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Vol. **44,** No. **1**	January 1969	
Vol. **44,** No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45,** No. **1**	March 1969	
Vol. **45,** No. **2**	April 1969	
Vol. **45,** No. **3**	May 1969	**(completing Vol. 45)**
Vol. **46,** No. **1**	June 1969	
Vol. **46,** No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47,** No. **1**	August 1969	
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Vol. **47,** No. **3**	October 1969	**(completing Vol. 47)**
Vol. **48,** No. **1**	November 1969	
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Photoionization studies by total ionization measurements. I. Benzene and its monohalogeno derivatives - J. Momigny, C. Goffart & L. D'Or (Liège, Belgium)

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Photoelectron spectra and ionic structure of carbon dioxide, carbon disulphide and sulphur dioxide - J.H.D. Eland & C.J. Danby (Oxford, Gt. Britain)

Ionization, preionization and internal energy conversion in CO_2, COS and CS_2 by photoelectron spectroscopy - J.E. Collin & P. Natalis (Liège, Belgium)

Fragmentation of some alkyl borates under electron impact - P.J. Fallon, P. Kelly & J.C. Lockhart (Newcastle upon Tyne, Gt. Britain)

Electron-impact studies of organometallic molecules. Part III. Some carbonylmetal halides and cyclopentadienyls - M.I. Bruce (Bristol, Gt. Britain)

Massenspektrometrische Element- und Isotopen-häufigkeitsanalysen zur Erforschung der Geschichte der Meteorite und des Planetensystems. Teil I und Teil II - H. Voshage (Mainz, Deutschland)

A mass spectrometric investigation of the high-temperature diffusion of uranium in tungsten and the allotropic phase transition in zirconium - E.C. Schwegler Jr. & F.A. White (Troy, N.Y., USA)

Mass spectrum of phenylboron dichloride and the ionic bond energy $D(\mathrm{PhBCl}^{+}\mathrm{Cl}^{-})$ - J.C. Lockhart & P. Kelly (Newcastle upon Tyne, Gt. Britain)

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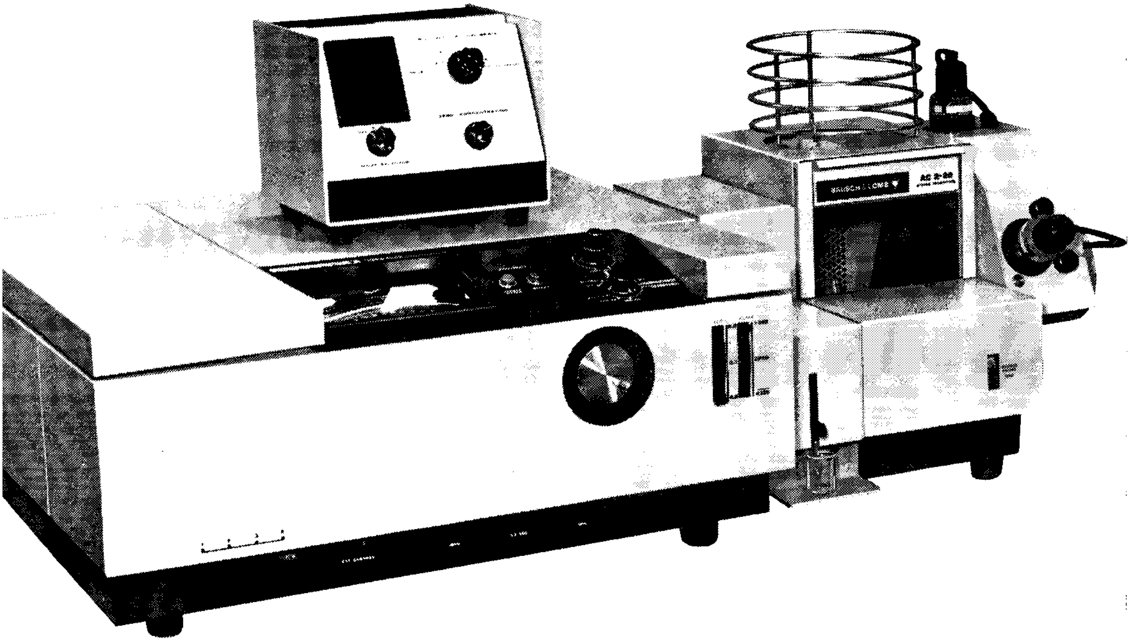

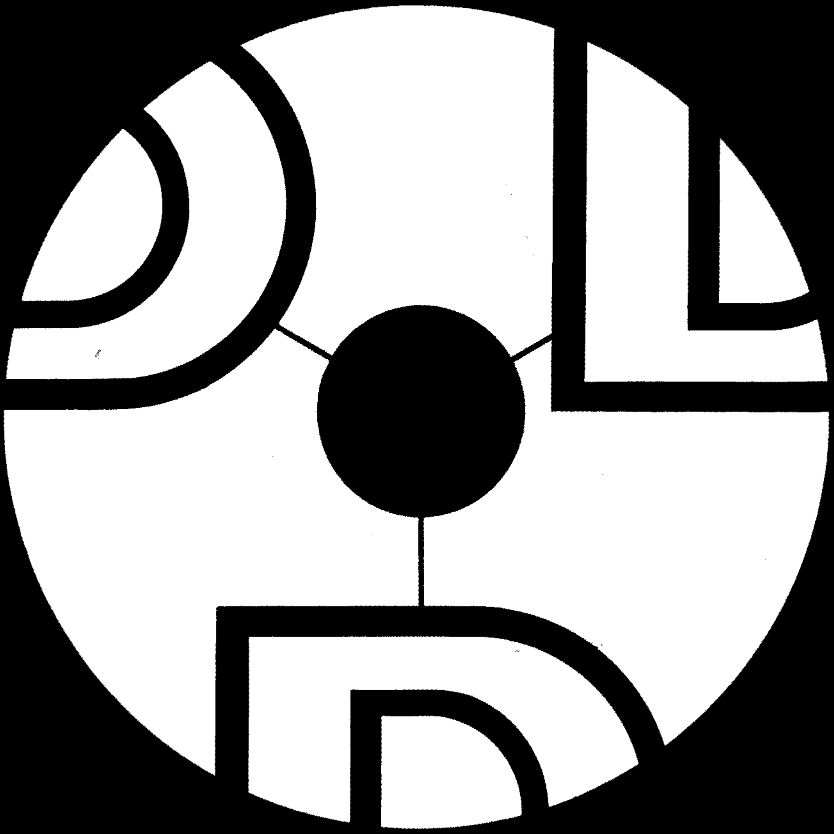

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 43, No. 3, December 1968

DIRECT DETERMINATION OF SUBMICROGRAM AMOUNTS OF OSMIUM AND RUTHENIUM IN SULPHIDE ORES BY NEUTRON ACTIVATION ANALYSIS

A neutron activation method, involving a radiochemical separation based upon two consecutive distillations, is described for the direct determination of nanogram amounts of osmium and ruthenium in selected sulphide ores. A loss of osmium due to volatilization occurred when the tracer solution was evaporated. A simple radiochemical method using iron(III) hydroxide precipitation was devised to prevent this loss. The proposed method was applied to ores expected to contain only traces of platinum metals. The addition of the active carrier was found to improve the separation of these two metals in the submicrogram range, although, no chemical yield determination was necessary.

K. S. CHUNG AND F. E. BEAMISH,
Anal. Chim. Acta, 43 (1968) 357–368

DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

I. SIMULTANEOUS DETERMINATION OF 16 TRACE ELEMENTS IN TITANIUM

The most important metallic impurities in titanium which give long-lived isotopes on neutron irradiation can be determined by a rapid anion-exchange separation of Ti, Sc, Cr, Na and Ag, after which the resin, containing most of the impurities, is counted on a high-resolution Ge(Li) γ-spectrometer. Cu, W, As, Ga, Au, Sn, Fe, Zn, Co, Ta, Mo and Ni can be determined in one measurement, while Na, Cr and Ag can be determined after an additional separation from the Sc isotopes, the major activities originating from titanium on neutron irradiation. Three different samples were analysed five times, and the reproducibility of the results was good.

R. NEIRINCKX, F. ADAMS AND J. HOSTE,
Anal. Chim. Acta, 43 (1968) 369–380

INTERNAL STANDARD ACTIVATION ANALYSIS OF SILICON IN STEEL

Non-destructive 14-MeV neutron activation analysis for silicon in steel has been applied with ^{56}Mn as internal standard. ^{56}Mn is formed from the iron matrix *via* the ^{56}Fe(n,p)^{56}Mn reaction. Several methods of internal standardisation *via* ^{56}Mn are discussed. The 0.84-MeV photopeak of ^{56}Mn is recommended if steel samples of about the same composition are to be analysed. Chemically analysed steel samples are used as silicon standards. A precision of 0.7% was obtained for an analysis plus standardisation time of 13 min. Special attention was paid to interferences produced by concentration changes of impurity elements. Several possible sources of errors were investigated.

R. VAN GRIEKEN, R. GIJBELS, A. SPEECKE AND J. HOSTE,
Anal. Chim. Acta, 43 (1968) 381–395

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART I. THE ANALYSIS OF SILICATE ROCKS,

The analysis of various inorganic siliceous materials of geological and industrial interest is discussed. The methods proposed are based on decomposition of a single sample by hydrofluoric acid and determination by atomic absorption spectrophotometry of up to 10 constituents. General procedures are described, and details are given for the determination of silicon, aluminium, total iron, magnesium, calcium, sodium, potassium, titanium and manganese in silicate rocks. Analytical data are given for the analysis of reference rocks G-2 and W-1.

F. J. Langmyhr and P. E. Paus,
Anal. Chim. Acta, 43 (1968) 397–408

A RAPID AND SPECIFIC DETERMINATION OF TRACES OF PLUTONIUM WITH A RECORDING SPECTROPHOTOMETER

A spectrophotometric method for the determination of plutonium in the range of 0.2–140 mg/l is described. The method is based on the measurement of the absorption of plutonium(VI) at 831 nm. A recording spectrophotometer with variable slit width, 10-cm cells and scale expansion facilities, is necessary. Uranium up to 20 g/l does not interfere.

K. Buijs, B. Chavane de Dalmassy and M. J. Maurice,
Anal. Chim. Acta, 43 (1968) 409–415

DI-2-PYRIDYLKETOXIME, A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

Di-2-pyridylketoxime is proposed for the spectrophotometric determination of iron(II). The complex is stable and exhibits an absorption maximum at 534 nm in an alkaline citrate medium. Beer's law is obeyed and the molar absorptivity is $1.5 \cdot 10^3$. Large amounts of copper and nickel can be tolerated. The method is simple, convenient and reproducible.

W. J. Holland, J. Bozic and J. T. Gerard,
Anal. Chim. Acta, 43 (1968) 417–422

A RAPID AND ACCURATE DETERMINATION OF TRACE QUANTITIES OF SULPHUR IN TIN

A method is described which permits the determination of 1–100 p.p.m. of sulphur in metallic tin. It is based on the complete combustion of the sample in a stream of oxygen and the determination of the change in electrical conductivity produced by the absorption of the gaseous combustion products (SO_2) in a suitable reaction liquid. Gas-borne tin(IV) oxide dust is removed from the oxidation products by electrostatic precipitation. The new technique is shown to be superior to the widely used methylene blue method.

E. Pell and H. Malissa,
N. A. Murphy and B. R. Chamberlain,
Anal. Chim. Acta, 43 (1968) 423–428

A RE-EVALUATION OF HYDROXYLAMMONIUM ACETATE AS A CARBONYL REAGENT — THE EFFECT OF DIELECTRIC CONSTANT CHANGE ON TITRATION ENDPOINTS

The determination of carbonyl groups with hydroxylammonium acetate in acetic acid has been re-examined. The reaction of hydroxylammonium acetate with acetic acid has been found to yield non-basic products, first acethydroxamic acid and eventually diacetylhydroxylamine, which do not interfere with the analyses. Calculations based on kinetics show that loss of the reagent is negligible in most cases, and in the extreme, involves only 0.9% of the amount originally present. Analyses in acetic acid media throughout are compared with those in which the titrations were conducted in benzene–acetic acid or carbon tetrachloride–acetic acid mixtures whose compositions were chosen to yield the most favorable titrations. The slopes of the titration curves were uniformly improved in the systems containing inert solvents, as predicted by consideration of the effect of dielectric constant change. Analytical precision was slightly improved except for aromatic aldehydes. Neither inert solvent system seemed superior to the other. The undesirable effect of small amounts of water is discussed.

TH. MEDWICK, C. R. ILLIAN AND L. G. WEYER,
Anal. Chim. Acta, 43 (1968) 429–439

THE SUBMICRO DETERMINATION OF CARBON, HYDROGEN AND NITROGEN BY A GAS-CHROMATOGRAPHIC METHOD

A method for the determination of carbon, hydrogen and nitrogen in organic samples weighing 40–80 μg is described. The sample is decomposed conventionally in a helium stream and the water formed is converted to acetylene. Nitrogen, carbon dioxide and acetylene are then separated on a silica-gel column, and the acetylene is burned to carbon dioxide by passage through copper oxide at 900° because the acetylene peak itself is not easily measured. Water from the second combustion is removed on silica gel and the three peaks emerging are measured by means of a micro thermistor cell. The standard deviations obtained for acetanilide are 0.31% for carbon, 0.28% for hydrogen and 0.11% for nitrogen. Results for other compounds are given and the parameters relevant to precision are discussed.

R. BELCHER, G. DRYHURST. A. M. G. MACDONALD, J. R. MAJER AND G. J. ROBERTS,
Anal. Chim. Acta, 43 (1968) 441–450

APPLICATION OF THE INTEGRATED ION-CURRENT TECHNIQUE TO THE STUDY OF RARE-EARTH CHELATES

Several substituted acetylacetones have been prepared and reacted with holmium to give tris chelates of the form HoL_3. One of these chelates has been converted to a tetrakis chelate of the form $NaHoL_4$. The mass spectra of these compounds have been studied and the integrated ion currents at significant m/e values have been related to the amounts of metal chelates evaporated into the ion source of the mass spectrometer. The shape of the integrated ion-current curve is shown to give information about the nature of the evaporation process. When the β-diketone (L) is asymmetrical as in the case of 1,1,1-trifluoro-5,5-dimethylhexan-2,4-dione, the existence of geometrical isomers of the chelate, HoL_3, is reflected in the shape of the integrated ion-current curve, which shows fine structure. The results of mass spectrometric studies are compared with those of the sublimation and gas chromatographic behaviour of the metal chelates.

R. BELCHER, J. R. MAJER, R. PERRY AND W. I. STEPHEN,
Anal. Chim. Acta, 43 (1968) 451–458

CATION-EXCHANGE SEPARATIONS IN ORGANIC SOLVENT–DITHIZONE MEDIA

Numerous elements can be adsorbed on a column of the strongly acidic cation-exchange resin Dowex 50 from a mixture consisting of tetrahydrofuran and 1 *M* nitric acid (19:1). These elements include Ag, Cu, Bi, Pb, rare earths, alkaline earth metals, alkali metals, U, Th, Fe, Co, Zn and Cd; Hg and Sb are not retained and so can be separated from the adsorbed elements. Fractionation of the adsorbed elements can be effected by using as eluent 0.01 *M* dithizone in tetrahydrofuran–1 *M* nitric acid (19:1); the dithizonates of silver, copper and bismuth are selectively eluted while the other adsorbed metal ions are still retained. The technique is suitable for the separation of tracer and macro amounts of elements.

K. A. Orlandini and J. Korkisch,
Anal.Chim Acta, 43 (1968) 459–463

QUANTITATIVE SEPARATION OF THE ALKALI METALS BY CATION-EXCHANGE CHROMATOGRAPHY WITH BIO-REX 40 RESIN

APPLICATION TO SILICATE ANALYSIS

The application of BIO-REX 40, a phenolformaldehyde resin, to the quantitative separation of Li, Na, K, Rb and Cs is described. All five elements can be separated in a single procedure by using a 25-g (62-ml) resin column and eluting lithium with 500 ml of 1.00 *M* hydrochloric acid in 80% ethanol, sodium with 500 ml of 0.20 *M* hydrochloric acid, potassium with 250 ml of 0.70 *M* hydrochloric acid, rubidium with another 450 ml of 0.70 *M* hydrochloric acid and cesium with 500 ml of 4.0 *M* hydrochloric acid. Procedures are described for the accurate determination of alkali metals in silicate minerals, plant material and water. Al, Fe, Ti, Zr, V, Mo and some other elements are first separated by absorption as oxalato complexes on a column of AG1-X8 resin. The alkali metals are finally determined by gravimetry or atomic absorption spectrometry. Tables of distribution coefficients and quantitative results of analyses of synthetic mixture and standard silicate samples are presented together with typical elution curves.

F. W. E. Strelow, C. J. Liebenberg and F. von S. Toerien,
Anal. Chim. Acta, 43 (1968) 465–473

A MODIFIED METHOD FOR DETERMINATION OF BORON WITH CURCUMIN AND A SIMPLIFIED WATER ELIMINATION PROCEDURE

The formation of boric acid ester with curcumin is usually performed in highly acidic solution in the absence of water. Small water contents are permissible, but the efficiency is lowered. The water content of a sample can be eliminated by a reaction with propionic anhydride catalyzed by oxalyl chloride, thus avoiding methyl borate distillation or evaporation processes. An advantage is that the reaction between boron and curcumin takes place in a completely homogeneous liquid medium. The excess of protonated curcumin is best destroyed with an ammonium acetate buffer. For trace amounts of boron, extraction of the coloured complex with a mixture of methyl isobutyl ketone, chloroform and phenol is recommended. Standard procedures for aqueous solutions with boron contents between 0.0033–40.0 μg B/l are described.

L. R. Uppström,
Anal. Chim. Acta, 43 (1968) 475–486

SPECIES FORMED IN THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH THORIUM OR LANTHANUM NITRATE AND FUNCTIONS SUITABLE FOR THE EVALUATION OF THE EQUIVALENCE POINTS

Calculations by means of SILLÉN's HALTAFALL program have been performed on experimental curves by LINGANE for the potentiometric titration of fluoride with thorium and lanthanum in different media. After adjusting the stability constants for some of the main species formed during the titration a good fit was obtained between the experimental data and the calculated titration curves. In the cases where the solution was buffered with acetate it was necessary to consider the formation of mixed fluoride–acetate complexes. Suitable functions for the evaluation of the equivalence point could be derived from the calculations. If the functions: $F_1 = (v_0 + v)[F^-]$ and $F_3 = (v_0 + v)[F^-]^{-3}$ are used before and after the equivalence point, respectively, it ought to be possible to determine fluoride very accurately by titration with lanthanum nitrate in an unbuffered solution. A value proportional to $[F^-]$ is obtained from 10 exp $(-EF/RT \ln 10)$, the Nernst e.m.f. equation.

T. ANFÄLT, D. DYRSSEN AND D. JAGNER,
Anal. Chim. Acta, 43 (1968) 487–499

EXTRACTION OF MANGANESE DITHIOCARBAMATE COMPLEXES FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

(Short Communication)

M. YANAGISAWA, M. SUZUKI AND T. TAKEUCHI,
Anal. Chim. Acta, 43 (1968) 500–502

A SELECTIVE METHOD FOR THE SEPARATION OF MERCURY(II) BY CHROMATOGRAPHY ON DEAE ION-EXCHANGE PAPER

(Short Communication)

J. SHERMA AND A. D. FINCK,
Anal. Chim. Acta, 43 (1968) 503–505

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE.
PART II. THE ANALYSIS OF SILICA

(Short Communication)

F. J. LANGMYHR AND P. E. PAUS,
Anal. Chim. Acta, 43 (1968) 506–507

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE.
PART III. THE ANALYSIS OF BAUXITE

(Short Communication)

F. J. LANGMYHR AND P. E. PAUS,
Anal. Chim. Acta, 43 (1968) 508–510

ARSENAZO III AS A METALLOCHROMIC INDICATOR FOR THE DIRECT DTPA TITRATION OF LANTHANONS IN ALUMINO-SILICATE ZEOLITES

(Short Communication)

W. W. Marsh, Jr. and G. Myers, Jr.,
Anal. Chim. Acta, 43 (1968) 511–514

NON-AQUEOUS SPECTROPHOTOMETRIC DETERMINATION OF CARBONYL FUNCTIONS

(Short Communication)

J. Belisle,
Anal. Chim. Acta, 43 (1968) 515–518

APPARATUS FOR THE RAPID DEGASSING OF LIQUIDS. PART II

(Short Communication)

R. Battino, F. D. Evans and M. Bogan,
Anal. Chim. Acta, 43 (1968) 518–520

DETERMINATION OF NITRILOTRIACETIC ACID AND ETHYLENEDIAMINETETRAACETIC ACID IN GRANULAR DETERGENT FORMULATIONS

(Short Communication)

G. G. Clinckemaille,
Anal. Chim. Acta, 43 (1968) 520–522

SIMULTANEOUS DETERMINATION OF RUBIDIUM AND CESIUM IN ROCK SAMPLES BY NEUTRON ACTIVATION ANALYSIS WITH A LITHIUM-DRIFTED GERMANIUM DETECTOR AFTER CHEMICAL GROUP-SEPARATION

(Short Communication)

K. Tomura, H. Higuchi, H. Takahashi, N. Onuma and H. Hamaguchi,
Anal. Chim. Acta, 43 (1968) 523–526

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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

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

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

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

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

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

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

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THE MASS SPECTRA OF ORGANIC MOLECULES

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

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

Contents: 1. The principles and methods of mass spectrometry. 2. Types of ions in the mass spectra of organic compounds. 3. The mass spectra of hydrocarbons. 4. The mass spectra of oxygenated compounds. 5. The mass spectra of nitrogen compounds. 6. The mass spectra of sulphur compounds. 7. The mass spectra of halogenated compounds. 8. The mass spectra of boron compounds. 9. The mass spectra of phosphorus compounds. 10. The mass spectra of silicon compounds. 11. Examples of structure determination from mass spectra. Appendix 1. Peaks commonly encountered in the mass spectra of organic compounds. Appendix 2. The masses and abundances of nuclides commonly encountered in the mass spectra of organic compounds. References. Indexes.

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. Ahearn, Member of Technical Staff, Bell Telephone Laboratories, Inc.,
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by A. B. P. LEVER, Associate Professor of Chemistry,
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DIRECT DETERMINATION OF SUBMICROGRAM AMOUNTS OF OSMIUM AND RUTHENIUM IN SULPHIDE ORES BY NEUTRON ACTIVATION ANALYSIS

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(Received June 5th, 1968)

Experimental procedures which allow the quantitative distillation of microgram amounts of osmium and ruthenium have already been reported[1]. The procedures have been applied in this work for the direct determination of these two metals in sulphide ores.

The proportions of total platinum metals in the type of ores examined are of the order of nanograms/ounce of ore. The direct determination of the two metals in such samples, without preconcentration, has not been accomplished by conventional methods. In recent years, the neutron activation technique, with distillation[2,3] or anion exchange[4] as a means of separation, has been applied for the determination of osmium and ruthenium in terrestrial sources. However, with ore samples, the analytical approaches were lengthy, requiring about 20 h for duplicate determinations[3] and, furthermore, the separation of osmium and ruthenium by distillation was not confirmed by adequate data.

The present work has shown that osmium is easily lost by volatilization during evaporation. A simple radiochemical method was devised to prevent this loss. Inactive carrier was added during the distillation process but no chemical yield determination was required. The overall processing time for the determination of the two metals was about 3 h.

NUCLEAR DATA

The nuclear data pertinent to the present work are shown in Table I[5-7].

EXPERIMENTAL

Apparatus

A scintillation counter (Nuclear Chicago Model 8725 Analyzer/Scaler) was used with a single-channel analyzer. The detector used was a 2 × 2 in NaI(Tl) well-type crystal, Model 422 type. A 400-channel γ-ray analyzer (RIDL Model 34-27) was used in conjunction with 3 × 3 in NaI(Tl) detector. Radiation measurements were also made with a 22-cm^3 Ge(Li) detector (provided with a 1.5-cm^2 thick aluminum absor-

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TABLE I

PRINCIPAL RADIONUCLIDES OF OSMIUM AND RUTHENIUM

Stable isotope	*Isotopic abundance* (%)	*Activation cross-section* (b)	*Radionuclide produced by* (n,γ) *reaction*	*Half-life of radionuclide*	*Radiation* (keV)
^{184}Os	0.018	< 200	^{185}Os	93.6 d	E.C. γ's (646)
^{190}Os	26.4	— 8±3	^{191m}Os ^{191}Os	14 h 16 d	I.T. (74) β^- (142)
^{192}Os	41	1.6±0.4	^{193}Os	31 h	β^-'s (677–1136) γ's (73–558) (esp. 281, 321, 388, 460, 558)
^{96}Ru	5.7	0.21±0.02	^{97}Ru	2.88 d	E.C. γ's (216)
^{102}Ru	31.3	1.44±0.16	^{103}Ru	39.8 d	β^-'s (220) γ's (55–610) (esp. 498, 610)
^{104}Ru	18.3	0.7±0.2	^{105}Ru	4.5 h	β^-(1150) γ (726)

ber) in conjunction with a 400-channel analyzer. Sartorius MPR 5/2 Microbalance. Distilled water and distillation apparatus were described previously[1].

Reagents

Hydrogen peroxide (30%), sulphuric acid, sodium peroxide, and sodium bromate were A.R.-grade reagents.

The carrier solutions for osmium and ruthenium were prepared by fusing, in a nickel crucible, 50 mg of finely divided osmium or ruthenium sponge with sodium peroxide as described below. The cold melt was diluted to about 50 ml with dilute sulphuric acid (*ca.* 5 *N*) (1 mg of each metal/ml). Iodine-131 was supplied from the Ames Co., Miles Laboratories Inc., Elkhart, Indiana, U.S.A.

Iron(II) sulphate (A.R.) was dissolved in water with a minimum amount of sulphuric acid (10 mg of iron/ml).

Sampling

About 100 pounds of sulphide ore, collected from several Canadian Mining Companies, were pulverized to 100–200 mesh. Each sample was split by hand-riffling and two of the portions were accepted if their weights differed by less than 1%; otherwise, the portions were recombined and the process repeated. The sample weights were reduced to about 10 g by continued sub-division. When coarse granules were found, the sample was ground in an agate mortar, as during the preliminary distillations any small amount of undissolved ores was usually associated with low recovery of osmium and ruthenium.

Standard and tracer solutions of osmium and ruthenium

The two metals were each purified as previously reported[1]. Their radiochemical purity was confirmed by γ-ray spectrometry. About 1 mg of purified sponge of each metal was added to quartz vials and weighed. After irradiation, they were treated by the method described below. The tracer and standard solutions were diluted to 100 ml with *ca.* 5 *N* sulphuric acid. The appropriate aliquot was diluted to 25 ml in a volumetric flask, and the activity was measured. This was also used as a tracer solution for the distillation of both metals. As shown in Fig. 1, the osmium tracer solution showed the γ-peaks of osmium-191 (half-life 16 d) at 45 and 130 keV, and also that of osmium-185 (half-life 94 d) at 646 and 875 keV. The ruthenium tracer solution showed the γ-peaks of ruthenium-103 (half-life 40 d) at 498 and 615 keV.

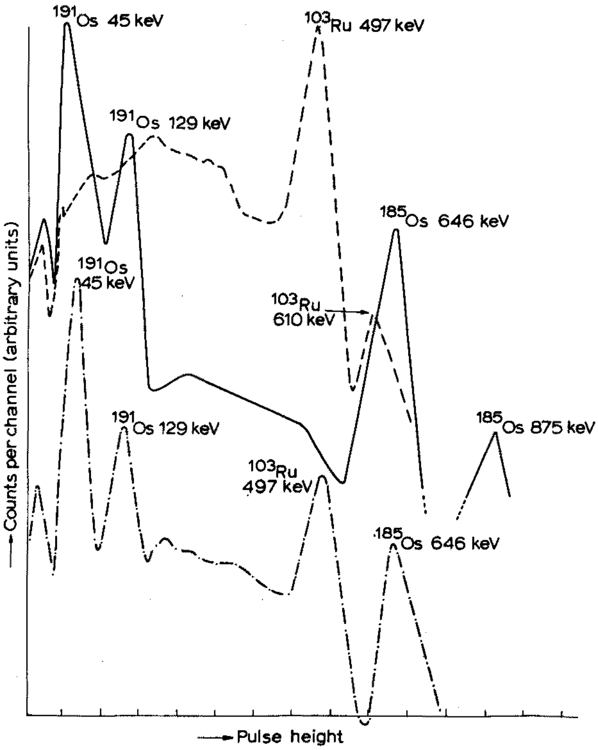

Fig. 1. γ-Spectra of standard solutions of osmium and ruthenium. (— — — —) Ru; (————) Os; (— . — . — . —) Ru + Os.

Counting

The activities of the sample solution, distillate and standard solution, were measured by γ-scintillation counting after the solution had been diluted with water to 25 ml in a volumetric flask. The flask was placed directly on the scintillation counter and the countings were continued until at least 10^4 counts were collected, in order to obtain good counting statistics. The radiochemical purity of the sample solution was confirmed with the multichannel analyzer.

Irradiation

About 100 mg of sulphide ore and *ca.* 1 mg of standard osmium and ruthenium were accurately weighed and added to tared quartz vials. Each set of ore samples, together with one standard of osmium and ruthenium, was placed in an aluminum capsule and irradiated for 4–5 days at a neutron flux of approximately $5 \cdot 10^{12}$

n cm^2 sec in the McMaster University Reactor, Hamilton, Ontario, Canada. In the case of ore samples, the irradiated materials were processed after a cooling period of about 4–5 days.

Fusion and dissolution of ore and of standard osmium and ruthenium metals

After irradiation, the quartz vials were opened in a glove box and the contents were transferred to the tared crucible by gentle tapping. To eliminate the possibility of loss, the irradiated materials were re-weighed. Sodium peroxide (*ca.* 1.5 g) was added and the sample and the flux were mixed thoroughly with a thin glass rod. The moist material adhered to the glass rod and was carefully scraped off with another glass rod. Mixing the ore with the fusion flux was advisable for complete decomposition of ore. The crucible was covered with a lid and the low temperature flame of a Meker burner was applied for about 2 min until the mixture just melted. The heat was gradually raised, using a medium flame, for about a further 2 min when the bottom of the nickel crucible became a dull red colour. At this stage, the melt usually reached a quiet fusion and the resulting molten mass appeared homogenous. If the fusion was carried out with the full flame of a Meker burner, the resulting melt was difficult to dissolve. The molten mass was cooled by rotating the crucible so that the mass solidified in a layer on the wall. About 10 ml of water was carefully added through a dropper to disintegrate the melt, the crucible being covered with a lid to avoid the loss by spurting. By repeating this procedure with the total 20 ml of water, the disintegrated melt was transferred to the distillation flask. During this manipulation, the crucible and the flask were cooled in an ice bath to avoid any loss of osmium by the heat of decomposition. The slight residue remaining in the crucible was dissolved by gently warming the crucible on a water bath for about 1 min with a minimum amount of sulphuric acid. The washings of the crucible were added to the flask. After this treatment, the activity from irradiated materials remaining in the crucible was found to be negligible.

Distillation procedure for osmium and ruthenium

The black slurry was dissolved by 40 ml of sulphuric acid (1:2). Hydrogen peroxide (20 ml) was added and a slow air current was drawn through the distillation apparatus. The flask was electrically heated for 10–15 min. When the temperature of the flask reached 75–80°, about 30 ml of hydrogen peroxide (30%) were added dropwise to the flask during the remainder of the distillation. At this stage, the temperature usually rose quickly to about 105°, at which temperature the distillation was maintained for 40 min. The heating was discontinued and an air current was drawn through for a further 10 min. The distillate absorbed in the two receivers, each containing 5 ml of 9 *N* sodium hydroxide, was diluted to 25 ml in a volumetric flask. The activities of the distillate were measured with a scintillation counter by comparison with the standard solution prepared above. Each absorbing tube was refilled with 5 ml of 9 *N* sodium hydroxide, and the ruthenium was distilled as follows: about 5 ml each of sodium bromate (20%) and concentrated sulphuric acid were added to the flask and the air current was again drawn through the apparatus. The distillation flask was carefully heated to avoid the violent evolution of bromine and the temperature was gradually raised to about 100°. For the remainder of the distillation, 15 ml of sodium bromate (20%) was added dropwise. The distillation was continued for 1 h and the distillate was then diluted to 25 ml in a volumetric flask.

RESULTS

Separation of osmium and ruthenium by distillation

The above distillation was applied to synthetic mixtures of osmium and ruthenium (Table II).

The mutual separation of these two elements was confirmed by examining the γ-spectra of both distillates with the γ-ray multichannel analyzer. All of the activity of both distillates was always collected in the first receiver.

TABLE II.

SEPARATION OF OSMIUM AND RUTHENIUM BY DISTILLATION

(No carrier added; the duration of the distillation was 40 min for osmium and 60 min for ruthenium)

Amount added (μg)		*Temp. (°C)*		*% Distilled*	
Os	*Ru*	*Os*	*Ru*	*Os*	*Ru*
3.5	11.2	104–107	103–108	99.0	99.6
3.5	11.2	104–107	102–107	99.4	100.3

TABLE III

DISTILLATION OF OSMIUM AND RUTHENIUM TRACERS FROM THE SOLUTION OF SULPHIDE ORE

(Duration of the distillation was 40 min for osmium and 60 min for ruthenium)

Tracer added (10^{-6} g)		*Temp. (°C)*		*% Distilled*		*Ore*
Os	*Ru*	*Os*	*Ru*	*Os*	*Ru*	
3.5	11.2	104–106	103–107	98.0	98.5	Sudbury
3.5	11.2	103–106	103–107	99.0	97.8	HCGM*
3.5	11.2	103–107	103–106	99.0	98.5	HCGM

Distillation of osmium and ruthenium from solutions of ore samples.

In order to apply the above method to the ore samples, the two metals were distilled from the dissolved solution of sulphide ore as follows. About 100 mg each of ore from two different locations, the Sudbury ore and HCGM* ore, were decomposed and the fused mass was dissolved with sulphuric acid as described above. The solution of ore sample was added to the flask and the osmium and ruthenium tracer solutions, respectively, 3 μg and 11 μg, were added. The distillation was carried out as described above (Table III).

As shown in Table III, the dissolution procedure for the ore samples showed no retarding effect on the distillation behaviours of osmium and ruthenium under the stated conditions. In order to verify further the applicability of the distillation method to ore analysis, the mixture of osmium and ruthenium tracer was evaporated and fused together with ore samples and the distillation behaviours were examined as follows. About 0.1 g of finely pulverized ore was added to the nickel crucible which was spiked with 5 ml each of osmium and ruthenium solutions, each containing about

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* Hollinger Consolidated Gold Mines, Ltd., Timmins, Ontario, Canada.

3 μg and 11 μg of these metals, respectively. The solutions were slowly evaporated on the water bath. After dryness, 1.5 g of sodium peroxide was added. The fusion, dissolution and distillation were as described above. The result showed about 60% recovery of osmium. This was repeated with about 78% recovery of osmium. Osmium was shown to be lost during evaporation, as follows: the same amount of osmium and ruthenium tracer solution were added to a 15-ml beaker and evaporated slowly on the water bath. Almost no activity remained in the beaker after evaporation. It has been reported[7] that the addition of iron(II) sulphate or chloride stops loss of osmium by volatilization, but in the present work losses were found even after the addition of iron(II) sulphate (Table IV). In contrast to osmium, 100% retention of ruthenium was always obtained.

TABLE IV

LOSS OF OSMIUM BY EVAPORATION IN THE PRESENCE OF IRON(II) SULPHATE[a]

	Immediately after			*24 H after*			*Remarks*
20 mg of iron(II) present							
Os activity added	12,748	12,403	12,436	12,754	12,537	12,649	The osmium tracer solution was evaporated in the presence of 20 mg of Fe^{2+}
Os activity recovered	11,233	11,941	11,836	12,043	11,925	11,945	
Recovery (%)	88.1	96.3	95.2	94.4	95.1	94.4	
50 mg of iron(II) present							
Os activity added	12,077	12,329	12,070	12,113	12,408	12,287	The osmium tracer solution was evaporated in the presence of 50 mg of Fe^{2+}
Os activity recovered	11,777	11,886	11,159	11,649	12,061	11,789	
Recovery (%)	97.5	96.4	92.5	96.2	97.2	95.9	
20 mg of iron(II) present							
Ru activity added	20,998	20,719	20,669				The ruthenium tracer solution was evaporated in the presence of 20 mg of Fe^{2+}
Ru activity recovered	21,186	20,816	20,831				
Recovery %	100.9	100.5	100.8				

[a] The osmium and ruthenium tracer contained 3.5 μg and 11.2 μg of the respective metals. The tracer solution (each 5 ml) and iron(II) sulphate solution were added to a 15-ml beaker and evaporated slowly on the water bath. After dryness, the residue was dissolved with dilute sulphuric acid and diluted to 25 ml in a volumetric flask. The activity was compared with the reference standard.

As shown in Table IV, 2–12% of osmium was always lost during evaporation and there was no improvement on ageing the solution by allowing to stand overnight.* The loss of osmium by volatilization was prevented by an iron(III) hydroxide precipitate formed by the addition of sodium hydroxide to the tracer solution as described below (Table V).

The distillation of osmium and ruthenium tracer was then carried out as described above except that iron(III) hydroxide was precipitated (Table VI). The low recovery of osmium by distillation, 60% and 78%, seems to be due to the volatilization of osmium rather than to any peculiar distillation characteristics.

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* It is known that during ageing, the complex, $[Ru(H_2O)Cl_5]^{2-}$, undergoes gradual hydration involving progressive replacement of the Cl^- group of the complex by an aquo-group[8].

TABLE V

RETENTION OF OSMIUM BY IRON(III) HYDROXIDE PRECIPITATION DURING EVAPORATION[a]

	Osmium (5 μg)			*Ruthenium (11.2 μg)*		
Activity added	10,928	10,727	10,601	20,942	20,976	20,794
Activity recovered	10,909	10,805	10,495	21,087	20.993	20,730
Recovery %	99.8	100.7	99.0	100.7	100.1	98.9

[a] The precipitation procedure is described below.

TABLE VI

DISTILLATION OF OSMIUM TRACER FROM FUSED SULPHIDE ORE

Distillation no.	*Os added (3.5 μg) (activity)*	*Os recovered (activity)*	*Recovery (%)*
1	10,083	9,997	99.2
2	10,280	10,096	98.2
3	10,162	10,018	98.6

TABLE VII

ACTIVATION ANALYSIS OF OSMIUM AND RUTHENIUM IN SULPHIDE ORE (IN THE ABSENCE OF CARRIER)[a]

Expt.	*Sulphide ore*	*Weight of sample (mg)*	*Os found (ng)*	*Os (p.p.m.)*	*Ru found (ng)*	*Ru (p.p.m.)*
A 1	HCGM 200′ level	129.16	5.9	0.05	—	—
A 2	HCGM 200′ level	152.82	3.6	0.02	10	0.07
A 3	HCGM 2,000 level	127.50	0.8	0.01	—	—
A 7	Sudbury ore	184.40	8.5	0.05	36	0.2
A 8	Sudbury concentrate	164.90	11.8	0.07	20	0.1
A 9	Sudbury concentrate	106.27	14.0	0.13	58	0.5

[a] A small amount of ruthenium and ^{131}I contamination were noticed in the osmium distillate. The resulting small error was not considered in the above results.

Activation analysis of osmium and ruthenium in sulphide ores (in the absence of a carrier)

A trial analysis by neutron activation was carried out for the determination of the two metals in sulphide ores. Six samples from different locations were analyzed (Table VII).

As shown in Fig. 2, the osmium distillate from the above determinations was contaminated with ruthenium and iodine-131 activity. The amount of ruthenium contamination was estimated roughly by γ-ray multichannel analyzer to be in the range 10–40 ng of ruthenium. The distillate of ruthenium was, however, always found to be radiochemically pure. It was interesting to notice in this experiment that iodine-131 was also present in the osmium distillate. The identity of iodine-131 was confirmed by comparing its γ-spectrum with of the standard iodine-131 obtained from the Ames Co. While the concentrates of sulphide ores from Sudbury, Ontario showed the presence of ^{131}I activity, the latter was absent form the HCGM sample. Iodine-131 seemed to be radiogenically produced from tellurium present in the ore by the reaction,

$$^{130}\text{Te}\ (\text{n},\gamma)\ ^{131}\text{Te} \xrightarrow{\beta^-} {}^{131}\text{I}\ .$$

It was possible that the codistillation of ruthenium was due to the extremely low amounts of these two metals in the ore. Therefore, further experiments were carried out with the addition of carrier.

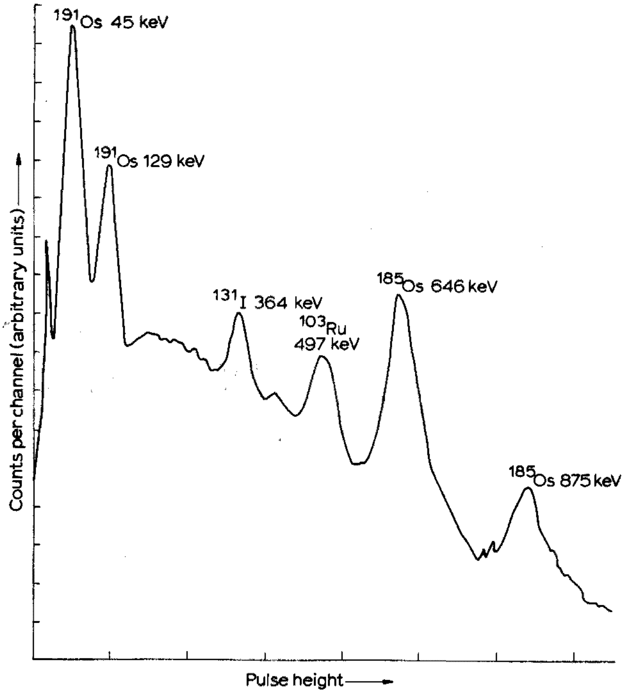

Fig. 2. γ-Spectrum of an osmium distillate from Sudbury sulphide ore (with osmium and iodine contamination). 5-h data accumulation with a 3 × 3 in scintillator 10 days after the end of irradiation of the ore.

Distillation of nanogram amount of osmium and ruthenium in the presence of carrier

To a 30-ml nickel crucible, 0.5 mg each of the carrier and 60 ng of active osmium tracer and 110 ng of ruthenium tracer were added. After the addition of 100 mg of sulphide ore and 20 mg of iron as iron(II) sulphate, the iron was precipitated as iron(III) hydroxide by the dropwise addition of 2 ml of *ca.* 1.3 *M* sodium hydroxide solution. The solution was carefully evaporated on a water bath and the residue fused with sodium peroxide. The distillation results are shown in Table VII.

Activation analysis of osmium and ruthenium in the HCGM sulphide ores (in the presence of carrier)

As shown in Table VIII, the separation of nanogram amounts of ruthenium

TABLE VIII

DISTILLATION OF NANOGRAM AMOUNTS OF OSMIUM AND RUTHENIUM FROM FUSED SULPHIDE ORE

(60 ng of osmium and 110 ng of ruthenium added; 0.4 mg Os carrier and 0.4 mg Ru carrier added)

Distillation no.	*Activity added (c.p.m.)*[a]		*Activity recovered (c.p.m.)*[b]		*Recovery (%)*	
	Os	*Ru*	*Os*	*Ru*	*Os*	*Ru*
1	1,103	2,016	1,072	1,978	97.2	98.1
2	1,095	2.030	1,080	1,969	98.6	97.0
3	1,108	2,053	1,086	2,024	98.0	98.6

[a] Because of the low activity counting, the tracer solution was freshly prepared.

[b] The radiochemical purity of each distillate was confirmed by 10-h counting with a multichannel analyzer. No activity was detected either in the crucible or the distillation flask after distillation.

TABLE IX

DETERMINATION OF NANOGRAM AMOUNTS OF OSMIUM AND RUTHENIUM IN SULPHIDE ORE BY NEUTRON ACTIVATION ANALYSIS WITH THE ADDITION OF CARRIER

Expt. no.	*Sample (mg)*	*Os found (ng)*	*Ru found (ng)*	*Os (p.p.m.)*	*Ru (p.p.m.)*
1	127.3	4.46	28.0	0.035	0.220
2	126.9	2.82	83.0	0.022	0.654
3	158.5	2.56	61.0	0.016	0.385
4	128.0	4.91	27.4	0.038	0.214
5	109.4	1.43	16.2	0.013	0.148
6	120.0	2.22	14.9	0.019	0.124
Average:				0.024 ± 0.010	0.290 ± 0.20
Coefficient of variation[a]:				43%	69%

[a] This is S.D./average.

and osmium was feasible under these conditions. The proposed procedure with the addition of inactive carrier and iron(III) hydroxide precipitation was applied to the determination of these two metals in sulphide ores. The samples were selected from the HCGM ore which was found to contain no ^{131}I activity. The samples were finely ground in an agate mortar and after irradiation, the sample was treated with the addition of inactive carriers and iron(III), etc., as described above. The results are shown in Table IX.

DISCUSSION

The analytical results (Table IX) indicate that the average content of osmium in the sulphide ore (0.024 ± 0.01 p.p.m.) was an order of magnitude smaller than that of ruthenium (0.29 ± 0.2 p.p.m.). Compared with the results of MORGAN[4] for the osmium content in the standard rocks, G-1 and W-1, the osmium concentration in sulphide ore reported here is about an order of magnitude higher.

Comparable data concerning the sulphide ore analysis are not available, and the accuracy of the present results cannot therefore be evaluated. If, however, the error involved in the analysis by Morgan[4] were of the same order of magnitude as in the present work, the osmium results with the coefficient of variation 43%, are reasonably close to MORGAN's results (standard deviation of 20–50%).* While the osmium results are reasonably close to each other, the ruthenium results show a coefficient of variation of 69%. However, with the exception of result no. 2, the precision of ruthenium analysis is similar to that of the osmium determination.

In view of the possible effect of neutron self-shielding[9], is was originally intended to irradiate the submicrogram amount of the standard as suggested by HOSTE[7], MORGAN[4] and MORRIS[10] who evaporated the small amount of osmium solution on filter paper[7] or Specpure silica[4]. This idea was abandoned because of the osmium loss observed in the present work. Moreover, when Whatman paper No. 1, spotted with osmium solution and wrapped in Mylar paper[7], was irradiated in the reactor for 4 days, both the filter and Mylar paper were so easily crumbled that it was difficult to transfer quantitatively from the quartz vial.

As stated above, the ruthenium contamination in the osmium distillate was very small, *i.e.* in the range 0.5–1.5 ng (Table VII). The presence of ruthenium contamination was confirmed only by the simultaneous counting of the combined osmium distillates. The above data for ruthenium contamination were estimated roughly from the photopeak area of the 498-keV peak of ^{103}Ru compared with that of known amounts of standards after counting for 10 h by multichannel analyzer. The effect of ^{131}I activity on the determination of osmium was similarly evaluated, and found to be very small. However, the sample containing the ^{131}I activity was avoided in this work because it was primarily intended to examine the applicability of the distillation

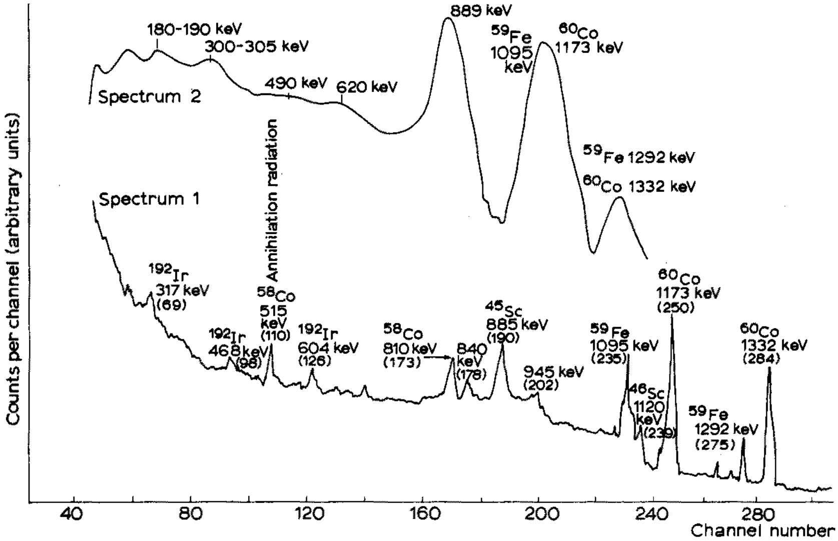

Fig. 3. γ-Spectra of residue in the flask after distillation of osmium and ruthenium from sulphide ore (Sudbury ore, Ontario, Canada). Spectrum 1: 20-min data accumulation using a 22 cm^3 Ge(Li)-detector, 12 days after 5 days irradiation. Spectrum 2: 100-min data accumulation using 3 × 3 in sodium iodide scintillator.
(The numbers in parentheses correspond to the exact channel number.)

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* This was taken by the present author as the coefficient of variation.

method as the separation procedure in the submicrogram range. Throughout the experiments, all the activity of the distillate was always collected in the first receiver.

At the beginning of the experiments, difficulty was encountered in distilling the last trace of osmium from ruthenium[11]. To rectify this, several distillations were carried out with the addition of potassium permanganate[11] to decompose hydrogen peroxide before the ruthenium distillation. Although this treatment gave a satisfactory removal of osmium, the permanganate treatment was abandoned when it was found that careful manipulation of the distillation procedure effected satisfactory separation of osmium (Tables III, VI, VIII and IX).

In the present work, the determination of chemical yield was purposely avoided although the addition of carrier was found to be necessary. The reason has been pointed out in a review[12] in which the inadequacy of the currently used procedures for the yield determination was emphasized.

It has been reported[7] and was also indicated by the γ-spectra of irradiated samples after distillation (Fig. 3), that platinum, iridium, palladium and rhodium are not distilled by this method. The possible interferences relevant to the present work in the neutron activation are as follows[9,13]: ^{193}Ir (n, p)^{193}Os, ^{196}Pt(n, α)^{193}Os, ^{191}Ir (n, p)^{191}Os, ^{108}Pd (n, α)^{105}Ru and ^{235}U (n, f)^{105}Ru.

However, the irradiations were made in a predominantly thermal flux, where the cross-sections for these reactions were generally quite low compared to the (n, γ) activation cross-section. Therefore, it was unlikely that these interfering reactions were sources of error.

It is a pleasure to acknowledge indebtedness to Dr. R. E. JERVIS and his group at the Department of Chemical Engineering and Applied Chemistry, University of Toronto, for the use of their counting equipment.

SUMMARY

A neutron activation method, involving a radiochemical separation based upon two consecutive distillations, is described for the direct determination of nanogram amounts of osmium and ruthenium in selected sulphide ores. A loss of osmium due to volatilization occurred when the tracer solution was evaporated. A simple radiochemical method using iron(III) hydroxide precipitation was devised to prevent this loss. The proposed method was applied to ores expected to contain only traces of platinum metals. The addition of the active carrier was found to improve the separation of these two metals in the submicrogram range, although, no chemical yield determination was necessary.

RÉSUMÉ

On décrit une méthode par activation aux neutrons, comprenant une séparation radiochimique basée sur deux distillations consécutives, pour le dosage de teneurs en osmium et en ruthénium, de l'ordre du nanogramme, dans des minérais sulfurés. Il peut se produire une perte en osmium par volatilisation; en peut l'éviter en utilisant une simple méthode radiochimique par précipitation d'hydroxyde de fer(III). Ce procédé est appliqué à des minerais ne renfermant que des traces de métaux du platine. L'addition d'un entraîneur permet d'améliorer la séparation.

ZUSAMMENFASSUNG

Es wird die direkte Bestimmung von Submikrogrammen Osmium und Ruthenium in sulfidischen Erzen mittels der Neutronenaktivierungsanalyse beschrieben. Zur direkten Bestimmung von Nanogrammen wird eine radiochemische Abtrennung durch zweifache Destillation durchgeführt. Beim Eindampfen der Lösungen tritt ein Verlust von Osmium durch Verdampfung auf. Durch Ausfällen von Eisen(III)-hydroxid wird dieser Verlust vermieden. Die vorgeschlagene Methode wurde nur für Erze mit Spuren von Platinmetallen verwendet. Durch Zugabe eines aktiven Trägers wurde die Trennung verbessert.

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DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

I. SIMULTANEOUS DETERMINATION OF 16 TRACE ELEMENTS IN TITANIUM

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Titanium metal is of importance, for instance, in the aeronautical industry and for a number of applications where its low specific weight, high corrosion resistance and high melting point justify its use. Most methods for the determination of impurities in this metal employ time-consuming precipitation of titanium with cupferron and subsequent extraction with chloroform, after which the impurities are determined by colorimetric, titrimetric or polarographic methods[1].

A spectrographic method for the determination of Al, Mo, Cr, Mn, Fe and Si in titanium compounds was described by TARASEVICH AND MOSELI[2]. The concentrations determined were never lower than 600 p.p.m. An anion-exchange separation of titanium from many elements was devised by DIXON AND HEADRIDGE[3], who used six consecutive elution steps. THOMPSON[4] determined some impurities in titanium by precipitation reactions. BROOKSBANK, LEDDICOTTE AND REYNOLDS[5] carried out activation analyses for W, Cl, V, Ni, Mn and Si; one element at a time was determined in their work and their separations were by precipitation reactions.

In the present work, a fast separation of the trace impurities from titanium and their simultaneous determination is described. The method is based on activation analysis and γ-spectrometry with a high resolution Ge(Li)-detector after anion-exchange separation into different groups. Ge(Li)-detectors allow an accurate and sensitive analysis of increasingly complex γ-spectra. Unfortunately, very high activities formed either by the activation of the matrix by (n,γ) or threshold reactions, or the presence of easily activated impurities in large concentrations, prevent the general use of non-destructive activation analysis by high-resolution γ-ray spectrometry.

The specific separation of large activities can, however, provide a possible analysis of a large number of impurities. One example is the determination of trace constituents in biological material, where the presence of large concentrations of sodium, and to a lesser extent of bromine and chlorine, prevent the use of instrumental methods based on high-resolution γ-ray spectrometry. In this case specific separations of sodium allow the ready determination of a large number of trace constituents.

The size and, consequently, the detection efficiency of Ge(Li)-detectors has considerably increased during recent years. Nevertheless, the detection efficiency remains approximately one order of magnitude smaller than for NaI(Tl) scintillation spectrometry. Chemical separations, which allow the measurement in geometrical conditions as favourable as possible, are thus desirable.

NUCLEAR DATA AND INTERFERENCES

Titanium has five stable isotopes, namely ^{46}Ti (8%), ^{47}Ti (7.3%), ^{48}Ti (74%), ^{49}Ti (5.5%) and ^{50}Ti (5.2%). The nuclear data of the isotopes, formed by reactor irradiation of titanium, are summarized in Table I.

The only radioactive titanium isotopes produced by reactor irradiation of pure titanium are ^{51}Ti and ^{45}Ti. Because of the short half-life (5.8 min) of ^{51}Ti, this isotope can only be a source of difficulties for the determination of those im-

TABLE I

NUCLEAR DATA OF THE ISOTOPES FORMED BY REACTOR IRRADIATION OF TITANIUM

Reaction	*Cross-section (barn)*	*Half-life*	*Decay and energy (MeV)*
^{46}Ti(n,2n)^{45}Ti	$5 \cdot 10^{-6}$	3.07 h	β^+ 1.02; EC γ 0.718; 1.238; 1.408
^{46}Ti(n,p)^{46}Sc	$8 \cdot 10^{-3}$	84 d	β^- 0.357; γ 0.8894; 1.1203
^{47}Ti(n,p)^{47}Sc	$1.5 \cdot 10^{-2}$	4.4 d	β^- 0.439; γ 0.1600
^{48}Ti(n,p)^{48}Sc	$4 \cdot 10^{-3}$	1.83 d	β^- 0.65; γ 0.9835; 1.0376; 1.3118
^{50}Ti(n,γ)^{51}Ti	0.14	5.8 min	β^- 2.13; γ 0.3200; 0.6084; 0.9285
^{50}Ti(n,α)^{47}Ca $\rightarrow$ ^{47}Sc	$4 \cdot 10^{-7}$	4.7 d (^{47}Ca)	β^- 0.67; γ 1.2969 (^{47}Ca)

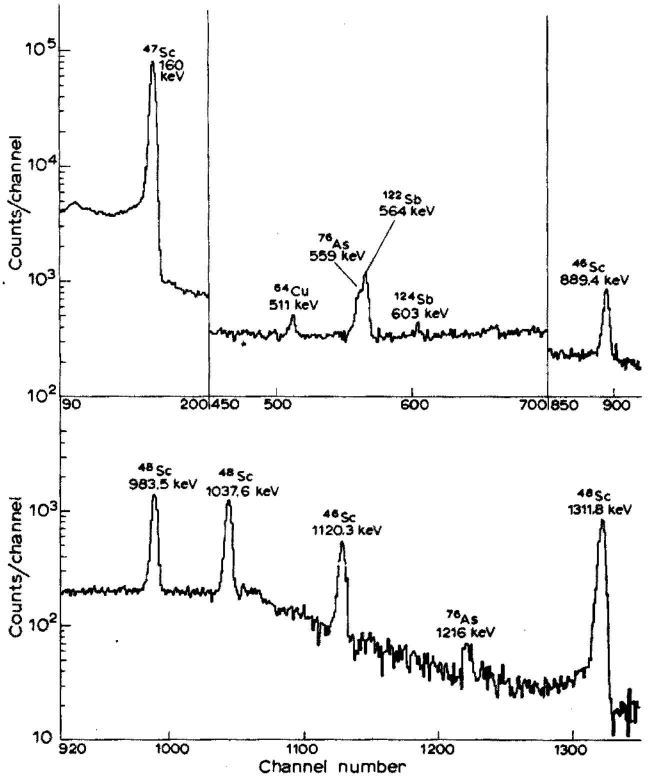

Fig. 1. γ-Ray spectrum of unseparated titanium metal four days after reactor irradiation.

purities which give rise to short-lived isotopes upon neutron irradiation. For the long-lived isotopes ($T_{\frac{1}{2}} > 2$ h), the radioactive ^{51}Ti is of no importance since a cooling period of 1 h is sufficient for the complete decay of the matrix activity. The cross-section for the formation of ^{45}Ti is too low to be of any importance.

^{46}Sc, ^{47}Sc and ^{48}Sc will contribute the major activity after a reactor irradiation. Figure 1 shows a γ-spectrum, measured during 1 h, of a titanium sample, 4 days after an irradiation of 4 h in the "Thetis" reactor, at a flux of $8 \cdot 10^{10}$ n cm^{-2} sec^{-1}.

In order to make possible accurate determinations of impurities in titanium, it will thus be necessary to remove scandium quantitatively. Moreover, a qualitative analysis of the titanium revealed a high concentration of sodium in several of the titanium sponge samples. For the simultaneous determination of a large number of trace impurities, a sodium separation, preferably simultaneous with the scandium separation, is desirable. On the other hand, some titania samples have high concentrations of antimony (0.01%). This precludes the same separation scheme being applicable for both titanium and titanium dioxide.

The nuclear data of the radionuclides, produced from trace and minor constituents of titanium metal and titanium sponge by neutron irradiation, are shown in Table II. A list of the γ-rays used for the quantitative determinations of the elements is included.

TABLE II

IMPURITIES IN TITANIUM METAL AND TITANIUM SPONGE: NUCLEAR DATA

Element	*Concn. range (p.p.m.)*	*Target nuclide*	*Reaction product*	*Activation cross-section (barn)*	*Half-life*	*γ-Radiations used (MeV)*
Na	1	^{23}Na	^{24}Na	0.54	14.8 h	1.3684; 2.7536
Cu	1	^{63}Cu	^{64}Cu	3.0	12.8 h	0.5110; 1.3455
W	0.1	^{186}W	^{187}W	34	23.9 h	0.1343; 0.4793; 0.6857
As	5	^{75}As	^{76}As	4.3	26.5 h	0.5592; 0.6570; 1.2158
Ga	10^{-4}	^{71}Ga	^{72}Ga	3.4	14.2 h	0.6301; 0.8341; 2.2014
Au	10^{-3}	^{197}Au	^{198}Au	96	2.7 d	0.4118
Sn	100	^{112}Sn	$^{113}\text{Sn} \xrightarrow{\text{EC}} {}^{113m}\text{In}$	1.3	112 d (^{113}Sn)	0.3914 (^{113m}In)
Fe	300	^{58}Fe	^{59}Fe	0.9	45.1 d	1.0986; 1.2915
Zn	1	^{64}Zn	^{65}Zn	0.25	254 d	0.5110; 1.1154
Co	0.1	^{59}Co	^{60}Co	36	5.2 y	1.1731; 1.3324
Ta	0.1	^{181}Ta	^{182}Ta	19	111 d	0.0677; 0.1003; 1.1212; 1.2216
Sb	1	^{121}Sb	^{122}Sb	3.7	2.8 d	0.5640; 0.6925; 1.1405
Mo	5	^{98}Mo	^{99}Mo	0.13	67 h	0.1406; 0.1809; 0.7399
Cr	1	^{50}Cr	^{51}Cr	11	27.8 d	0.3200
Ag	0.1	^{109}Ag	^{110m}Ag	2.8	270 d	0.6578; 0.8845; 0.9372
Ni	10	^{58}Ni	^{58}Co	0.105	71 d	0.5110; 0.8103

SELF-SHIELDING EFFECT

The self-shielding effect for a spherical sample, with radius r, can be calculated from the formula

$$f = 1 - \tfrac{3}{4} n \sigma r$$

where f = fraction of beam-intensity of an isotopic neutron flux in the middle of a sphere with radius r, of a material with absorption cross-section, σ; n = number of atoms/cm^3 = $5.5 \cdot 10^{21}$ for TiO$_2$-powder (Anatase); σ = thermal total absorption cross-section = $5.6 \cdot 10^{-24}$ cm^2.

Application of the formula leads to a 0.23% decrease in specific activity for a titanium sphere of 1 mm radius.

Experimentally, the specific activity of cobalt–aluminum alloy wire, containing 1% cobalt, placed in the middle of a titania-filled quartz-tube, was compared with that of a similar wire outside the tube. The diameter of the titania layer was 4.5 mm. No decrease in specific activity could be detected. Further, five pieces of titanium foil, each with 0.18-mm thickness, were placed on top of each other, and irradiated for 1 h at a flux of $5 \cdot 10^{10}$ n cm^{-2} sec^{-1}. After cooling for 2 h, the specific activity, from ^{56}Mn, of each of the metal foils was measured. Again, no difference in specific activity between the outer and the inner foils could be detected. It therefore appears that in titanium metal, as in titanium dioxide, there is no detectable decrease of neutron flux throughout the material.

EXPERIMENTAL

For the separation of titanium, scandium and sodium, an ion-exchange method was chosen. The strongly basic Dowex 1-X8, 100–200 mesh was used as anion-exchange resin, while a mixture containing 1 *M* hydrofluoric acid and 9 *M* hydrochloric acid was chosen as eluant. The column was made of a polythene tube, with a diameter of 1 cm and height of 25 cm.

To a solution of 100 mg of titanium metal in 15 ml of the above eluant, suitable amounts of different tracers were added. The weights never exceeded 100 μg for each element, except in the case of iron, where 500 μg were used. This solution was placed on the equilibrated column and a total volume of 40 ml of eluant solution was collected. To obtain the highest accuracy on the yield determinations, the fraction that should be free of the tracer was counted for residual activity on a NaI(Tl)-detector.

The results of the tracer experiments are shown in Table III.

The only impurities in titanium that are eluted with scandium and titanium are chromium, sodium and silver. Thus an additional separation of these elements is necessary. An identical column can be used, with 1 *M* hydrofluoric acid as the eluant. Distribution constants, listed by FARIS[6], show that in this way chromium, silver and sodium will be eluted, while scandium and titanium(IV) remain on the resin. The chromium and silver can then be determined directly, if the sodium content in the sample is not too unfavourable, otherwise a waiting-time of 1–3 days insures sufficient decay of ^{24}Na. The results of such tracer experiments are also shown in Table III.

Instrumental

Two Ge(Li)-detectors were used for the measurements. Both were of the coaxial type, with a volume of 18 cm^3 and 40 cm^3, respectively, and were constructed in this laboratory. The detectors were used with a commercial preamplifier–amplifier combination coupled to a 20 Mc analog-to-digital converter and a 4096-channel analyser. Integration and differentiation time constants were 1.6 μsec for counting

TABLE III

ELUTIONS WITH 1 *M* HYDROFLUORIC ACID + 9 *M* HYDROCHLORIC ACID AND 1 *M* HYDROFLUORIC ACID ON DOWEX 1-X8

Element	*Tracer used*	*% in 1 M HF–9 M HCl fraction (40 ml)*	*% on resin*
Ti(III) + Ti(IV)	^{51}Ti	>99.4	
Sc	^{46}Sc	>99.6	
Cr	^{51}Cr	>99.3	
Na	^{24}Na	>99.2	
As	^{76}As		>99.98
Sb	$^{122+124}$Sb		>99.3
W	^{187}W		>99.2
Cu	^{64}Cu		>99.99
Ta	^{182}Ta		>99.5
Zn	^{65}Zn		>99.8
Co	^{60}Co		>99
Fe	^{59}Fe		>98.7
Au	^{198}Au		>99
Sn	^{117m}Sn		>99.5
Mo	^{99}Mo		>99.5
Ag	^{110m}Ag	>98	
		% in 1 M HF fraction (40 ml)	
Ti(IV)	^{51}Ti		>99.3
Sc	^{46}Sc		>99.9
Ag	^{110m}Ag	>96	
Cr	^{51}Cr	>99.1	
Na	^{24}Na	>99.8	

rates not exceeding 1000 counts/sec, whereas a doubly-differentiated pulse shape was chosen to insure a symmetrical peak and to prevent any errors in the determinations caused by pulse pile-up in the case of higher count rates. To find out if the variations in dead-time for the different samples may lead to mistakes in the determinations, measurements with different dead-time corrections were made. For these, increasingly active ^{60}Co-sources were placed on the Ge(Li)-detector and the number of counts in the 1.3324-MeV photo-peak determined. The number of counts was plotted against the relative activity of the sources. For the experimental conditions used, the resulting curve deviated from the straight line only for dead-times higher than 12%. Consequently, care was taken not to exceed a 10% dead-time correction; this corresponds to 3,000 counts/sec.

The gain was adjusted to provide 1 keV per channel. The detector was shielded with a 5-cm thick lead castle. All the equipment was used in a temperature-controlled counting room (within ±0.1°). During a working day, the peak positions were thus kept constant to better than 0.2 keV. The energy resolution with the 18-cm^3 detector was 3.0 keV for the 0.6616 MeV transition of ^{137}Cs, while with the 40-cm^3 detector the resolution was 4 keV, as a result of the higher detector capacitance and the higher excess of noise from the surface leakage current.

Preparation of the standards

In view of the large number of standards to be irradiated with the samples, they were divided into 4 groups: those soluble in hydrochloric acid (CuO, Co, Fe, ZnO, Ga_2O_3, Au, NiO, Sn), soluble in ammonia (As_2O_3, Sb_2O_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, WO_3) and soluble in dilute nitric acid (Na_2CO_3, Cr_2O_3, $AgNO_3$). Tantalum was treated separately by fusion with potassium hydrogen sulfate and dissolution in oxalic acid. A solution of each group was made, containing a concentration of each element, such as to insure that peak areas of the main gammas were of comparable heights; 10 μl were placed into a quartz-tube and evaporated to dryness. The concentration of each element is shown in Table IV. After irradiation, the content of each tube was dissolved in 20 ml of hydrochloric acid, ammonia solution, water, or oxalic acid solution, and measured on the Ge(Li)-detector in the same geometrical conditions as the 20 cm³ of resin containing the trace elements.

TABLE IV

CONCENTRATION OF THE STANDARD SOLUTIONS

Solvent	*Element*	*Concn. ($\mu g/10\ \mu l$)*
6 *N* HCl	Cu	1
	Co	19
	Fe	2400
	Zn	23.5
	Ga	0.023
	Au	$0.75 \cdot 10^{-3}$
	Ni	365
	Sn	2000
6 *N* NH_4OH	As	1.35
	Sb	0.75
	W	0.17
	Mo	15
1 *N* HNO_3	Na	3.1
	Ag	1.5
	Cr	8.2
$KHSO_4$-fusion dissolved in 5% oxalic acid	Ta	1.9

Irradiation conditions

Samples of titanium (100 mg) were enclosed in quartz tubes. The irradiations were carried out in the BR-2 reactor at the S.C.K. (Mol) either at a flux of 10^{14} n cm^{-2} sec^{-1} during 15 h, or at a flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} during 1 week.

The separations were started about 24 h after the end of the irradiation. This long waiting period, caused by the transfer of the samples from Mol to Ghent, prevented the determination of short-lived species. Long-lived isotopes were measured after a decay period of 1–3 days. A typical γ-spectrum is shown in Fig. 2.

Procedure

Transfer the samples to a Teflon reaction vessel and dissolve in 15 ml of 1 *M* hydrofluoric acid + 9 *M* hydrochloric acid. Use a water-cooled polythene tube to avoid evaporation of volatile compounds. Transfer the solution to the anion-exchange column and elute with an additional 25 ml of the eluant. Extrude the resin from the column and measure on the Ge(Li)-detector.

Evaporate the eluate to dryness on a water bath. Redissolve the residue in 1 ml of 22 *M* hydrofluoric acid, dilute to 1 *M* hydrofluoric acid and place this solution on an anion-exchange column Dowex 1-X8, 100–200 mesh. Elute with an additional 20 ml of 1 *M* hydrofluoric acid.

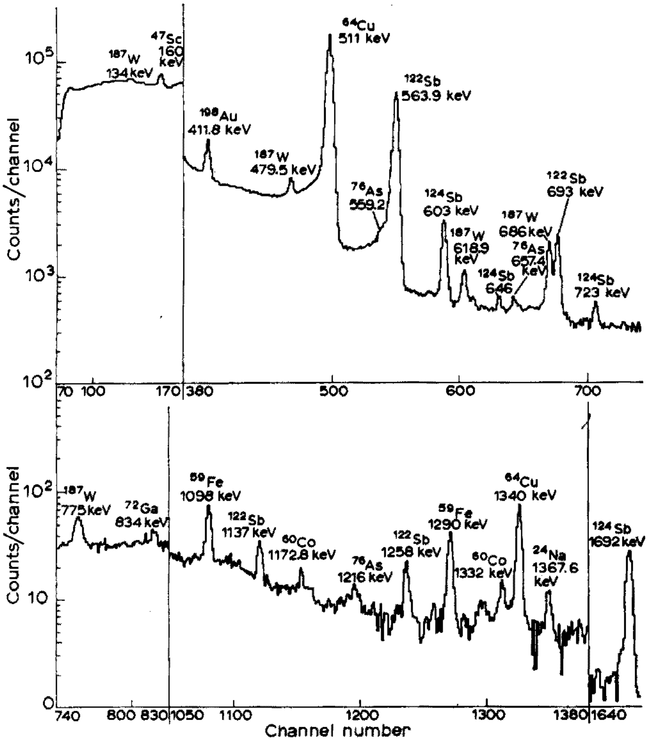

Fig. 2. γ-Ray spectrum of the impurity fraction of reactor irradiated titanium metal, after separation from Sc, Ti, Ag, Cr and Na.

Calculation of the results

The concentrations were calculated by the ratios of the photo-peak areas for samples and standards. The background was obtained by graphical extrapolation of the channels neighbouring the full energy peak. This can of course be more or less subjective. Also, the calculation of the peak areas and of confidence limits for 2048-channel γ-ray spectra is a tedious task.

A computer program developed by OP DE BEECK[7] for IBM 360-30 was therefore applied on a number of spectra. The calculation consists of a search for every statistically significant peak, after data smoothing and differentiation, followed by the calculation of the photo-peak areas. A comparison of results obtained by the program and by the manual method are given in Table V. Except for the determination of gallium, the results obtained by both methods agree within the errors caused by the counting statistics. The activity from gallium is very small, since only 268 counts are located on a background distribution of 9000 counts.

TABLE V

COMPARISON OF THE CONCENTRATIONS (p.p.m.) FOR VARIOUS ELEMENTS FOUND BY CONVENTIONAL CALCULATIONS AND A COMPUTER ROUTINE

Element	*Concn. (p.p.m.) and standard deviation*		
	IBM 360-30	*σ (%)*	*Graphical*
Cr	1.05	18.9	1.11
Au	$2.57 \cdot 10^{-3}$	1.7	$2.55 \cdot 10^{-3}$
W	0.122	12.1	0.131
Sb	4.06	3.7	3.70
As	5.33	2.5	5.19
Ga	$0.35 \cdot 10^{-3}$	30	$0.15 \cdot 10^{-3}$
Fe	454	3.8	408
Co	0.134	10.3	0.123

Calculation of lower limits

According to the convention of CURRIE[8], the number of counts, S, above the background, at the energy region of a photo-peak, is compared with the square root of the total number of counts in the background, N. If, within the energy region corresponding to the photo-peak, the ratio $S/\sqrt{N}$ is higher than 4.65, a quantitative determination can be performed. The standard deviation on such a determination varies from 30% ($S/\sqrt{N}=4.65$) to 10% ($S/\sqrt{N}=14.1$). For ratios between 4.65 and 14.1, the theoretical standard deviation is calculated. For ratios smaller than 4.65, a detection limit ($L_D=4.65\sqrt{N}$) is calculated. The lower concentration limit (C_D) is calculated from the L_D values. Concentrations higher than C_D can be determined with a standard deviation better than 30%.

TABLE VI

CONCENTRATION OF IMPURITIES IN TITANIUM FOIL

Element $S/\sqrt{N} \geqslant 14.1$	*Concn. (p.p.m.)*											
	1		*2*		*3*		*4*		*5*		$\bar{x}$	*σ (%)*
Au	$2.55 \cdot 10^{-3}$		$3.01 \cdot 10^{-3}$		$2.12 \cdot 10^{-3}$		—		—		2.56	10
As	5.19		5.48		7.74		4.67		4.98		5.61	10
W	0.131		0.130		0.115		0.170		0.133		0.136	7
Cu	37.8		37.6		35.5		34.6		36.0		36.3	2
Fe	408		283		359		368		364		356	5
Co	0.123		0.125		0.099		0.115		0.109		0.114	4
Sb	3.7		4.0		4.0		5.7		4.9		4.5	8
Cr	1.11		1.07		1.09		1.55		1.26		1.22	7
$S/\sqrt{N}>4.65$		*σ*				*σ*						
Ga	$0.15 \cdot 10^{-3}$	20%	—	—	$0.13 \cdot 10^{-3}$	20%	—	—	—	—	$0.14 \cdot 10^{-3}$	
Na	—	—	—	—	—	—	0.21	—	0.26	—	0.23	
$S/\sqrt{N}<4.65$	C_D		C_D		C_D		C_D		C_D			
Zn	0.34		0.40		0.64		0.44		0.24			
Ta	$3 \cdot 10^{-3}$		$2 \cdot 10^{-3}$		$2 \cdot 10^{-3}$		0.4		0.2			
Mo	1.8		2.6		2.2		27.2		15.8			
Ni	—		—		—		35.6		21			
Ag	0.46		0.62		—		0.2		0.2			
Ga	—		$0.8 \cdot 10^{-3}$		—		$32 \cdot 10^{-3}$		$32 \cdot 10^{-3}$			

RESULTS

Three titanium samples, one titanium foil and two titanium sponges, were analysed for Na, Cu, W, As, Ga, Au, Sn, Fe, Zn, Co, Ta, Sb, Mo, Cr, Ag and Ni.

Five analyses were made of the titanium foil. The spectrum of these isotopes, remaining on the Dowex 1-X8 resin, after the removal of Sc, Ti, Ag, Cr and Na is shown in Fig. 2. Ten elements could be detected, while for five other elements, lower limits were calculated. The results of these five analyses are listed in Table VI.

Nine elements could be detected in titanium sponge no. 1, and for seven others, lower limits were determined. The results are listed in Table VII.

Five analyses were also made on titanium sponge no. 2. Nine elements could be detected and for seven others, upper limits were calculated. The results are given in Table VIII.

The results show a good reproducibility. The more important fluctuations on the lower limit determinations are due to the variations of the Compton continuum, as the measurements were made at different times after the end of the irradiation and during different measuring times.

DISCUSSION

The results of the separations and determination of up to 16 impurities in titanium metal and titanium sponge appear to be satisfactory. The separation procedure is rapid. In one hour the elution with a solution containing 1 *M* hydrofluoric acid and 9 *M* hydrochloric acid is completed. Measurements take 30 min for the highest activities in each sample and 4 h for the lower concentrations or for less sensitive elements. The sensitivity of the method is from 10^{-4} μg (1 p.p.b. in 100 mg of sample) for gold, up to 1 μg for molybdenum and nickel.

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SUMMARY

The most important metallic impurities in titanium which give long-lived isotopes on neutron irradiation can be determined by a rapid anion-exchange separation of Ti, Sc, Cr, Na and Ag, after which the resin, containing most of the impurities, is counted on a high-resolution Ge(Li) γ-spectrometer. Cu, W, As, Ga, Au, Sn, Fe, Zn, Co, Ta, Mo and Ni can be determined in one measurement, while Na, Cr and Ag can be determined after an additional separation from the Sc isotopes, the major activities originating from titanium on neutron irradiation. Three different samples were analysed five times, and the reproducibility of the results was good.

RÉSUMÉ

Il est possible de doser les impuretés métalliques les plus importantes du titane, donnant des isotopes de longue période, par irradiation aux neutrons, avec séparation rapide par échangeur d'anions du Ti, Sc, Cr, Na et Ag. La résine contenant les

TABLE VII

CONCENTRATION OF IMPURITIES IN TITANIUM SPONGE NO. 1 (p.p.m.)

Element	*Concn. (p.p.m.)*											
$S/\sqrt{N} \geq 14.1$	*1*		*2*		*3*		*4*		*5*		$\bar{x}$	σ(%)
Na	1195		1102		1522		1018		1218		1211	7
Cu	3.71		4.52		3.91		4.10		4.40		4.13	4
As	6.9		5.9		6.6		5.3		5.3		6.0	5
Sb	4.2		3.4		5.1		3.6		4.7		4.2	7
Sn	76		105		96		83		100		92	5
Fe	21.6		25.0		22.0		23.7		32.7		25.0	8
Cr	0.160		0.166		—		0.188		—		0.171	5
$S/\sqrt{N} > 4.65$		σ (%)		σ (%)		σ (%)		σ (%)		σ (%)	$\bar{x}$	σ(%)
Au	$2.8 \cdot 10^{-3}$	19	$2.4 \cdot 10^{-3}$	28	—	—	—	—	$3.0 \cdot 10^{-3}$	26	$2.7 \cdot 10^{-3}$	6
Zn	0.3	21	—	—	0.3	25	0.5	22	0.2	27	0.3	20
Co	$19 \cdot 10^{-3}$	24	$37 \cdot 10^{-3}$	17	$32 \cdot 10^{-3}$	22	$30 \cdot 10^{-3}$	28	$24 \cdot 10^{-3}$	16	$28 \cdot 10^{-3}$	11
$S/\sqrt{N} < 4.65$	C_D		C_D		C_D		C_D		C_D			
W	$6.4 \cdot 10^{-2}$		0.17		0.11		0.11		0.13			
Ga	$5.2 \cdot 10^{-2}$		$3.6 \cdot 10^{-2}$		0.15		0.2		0.2			
Ta	0.24		0.14		0.30		0.34		0.16			
Mo	10.4		7		13.4		17.2		7.4			
Ni	14.8		10.0		18.8		24		10			
Ag	0.02		0.02		0.02		0.08		0.02			
Au	—		—		$2.6 \cdot 10^{-3}$		$2.4 \cdot 10^{-3}$		—			

TABLE VIII

CONCENTRATION OF IMPURITIES IN TITANIUM SPONGE NO. 2 (p.p.m.)

Element	*Concn. (p.p.m.)*											
$S/\sqrt{N} \geq 14.1$	*1*		*2*		*3*		*4*		*5*		$\bar{x}$	$\sigma(\%)$
Cr	2.32		1.73		2.44		1.64		2.31		2.09	7
Cu	1.33		1.70		1.16		1.47		1.53		1.44	7
As	5.0		6.3		4.9		5.4		6.0		5.5	5
Sb	5.1		5.5		4.9		5.6		5.0		5.2	8
Sn	107.5		132		—		116		144		125	6
Fe	21.4		19.9		23.8		—		22.4		21.9	4
Zn	0.7		—		0.3		—		—		0.5	—
Na	1053		987		1155		1364		1054		1123	6
$S/\sqrt{N} > 4.65$		$\sigma(\%)$		$\sigma(\%)$				$\sigma(\%)$		$\sigma(\%)$	$\bar{x}$	$\sigma(\%)$
Zn	—	—	0.6	17	—	—	0.5	24	0.5	16	—	—
Co	$1\cdot10^{-2}$	28	$1.7\cdot10^{-2}$	27	—	—	$2\cdot10^{-2}$	13	$1.7\cdot10^{-2}$	31	$1.6\cdot10^{-2}$	13
$S/\sqrt{N} < 4.65$	C_D		C_D		C_D		C_D		C_D			
W	$5.8\cdot10^{-2}$		0.2		$4\cdot10^{-2}$		0.28		$6\cdot10^{-3}$			
Ga	$4.2\cdot10^{-2}$		0.4		$4\cdot10^{-2}$		$4\cdot10^{-2}$		$4\cdot10^{-3}$			
Au	$3\cdot10^{-3}$		$2\cdot10^{-3}$		$2\cdot10^{-3}$		$4\cdot10^{-3}$		$2\cdot10^{-3}$			
Ta	0.2		0.4		0.2		0.4		0.4			
Mo	10		4		8		18		18			
Ni	14		24		12		26		24			
Co	—		—		10^{-2}		—		—			
Ag	0.02		0.02		0.04		0.02		0.03			

impuretés est comptée par spectrométrie-γ. Cu, W, As, Ga, Au, Sn, Fe, Zn, Co, Ta, Mo et Ni peuvent être dosés en une mesure, tandis que Na, Cr et Ag peuvent être dosés après une séparation additionnelle des isotopes Sc d'avec les principales activités provenant du titane, par irradiation neutronique. Trois échantillons différents ont été analysés cinq fois, la reproductibilité des résultats est bonne.

ZUSAMMENFASSUNG

Die wichtigsten metallischen Verunreinigungen im Titan, welche langlebige Isotopen bei der Neutronenaktivierung ergeben, können mit einem Anionenaustauscher schnell von Ti, Sc, Cr, Na und Ag abgetrennt werden. Danach wird das Harz, welches die meisten Verunreinigungen enthält, in einem hoch auflösendem Ge(Li)-γ-Spektrometer gezählt. Cu, W, As, Ga, Au, Sn, Fe, Zn, Co, Ta, Mo und Ni können in einer Messung bestimmt werden, während Na, Cr und Ag nach einer zusätzlichen Abtrennung von den Sc-Isotopen bestimmt werden können. Drei verschiedene Proben wurden fünfmal analysiert und ergaben gute und reproduzierbare Ergebnisse.

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INTERNAL STANDARD ACTIVATION ANALYSIS OF SILICON IN STEEL

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In the production of grain-oriented magnetic steel sheet, a rapid and precise determination of silicon is desirable, for its 3% content must be kept within 0.04% to achieve optimal physical properties. Wet chemical analysis is relatively time-consuming while the precision of most instrumental methods is inadequate. For routine silicon determination in this type of steel, a non-destructive activation analysis with 14-MeV neutrons with the reaction ^{56}Fe(n,p)^{56}Mn as an internal standard, appears attractive. The internal standard technique was introduced in activation analysis by LELIAERT *et al.*[1] and has since been applied by other authors. The use of iron as internal standard for silicon determination in steel, was proposed by WOOD AND ROPER[2].

If the element to be determined and the internal standard are homogeneously distributed throughout the sample, the method eliminates errors from variations in flux intensity and geometry, and from variations in positioning of standard and sample during irradiation and measurement. A major requirement in the internal standard method of analysis is that the ratio of the measured specific activities induced in the element to be determined and in the standard element should be constant. This condition is fulfilled if the irradiation time is short compared to the half-lives of the radionuclides of interest and if the neutron spectrum is constant, which is obviously the case for the "mono-energetic" 14-MeV neutrons. Moreover, the content of the element used as internal standard should be known and/or be constant. This is the case for grain-oriented magnetic steels, as they contain 96.3–96.8% of iron, and 3.0–3.3% of silicon, the total amount of other elements varying from 0.2 to 0.4%.

If for such samples, the precision is mainly governed by counting statistics, a relative standard deviation of about 1% can be expected if reasonably high activities are induced. An additional advantage of the internal standard method is that no weighing of the samples is required.

Flux monitoring, *e.g.*, by α-particle counting of the ^{3}H(d,n)^{4}He reaction[3] or with a low geometry BF_3 counter[4], or even a simultaneously irradiated oxygen flux monitor[5], yields a precision not better than 2–3% even for high counting rates. A precision almost exclusively determined by counting statistics can also be obtained by spinning sample and flux monitor during irradiation[6,7]. In this case, however, an intricate rotation system has to be built, and much smaller activities are induced because of the greater distance from the neutron source.

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NUCLEAR REACTIONS

When silicon is bombarded with 14-MeV neutrons, the most important radionuclide formed is ^{28}Al, by the reaction ^{28}Si(n,p)^{28}Al; ^{28}Al has a half-life of 2.3 min and emits a γ-ray at 1.78 MeV. Iron yields mainly ^{56}Mn, by the reaction ^{56}Fe(n,p)^{56}Mn; ^{56}Mn has a half-life of 2.58 h. The most important γ-rays emitted by ^{56}Mn have energies of 0.84, 1.81 and 2.11 MeV (relative intensities 100, 29.6, 15.7, respectively), each of which photopeaks can, in principle, be used for internal standardisation.

The condition of short irradiation time compared to the half-lives of the radioisotopes produced — which is a prerequisite of the internal standard method — is fulfilled by irradiation for 5 sec. A γ-spectrum of a 3% silicon steel sample, irradiated and counted under conditions similar to those used here has been given previously[5].

APPARATUS

14-MeV neutrons were produced by the ^{3}H(d,n)^{4}He reaction in a 150-kV Sames Type J accelerator, at a flux of *ca.* 10^9 n cm^{-2} sec^{-1}. Samples were transferred pneumatically *via* an aluminium tube with rectangular section. The generator and transfer system were described in detail previously[8]. The temperature in the counting room was kept constant at $23 \pm 0.5°$ to avoid drift on the counting equipment.

Samples were cylindrical, with a diameter of 26 mm, a thickness of 9 mm and a weight of about 36 g.

The counting was carried out with a 3×3 in NaI(Tl) detector (resolution 8.0%), coupled to a 400-channel analyser or two single-channel analysers with a linear amplifier.

INTERNAL STANDARDISATION WITH THE 1.81-MeV PHOTOPEAK OF ^{56}Mn

When a NaI(Tl) detector is used, the 1.81-MeV photopeak of ^{56}Mn cannot, of course, be distinguished from the 1.78-MeV photopeak of ^{28}Al. To evaluate the contribution of each radioisotope in the complex photopeak, it is possible to take advantage of the difference in half-lives by applying two successive countings of the 1.8-MeV activity.

Let $A(1)$ be the total number of counts in the 1.8-MeV region observed during the first count, starting t_1 min after the end of the irradiation; then

$$A(1) = A_{\mathrm{Si}}(1) + A_{\mathrm{Fe}}(1) \tag{1}$$

where $A_{\mathrm{Si}}(1)$ = number of counts from ^{28}Al (produced from silicon) during the first measurement; and $A_{\mathrm{Fe}}(1)$ = number of counts from ^{56}Mn (produced from iron) during the first measurement.

Let $A(2)$ be the total number of counts during the second counting, t_2 min after the end of the irradiation, for the same counting time:

$$A(2) = A_{\mathrm{Si}}(2) + A_{\mathrm{Fe}}(2) = A_{\mathrm{Si}}(1) \cdot \exp[-\lambda_{\mathrm{Si}}(t_2 - t_1)] + A_{\mathrm{Fe}}(1) \cdot \exp[-\lambda_{\mathrm{Fe}}(t_2 - t_1)] \tag{2}$$

where λ_{Si} and λ_{Fe} = decay constants of ^{28}Al and ^{56}Mn, respectively.

The ratio $A_{\mathrm{Si}}(1)/A_{\mathrm{Fe}}(1)$ equals

$$\frac{A(1)\cdot\exp[-\lambda_{\mathrm{Fe}}(t_2-t_1)]-A(2)}{A(2)-A(1)\cdot\exp[-\lambda_{\mathrm{Si}}(t_2-t_1)]} \tag{3}$$

and is proportional to the ratio of the silicon to the iron weight. Suitable correction factors can be included in eqn. (3) if the counting times for $A(1)$ and $A(2)$ are different.

Experimentally, a standard deviation of about 1.5% was found when $A(1)$ was counted during 1 min, 1 min after the end of irradiation, and $A(2)$ was counted during 4 min, 30 min after the end of the irradiation. Typical values of $A(1)$ and $A(2)$ were, respectively, 100,000 and 40,000 counts for a 5-sec irradiation at a beam intensity of 300 μA.

By carrying out the counting of $A(2)$ 10 min after the end of the irradiation in order to shorten the analysis time, the standard deviation increased to 2–2.5%. This was due to poorer statistics, because the difference between $A(1)$ and $A(2)$ decreased.

Although only one amplifier, discriminator and scaler is necessary, this method requires too long an analysis time to be suitable for industrial application.

INTERNAL STANDARDISATION WITH THE 2.11-MeV PHOTOPEAK OF ^{56}Mn

The activities in the 1.8-MeV and 2.1-MeV range can be simultaneously counted, with two single-channel analysers connected to the same detector. In the γ-spectrum of pure irradiated silicon, a small activity is, however, observed in the 2.1-MeV range; this is due to the broadening of the 1.78-MeV peak of ^{28}Al and to Compton scattering of the small 2.43-MeV photopeak of 6.6-min ^{29}Al, formed from ^{29}Si(n,p)^{29}Al. This silicon interference should be taken into account when the 2.11-MeV photopeak of ^{56}Mn is used for internal standardisation. The interference is negligible when the 2.11-MeV photopeak of ^{56}Mn is used only to evaluate the net ^{28}Al contribution in the complex 1.8-MeV peak[5]. Thus, the 2.1-MeV photopeak cannot be used directly for internal standardisation since it is not exclusively due to ^{56}Mn. The ^{28}Al contribution in the 2.1-MeV energy range can, in principle, be calculated.

Let k_{Si} be the ratio of the 1.8-MeV activity to the 2.1-MeV activity for pure silicon, and k_{Fe} be this ratio for pure iron (*ca.* 2). Let $A(1.8)$ and $A(2.1)$ be the total number of counts respectively in the 1.8-MeV and 2.1-MeV channels for a steel sample:

$$A(1.8)=A_{\mathrm{Si}}(1.8)+A_{\mathrm{Fe}}(1.8)=A_{\mathrm{Si}}(1.8)+k_{\mathrm{Fe}}A_{\mathrm{Fe}}(2.1) \tag{4}$$

$$A(2.1)=A_{\mathrm{Si}}(2.1)+A_{\mathrm{Fe}}(2.1)=\frac{A_{\mathrm{Si}}(1.8)}{k_{\mathrm{Si}}}+A_{\mathrm{Fe}}(2.1) \tag{5}$$

This system of equations leads to:

$$\frac{A_{\mathrm{Si}}(1.8+2.1)}{A_{\mathrm{Fe}}(2.1)}=(1+k_{\mathrm{Si}})\frac{A(1.8)-k_{\mathrm{Fe}}A(2.1)}{k_{\mathrm{Si}}A(2.1)-A(1.8)} \tag{6}$$

Again, this ratio is proportional to the ratio of weights of silicon and iron.

It was found, however, that the factor k_{Si} is not constant, but depends on the total activity, as pile-up occurs. For given experimental conditions, k_{Si} decreased from *ca.* 110 for an integral count rate of 100,000 counts/min to *ca.* 60 for 500,000 counts/min. The ratio, $A_{\mathrm{Si}}(1.8+2.1)/A_{\mathrm{Fe}}(2.1)$, thus becomes a complicated function of $A(1.8)$ and $A(2.1)$ since the factor k_{Si} depends on the total activity, and thus on the neutron output, the sample weight and the silicon content. Moreover, the results are strongly influenced by small shifts in gain of the counting equipment.

When samples of similar constitution and weight were analysed by this method, the neutron flux being kept as constant as possible, a standard deviation of *ca.* 1.5% was observed. The time required for one analysis cycle was about 7 min. Although the analysis time is quite short, this method can obviously not be recommended for industrial routine analysis.

INTERNAL STANDARDISATION WITH THE 0.84-MeV PHOTOPEAK OF ^{56}Mn

Several alloy elements can be expected to interfere in the 0.8-MeV energy region, either by photopeaks or by Compton scattering, *e.g.*, aluminium, chromium, manganese, copper. However, for similar steels, this method can be expected to be at least as short as standardisation with the 2.11-MeV peak of ^{56}Mn; moreover, the 0.84-MeV peak will yield much better statistics and will be less sensitive to pile-up and to small energy shifts.

In both the 0.8 and 1.8-MeV energy regions, mainly ^{56}Mn and ^{28}Al activities are measured, originating from iron and silicon. Let k_{Si} be the ratio of 1.8-MeV to 0.8-MeV activity for pure silicon (*ca.* 2), and k_{Fe} the ratio of 1.8-MeV to 0.8-MeV activity for pure iron (*ca.* 0.2). Let $A(1.8)$ be the total number of counts observed at 1.8 MeV for a steel sample, and $A(0.8)$ the total number of counts at 0.8 MeV:

$$A(1.8) = A_{\mathrm{Si}}(1.8) + A_{\mathrm{Fe}}(1.8) = A_{\mathrm{Si}}(1.8) + k_{\mathrm{Fe}}A_{\mathrm{Fe}}(0.8) \tag{7}$$

$$A(0.8) = A_{\mathrm{Si}}(0.8) + A_{\mathrm{Fe}}(0.8) = \frac{A_{\mathrm{Si}}(1.8)}{k_{\mathrm{Si}}} + A_{\mathrm{Fe}}(0.8) \tag{8}$$

This leads to:

$$\frac{A_{\mathrm{Si}}(1.8)}{A_{\mathrm{Fe}}(0.8)} = \frac{A(1.8) - k_{\mathrm{Fe}}A(0.8)}{A(0.8) - A(1.8)/k_{\mathrm{Si}}} = \frac{(A(1.8)/A(0.8)) - k_{\mathrm{Fe}}}{1 - (A(1.8)/A(0.8))k_{\mathrm{Si}}} \tag{9}$$

This ratio is proportional to the ratio of the weights of silicon to iron: $W_{\mathrm{Si}}/W_{\mathrm{Fe}}$, and thus proportional to $\%\mathrm{Si}/((100-Z)\% - \%\mathrm{Si})$, Z being the total percentage of alloy elements other than iron and silicon. If Z is known or negligible, the measurement of the 1.8-MeV and 0.8-MeV activities allows the determination of silicon. Indeed, from standards with a known silicon content, one can calculate a specific ratio, K:

$$K = \frac{A_{\mathrm{Si}}(1.8)/A_{\mathrm{Fe}}(0.8)}{W_{\mathrm{Si}}/W_{\mathrm{Fe}}} = \frac{(A(1.8)/A(0.8) - k_{\mathrm{Fe}})/(1 - (A(1.8)/A(0.8))/k_{\mathrm{Si}})}{W_{\mathrm{Si}}/W_{\mathrm{Fe}}} \tag{10}$$

The ratio of the silicon to the iron weight in an unknown sample X is obtained by dividing the normalized ^{28}Al activity by K:

$$\left(\frac{W_{\mathrm{Si}}}{W_{\mathrm{Fe}}}\right)_{\mathrm{X}} = \frac{\%\ \mathrm{Si_X}}{(100-Z)\% - \%\ \mathrm{Si_X}} = \frac{A_{\mathrm{Si}}'(1.8)/A_{\mathrm{Fe}}'(0.8)}{K}$$
$$= \frac{\left(\dfrac{A'(1.8)}{A'(0.8)} - k_{\mathrm{Fe}}\right)\Big/\left(1 - 1/k_{\mathrm{Si}} \cdot \dfrac{A'(1.8)}{A'(0.8)}\right)}{K} \tag{11}$$

If Z, k_{Fe} and k_{Si} are known, the measurement of $A(1.8)$ and $A(0.8)$ for the standards allows K to be calculated, whereas the measurement of $A'(1.8)$ and $A'(0.8)$ for the samples allows $\%\ \mathrm{Si}_x$ to be calculated.

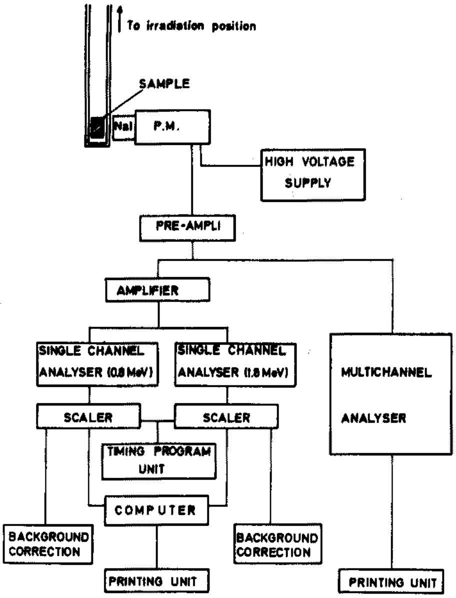

Fig. 1. Counting equipment.

Analysis cycle

With the experimental set-up shown in Fig. 1, the following analysis cycle was used:

(i) Transfer of the sample pneumatically to the irradiation position;

(ii) after the arrival of the sample: irradiation for 5 sec at a beam intensity of 300 μA by automatic pneumatic removal of the tantalum screen from the deuteron beam;

(iii) transfer of the sample automatically (pneumatically) from the irradiation site to the detection site;

(iv) after a waiting time of 90 sec, the counting of the 1.8-MeV and 0.8-MeV activities during 3 min starts automatically.

The total time required for one analysis cycle is thus *ca.* 4.5 min.

Observed counting rates were typically 100,000 counts in both energy regions for a 3% silicon steel.

With a higher neutron flux, the counting time necessary to record *ca.* 100,000 counts for each channel, can be reduced to 1.5 min, without overloading effects. Moreover, the counting can be started 60 sec after the end of the irradiation, if no appreciable interference of short-lived isotopes is expected. The total time required for one cycle is, in this case, shortened to 2.5 min.

Standards

The standards had an accurately known silicon content of about 3% and were of similar composition to the samples. The silicon content had been determined chemically by the perchloric acid method[9]. As repeated standardisation is desirable, several standards are necessary. Indeed, each sample may only be irradiated once in a 24-h period to avoid accumulation of ^{56}Mn (half-life, 2.58 h).

RESULTS

Six batches (A, B, C, D, E, F) of industrial grain-oriented magnetic steel (3% silicon) were analysed. Three discs (diameter 26 mm, thickness 9 mm) were machined from each batch. Accurate wet chemical determinations[9] were carried out on the chips and activation analyses were performed on each steel sample.

The sequence of irradiation was as follows: two standards, sample A1, sample A2, sample A3, two standards, sample B1, sample B2, sample B3, etc. The four surrounding standards were used to calculate the normalized specific activity, *K*.

Some typical data are given in Table I. The timing program was as follows: irradiation time 5 sec (beam intensity: adjusted to obtain *ca.* 100,000 for $A(0.8)$, *i.e.*, 300 μA for a new 4-Ci target with a diameter of 28 mm), waiting time 90 sec, counting time 180 sec. Results are listed in Table II.

TABLE I

TYPICAL DATA

$k_{Fe} = 0.20$ $k_{Si} = 1.80$
Standards: % Si = 3.07; $Z = 0.24\%$, thus $W_{Si}/W_{Fe} = 0.03175$

Sample	$A(1.8)$[a]	$A(0.8)$[a]	$\dfrac{A(1.8)/A(0.8) - k_{Fe}}{1 - \frac{1}{k_{Si}} A(1.8)/A(0.8)}$	*K*	$\dfrac{W_{Si}}{W_{Fe}}$[b]	*%Si*
Standard 1	110,259	102,385	2.180	68.65		
2	111,391	103,210	2.193	69.06		
Sample F1	110,847	102,789	2.188		0.03164	3.060
F2	110,070	101,456	2.224		0.03217	3.109
F3	117,791	108,455	2.231		0.03226	3.118
Standard 3	112,480	103,812	2.216	69.80		
4	115,780	107,285	2.196	69.04		
Sample A1						
A2						
A3						
etc.						

[a] Corrected for background.
[b] Calculated with the mean of the four *K*-values, nl. 69.14.

DISCUSSION

It can be seen from Table II that when four standardisations are carried out, the average value of the standard deviation for a single determination is 0.038% Si. Hence, the coefficient of variation is 1.18%. When three samples (A1, A2, A3)

TABLE II

RESULTS FOR SILICON IN STEELS

Sample	*% Si chemical*	*Mean*	*% Si activation analysis*	*Mean and S.D. for a single detn.*	
A1	3.19	3.185	3.264; 3.186; 3.148; 3.194; 3.148; 3.225; 3.180; 3.179	3.190 ± 0.039	3.195 ± 0.040
A2	3.18		3.179; 3.210; 3.183; 3.256; 3.227; 3.104	3.193 ± 0.053	
A3	3.185		3.206; 3.196; 3.178; 3.186; 3.255	3.204 ± 0.030	
B1	3.24	3.23	3.220; 3.217; 3.237; 3.199; 3.173; 3.255; 3.157; 3.287	3.218 ± 0.042	3.231 ± 0.038
B2	3.225		3.280; 3.200; 3.233; 3.248; 3.227; 3.226; 3.267; 3.221	3.238 ± 0.026	
B3	3.225		3.260; 3.220; 3.252; 3.231; 3.267; 3.203; 3.296; 3.236; 3.157	3.236 ± 0.040	
C1	3.15	3.17	3.189; 3.242; 3.192; 3.215; 3.142	3.196 ± 0.038	3.208 ± 0.036
C2	3.175		3.251; 3.256; 3.197; 3.224; 3.225; 3.181	3.222 ± 0.029	
C3	3.185		3.206; 3.244; 3.128; 3.216; 3.217	3.202 ± 0.044	
D1	3.20	3.202	3.156; 3.231; 3.122; 3.232; 3.179; 3.225	3.191 ± 0.046	3.204 ± 0.042
D2	3.215		3.279; 3.247; 3.226; 3.202; 3.176; 3.150	3.213 ± 0.047	
D3	3.19		3.231; 3.181; 3.206; 3.257; 3.172	3.209 ± 0.036	
E1	3.175	3.182	3.191; 3.182; 3.215; 3.250; 3.244; 3.179	3.210 ± 0.031	3.191 ± 0.030
E2	3.18		3.178; 3.162; 3.183; 3.199; 3.179	3.180 ± 0.013	
E3	3.19		3.179; 3.233; 3.151; 3.184; 3.153	3.180 ± 0.033	
F1	3.135	3.115	3.119; 3.096; 3.137; 3.056; 3.060	3.094 ± 0.035	3.098 ± 0.034
F2	3.100		3.085; 3.155; 3.052; 3.099; 3.109	3.100 ± 0.038	
F3	3.110		3.120; 3.147; 3.102; 3.047; 3.070; 3.118	3.101 ± 0.036	

produced from the same batch are analysed one after another, the expected coefficient of variation of the mean value is $1.18\%/\sqrt{3} = 0.68\%$.

It can be shown that for values of $A(1.8)$ and $A(0.8)$ approximately equal to 10^5 counts, $k_{Fe} \simeq 0.2$, $k_{Si} \simeq 2$, the coefficient of variation due to counting statistics is *ca.* 0.72% on eqn. (9). This same coefficient of variation on the final result (v_R)

will depend on the number of standardisations and the number of analyses on the same sample batch. It is given by

$$v_R = 0.72\sqrt{\frac{1}{n_S} + \frac{1}{n_X}} \qquad (12)$$

(n_S, n_X: number of standardisations and sample analyses).

The values of v_R for several modes of operation are listed in Table III.

TABLE III

PRECISION (%)

Sequences[a]	Counting statistics (v_R)	Computed ($v = \sqrt{v_R^2 + v_s^2 + v_c^2}$)	From Table II ($\sqrt{v_R^2 + v_s^2}$)	From chemical analysis (v_c)
SX	1.02	1.80		1.15
SSX	0.88	1.55		1.00
SXS	0.88	1.56		1.00
SSXX	0.72	1.29		0.81
SXXS	0.72	1.27		0.81
SXSXS	0.66	1.10		0.74
SSXXXSS	0.55	0.92	$1.18/\sqrt{3} = 0.68$	0.62

[a] S for a standard, X for each sample produced from the batch to be analysed.

The experimental coefficients of variation (v), also shown in Table III, were obtained by statistically analysing a total of 160 measurements, carried out over 11 days. For this purpose, no difference was made between standards and samples, as the silicon content of both was equally well known by chemical analyses. The results were listed in the order in which they were obtained. The daily coefficients of variation (v_a, v_b, ...) for each of the sequences mentioned in Table III were computed by comparing the normalized specific activities, taken in the closest possible order and moving up one measurement at a time through the series. The weighted average coefficient of variation (v) was calculated by:

$$v = \sqrt{\frac{av_a^2 + bv_b^2 + \ldots}{a + b + \ldots}} \qquad (13)$$

(a, b, c: number of analyses per day).

This can be resolved into three parts:

(i) counting statistics (v_R);

(ii) errors in the chemical analysis of the samples (v_c);

(iii) instability of the counting equipment: shift, etc. (v_s), *i.e.*,

$$v^2 = v_R^2 + v_c^2 + v_s^2 \qquad (14)$$

If one considers the average coefficient of variation for 3 analyses and 4 standardisations found from Table II, ($1.18\%/\sqrt{3} = 0.68\%$), and the coefficient of variation (v) found for the sequence SSXXXSS in Table III (0.92%), the difference between the two values is due only to the fact that the former is obtained by analysing a sample always *versus* the same standards, whereas in the latter case, the choice of standards and samples is made purely arbitrarily, as already stated above. The coefficient of variation caused by errors in the chemical analysis (v_c) is thus:

$$v_c = \sqrt{(0.92\%)^2 - (0.68\%)^2} = 0.62\%.$$

For one measurement, this same coefficient of variation, v_c, is thus

$$0.62/\sqrt{\tfrac{1}{4}+\tfrac{1}{3}} = 0.81\%.$$

The values of v_c for the other modes of analysis can be calculated by

$$v_c = 0.81 \sqrt{\frac{1}{n_s} + \frac{1}{n_x}} \tag{15}$$

Eventually, the error due to the equipment is given by eqn. (16) and was *ca.* 0.5%

$$v_s = \sqrt{v^2 - v_c^2 - v_R^2} \tag{16}$$

The expected coefficient of variation for the activation analysis ($v_{A.A.}$) is:

$$v_{A.A.} = \sqrt{v_R^2 + v_s^2} = \sqrt{v^2 - v_c^2} \tag{17}$$

The values of $v_{A.A.}$ are shown in Table IV for several modes of operation, together with the duration. Indeed, precision and duration will be a compromise. It is obvious that the duration can be reduced by reducing waiting and counting time and increasing the neutron output, but only at the cost of faster target depletion. The analysis time will, of course, be different for a single analysis and for a series, as in this case, the last standardisation(s) of a former analysis can serve for the next one.

TABLE IV

PRECISION AND DURATION

Sequence	*Expected % coeff. of variation on the activation analysis* $v_{A.A.} = \sqrt{v_R^2 + v_s^2} = \sqrt{v^2 - v_c^2}$	*Duration (min)*[a]			
		(1)	*(2)*	*(3)*	*(4)*
SX	1.4	9.5	9.5	5.5	5.5
SXX	1.2	14.3	14.3	8.3	8.3
SXS	1.2	14.3	9.5	8.3	5.5
SSXX	1.0	19	19	11	11
SXXS	1.0	19	14.3	11	8.3
SXSXS	0.8	23.8	19	13.8	11
SSXXXSS	0.68[b]	33.3	23.8	19.3	13.8

[a] (1) 5-sec irradiation, 90-sec waiting time, 180-sec counting time.
(2) As (1), but for a series of analyses.
(3) 5-sec irradiation, 60-sec waiting time, 90-sec counting time; neutron output adjusted to obtain about 10^5 counts for $A(1.8)$ and $A(0.8)$.
(4) As (3); for a series of analyses.

[b] Found from Table II, while the other values are calculated as mentioned above.

Assuming approximately equal silicon concentrations in samples and standards (*e.g.*, 3–3.4%), it can be shown that the values of k_{Fe} and k_{Si} need not be known very accurately, as they are used in the same way for the calculations of both standards and samples. If a result is, for example, recalculated with a k_{Si}-value increased by

5%, and a k_{Fe} value decreased by 5%, the error does not exceed 0.1% (relative to the 3% silicon content). This is obviously negligible.

When counting is done with single-channel analysers, the results are independent of reasonable changes (a factor of two) in the total counting rate, and thus on variations of the neutron flux. From this it can be concluded that flux normalization by means of this internal standard method is satisfactory.

Samples of different thicknesses (8.2–9.2 mm) and different diameters (25.0–26.2 mm) were analysed. No systematic deviation could be observed.

Calculations can be simplified by assuming the iron content to be constant. In this case, eqns. (10) and (11) can be replaced, for standards, by:

$$K = \frac{(A(1.8)/A(0.8) - k_{Fe})/(1 - (A(1.8)/A(0.8))/k_{Si})}{\%\ \mathrm{Si}_{st}} \qquad (10a)$$

and, for samples, by

$$\%\ \mathrm{Si}_{sample} = \frac{(A'(1.8)/A'(0.8) - k_{Fe})/(1 - (A'(1.8)/A'(0.8))/k_{Si})}{K} \qquad (11b)$$

The error incurred depends on the difference in silicon content between standard and sample. Indeed, the percentage difference, Δ, in the silicon content found *via* the simplified and the correct calculations equals:

$$\Delta = \frac{100\%}{(100-Z)\%}\left(\%\ \mathrm{Si}_{sample} \cdot \frac{(100-Z)\% - \%\ \mathrm{Si}_{standard}}{(100-Z)\% - \%\ \mathrm{Si}_{sample}} - \%\ \mathrm{Si}_{standard}\right) \qquad (18)$$

For similar steels, this can be approximated as:

$$\Delta \simeq \%\ \mathrm{Si}_{sample} - \%\ \mathrm{Si}_{standard} \qquad (19)$$

Thus, for a 3.3% silicon steel sample with a 3% silicon steel as a standard, a relative error of 3.3—3.0 = +0.3% will be incurred, *i.e.*, 3.31% of silicon will be found instead of 3.30%.

Sources of error

In standards which are irradiated repeatedly, a low ^{54}Mn activity accumulates; ^{54}Mn produced from the reaction ^{54}Fe(n,p)^{54}Mn with a cross-section of *ca.* 350 mb, has a half-life of 303 d and emits γ-rays with an energy of 0.84 MeV, that interfere in the 0.8-MeV range. A correction can easily be carried out by counting the standards after the decay of ^{56}Mn. It appeared that under the conditions mentioned above, a relative error of +1% occurs after 100 irradiations of the standards.

The NaI(Tl) detector was surrounded by a lead shield to decrease the natural background. If the detector is placed in a room where the neutron flux is not negligible, a small ^{128}I activity may build up, owing to the reaction ^{127}I(n,γ)^{128}I ($\sigma_{th} = 5.4$ b). This isotope has a half-life of 25 min and emits γ-rays of 0.46 and 0.53 MeV and β-rays of 2.12 and 1.67 MeV. Consequently, the background increase during a series of analyses will particularly interfere in the 0.8-MeV energy range. By surrounding the detector with a cadmium sheet and a 5-cm paraffin cover, this effect was reduced by a factor of *ca.* 7. On average, the background in the 0.8-MeV range is then increased by about 5 counts/3 min after a 5-sec irradiation at 300 μA. This is almost negligible.

Automatic dead-time correction is provided in most multichannel analysers (life-time mode of counting). This method is, however, inadequate in the case of short-lived radionuclides, since the counts lost during the counting cannot be "recovered" by automatically extending the clock time[10]. The built-in correction device is only adequate if the fractional dead-time is very small and/or if the clock time is much smaller than the half-life. Hence, when the average counting rate, and thus the average fractional dead-time, is larger for standards than for samples, more counts will be lost for the standards, and thus, the silicon content found will be too high. Calculations and experimental results showed that for an average fractional dead-time of 10% for the standard and 5% for the sample (*e.g.*, owing to different neutron fluxes), a relative error of *ca.* +2.2% was made after a decay of 90 sec and a 3-min counting time in life-time mode of counting. When accurate determinations are required, two single-channel analysers must be preferred to a multichannel analyser, since they are much less sensitive to dead-time losses.

Timing can be incorrect, and may be different for sample and standard. When counting is started for a standard 90 sec after the irradiation and for a sample 95 sec after the irradiation, a relative error of *ca.* −2.5% is introduced; starting after 91 sec still causes an error of *ca.* −0.5%. This source of error can easily be avoided by using an electronic programmer controlling waiting time and start-up of the counting equipment.

The carrying of aluminium from the aluminium transfer tubes by the samples was investigated, for, in a fast neutron flux, aluminium yields ^{27}Mg which has a half-life of 9.5 min and emits γ-rays of 0.84 MeV. This effect was, however, found to be completely negligible.

TABLE V

INTERFERENCES FOR 3% SILICON STEELS

Interfering element	k_x	*Calculated relative error induced (%)*	
		For 0.1% concns.	*For contents normal in grain-oriented 3% Si steel*
P	2.27	+1.9	+0.095
Al	0.02	−1.8	−0.036
Cr	0.08	−0.66	−0.112
Cu	0.08	−0.50	−0.200
Mn	0.01	−0.20	−0.140
Mg	0.48	−0.057	—
Zr	0.09	−0.05	—
V	0.13	−0.03	−0.001
Sn	0.18	−0.03	−0.002
Mo	0.33	−0.025	−0.002
Co	0.21	−0.02	—
Pb	0.53	−0.02	—
Ni	0.23	−0.015	−0.007
Ti	0.33	−0.01	—
W,S,C	—	—	—

Interferences

As can be seen from eqn. (10), impurities that yield an activity ratio for 1.8: 0.8 MeV (k_x) equal to this ratio for the sample (k_s) to be analysed (*i.e.*, for a given silicon content), will not interfere for this particular silicon content. For elements with $k_X > k_S$, positive errors will be made; if $k_X < k_S$, negative errors are made. Thus, the percent interference for a given impurity (with a given k_X) depends on k_S, and so on the silicon content of the sample for a given timing program and given energy selections; k_S was about 1 for steel samples containing *ca.* 3% of silicon when the irradiation time was 5 sec, the decay time 90 sec, and the counting time 3 min. Energy ranges were *ca.* 0.73–0.95 MeV and 1.63–2.05 MeV.

The percent errors found under these conditions on the silicon determination are listed in Table V. In the third column, the difference in impurity concentration between sample and standard is assumed to be 0.1% (absolute). The fourth column was calculated on the assumption that the impurity concentration of the sample is twice that of a normal grain-oriented 3% silicon steel used as the standard. It must be noted that errors are only made when the concentration of the impurity of interest is different for sample and standard.

The errors induced by impurity content changes appear to be completely negligible for grain-oriented 3% silicon steel.

The phosphorus interference is a special one, as, by the reaction $^{31}P(n,\alpha)^{28}Al$, the same radionuclide is formed as by the (n,p) reaction on ^{28}Si. The ^{28}Al activity induced in phosphorus is about 60% of the ^{28}Al activity induced in the same weight of silicon. It is obvious that a given phosphorus content in the sample gives rise to the same absolute error for every silicon concentration, *i.e.*, a more important relative error when the silicon content decreases.

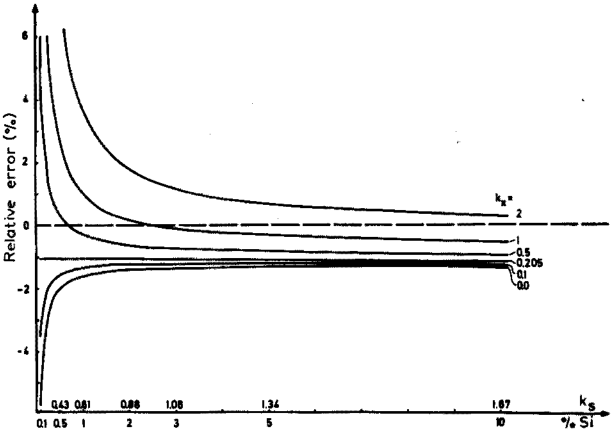

Fig. 2. Interferences by impurities with several k_X-values, as a function of the silicon content (for a given 0.8-MeV activity of the impurity).

For other elements, the variation of the percent interference as a function of the silicon content depends on the k_X-value of the interfering element.

Figure 2 represents the shape of calculated interference curves *versus* the silicon content for k_X-values of 0, 0.1, 0.205 ($=k_{Fe}$), 0.5, 1 and 2. First, consider an impurity X so that $k_{Fe} < k_X < k_{Si}$ (*e.g.*, $k_X = 0.5$ while $k_{Fe} = 0.205$ and $k_{Si} = 2.2$). If $k_S > k_X$, a negative error is made. For decreasing silicon contents, the 1.8:0.8 MeV activity ratio (k_S) decreases, approaching k_X. The relative error decreases, and even becomes zero when $k_S = k_X$; if $k_S < k_X$, *i.e.*, at lower silicon concentrations, positive errors occur. For an impurity with $k_x < k_{Fe}$ (*e.g.*, $k_x = 0.1$ in Fig. 2), however, a negative error occurs for any silicon concentration, as k_s cannot come below k_{Fe}, and thus not below k_x.

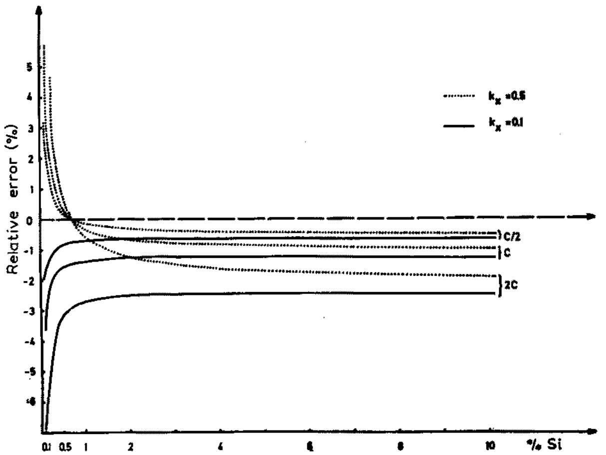

Fig. 3. As Fig. 2, but showing the influence of the impurity concn. ($c/2$, c, $2c$).

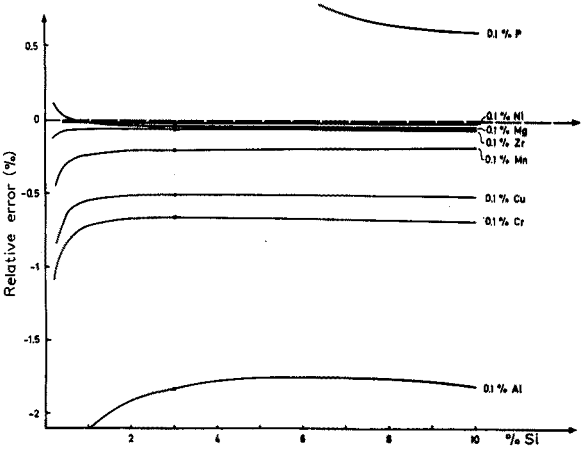

Fig. 4. Relative error caused by 0.1% of some alloy elements as a function of the silicon content.

The relative error is directly proportional to the interfering alloy element content as long as the activity induced in it is small compared to the ^{28}Al and ^{56}Mn activity. Figure 3 represents interference curves for interferences with a k_x of 0.1 and 0.5, for contents c, $c/2$ and $2c$.

Figure 4 shows the percent error curves as a function of the silicon content for some alloy elements mentioned in Table V. It can be seen that, except for phosphorus, the percent interferences calculated for a 3% silicon steel and listed in Table IV, are valid down to *ca.* 1.5% of silicon. For lower contents, the relative importance of a given difference in impurity concentration between sample and standard increases.

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SUMMARY

Non-destructive 14-MeV neutron activation analysis for silicon in steel has been applied with ^{56}Mn as internal standard. ^{56}Mn is formed from the iron matrix *via* the ^{56}Fe(n,p)^{56}Mn reaction. Several methods of internal standardisation *via* ^{56}Mn are discussed. The 0.84-MeV photopeak of ^{56}Mn is recommended if steel samples of about the same composition are to be analysed. Chemically analysed steel samples are used as silicon standards. A precision of 0.7% was obtained for an analysis plus standardisation time of 13 min. Special attention was paid to interferences produced by concentration changes of impurity elements. Several possible sources of errors were investigated.

RÉSUMÉ

Une méthode est proposée pour le dosage du silicium dans les aciers par activation au moyen de neutrons (14-MeV) avec ^{56}Mn comme étalon interne. ^{56}Mn est obtenu de la matrice de fer via la réaction ^{56}Fe(n,p)^{56}Mn. Le photopic 0.84-MeV du ^{56}Mn est recommandé si les échantillons d'acier à analyser sont d'une composition à peu près identique. Des échantillons d'acier analysés chimiquement sont utilisés comme étalon de silicium. On obtient une précision de 0.7% avec une durée d'analyse et d'étalonnage de 13 min. On examine les sources d'erreurs possibles.

ZUSAMMENFASSUNG

Silicium wurde im Stahl zerstörungsfrei durch Aktivierung mit 14-MeV-Neutronen bestimmt. Dabei wurde ^{56}Mn als innerer Standard verwendet, das durch die Reaktion ^{56}Fe(n,p)^{56}Mn in der Eisenmatrix gebildet wurde. Verschiedene Methoden des inneren Standards mit ^{56}Mn werden diskutiert. Es wird der 0.84-MeV-Photopeak des ^{56}Mn empfohlen, wenn Proben von etwa der gleichen Zusammensetzung analysiert werden sollen. Chemisch analysierte Stahlproben werden als Siliciumstandard verwendet. Es wurde eine Genauigkeit von 0.7% erhalten bei einer Standardisierungs- und Analyse-Zeit von 13 Min. Besondere Aufmerksamkeit wurde den Störungen, welche durch Konzentrationswechsel der Verunreinigungen gebildet wurden, gewidmet. Mehrere mögliche Störquellen wurden untersucht.

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THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART I. THE ANALYSIS OF SILICATE ROCKS

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During the last ten years atomic absorption spectrophotometry has become one of the most versatile methods of quantitative inorganic analysis. A detailed discussion of its use has been provided by ELWELL AND GIDLEY[1], and its applications to geological materials have been described[2].

For the decomposition of inorganic siliceous materials, hydrofluoric acid offers certain advantages which have been discussed in a previous paper[3], but the combination of decomposition by hydrofluoric acid and determination by atomic absorption spectrophotometry does not seem to have been fully utilized in the analysis of inorganic siliceous materials[2]. In a series of papers the analysis of various materials of geological and industrial interest will be described; the present paper contains the general part and methods for the analysis of silicate rocks.

The methods described are intended for the analysis of all types of inorganic siliceous materials decomposable by 38–40% hydrofluoric acid and containing, as main constituents, silicon, aluminium, iron, magnesium, calcium, sodium and potassium. In certain materials, analyses may be required for additional components, such as titanium, manganese, chromium, lead, tin, zinc, barium, zirconium, lithium, strontium, copper, vanadium and phosphorus. The determination of some of these elements has been incorporated in the present schemes. Except for phosphorus, it is highly probable that all of the constituents listed could be determined in samples decomposed by the present technique. For obvious reasons, methods for carbon dioxide, sulfide, sulfate, phosphorus, halogens, iron(II) and water are not described. Some of these components could, however, be determined, *e.g.* by spectrophotometry, in aliquot portions withdrawn from the sample solution.

The present methods are based on decomposition of a sample (normally 0.2000 g) by 5 ml of 38–40% hydrofluoric acid in a plastic vessel. After the decomposition boric acid solution* is added to dissolve precipitated fluorides, and the solution is diluted with water to a known volume (normally 100 ml). If the hydrofluoric acid, boric acid solution and water are added by pipette, the final sample solution does not have to be transferred to a volumetric flask. The atomic absorption measurements are made on the sample solution or on aliquot parts taken from it.

Interferences

Although atomic absorption has the important advantage of being practically

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* A volume of 50 ml saturated solution is normally added.

free from spectral interferences, some chemical interferences had to be taken into account in the development of the present methods. Table I lists the components for which methods will be given, the chemical interferences and disturbances encountered, and the steps taken to avoid these effects.

TABLE I

CONSTITUENTS DETERMINED, INTERFERENCES AND OTHER EFFECTS, AND THE REQUIRED PRECAUTIONS

Constituent determined	*Oxidizing gas*[a]	*Interferences etc.*	*Precautions needed*	*Ref.*
Silicon	N_2O	None		
Aluminium	N_2O	$HBF_4(H_3BO_3 + HF)$	H_3BO_3 and HF added[b]	1
Iron	air	None		
Magnesium	air	Si, Al, P	La added[c]	4
	N_2O	None		4
Calcium	air	Si, Al, P	La added[c]	4
	N_2O	Ionization	K added[c]	4
Sodium	air	Other alkalis	Cs added[c]	5
Potassium	air	Other alkalis	Cs added[c]	5
Titanium	N_2O	Al, $HBF_4(H_3BO_3 + HF)$	Al, H_3BO_3 and HF added[b]	4,6
Manganese	air	None		
Chromium	air	Fe	Fe added[b]	1
	N_2O	None		

[a] Acetylene was used throughout as the fuel gas.
[b] To standard solutions only.
[c] To both standard and sample solutions.

EXPERIMENTAL

Sampling and preparation of the sample

From the bulk material a representative sample of about 5 g passing a 120-mesh sieve is prepared according to the general rules for sampling. During these operations precautions should be taken to minimize the absorption of moisture and the introduction of contaminations from the equipment. It is recommended to use an air-dried sample for analysis, and to make a special determination of the moisture content.

Instruments

All measurements were made with a Perkin-Elmer model 303 atomic absorption spectrophotometer. Two types of burners were employed. A 3-slot Boling burner was used for acetylene–air flames and a nitrous oxide burner was used for acetylene–nitrous oxide flames.

Different types of source lamps were used. For the determination of silicon, a high-brightness lamp with a special power supply was employed; the alkalis were determined with separate arc discharge lamps. All other elements were determined with ordinary mono- or multi-element hollow-cathode lamps. The instrument was used without a recorder or a digital readout.

It should be noted that the use of other instruments, lamps or burners may necessitate changes in the present methods as to the preparation of the optimal sample and standard solutions.

Apparatus for decomposition

It is convenient to distinguish between equipment for decompositions below and above the boiling point (112.0°) of the azeotropic mixture of hydrogen fluoride and water (38.26% HF).

For decompositions below the boiling point, inexpensive plastic vessels (bottles or Erlenmeyer flasks (capacity 100–200 ml)) equipped with screw closures or stoppers, are suitable. It is recommended to use plastic materials capable of withstanding temperatures up to about 130°. The ordinary types of plastic materials, such as conventional polyethylene, general purpose polystyrene, styreneacrylonitrile and polyvinyl chloride, have temperature limits below 100°; the necessary equipment should therefore be made from linear polyethylene, polyallomer, polypropylene or polycarbonate. The latter material has the advantage of being clear.

When silicon is not going to be determined, decompositions can be done in the above heat-resistant plastic beakers loosely covered with plastic lids, with a capacity of 100–200 ml.

In some instances it may be desirable to remove completely silicon and fluorine by volatilization in the presence of perchloric acid. Because of the interfering effect of sulfate on many atomic absorption measurements, sulfuric acid should not be used for volatilization purposes. These evaporations must be made at temperatures in the range 150–250°, *i.e.* above the temperature limits for ordinary plastic materials. Polytetrafluoroethylene (PTFE) is the only plastic material which can be used at these temperatures; PTFE-beakers can be purchased or made. Evaporations can, of course, also be made in platinum vessels.

For decomposition above the boiling point of 38.26% hydrofluoric acid, and if silicon is to be determined, it is necessary to resort to a bomb technique. In the literature various types of PTFE- or platinum-lined bombs are described[3,7–11], the temperature of attack varying from 150° to 425°.

In the present work a bomb of a type previously described[1] was used; however, the inner PTFE vessel was enlarged to a volume of about 120 ml; this permitted dilution to 100 ml without transference of the solution to volumetric glassware. The bomb could be heated to a maximum temperature of $250 \pm 10°$; during the heating the contents were stirred with an electrically heated magnetic stirrer. The temperature was measured with a contact thermometer.

The plastic bottles, flasks or beakers were heated on or in an ordinary water bath (for decomposition purposes special water baths with magnetic stirrers situated in the bottom can be obtained).

Reagents

The standard solutions should be prepared from highly purified reagents. In the present investigations, the following spectrographically standardized compounds or high-purity metals (all with a purity better than 99.9%) were used. Silicon dioxide, magnesium oxide, calcium carbonate, sodium chloride and potassium chloride were obtained (Johnson, Matthey & Co., Ltd., London) as spectrographically standardized powders. Rods of aluminium and iron were supplied in the same quality from the same firm. High-purity titanium, manganese and chromium metals were obtained from A. D. Mackay, Inc., U.S.A., Electro Manganese Corp., U.S.A., and General Electric Company, U.S.A., respectively.

The reagent solutions should be prepared from chemicals of good reagent-grade quality. The following reagents were used.

Boric acid, crystals, purity 99.99%; only high-purity boric acid should be used.

Caesium chloride and potassium chloride, crystalline powders ("Suprapur" from E. Merck, Germany).

Calcium carbonate, powder. Reagent-grade qualities of calcium carbonate may contain appreciable amounts of alkali; a high-quality product, low in alkali, should be used.

Lanthanum oxide, powder. A product of purity not below 99.99% should be used.

Reagent-grade acids of the following concentrations were employed: hydrochloric acid, about 37%; hydrofluoric acid, 38–40%, maximum content of fluorosilicic acid 0.005%; nitric acid, about 65%; perchloric acid, about 70%. Twice-distilled water was used in the preparation of all solutions.

Primary standard solutions

Silicon standard solution I (2 mg SiO_2/ml). Ignite silicon dioxide to constant weight at 1150±50°, weigh 0.2000 g and transfer to a plastic bottle or flask. Add 5 ml of hydrofluoric acid by a plastic pipette, close the vessel and leave it at room temperature until the oxide is completely dissolved (a standing time of about 2 h is normally sufficient). Add 50 ml of saturated boric acid solution and 45 ml of water by pipette or burette and mix.

Aluminium standard solution I (2 mg Al_2O_3/ml). Transfer 1.0585 g of aluminium drillings to a beaker, add 50±5 ml of water and 50±1 ml of hydrochloric acid, cover the beaker and heat until the metal has dissolved. Cool the solution to room temperature, transfer to a 1-l volumetric flask and dilute to the mark with water.

Iron standard solution I (1 mg Fe_2O_3/ml). Transfer 0.6995 g of iron drillings to a beaker. Prepare the solution as described for the above aluminium solution.

Magnesium standard solution I (1 mg MgO/ml). Ignite magnesium oxide to constant weight at 700±25° and transfer 1.0000 g to a beaker. Add 25±1 ml of hydrochloric acid, cover the beaker and heat to dissolve the oxide. Cool the solution to room temperature, transfer to a 1-l volumetric flask and dilute to volume with water.

Calcium standard solution I (0.5 mg CaO/ml). Dry calcium carbonate to constant weight at 110±5°, transfer 0.8924 g to a beaker, suspend the salt in 50±5 ml of water, cover the beaker and add 50±1 ml of hydrochloric acid. Heat to boiling and boil until all carbon dioxide is removed. Cool the solution to room temperature, transfer to a 1-l volumetric flask and dilute to volume with water.

Sodium standard solution I (0.1 mg Na_2O/ml). Ignite sodium chloride to constant weight at 550±50°, transfer 0.1886 g to a 1-l volumetric flask and dissolve in water. Dilute the solution to volume with water.

Potassium standard solution I (0.1 mg K_2O/ml). Ignite potassium chloride to constant weight at 550±50°, transfer 0.1583 g to a 1-l volumetric flask, dissolve in water, and make up to the mark with water.

Titanium standard solution I (1 mg TiO_2/ml). Transfer 0.5995 g of metal to a beaker. Prepare the solution as described for the aluminium solution, except that hydrochloric acid (1+100) must be used for washing the beaker and for diluting the solution to the mark.

Manganese standard solution I (1 mg MnO/ml). Transfer 0.7745 g of the metal to a beaker, add 25 ± 5 ml of water and 25 ± 5 ml of hydrochloric acid, cover the beaker and heat until the metal has dissolved. Cool to room temperature, transfer to a 1-l volumetric flask and dilute to volume with water.

Chromium standard solution I (1 mg Cr_2O_3/ml). Transfer 0.6842 g of the metal to a beaker. Prepare the solution as described for the above aluminium solution.

Reagent solutions

Aluminium reagent solution (4 mg Al_2O_3/ml — this solution is required only for the determination of titanium in bauxite). Weigh out 2.12 g of aluminium drillings, dissolve and dilute as described above for the primary aluminium standard solution.

Boric acid solution (saturated). Weigh out 200 ± 5 g boric acid and transfer to a large beaker, add 1000 ± 50 ml of water, cover the beaker and heat until the acid has dissolved. Cool to 40 ± 10° and decant into a bottle.

Combined boric acid–hydrofluoric acid reagent solution. Mix 500 ± 5 ml of saturated boric acid solution, 50 ± 1 ml of hydrofluoric acid and 450 ± 5 ml of water in a 1-l plastic bottle.

Caesium reagent solution (10 mg Cs_2O/ml). Transfer 11.95 g of caesium chloride to a 1-l volumetric flask, dissolve and dilute to volume with water.

Calcium reagent solution (31.5 mg CaO/ml — this solution is required only for the analysis of cement, klinker, raw mix and siliceous limestone). Dry calcium carbonate at 110 ± 5° for 3 ± 1 h, transfer 56.3 g to a beaker, suspend the salt in 500 ± 50 ml of water, cover the beaker and add 100 ± 5 ml of hydrochloric acid. Boil until all carbon dioxide is removed, cool to room temperature, and dilute to 1 l in a volumetric flask with water.

Lanthanum reagent solution (50 mg La/ml). Suspend 58.7 g of lanthanum oxide in 250 ± 25 ml of water, cover the beaker and add 250 ± 5 ml of hydrochloric acid. Heat until the oxide has dissolved, cool to room temperature, and dilute to 1 l in a volumetric flask with water. The amounts of lanthanum added to the sample and standard solutions should always be taken from the same reagent solution.

Potassium reagent solution (10 mg K/ml). Dissolve 19.07 g of potassium chloride in water and dilute to 1 l in a volumetric flask with water.

Methods of decomposition

In the literature[3,7–10,12–14], data are given on the decomposition of siliceous materials in hydrofluoric acid; from these data the proper equipment and procedure can be chosen. However, it should be noted that for a number of materials the decomposibility has only been established with the use of the bomb technique. Some of these materials may also be decomposable at temperatures below the boiling point of 38–40% hydrofluoric acid.

If nothing is known about the ease of decomposition of the material to be analyzed, the following general technique is recommended.

Decomposition method 1. Many naturally occurring and industrially important siliceous materials can be readily decomposed by cold, dilute or concentrated, hydrofluoric acid. To increase the rate of attack, it is recommended to heat the reaction mixture, either on or in the boiling water bath, or in a bath maintained at 110 ± 2°; it is also advantageous to stir the reaction mixture. Many materials succumb to 15–30 min heating on the boiling water bath. The decompositions are conveniently made in plastic bottles with screw closures, or in Erlenmeyer plastic flasks with stoppers.

If a clear solution is obtained after the decomposition, saturated boric acid solution and water are pipetted into the decomposition vessel (the hydrofluoric acid was also added by pipette) and the solution is mixed.

If the decomposition results in the formation of a precipitate, boric acid solution is added by pipette and the closed decomposition vessel is reheated on the water bath until a clear solution is obtained (15–30 min is normally sufficient). The solution is cooled somewhat, 45 ml of water are added by pipette and the solution is mixed.

If the decomposition is unsuccessful, as apparent from a residue present after the treatment with boric acid, two modes of action are open, *i.e.* either to repeat the attack with material ground to a finer state of subdivision and a prolonged decomposition time, or to resort to the bomb technique described below. The former method is recommended when small amounts of undecomposed material are present, whereas comparatively large amounts call for the use of the bomb.

Decomposition method 2. The bomb technique is used to open up samples resistant to the above attack. Samples must always be finely ground.

If silicon is to be determined, the sample is attacked for 30–60 min in a PTFE-lined bomb at a temperature in the range 150–250°; during the attack the content is continually stirred with a magnetic stirrer. The bomb is then cooled to room temperature under running water and opened. The further procedure is the same as that given in decomposition method 1. After being diluted to 100 ml and mixed, the solution is transferred to a plastic bottle. If a residue of undecomposed material is visible after the first attack in the bomb, the operation must be repeated with a sample ground to an impalpable powder, and a prolonged heating time at the maximum temperature of attack.

Decomposition method 3. If silicon is not to be determined, the decompositions can be done in plastic beakers equipped with plastic covers. In such cases, the general procedure is to heat the covered beaker for about 30 min on the boiling water bath. If a clear solution is obtained, 50 ml of saturated boric acid solution are added by pipette, the solution is transferred to a 100-ml volumetric flask and immediately diluted to 100 ml with water. The sample solution is then transferred to a plastic bottle.

If a precipitate is observed after the decomposition, boric acid is added and the covered beaker is heated on the water bath until a clear solution is obtained. The solution is then cooled to room temperature, transferred to a 100-ml volumetric flask, diluted without delay to 100 ml with water and directly transferred to a plastic bottle.

Decomposition method 4. The treatment described in method 2 may fail to open up the most resistant types of siliceous materials. In such cases, the samples are first ground to the finest possible powder, and the attack is made in open evaporation dishes of PTFE or platinum with a mixture of about 5 ml of hydrofluoric acid and about 0.5 ml of perchloric acid. The reaction mixture is heated to dryness on the hot plate (with the PTFE dish the temperature must not exceed 280°). The evaporation is repeated with a new portion of hydrofluoric and perchloric acids. The residue, from which silicon and fluorine have now been quantitatively removed, is cooled and moistened with hydrochloric acid, water is added and the salts are brought into solution by heating. The clear solution is cooled to room temperature, transferred to a 100-ml volumetric flask and diluted with water to 100 ml.

General technique for atomic absorption

The instrumentation was used as suggested by the manufacturers; the gas pressures, gas flows, slits, wavelengths and other controls were adjusted to the values recommended in the manual.

After the normal zero point adjustment, a sample solution of suitable concentration is sprayed and the extinction is read or calculated. A series of secondary standard solutions is then measured, and two contiguous solutions are selected, one with a higher extinction ("upper standard") and the other with a lower extinction ("lower standard") than the sample solution. The following four series of measurements are then made: (1) zero adjustment with water, "lower standard", sample solution, "upper standard"; (2) zero adjustment, "upper standard", sample solution, "lower standard"; (3) as (1); (4) as (2).

For each series the content C (in percent by weight) of the sample is calculated from the following general equation:

$$C = A + k\frac{E_x - E_1}{E_2 - E_1}$$

where A is the % by weight in the "lower standard", k is the difference in weight percent between the "upper" and the "lower" standard, and E_x, E_1 and E_2 are the extinctions of the sample solution, the "lower standard" and the "upper standard", respectively. The arithmetical mean of the four series of measurements is finally calculated.

The content in the reagents of the constituents being determined, must be taken into account. In some measurements, the same amount of a reagent (taken from the same bottle) is present in both the sample and the standard solutions, and in these cases any interference is automatically compensated. Reagents present only in the sample solution should always be tested for impurities.

THE ANALYSIS OF SILICATE ROCKS

A large number of complete analyses of silicate rocks is carried out in geochemical laboratories. The principles of rock analysis are also followed in the analysis of various industrial raw materials and products. The partial analysis of silicate minerals and rocks by atomic absorption spectrophotometry has been described in previous papers[5,15–23].

The present methods are intended for the analysis of all types of silicate rocks decomposable by hydrofluoric acid and containing as essential components the 14 constituents normally expected. In certain rocks some components may be present in concentrations outside the range covered by the standard solutions described below; in these instances, different aliquot portions of the main solution will usually overcome the difficulty.

Methods are given for the determination of silicon, aluminium, total iron, magnesium, calcium, sodium, potassium, titanium and manganese.

Reagents and solutions

The reagents, primary standard solutions and other solutions required are listed in the general part above. The compositions of the series of secondary standard solutions are given below. Each of these series is designed to correspond to a definite dilution of the sample solution; this dilution is indicated in each case.

Secondary standard solutions

Silicon. (Sample solutions diluted 4 times) Transfer by plastic pipette 10–20 ml, in steps of 0.5 ml, of primary silicon standard solution I to plastic bottles and dilute with water to 100 ml. The series covers the range 40–80% SiO_2, in steps of 2%.

Aluminium. (Sample solutions diluted 4 times) Dilute primary aluminium standard solution I with water to give a concentration of 0.5 mg Al_2O_3/ml. Transfer 10–25 ml, in steps of 1 ml, of this solution to plastic bottles, add by plastic pipette 25 ml of the combined boric acid–hydrofluoric acid reagent solution and dilute with water to 100 ml. The series covers the range 10–25% Al_2O_3, in steps of 1%.

Iron. (Sample solutions diluted 10 times) Dilute primary iron standard solution I with water to give a concentration of 0.1 mg Fe_2O_3/ml. Transfer up to 30 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks and dilute to 100 ml with water. The series covers the range up to 15% Fe_2O_3, in steps of 1%.

Magnesium. Dilute primary magnesium standard solution I with water to give a concentration of 0.01 mg MgO/ml. Transfer up to 30 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution and dilute to volume with water. If sample solutions are diluted 10 times, this series covers the range up to 1.5% MgO in steps of 0.1%; if the sample solutions are diluted 100 times, the series covers the range up to 15% MgO, in steps of 1%.

Calcium. Dilute primary calcium standard solution I to a concentration of 0.02 mg CaO/ml with water. Two series of secondary standard solutions are prepared. Prepare Series I by transferring up to 30 ml, in steps of 2.5 ml, of the diluted primary standard solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution and dilute to the mark with water. If sample solutions are diluted 10 times, Series I covers the range up to 3% CaO, in steps of 0.25%.

Prepare Series II similarly by transferring 3–12 ml, in steps of 1 ml, of the diluted primary standard solution to 100-ml volumetric flasks, etc. With 100-fold dilution of the sample solution, Series II covers the range 3–12% CaO, in steps of 1%.

Sodium. (Sample solutions diluted 100 times) Dilute sodium standard solution I to a concentration of 0.01 mg Na_2O/ml with water. Transfer up to 16 ml, in steps of 1 ml, of this solution to 100-ml volumetric flasks, add 10 ml of caesium reagent solution and dilute to volume with water. The series covers the range up to 8% Na_2O, in steps of 0.5%.

Potassium. (Sample solutions diluted 50 times) Dilute potassium standard solution I to a concentration of 0.01 mg K_2O/ml with water. Transfer up to 32 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks, add 10 ml of caesium reagent solution and dilute to volume with water. The series covers the range up to 8% K_2O, in steps of 0.5%.

Titanium. (Undiluted sample solutions) Dilute primary titanium standard solution I to a concentration of 0.1 mg TiO_2/ml with water. Transfer up to 30 ml, in steps of 2 ml, of this solution to plastic bottles, add a volume of primary aluminium standard solution I corresponding approximately to the amount of aluminium present in the sample solution, add by plastic pipette 5 ml of hydrofluoric acid, add 50 ml of saturated boric acid solution and finally add water to give a final volume of 100 ml. The series covers the range up to 1.5% TiO_2, in steps of 0.1%.

Manganese. (Undiluted sample solutions) Dilute primary manganese standard solution I to a concentration of 0.01 mg MnO/ml with water. Transfer up to 90 ml, in steps of 10 ml, to 100-ml volumetric flasks and dilute to volume with water. The series covers the range up to 0.45% MnO, in steps of 0.05%.

Procedure

If nothing is known about the ease of decomposition of the rock sample, decompose 0.2000 g of the rock by decomposition method 2. Make the separate determinations as follows.

Determine titanium and manganese in the main solution. For the determination of silicon and aluminium, pipette 25 ml of the main solution into a dry plastic bottle, add 75 ml of water by pipette or burette and mix well.

Determine iron by pipetting 10 ml of the main solution into a 100-ml volumetric flask and diluting to the mark with water.

Determine sodium and potassium in the solution prepared for the determination of iron. Determine sodium or potassium by pipetting 10 ml or 20 ml, respectively, into a 100-ml volumetric flask, add 10 ml of caesium reagent solution and dilute to 100 ml with water.

Determine magnesium and calcium by pipetting 10 ml of the main solution into a 100-ml volumetric flask, add 10 ml of potassium reagent solution and dilute the solution to volume with water. This dilution is suitable for samples containing up to about 3% CaO and 1.5% MgO. Higher contents of one or both of these components call for a further dilution, made as follows. Pipette 10 ml of the solution prepared for the determination of magnesium and calcium into a 100-ml volumetric flask, add 9 ml of potassium reagent solution by pipette or burette, and dilute to 100 ml with water.

Determine silicon, aluminium, magnesium, calcium and titanium with an acetylene–nitrous oxide flame; for the determinations of iron, sodium, potassium and manganese, use an acetylene–air flame. Measure and calculate the results as described above in the general part.

Applications

The present methods were used in the analysis of the U.S. Geological Survey reference samples G-2 (a granite) and W-1 (a diabase). The results of these analysis are given in the Tables II and III; for comparison these tables also contain published and preferred values.

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TABLE II

ANALYTICAL DATA FOR U.S. GEOLOGICAL SURVEY REFERENCE SAMPLE G-2 (A GRANITE)

Split/Position 88/30
The analyses were made on an air-dried sample with a content of moisture of 0.16%

Sample No.	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Na as Na_2O (%)*	*K as K_2O (%)*	*Ti as TiO_2 (%)*	*Mn as MnO (%)*
1	69.28	15.85	2.71	0.756	1.86	3.96	4.51	0.43	0.034
2	69.59	15.51	2.73	0.751	1.82	4.01	4.49	0.46	0.032
3	68.92	15.44	2.69	0.741	1.81	3.87	4.34	0.47	0.034
4	68.81	15.59	2.71	0.730	1.85	4.32	4.62	0.44	0.033
5	68.91	15.63	2.67	0.762	1.82	3.87	4.32	0.46	0.033
Averages	69.10	15.60	2.70	0.748	1.83	4.00	4.45	0.46	0.033
Standard deviation	0.32	0.15	0.02	0.013	0.02	0.18	0.12	0.02	0.0008
Relative deviation	0.46	0.96	0.75	1.7	1.1	4.5	2.7	4.3	2.3
Published values[a]	69.20	15.42	2.67	0.75	1.95	4.05	4.46	0.48	0.04

[a] Taken from F. J. FLANAGAN, *Geochim. Cosmochim. Acta*, 31 (1967) 289, Table 2, Conventional analysis of Split/Position 20/16.

TABLE III

ANALYTICAL DATA FOR U.S. GEOLOGICAL SURVEY REFERENCE SAMPLE W-1 (A DIABASE)

The analyses were made on an air-dried sample with a content of moisture of 0.15%

Sample No.	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Na as Na_2O (%)*	*K as K_2O (%)*	*Ti as TiO_2 (%)*	*Mn as MnO (%)*
1	52.64	15.50	11.53	6.67	10.63	2.12	0.609	1.08	0.166
2	52.69	15.26	11.29	6.68	10.92	2.13	0.606	1.10	0.171
3	52.52	15.14	11.20	6.59	10.67	2.12	0.599	1.07	0.172
4	52.66	15.16	10.92	6.47	10.77	2.09	0.595	1.08	0.167
5	52.72	15.27	11.10	6.53	11.15	2.10	0.584	1.09	0.164
Averages	52.65	15.27	11.20	6.59	10.83	2.11	0.598	1.08	0.167
Standard deviation	0.09	0.15	0.22	0.09	0.21	0.02	0.009	0.01	0.003
Relative deviation	0.17	0.98	2.0	1.4	1.9	0.95	1.5	0.92	1.8
Preferred values[a]	52.64	14.85	11.17	6.62	10.96	2.07	0.64	1.07	0.16

[a] Taken from M. FLEISCHER, *Geochim. Cosmochim. Acta*, 29 (1965) 1263.

SUMMARY

The analysis of various inorganic siliceous materials of geological and industrial interest is discussed. The methods proposed are based on decomposition of a single sample by hydrofluoric acid and determination by atomic absorption spectrophotometry of up to 10 constituents. General procedures are described, and details are given for the determination of silicon, aluminium, total iron, magnesium, calcium, sodium, potassium, titanium and manganese in silicate rocks. Analytical data are given for the analysis of reference rocks G-2 and W-1.

RÉSUMÉ

On examine l'analyse de divers produits inorganiques silicieux présentant un intérêt géologique et industriel. Les méthodes proposées sont basées sur la décomposition de l'échantillon par l'acide fluorhydrique et dosage de 10 constituants au moins par spectrophotométrie par absorption atomique. Des procédés généraux sont décrits; des détails sont donnés pour le dosage du silicium, de l'aluminium, du fer total, du magnésium, du calcium, du sodium, du potassium, du titane et du manganèse dans des roches silicatées. Des résultats d'analyse sont donnés pour des roches étalons G-2 et W-1.

ZUSAMMENFASSUNG

Es wird die Analyse anorganischer, silikatischer Materialien mit der Flammenabsorptionsanalyse beschrieben. Dazu wird nur eine Probe in Flusssäure gelöst und bis zu 10 Bestandteilen nacheinander bestimmt. Das allgemeine Verfahren wird beschrieben und besondere Angaben zur Bestimmung folgender Elemente gemacht: Silicium, Aluminium, Eisen, Magnesium, Calcium, Natrium, Kalium, Titan und Mangan. Die analytischen Werte für die Standardgesteine G-2 und W-1 werden angegeben.

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A RAPID AND SPECIFIC DETERMINATION OF TRACES OF PLUTONIUM WITH A RECORDING SPECTROPHOTOMETER

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Plutonium in aqueous solution in the mg/l range is usually determined by α-counting or photometry. The α-counting method suffers from the drawback that the presence of a high overall salt concentration or of other α-emitters such as americium necessitates preliminary separations. For the photometric determination[1-3] several reagents have been proposed and molar extinction coefficients as high as 140,000 have been reported[1], but these reagents (arsenazo III and chlorophosphonazo) are inselective and uranium interferes strongly, so that chemical separations are again necessary.

It is well known that plutonium(VI) has a strong absorption band at 831 nm. This band is in principle very convenient for the determination of plutonium in the presence of other elements, because its position in the near infrared diminishes the chance of overlapping by absorption bands from accompanying elements or complexes. If the spectrum in the wavelength interval containing the 831-nm band is recorded, a graphical correction for background absorption can be applied. The sharpness of the peak, however, is inconvenient because the observed absorbance is dependent on the slit width of the spectrophotometer. Moreover, it necessitates the use of a recording spectrophotometer.

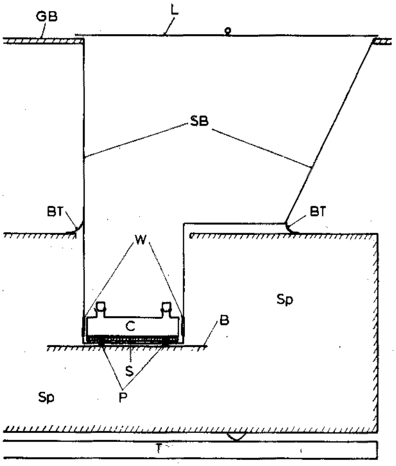
The detailed study carried out to assess the possibilities of the above measurement for a rapid and relatively simple determination of microgram amounts of plutonium in solutions of widely varying compositions, is described in this paper. It should be noted that the concentrations of the various valency states of plutonium in aqueous solutions are usually determined from the characteristic bands in the absorption spectra of the different ionic species[4-7].

EXPERIMENTAL

Apparatus

The spectra were recorded with a Beckman DK-2A recording spectrophotometer, scale expansion being possible for the measurement of low absorbances. This instrument does not allow double beam operation with preset slit widths, but the value of the slit width can be read continuously.

In view of the health hazards caused by the extreme toxicity of plutonium, all solutions containing this element were kept sealed off from the environment. This was done by substituting a closed stainless steel box provided with four quartz windows for the standard sample holder of the spectrophotometer (Fig. 1). The box was welded directly to the bottom plate of a glove box placed partly over the spectrophotometer. All preparative work and handling of samples was carried out in this glove box and in similar boxes connected with it. The spectrophotometer was placed on a table, the height of which could be hydraulically adjusted, so that the spectrophotometer could easily be freed for work with inactive substances and for maintenance.



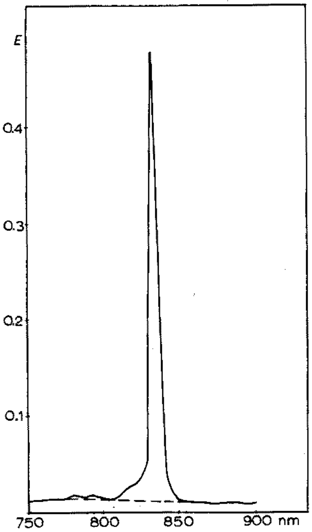


Fig. 1. Arrangement of spectrophotometer under the glove box. GB: Glove box bottom. L: Lid. SB: Stainless steel box. BT: Black tape. W: Windows. C: 10-cm cell. S: Support for cell. B: Bottom of spectrophotometer sample compartment. P: Positioning pins. Sp: Spectrophotometer. T: Table.

Fig. 2. Absorption band of plutonium(VI) in 4 *N* nitric acid.

TABLE I

THE DEPENDENCE OF PLUTONIUM(VI) ABSORBANCE AT 831 NM ON NITRIC ACID CONCENTRATION

HNO_3 concn. (*N*)	1.98	2.90	3.87	4.85	5.87
Pu(VI) absorbance[a]	0.481	0.478	0.467	0.445	0.397

[a] Absorbance measured at constant slit width; 2.88 mg Pu(VI)/ml.

Selection of conditions

The oxidation of plutonium to the hexavalent state was accomplished with silver(II) oxide[8] in nitric acid medium as described by LINGANE AND DAVIES[9]. The reagent was prepared as described by CORPEL AND REGNAUD[10].

Nitric acid (4 *N*) was chosen as the medium for the measurements because the absorbance is then not very sensitive to small variations in acidity (Table I). Furthermore, this acidity makes it possible to take relatively large aliquots of sample solutions which are strong in nitric acid. Finally, the effect of potential interferences such as fluoride and phosphate, is reduced as they are largely transformed to undissociated acids. The solutions were found to be stable for at least 24 h and to withstand boiling for 1 h.

A typical spectrum of plutonium(VI) in the 800 nm region is shown in Fig. 2; the wavelength of the peak maximum lies at 831 nm. In order to obtain a reproducible interpolation of the base line, as drawn in Fig. 2, the spectrum should be recorded in the interval from 750 to 900 nm.

Interferences

Two types of interference are possible: species can interfere by chemical interaction, *e.g.* by formation of plutonium complexes, or their absorption spectra may interfere with the measurement of the plutonium peak. Common anions such as sulphate, phosphate, chloride, fluoride, and oxalate belong to the first group. Oxalate is rapidly destroyed by the oxidation; if large amounts of reducing anions are present, consumption of excessive amounts of silver(II) oxide may be avoided by using this reagent in combination with persulphate, but the amount of persulphate is restricted by the criteria for interference of sulphate. The presence of chloride ions is immediately evident from the appearance of a precipitate at the oxidation step; once this precipitate has been centrifuged off, the analysis can be carried on without difficulty. The effects of the other anions on the determination of 0.35–5 mg of plutonium are listed in Table II. Phosphate and sulphate up to 5 mmoles can be tolerated; the absorbances found in the presence of higher concentrations of these ions are rather erratic, and

TABLE II

EFFECT OF ANIONS ON PLUTONIUM DETERMINATION (the absorbance values listed in the last column apply to the slit widths at which the corresponding absorbances in the fourth column have been measured)

Anion	*Anion concentration mmol/50 ml*	*Plutonium concentration mg/50 ml*	*Absorbance in presence of anion*	*Absorbance in absence of anion*
PO_4^{3-}	5	3.69	0.700	0.690
	25	3.69	0.728	0.690
	45	2.68	0.493	0.446
	50	3.69	0.709	0.676
	50	4.79	0.899	0.820
	50[a]	4.79	0.790	0.820
	110	2.68	0.527	0.452
	350	2.68	0.254	0.446
SO_4^{2-}	5	4.79	0.828	0.820
	25	3.69	0.625	0.696
	50	4.79	0.773	0.820
	50[a]	4.79	0.697	0.830
	50[b]	4.79	0.565	0.820
F^-	2	0.35	0.056	0.056
	4	0.35	0.032	0.056
	10	0.35	<0.002	0.056
	6[c]	0.54	0.083	0.082
	25[d]	0.54	0.080	0.082

[a] In presence of 34 mmol of $Al(NO_3)_3$.
[b] In presence of 68 mmol of $Al(NO_3)_3$.
[c] In presence of 7.5 mmol $Al(NO_3)_3$.
[d] In presence of 25 mmol $Al(NO_3)_3$.

addition of a complex-forming metal such as aluminium has little effect. As little as 4 mmoles of fluoride interferes, but even at higher concentrations, the addition of enough aluminium restores the observed absorbance to its normal value. Solutions with high fluoride concentrations were measured in cells made from polyvinylchloride and fitted with transparent windows (thickness 2 mm) of the same material. The absorbance due to such a cell varies smoothly between 0.18 and 0.40 in the wavelength interval 400–1100 nm.

Cations fall only into the second group of interfering substances, except for uranium which at high concentrations had a detrimental effect on the oxidation of plutonium by silver(II) oxide. The results of measurements carried out in the presence of various metals are listed in Table III. The interference of manganese is due to the slope in the base line caused by the permanganate absorption band; the improved value after 20 h results from slow decomposition of the permanganate. The absorption caused by 10 mg of permanganate in 50 ml lifts the base-line absorbance to about 0.350. The resulting error of only 0.030 in the plutonium absorbance may be considered good proof of the advantage of the base-line technique.

TABLE III

EFFECT OF METALS ON PLUTONIUM DETERMINATION (the absorbance values listed in the last column apply to the slit widths at which the corresponding absorbances in the fourth column have been measured)

Metal	*Metal concentration mg/50 ml*	*Plutonium concentration mg/50 ml*	*Absorbance in presence of metal*	*Absorbance in absence of metal*
U	25	0.054	0.0118	0.0115
	25	0.054	0.0101	0.0115
	100	0.14	0.0240	0.0295
	100	2.68	0.455	0.459
	250	2.68	0.459	0.459
	500	2.68	0.455	0.459
	1000	2.68	0.450	0.459
Mn	2.50	2.68	0.454	0.454
	5.00	2.68	0.451	0.454
	10.00	2.68	0.423	0.454
	10.00	2.68	0.442[b]	0.454
Mixture[a]		1.75	0.344	0.340

[a] A mixture containing 72 mg each of U and Th, and 15 mg each of Al, Ce, Co, Cr, Cu, Fe, Mo, Ni, V, Zr in 50 ml.

[b] After 20-h standing.

RECOMMENDED PROCEDURE

Make the sample solution containing from 0.01–7 mg of plutonium 4 *N* in nitric acid, taking care that the final volume does not exceed 40 ml. Add with stirring enough silver(II) oxide to give a black colour that persists for 5 min. After 5 min, heat slowly to near boiling until the colour has disappeared. Cool, transfer to a 50-ml volumetric flask, and make up to volume with 4 *N* nitric acid. Record the absorption spectrum of this solution from 750 to 900 nm in a 10-cm cell, against 4 *N* nitric acid as a blank. Read the slit width at the moment that the recorder indicates the maximum of the absorption peak. Construct the base line on the recorded spectrum and measure the difference in absorbance between the peak maximum and the corresponding background. If scale expansion is used, convert the transmission values measured into absorbance values before making the background correction. From the plutonium absorbance thus determined and the measured slit width determine the amount of plutonium with the aid of either calibration graphs or an equation (see below).

Calibration graphs

A series of calibration curves was constructed by the above method. For different values of the slit width, different calibration curves were obtained (Fig. 3). For 0.014–7 mg of plutonium per 50 ml of final volume, the absorbances varied between 0.0030 and 0.975. The calibration curves were verified by measurements on solutions prepared from N.B.S. plutonium standard no. 949 a.

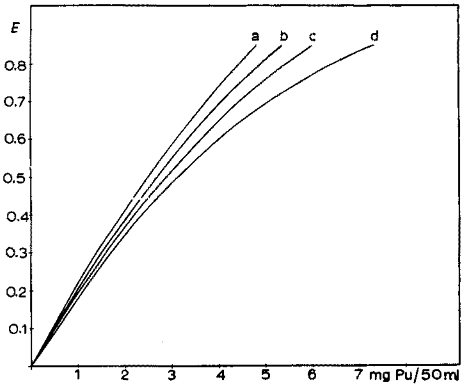


Fig. 3. Calibration graphs for the determination of plutonium(VI) at 831 nm. Slit widths: (a) 0.035 mm, (b) 0.040 mm, (c) 0.045 mm, (d) 0.050 mm.

Because the slit width is a variable, a numerical expression relating the observed absorbance to plutonium concentration and slit width was sought. Figure 3 shows that, for each slit width, the relation between concentration, C, and absorbance, E, can be represented by

$$E = \mathrm{e}C + \mathrm{d}C^2 \qquad (1)$$

where e and d are constants. Furthermore, it was found that

$$\mathrm{e} = \mathrm{a} + \mathrm{b}F \qquad (2)$$

where F is the slit width and a and b are constants.

From a combination of these equations and a least-squares calculation involving 153 observations, the following equation was found:

$$E = 0.307\,C - 2.29\,FC - 0.0107\,C^2 \qquad (3)$$

where E is the absorbance measured in a 10-cm cell, C is the concentration expressed in mg/50 ml, and F is the slit width in mm.

DISCUSSION

When C is expressed in moles per litre, eqn (3) becomes

$$E \cdot 10^{-4} = 0.368\,C - 2.74\,FC - 152.3\,C^2 \qquad (4)$$

From this equation, the molar absorptivity, extrapolated to zero slit width and zero concentration, amounts to 368; this figure agrees well with the values varying between 500 and 300 found in 2 N nitric acid for other instruments[5,7].

The precision of the method was determined by calculating the standard. deviation $s\{C_0\}$, of a concentration C_0, determined with the aid of eqn (2) according to

$$s\{C_0\} = \frac{C_0}{E}\sqrt{s_E{}^2 + C_0{}^2 b^2 s_F{}^2} \qquad (5)$$

where s_E = standard deviation of an absorbance measurement, E = measured absorbance corresponding to C_0, and s_F = standard deviation of a slit width reading. $s\{C_0\}$ was found to be 0.007 mg/50 ml for the C_0-range from 0.01 to 0.35 mg/50 ml and so the coefficient of variation varied from 35 to 2%. For the C_0-range from 0.35 to 7.0 mg/50 ml, $s\{C_0\}$ varied from 0.010 to 0.137 mg/50 ml whereas the coefficient of variation was constant and amounted to 1.7%.

The limit of detection, δC, can be defined as[11]

$$\delta C = \frac{1.645\,C\,s_E}{E} \qquad (6)$$

For the lower concentration range the factor C/E can be considered constant for a given slit width, thus the quadratic term in eqn (3) can be neglected. For an s_E-value of $14 \cdot 10^{-4}$ it was found that δC increases regularly from 0.009 to 0.012 mg of plutonium per 50 ml as the slit width increases from 0.020 to 0.050 mm.

From the above results, the scope of the method can be defined as 0.01–7 mg of plutonium per 50 ml, when 10-cm cells are used. Obviously, the scope can be extended to higher concentrations by using cells with shorter optical paths. Equations (1) and (2) can still be used provided that the measured absorbance is substituted in it and the calculated concentration, C_0, is multiplied afterwards by the ratio of the optical path length of the 10-cm cell to that of the cell used. This procedure is valid while in the system described the apparent deviations from Lambert's law and from Beer's law are identical. A detailed paper on this matter will be published later.

SUMMARY

A spectrophotometric method for the determination of plutonium in the range of 0.2–140 mg/l is described. The method is based on the measurement of the absorption of plutonium(VI) at 831 nm. A recording spectrophotometer with variable slit width, 10-cm cells and scale expansion facilities, is necessary. Uranium up to 20 g/l does not interfere.

RÉSUMÉ

On décrit une méthode spectrophotométrique pour le dosage du plutonium dans le domaine de 0.2 à 140 mg/l. La méthode est basée sur la mesure de l'absorption du plutonium(VI) à 831 nm. Un spectrophotomètre enregistreur, muni d'une fente de largeur variable et connue, et avec possibilité d'expansion d'échelle est indispensable. On doit d'autre part pouvoir y adapter des cuves de 10 cm. L'uranium ne gêne pas tant que sa concentration ne dépasse pas 20 g/l.

ZUSAMMENFASSUNG

Eine spektrophotometrische Methode für die Bestimmung von Plutonium in dem Bereich von 0.2 bis 140 mg/L wird beschrieben. Die Methode gründet sich auf die Messung der Absorption des Plutonium(VI) bei 831 nm. Ein registrierendes Spektrophotometer mit ablesbarer Spaltbreite, 10-cm-Küvetten und der Möglichkeit, die Skala zu spreizen, ist unbedingt erforderlich. Uran stört nicht bis zu 20 g/L.

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DI-2-PYRIDYLKETOXIME, A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

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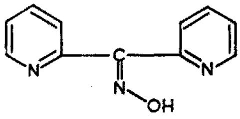
Numerous spectrophotometric methods have been proposed for the determination of iron[1-3]. Of these, the *o*-phenanthroline method[4] is well established for the determination of traces of iron in a variety of substances, but this reagent cannot tolerate large amounts of copper, nickel, cobalt, tin, tungstate or phosphate and a strict pH control is necessary especially if more than one of the ions are present with iron. The molar absorptivity of the *o*-phenanthroline complex is $1.1 \cdot 10^3$ compared to $1.5 \cdot 10^3$ for the di-2-pyridylketoxime complex.

o-Phenanthroline contains the atomic grouping, $-N{=}C{-}C{=}N-$, which has found widespread application in the determination of iron. Other reagents in this class are 2,2′-bipyridine[5], phenyl-2-pyridylketoxime[6], and 2,4,6-tripyridyl-s-triazine[7].



I

Di-2-pyridylketoxime (I), which also contains the above characteristic grouping, has been reported as a new reagent for the spectrophotometric determination of gold[8], palladium[9], and cobalt[10]. It also gives a highly sensitive colour reaction with iron(II) in an alkaline citrate medium. One of the objects of this investigation was to establish a simple and rapid procedure for the determination of trace amounts of iron(II) in the presence of large amounts of copper, nickel and cobalt.

Di-2-pyridylketoxime has the advantages that its ethanolic solution is stable indefinitely, soluble in hot water, and that its symmetry precludes syn and anti isomers. Furthermore, the ketone is commercially available and preparation of the oxime is simple and rapid.

EXPERIMENTAL

Apparatus

Spectral studies and light absorbance measurements were made with a Hitachi Perkin Elmer model 139 spectrophotometer and a Beckman DB spectrophotometer equipped with a Sargent model SRL recorder attachment. All absorption measurements were obtained with matched silica cells of 1 cm path length. The pH studies were made with a Corning model 12 pH meter equipped with standard glass–calomel electrodes. A Buchler universal electrophoresis cell was used for the electrophoresis experiment.

Reagents

Preparation of di-2-pyridylketoxime. The parent ketone was either prepared[8,11] or purchased (Aldrich Chemical Co.) and converted directly to the oxime by refluxing for 5 min with hydroxylamine hydrochloride. The oxime was used as a 1% solution in 95% ethanol. The solution is colourless and indefinitely stable towards light. The water-soluble dihydrochloride salt of di-2-pyridylketoxime was also prepared by dissolving the oxime in hydrochloric acid, evaporating to dryness, and vacuum drying. Analysis: calcd. for $C_{11}H_{11}ON_3Cl_2$: 45.55% C, 4.07% H, 26.06% Cl; found: 45.38% C, 4.06% H, 26.05% Cl.

Standard iron solution. The standard iron solution was prepared by dissolving electrolytic iron wire in dilute hydrochloric acid and diluting to 1 l with twice distilled water. This solution was further diluted to give a standard solution of 10 μg of iron/ml.

Other reagents. Reagent-grade chlorides or nitrates were used to make solutions of diverse cations, and potassium or sodium salts for anion solutions, unless otherwise specified. ACS grade sodium citrate and hydroxylamine hydrochloride were used without further purification.

Spectral characteristics of the complex

The absorption spectra of the aqueous iron(II)–di-2-pyridylketoxime complex were determined at various pH values between 3.0 and 14.0 in dilute potassium hydroxide or hydrochloric acid media. The complex exhibited absorption maxima at 524 nm at pH 3.2, 527 nm at pH 6.2 and 534 nm at pH 12.5 with a sharp increase in the absorbance at the higher pH. That the absorption maxima shift with an increase in pH is evidence for more than one type of complex produced. At pH 6.5 the complex is completely extracted into methylene chloride but not extracted into a variety of solvents at pH 10.5–13.5. Furthermore, at the lower pH a precipitate forms when the complex is heated but in highly alkaline conditions (pH 10.5–13.5) colour development is increased and stable even in boiling solution.

Continuous variations and molar ratio studies also indicated that more than one species is formed when a large excess of reagent is not present. When excess of reagent is present, the probable species is a 3:1 ligand: iron anionic complex of the type FeL_3^-. An ionic complex is inferred by its high solubility in water and its non-extractability into organic solvents[12,13] at the optimum pH 10.5–13.5. That the complex is anionic, was proved conclusively by its anodic migration in a filter paper electrophoresis experiment.

The absorption maximum at 534 nm was employed in all subsequent investigations and at this wavelength there was no absorption due to reagent (Fig. 1). Beer's law is obeyed up to 4.0 p.p.m. of iron; the molar absorptivity at 534 nm is $1.5 \cdot 10^3$ and the Sandell sensitivity[14] is 0.0027 μg cm^{-2}.

Effect of pH

The effect of pH was studied by developing the complex for 20–30 min at almost boiling temperature, transferring to 25-ml volumetric flasks and recording the absorbance at 534 nm. The results are summarized in Table I. The optimum pH range is 10.5–13.5.

Development of complex

At the optimum pH range of 10.5–13.5, the iron(II)–di-2-pyridylketoxime complex is completely developed after 15 min at almost boiling temperature on a hot plate. Heating for 1 h also gave satisfactory results. Low absorbance readings were obtained unless the complex was heated for at least 15 min. When no heating was employed, colour development was incomplete even after 1 h.

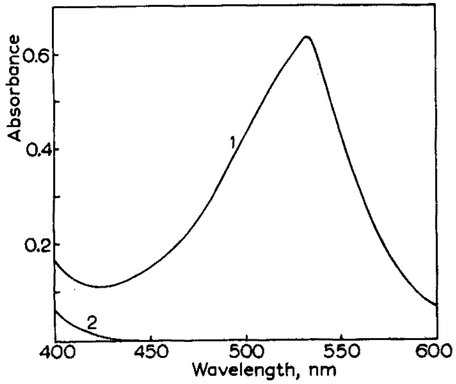


Fig. 1. Absorption spectra of iron(II)–di-2-pyridylketoxime complex (2.4 p.p.m.). (1) Complex *vs.* reagent blank, (2) reagent *vs.* water.

TABLE I

EFFECT OF pH ON ABSORBANCE

(534 nm, 1.6 p.p.m. iron)

pH	*Absorbance*	*pH*	*Absorbance*
5.0	Precipitate	11.7	0.423
7.4	Precipitate	12.7	0.423
8.2	0.394	13.0	0.427
9.1	0.402	13.7	0.424
10.1	0.418	>14	0.364
10.7	0.424		

Effect of reagent

A large excess of reagent (1% in 95% ethanol) was used. There was no significant change in absorbance when 1 ml or 5 ml of the reagent solution was used.

Stability of the complex

The colour of the complex was found to be stable for 24 h in direct light and after 1 week the absorbance decreased by approximately 5%. In the dark, the complex was stable for at least 2 weeks.

Reproducibility of the method

The reproducibility of the method was studied by replicate analyses of solutions containing known amounts of iron. The relative standard deviations of absorbances are summarized in Table II.

TABLE II

REPRODUCIBILITY DATA

Experiment	*Iron taken (p.p.m.)*	*Absorbance*	*Rel. S.D. (%)*
1	0.40	0.110	1.82
2	1.60	0.426	0.70
3	2.80	0.738	0.27

Recommended procedure

Dissolve the sample by appropriate means and place an aliquot containing 6–60 μg of iron into a 100-ml beaker. Add 1 ml of 10% hydroxylamine hydrochloride to reduce all the iron to iron(II). Add 2–3 ml of 40% sodium citrate to complex most metals and 2 ml of 1% reagent solution. Adjust the pH to 10.5–13.5 with dilute potassium hydroxide or hydrochloric acid and heat almost at boiling for 20–30 min. Cool, transfer to a 25-ml volumetric flask, and dilute with distilled water to the mark. Prepare a blank similarly. Measure the absorbance at 534 nm and read off the amount of iron from a previously prepared calibration curve.

TABLE III

FOREIGN IONS

Ion	*Maximum tolerable concentration (p.p.m.)*	*Ion*	*Maximum tolerable concentration (p.p.m.)*	*Ion*	*Maximum tolerable concentration (p.p.m.)*
Acetate	4000	F^-	400	$P_2O_7^{2-}$	4000
Al^{3+}	200	Ga^{3+}	200	Pt^{4+}	20
As^{3+}	200	Hf^{4+}	10	Re^{7+}	100
Au^{3+}	6	Hg^{2+}	10	Rh^{3+}	10
Ba^{2+}	200	Ir^{3+}	10	Sb^{3+}	200
Be^{2+}	16	K^+	200	SCN^-	4000
Bi^{3+}	200	Li^+	200	Se^{4+}	200
BO_3^-	1000	Mg^{2+}	200	Sn^{4+}	200
Br^-	4000	Mn^{2+}	200	SO_4^{2-}	4000
Ca^{2+}	200	MoO_4^{2-}	200	$S_2O_8^{2-}$	4000
Cd^{2+}	200	Na^+	200	SO_3^{2-}	4000
Ce^{3+}	60	Nb^{5+}	80	$S_2O_3^{2-}$	4000
Citrate	40000	Ni^{2+}	900	Sr^{2+}	200
ClO_4^-	4000	NH_4^+	200	Ta^{5+}	10
Co^{2+}	20	NO_2^-	4000	Tartrate	8000
CO_3^{2-}	4000	NO_3^-	3000	Th^{4+}	100
Cr^{3+}	50	Os^{8+}	40	Ti^{3+}	2
$Cr_2O_7^{2-}$	100	Oxalate	4000	Tl^+	200
Cu^{2+}	900	Pb^{2+}	200	WO_4^{2-}	200
EDTA	10000	Pd^{2+}	1	Zn	200
		PO_4^{3-}	200	Zr	40

Effect of diverse ions

A large number of foreign ions was studied to make the procedure as diversified as possible. Sodium citrate, EDTA, or potassium cyanide proved to be very satisfactory for masking most metals under alkaline conditions. The interference of ions was studied by adding various cations or anions to 40 μg of iron (1.6 p.p.m.) and following the outlined procedure; a maximum error of 2% was considered tolerable. The results are summarized in Table III. For copper and nickel ions, a larger excess of reagent was used and after normal colour development, potassium cyanide was added which destroyed the di-2-pyridylketoxime complexes of nickel and copper but not the iron complex. Magnesium, calcium, strontium, barium, and zinc were masked with 5 ml of 5% EDTA solution. Cerium and thorium were masked with 1.7 ml of 1% sodium fluoride solution. Molybdenum, osmium, arsenic, rhenium, and selenium were added as their oxides.

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SUMMARY

Di-2-pyridylketoxime is proposed for the spectrophotometric determination of iron(II). The complex is stable and exhibits an absorption maximum at 534 nm in an alkaline citrate medium. Beer's law is obeyed and the molar absorptivity is $1.5 \cdot 10^3$. Large amounts of copper and nickel can be tolerated. The method is simple, convenient and reproducible.

RÉSUMÉ

On propose l'utilisation de la di-2-pyridylcétoxime pour le dosage spectrophotométrique du fer(II). Le complexe est stable et présente un maximum d'absorption à 534 nm en milieu citrate alcalin. La loi de Beer est suivie; l'absorption molaire est de 1.5×10^3. Le cuivre et le nickel ne gênent pas. Cette méthode est simple et reproductible.

ZUSAMMENFASSUNG

Zur spektralphotometrischen Bestimmung von Eisen(II) wird Di-2-pyridylketoxim vorgeschlagen. Der Komplex ist stabil und besitzt in alkalischer Citratlösung ein Absorptionsmaximum bei 534 nm. Das Beersche Gesetz wird befolgt. Die molare Extinktion beträgt 1.5×10^3. Grosse Mengen von Kupfer und Nickel sind zulässig. Die Methode ist einfach, bequem und reproduzierbar.

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A RAPID AND ACCURATE DETERMINATION OF TRACE QUANTITIES OF SULPHUR IN TIN

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The demands for pure materials of all types are increasing daily, and tin is no exception. A particularly undesirable contaminant of tin is sulphur. The usual chemical methods for the analysis of very low levels of contamination are inadequate since the standard deviation is frequently of a similar order of magnitude.

During the past decade a relative-conductimetric method has been developed for the determination of sulphur in ferrous[1] and organic[2] materials, which involves the combustion of the sample in oxygen. The evolved sulphur dioxide is absorbed in a conductivity cell containing acidified hydrogen peroxide and the change in conductivity is a measure of the sulphur content of the material. This paper describes an extension of this technique to handle the low concentrations of sulphur found in refined tin.

EXPERIMENTAL

Apparatus

Unglazed porcelain boats (5 cm × 1 cm × 1 cm) (H. Wösthoff O.H.G. Bochum, Germany);

Wösthoff Sulmhograph 12, Sulphur Analyser (0–20 p.p.m.);

Wösthoff Gas Dosing Device, consisting of a cascade of gas dilution pumps.

Reagents

Absorption reagent: 0.5 ml of 30% (w/w) hydrogen peroxide per litre of 0.002 *N* sulphuric acid (both analytical-reagent-grade).

Microanalytical-reagent-grade sulphanilic acid.

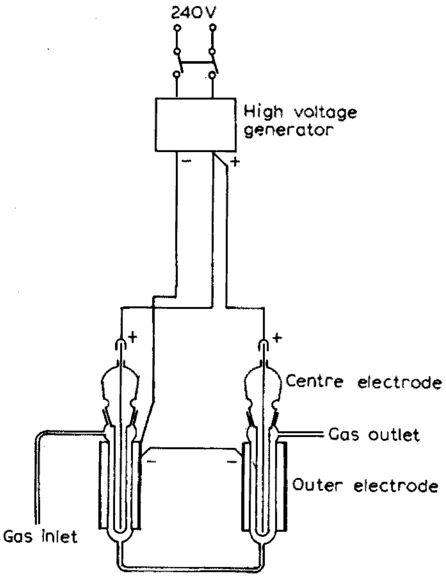
Procedure

Reduce the tin to fine turnings. Wash well with acetone to remove any grease, and dry. Place a porcelain boat in the secondary furnace tube and condition in oxygen at 1350° for 10 min. Remove the boat and allow it to cool. Accurately weigh *ca.* 1 g of tin and transfer to the boat, distributing the turnings evenly. Fill the conductivity cell and introduce the boat into the combustion tube (1350°).

Combustion is complete in a few seconds. Calibrate the instrument against sulphur dioxide with the dosing device, or by burning accurately weighed 300–500 μg quantities of sulphanilic acid in a platinum crucible.

Electrostatic filter

Exploratory experiments revealed the disastrous effects of tin(IV) oxide carry-over into the absorbing solution, because of the high combustion temperature needed and the high gas flow for which the instrument is designed. A porous plug filter rapidly became sealed by the finely divided oxide particles. An electrostatic filter was designed and found to be satisfactory.



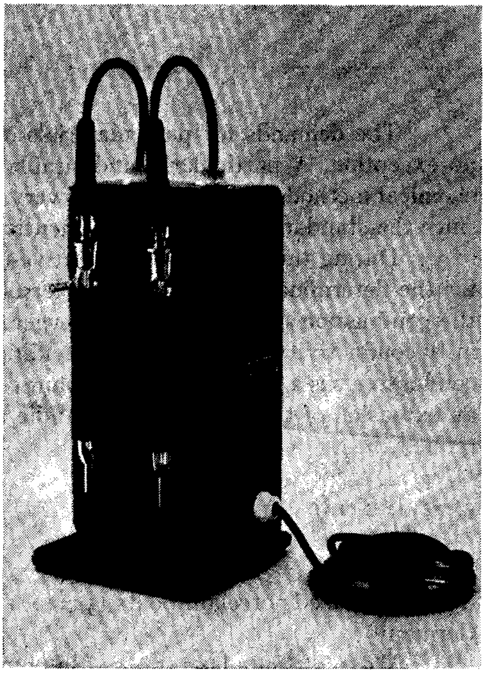


Fig. 1. Arrangement for electrostatic precipitator.

Fig. 2. Electrostatic precipitator.

The high voltage (5–10 kV) for the filter is produced by a transistor generator and is rectified (see Figs. 1 and 2). This filter has a maximum gas throughput of 100 l/h, a maximum dust extraction of 150 mg/min and a maximum dust loading of 1 g. There is no pressure drop across the filter. Before operation the ground joints are greased and secured and the high voltage leads attached. The apparatus is ready for use 20–30 sec after switching on.

Although the apparatus was designed for operation with the two units in series, one is usually sufficient and advantageous in that the idle unit can be dismantled for cleaning. When two units are used in series the filter efficiency is dependent on the cleanliness of the first unit since the main load is on this filter. Cleaning is achieved by dismantling each unit and either brushing or blowing out the deposit.

RESULTS

A series of tin samples was investigated in accordance with the method described and the results were evaluated by calculation of the standard deviation and the coefficients of variation.

The three types of tin used can be classified as follows: commercial-grade tin, sulphur-doped tin, and analytical-reagent tin. The commercial grades of tin investigated were: wire, foil and granular tin. These materials are used as a flux in the combustion of steel during analysis. Table I summarises the results obtained for sulphur.

TABLE I

ANALYSIS OF COMMERCIAL-GRADE TIN

Sample	*Mean value* $\bar{x}$ *(p.p.m. S)*	*Standard deviation s (p.p.m. S)*	*Coefficient of variation v (%)*
Tin-wire	5.1	0.7	12.7
Tin-foil	3.0	0.6	21.7
Tin-granule	3.0	0.3	8.7

When the analysis of commercial-grade tin proved successful, an investigation was carried out to explore the possibility of analysing material with higher levels of contamination. This involved the development of a method for the preparation of samples containing up to *ca.* 100 p.p.m. sulphur. The procedure adopted was as follows.

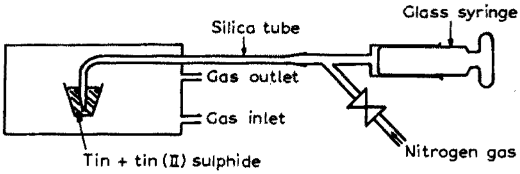


Fig. 3. Schematic arrangement of doping apparatus.

The required amounts of tin(II) sulphide and analytical-reagent-grade tin chippings were weighed into a porcelain crucible and were melted at 600° under an atmosphere of 90% nitrogen:10% hydrogen. Nitrogen gas was also slowly bubbled through a silica tube into the melt to ensure adequate mixing (Fig. 3). After a suitable melting time, the flow of nitrogen was stopped and the sample sucked into the silica tube with the aid of the glass syringe. The tube was then immediately withdrawn and water-quenched to obviate inhomogeneity, and the silica cracked away.

In this manner samples were prepared containing *ca.* 10, 25, 50 and 100 p.p.m. sulphur. Electron-probe microanalysis of the 100-p.p.m. sample gave no evidence of inhomogeneity. The results from ten consecutive analyses of three individual samples are given in Table II. The final column gives the comparative results for Sample 3 obtained by the methylene blue method.

The sensitivity of the relative-conductimetric method is dependent on the concentration of the sulphuric acid in the absorbing solution. It was therefore important to determine the concentration giving the optimum conditions of sensitivity and precision. A series of analyses was carried out on the following samples of low sulphur content: sample 4 doped tin (10 p.p.m. S), sample 5 refined tin, and sample 6 analytical-reagent tin.

TABLE II

ANALYSIS OF SULPHUR-DOPED TIN

(Results expressed as p.p.m. S)

Analysis	*Sample 1*	*Sample 2*	*Sample 3*	*Sample 3 MB-method*
1	24.9	42.4	101.1	96
2	24.9	42.9	100.4	88
3	24.3	42.6	103.3	81
4	24.3	43.2	112.9	100
5	22.9	45.1	111.5	108
6	23.7	43.4	108.6	105
7	23.5	43.0	108.1	106
8	22.8	42.8	114.1	107
9	23.8	44.2	112.3	108
10	22.7	45.1	114.3	104
$\bar{x}$ p.p.m. S[a]	23.8	43.5	107.7	100.3
s p.p.m. S	0.8	1.0	5.1	9.3
v %	3.4	2.2	4.7	9.3

[a] For symbols used, see Table I.

TABLE III

ANALYSIS OF LOW-SULPHUR TIN. OPTIMUM CONDITIONS FOR SENSITIVITY AND PRECISION

	Relative-conductimetric method									*Methylene blue method*		
	Sample 4			*Sample 5*			*Sample 6*					
	a[a]	*b*[b]	*c*[c]	*a*	*b*	*c*	*a*	*b*	*c*	*4*	*5*	*6*
$\bar{x}$ p.p.m. S	8.9	8.4	8.6	1.5	1.5	1.6	0.9	0.9	1.0	8.7	1.0	0.8
s p.p.m. S	0.4	0.2	0.5	0.3	0.1	0.1	0.1	0.2	0.1	1.5	0.4	0.3
v %	4.5	2.1	5.8	20	8.2	6.3	13	22	10	17	40	38

[a] Solution *a* 0.002 *N* sulphuric acid.
[b] Solution *b* 0.0002 *N* sulphuric acid.
[c] Solution *c* 0.0001 *N* sulphuric acid.

Three absorbing solutions were used: (*a*) 0.002 *N*, (*b*) 0.0002 *N*, and (*c*) 0.0001 *N* sulphuric acid. For each absorbing solution, samples 4, 5 and 6 were each analysed ten times in the random sequence: 465655454444466665446556564565. This sequence was followed for each series. The samples were also analysed by the methylene blue method in the same sequence. Table III summarises the results.

The values for solution *a* were obtained from one instrument standardised against sulphanilic acid, whilst those for solutions *b* and *c* were from a second instrument standardised against sulphur dioxide. The results from the methylene blue method are given for comparison.

A reduction in the sulphuric acid concentration from 0.002 N to 0.0002 N gave an increase in sensitivity from 0–200 μg for full-scale deflection to 0–20 μg, together with a decrease in the standard deviation; a further reduction to 0.0001 N (0–10 μg) showed a slight increase of the standard deviation. A sulphuric acid concentration of 0.0002 N is therefore recommended for maximum precision.

Although the precision of the methylene blue method is very good, that of the relative-conductimetric method is superior. It can be seen that the mean values obtained by the two techniques agree. Since the techniques are entirely different and were calibrated against unrelated standards it must be assumed that, within the limits of precision, the results are accurate.

Methylene blue method

The tin was dissolved in dilute hydrochloric acid in a distillation flask. The liberated hydrogen sulphide was absorbed in a buffered solution of zinc acetate and was then reacted with *p*-aminodimethylaniline sulphate in the presence of dilute hydrochloric acid and iron(III) chloride. The intensity of the resulting methylene blue colour was then determined spectrophotometrically. Calibration was by means of standardised solutions of sodium sulphide.

Time for analysis

A single analysis by the methylene blue method takes approximately 30 min after standardisation whilst the instrumental method takes 5–10 min.

The authors wish to thank Professor G. WAGNER, *Institut für Analytische Chemie und Microchemie der T.H.-Wien*, for designing the prototype electrostatic precipitator, Messrs. H. WÖSTHOFF O.H.G., Bochum, Germany, for providing the drawing and the photograph of the electrostatic precipitator, and the *Central Analytical Laboratory, Pilkington Brothers, Ltd., St. Helens, Lancashire*, for its co-operation in carrying out the methylene blue analyses. N.A.M. and B.R.C. wish to thank the Directors of Pilkington Brothers, Ltd., for permission to participate in this publication, and Mr. H. COLE for his encouragement and for making facilities available.

SUMMARY

A method is described which permits the determination of 1–100 p.p.m. of sulphur in metallic tin. It is based on the complete combustion of the sample in a stream of oxygen and the determination of the change in electrical conductivity produced by the absorption of the gaseous combustion products (SO_2) in a suitable reaction liquid. Gas-borne tin(IV) oxide dust is removed from the oxidation products by electrostatic precipitation. The new technique is shown to be superior to the widely used methylene blue method.

RÉSUMÉ

Une méthode est décrite permettant le dosage du soufre (1–100 p.p.m.) dans l'étain métallique. Elle est basée sur la combustion complète de l'échantillon, dans un courant d'oxygène et sur la mesure de la variation de conductivité électrique, produite par absorption des produits de combustion gazeux (SO_2) dans un réactif approprié. La poussière d'oxyde stannique est séparée des produits d'oxydation par précipitation électrostatique. Cette nouvelle technique se montre supérieure à la méthode bien connue au bleu de méthylène.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, mit der 1–100 p.p.m. Schwefel in metallischem Zinn bestimmt werden können. Dazu wird die Probe im Sauerstoffstrom vollständig verbrannt und der durch die Absorption von SO_2 in einer geeigneten Flüssigkeit hervorgerufene Wechsel der elektrischen Leitfähigkeit bestimmt. Zinnoxidstaub wird durch elektrostatischen Abscheidung von den Oxydationsprodukten abgetrennt. Diese neue Technik ist besser als die Methylenblau-Methode.

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A RE-EVALUATION OF HYDROXYLAMMONIUM ACETATE AS A CARBONYL REAGENT — THE EFFECT OF DIELECTRIC CONSTANT CHANGE ON TITRATION END-POINTS

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Many of the procedures for the analysis of aldehydes and ketones involve oximation. Hydroxylammonium acetate[1], hydroxylammonium formate[2,3] and hydroxylammonium chloride[4] have been studied as oximating reagents in recent years. The hydroxylammonium acetate reagent[1] provides a simple and useful method for carbonyl analysis in the presence of organic acids. However, this procedure has been criticized because of reagent instability and poor potentiometric endpoints, particularly in the case of aliphatic ketone analysis[2,3].

The purpose of this work is to re-examine the HIGUCHI AND BARNSTEIN[1] procedure, particularly with a view toward the points under criticism. The question of reagent stability is considered from the original kinetic data[1] and the products are identified. Finally, the quality of the endpoint is quantitatively evaluated; improved endpoints are sought by the use of inert solvent–acetic acid titration media.

EXPERIMENTAL

Apparatus

The potentiometric titrations were performed with the automatic titrator and titration vessel described previously[5].

The following glass electrodes were used: Beckman (40498), Corning (476022), Leeds and Northrup (117169). The reference electrode was a Beckman inverted sleeve calomel electrode (43462), the saturated aqueous potassium chloride solution having been replaced by 0.1 *M* acetous lithium perchlorate.

Sargent Model V oscillometer for measurements of dielectric constant.

Sargent Model S-84810, thermostatic bath, ±0.005°, Thermistor detector, Thermonitor, reactor controlled.

Chemicals and solutions

Hydroxylammonium acetate (Eastman White Label) was stored in a vacuum desiccator.

Triphenylguanidine (Matheson, Coleman and Bell) was recrystallized twice from ethanol and dried under vacuum (m.p. 144.5°).

Diacetylhydroxylamine (m.p. 87.5–89°, lit. m.p. 89°) was synthesized by the method of HANTZSCH[6].

Acethydroxamic acid was prepared by two methods.

Equal volumes of saturated barium hydroxide solution and an alcoholic solution of diacetylhydroxylamine (10 mg/ml) were mixed and allowed to stand for 1 h to insure sufficient hydrolysis[7].

The second method was similar to a published procedure[8], but more concentrated reagents were used in order to obtain a sufficient level of product for chromatographic studies. Ethyl acetate (1 ml) was diluted to 25 ml with methanol. A 1-ml aliquot of the methanolic solution was diluted to 20 ml with anhydrous ether. The hydroxylamine hydrochloride was prepared as directed. The ether solution of the ester (10 ml) was then mixed with 6 ml of the hydroxylamine reagent and the mixture was allowed to stand for 30 min before use.

In both of these procedures, no attempt was made to isolate the product but the subsequent chromatographic studies verified its presence.

Glacial acetic acid (Fisher Certified Reagent) was stored in a 2-l flask equipped with a glass tubing inlet–outlet arrangement which permitted the acid to be dispensed by dry air pressure.

Acetous perchloric acid titrant was prepared by the acetic anhydride method described by FRITZ[9] and was standardized against triphenylguanidine.

All other chemicals were reagent or White Label grade. Liquids were distilled under reduced pressure immediately before use.

Procedures

Paper chromatographic studies. These were accomplished with circular chromatographic chambers, Whatman No. 1 paper, and the technique described by MEDWICK *et al.*[10]. A butanol–acetic acid–water (4:1:5) system[11] was used. The detection reagent, 3% iron(III) chloride in ethanol, produced purple colored bands with hydroxylamine, acethydroxamic acid and diacetylhydroxylamine.

The chromatographic studies of the reaction kinetics were conducted on samples of acetous hydroxylammonium acetate solution, *ca.* 0.15 *N*, which were kept in a constant temperature mineral oil bath set at 50.0°, 60.0° or 80.0° ± 0.05°, as desired. Samples were removed from the thermostatted flask by pipette and frozen solid until ready for chromatography. The sample sizes taken for chromatography were usually 0.02 ml.

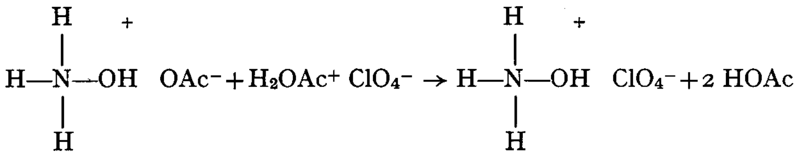
Karl Fischer water determinations. A Leeds and Northrup model 7401 pH indicator[12] was used. Although the system is usually swept with nitrogen during the entire titration, it was found that a much better endpoint was obtained when the flow of gas was not continued during the titration. Potential readings were taken 10 or 15 sec after the addition of each 0.5-ml increment of titrant. A plot of potential *vs.* volume was obtained and the line indicating potential change was extrapolated to the volume axis. This extrapolated value was taken as the end-point.

Procedure for determination of carbonyl. Two 10-ml aliquots of either 0.5 *N* or 0.75 *N* acetous hydroxylammonium solution were transferred to two 100-ml volumetric flasks. Then 2.5 or 3.75 meq of carbonyl compound, respectively, was added to one flask, leaving the other as a blank. After sufficient time for complete oximation had elapsed[1], the solutions were diluted to volume. Three 10-ml samples of blank solution were withdrawn, transferred to 250-ml titration vessels, diluted with 50 ml of acetic acid and covered; a second group of three 10-ml blank samples were taken but were diluted with 20 ml of acetic acid and 30 ml of benzene or carbon tetrachloride (other solvent mixtures could be used, if desired). The carbonyl-containing solution was sampled and treated identically. These solutions were titrated potentiometrically with standard acetous perchloric acid, *ca.* 0.1 *N*.

THEORY

The effect of dielectric constant on a chemical reaction may be qualitatively predicted[13]. In general, reactions leading to the elimination of charge proceed more favorably in low dielectric constant solvents whereas the production of charge is inhibited in these media. No effect should be noted when a system undergoes no change in the charge make-up of reactants *versus* products; however, the nature of the transition state may cause some small change, as is noted later[14].

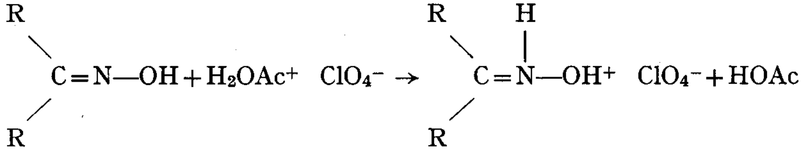
The reactions encountered in the carbonyl method under study may be interpreted with respect to the effect of dielectric constant. The neutralization of residual hydroxylammonium acetate with perchloric acid is common to the analysis of each of the various types of carbonyls. Since hydroxylamine has a pK_b (H_2O) value of 6.03 [15], it is expected to be in the levelling region of acetic acid[16] and should be present largely in the form of an ion pair. Thus, the neutralization reaction may be written as eqn. (1). Clearly, a reduction of charge is involved



$$\mathrm{H{-}\overset{\displaystyle H\;{}^{+}}{\underset{\displaystyle H}{N}}{-}OH\;\; OAc^{-} + H_2OAc^{+}\; ClO_4^{-} \rightarrow H{-}\overset{\displaystyle H\;{}^{+}}{\underset{\displaystyle H}{N}}{-}OH\;\; ClO_4^{-} + 2\,HOAc} \tag{1}$$

leading to the prediction that a lower dielectric constant will favor this reaction.

A second reaction which should be considered occurs only in the analysis of aliphatic ketones. Generally, oximes are substantially less basic than the parent hydroxylamine; this is verified by the fact that, except for the aliphatic ketoximes, no consumption of titrant is evident potentiometrically after the residual hydroxylammonium acetate reagent has been reacted. The aliphatic ketoximes do exhibit basicity sufficient to permit titration. However, the more weakly basic ketoxime is thought to be outside of the levelling region of acetic acid and does not exist as the ion pair. Therefore, its neutralization reaction may be written as eqn. (2). Clearly, no change in charge nature is involved



$$\mathrm{\overset{\displaystyle R}{\underset{\displaystyle R}{\;}}\!\!>C{=}N{-}OH + H_2OAc^{+}\;\; ClO_4^{-} \rightarrow \overset{\displaystyle R}{\underset{\displaystyle R}{\;}}\!\!>C{=}\overset{\displaystyle H}{N}{-}OH^{+}\;\; ClO_4^{-} + HOAc} \tag{2}$$

and thus dielectric constant should have little or no effect. It may be mentioned that such reactions often involve a dispersal of charge in the transition state and thus proceed more favorably in lower dielectric constant medium[14]. However, any observed effect is generally much less marked than in reactions involving diminution of charge.

A useful means of characterizing end-point quality is the sharpness index. This quantity, usually given the symbol η, is defined as the magnitude of the slope of the titration curve, and, when the course of the titration is followed by means of potential values, is written as $dE/d\phi$, where E is the potential and ϕ the fraction of the sample titrated. A titration curve having a larger slope, and consequently a larger sharpness index, will give a smaller titration error. TANAKA AND NAKAGAWA[17] have shown that the maximum value of the sharpness index for a base titration in acetic acid generally occurs at the equivalence point whether a second base is present or not. Thus, the quality of end-points in the systems under study may be examined and compared in terms of relative sharpness index values.

RESULTS AND DISCUSSION

Decomposition of the hydroxylammonium acetate reagent

The stability of hydroxylammonium acetate is considered below, both from the point of view of the rate of reaction of the reagent with acetic acid, and of the products formed by this reaction. The reaction kinetics studied by HIGUCHI AND BARNSTEIN[1] in terms of the rate of loss of basicity with time are useful in predicting the extent of reaction. In this work, the reaction products have been identified and support the kinetic data.

The kinetics of the reagent stability indicate that, even when long reaction times are required for oximation, the amount of reagent lost by this undesirable reaction is less than 1%. Since many of the carbonyl compounds require about 20 min for complete reaction at 25°, the loss of reagent is negligible when calculated from the pseudo-first order rate constant, 0.000388 h^{-1} [1]. In the case where benzil, a sterically-hindered ketone, needs a reaction time of 24 h, only 0.9% of the reagent is lost by decomposition. It is, of course, clear that the blank titration compensates for the reagent lost in each case. On the basis of these findings, it may be concluded that the hydroxylammonium acetate reagent is sufficiently stable to present no problem. Naturally, reagent solutions should be prepared as needed.

TABLE I

R_F-VALUES OF HYDROXYLAMINE COMPOUNDS

Compound	R_F
Hydroxylammonium acetate	0.49 ± 0.01 (2)[a]
Acethydroxamic acid	0.68 ± 0.01 (4)
Diacetylhydroxylamine	0.86 ± 0.01 (2)
	0.67 ± 0.00 (2)[b]

[a] The number in parentheses indicates the number of trials used to determine the reported average and its average deviation.

[b] This compound is acethydroxamic acid, an impurity.

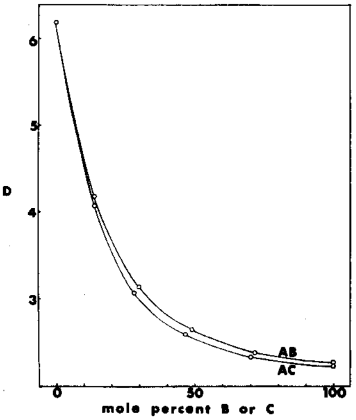
The products of the reaction of hydroxylammonium acetate with acetic acid were identified by paper chromatography. The relative mobilities of known compounds are shown in Table I. It is seen that the separation is excellent. In order to permit convenient study of the products being formed, reactions were conducted at 50°, 60° and 80°, as well as at room temperature. The reactions were followed by paper chromatography and the results are presented in Table II. From these data it seems that the primary reaction between hydroxylammonium acetate and acetic acid yields the mono-acetylated hydroxylamine, acethydroxamic acid. However, if enough time is permitted to elapse, a diacetylated product, diacetylhydroxylamine is observed. On the basis of this study, it is seen that the products formed by this side reaction of hydroxylamine are not basic and will not interfere with either the desired carbonyl reaction or the titration with perchloric acid.

TABLE II

PAPER CHROMATOGRAPHIC STUDIES OF REACTION PRODUCTS AS A FUNCTION OF TIME

Condition of sample (time, temp.)	*% of reaction*[a]	R_F
5 h, 50°	4	0.68
45 h, 50°	29	0.67
165 h, 50°	72	0.69
2 h, 60°	4	0.49 0.67
10 h, 60°	19	0.50 0.68
22 h, 60°	36	0.48 0.67
35 h, 60°	51	0.48 0.67
1 h, 80°	15	0.68
4 h, 80°	47	0.67
12 h, 80°	81	0.68
8 months, room temp.	—	0.67 0.85

[a] Calculated from the reported rate constants[1] and reaction times.



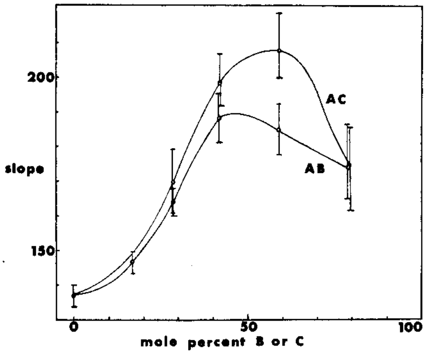


Fig. 1. Relationship of dielectric constant (D) to mole% of benzene (B) in benzene–acetic acid (AB) and mole% of carbon tetrachloride in carbon tetrachloride–acetic acid (AC).

Fig. 2. Relationship of vanillin titration curve slopes (mV/ml) to mole% of benzene (B) in benzene–acetic acid (AB) and mole% of carbon tetrachloride (C) in carbon tetrachloride–acetic acid (AC). Each chord represents the range of observed slopes and the average values are connected to give the curves.

Effect of dielectric constant on titration end-points

The dielectric constants of various acetic acid–benzene and acetic acid–carbon tetrachloride mixtures were measured. Figure 1 is a plot of dielectric constant as a function of mole per cent for each mixture. As might be expected, the carbon tetrachloride solutions exhibited slightly lower dielectric constants than corresponding benzene solutions.

In order to choose a favorable solvent mixture for analysis, the relationship between sharpness index (practically taken as the titration curve slope) and dielectric constant was studied. Vanillin was chosen as the test compound since it is a conveniently weighed solid which is relatively stable and is obtainable in a high state of purity. Vanillin analyses were carried out in both acetic acid–benzene and acetic acid–carbon tetrachloride solutions of varying compositions. Figure 2 is a plot of the slopes of the titration curves obtained during the vanillin analyses as a function of the mole percentage of benzene or carbon tetrachloride. The mole percentages used in Fig. 2 represent the solvent composition at the titration end-points. The benzene solvents show a maximum at about 45–50 mole% of benzene whereas the carbon tetrachloride system has a peak at *ca.* 50–55 mole% of carbon tetrachloride. A similar plot, not shown here, indicates that a maximum is also present at the same points if the slopes are plotted *versus* dielectric constant. Both systems show a decrease after the maximum.

The fact that the titration curve slope decreases while the dielectric constant increases slightly after the maximum, indicates that other considerations are involved. A factor that must be recognized is the solvating ability of the solvent. If a solvent cannot solvate reaction products, then the reaction will not proceed successfully. For inert solvent–glacial acetic acid mixtures, the occurrence of a dimer–monomer equilibrium is well established[18]. As the mole fraction of acetic acid decreases, the activity of monomer, which is felt to be more successfully solvated by inert solvents than the dimer, increases. This solvent–solvent type interaction may compete with the solute–solvent relationship, resulting in less successful solvation of the products. Needless to say, the role of the solvent is very complex.

On the basis of this work, the use of a 42 mole% inert solvent–acetic acid system was chosen as a good end-point reaction medium. This corresponds to a 53%(v/v) mixture at the end-point, but a 50%(v/v) mixture as initially added. For both the benzene–acetic acid and carbon tetrachloride–acetic acid solvents, this choice was a compromise between maximum slope and minimum electrical noise which increased beyond this point, in spite of careful grounding and shielding, making the measurements trying, difficult and somewhat erratic. These studies emphasize that the choice of a solvent thought to be useful in improving titration endpoints cannot be made arbitrarily. Since the role of the solvent is very complicated, only actual laboratory experience can determine the over-all result.

Table III is a summary of the analytical results, the measured slopes and the relative changes in slope which were observed during the study of seven different carbonyl compounds. The first group of 5 compounds are those in which only one end-point was found, whereas the last 2 compounds are those whose titration curve is characterized by two end-points.

An examination of the slope values for the first end-points for each compound indicates a favorable effect when the results obtained in the mixed solvent system are compared with those achieved in glacial acetic acid. In general the slope of the titration curve end-point is increased; even though different concentrations were used in some of the analyses which would lead to a variation in sharpness index or slope as is evident[17], the relative percent changes in slope are comparable since the concentration factor is negated. The results indicate that the choice of eqn. (1) as the phenomenon taking place during the titration of residual reagent in each case of carbonyl analysis is accurate, at least as far as charge nature is concerned.

The behavior of the individual compounds permits some limited comment. In the case of the poorest slopes in acetic acid, the aliphatic ketones, some improvement is noted when inert solvents are used, but the absolute values of the slopes are still small. The improvement is visually evident from the titration curve (Fig. 3).

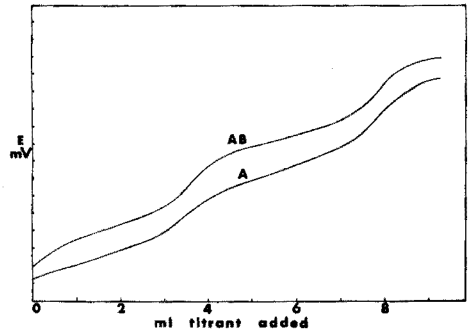


Fig. 3. Titration curves of reaction mixture–methyl ethyl ketone analyses in acetic acid (A) and benzene–acetic acid solvents (AB). The ordinate or potential, E, axis (each cm = 27.40 mV) is shifted to permit presentation of curves as shown.

When the effects of benzene and carbon tetrachloride are compared, there are 3 cases (piperonal, benzil and diethyl ketone) in which carbon tetrachloride produces an effect more than twice as great as benzene. In the other cases, the effects of the two non-polar solvents are similar. The variation in slope when different compounds are compared will not be dealt with here, since specific types of solute–solvent interactions are probably involved and these phenomena have not been examined in this work.

The results for the last 2 compounds listed in Table III, both aliphatic ketones, include data for a second titration end-point. As noted in the THEORY section, the results are different in nature from those observed for the first end-point. The effect of going from acetic acid to a mixed solvent is much less pronounced in terms of the effect on the second end-point slope; both mixed solvents produced a small decrease in the case of diethyl ketone whereas, in the case of methyl ethyl ketone, the benzene system showed a small increase and the carbon tetrachloride system exhibited no effect. The change in the methyl ethyl ketone end-points may be seen in Fig. 3. Again, these results reaffirm the choice of eqn. (2) as describing the ketoxime titration.

Analytical results were calculated from the end-points that represent the titration of the residual hydroxylammonium acetate reagent (Table III). Comparison of the various average values indicates that the three solvents yield equivalent results in most cases. The relative standard deviations which are included were calculated

TABLE III

QUANTITATIVE ANALYSIS OF CARBONYL COMPOUNDS

Compound	*% Found*[a]			*Slope of titration curve (mV/ml)*[b]			*% Slope change, relative to HOAc*	
	HOAc	*C_6H_6–HOAc*	*CCl_4–HOAc*	*HOAc*	*C_6H_6–HOAc*	*CCl_4–HOAc*	*C_6H_6–HOAc*	*CCl_4–HOAc*
Vanillin	98.6 ± 1.1 (3)[c]		98.3 ± 1.3[c]	161 ± 6		217 ± 8		+35
	99.8 ± 1.3 (3)	99.7 ± 1.8		134 ± 2	188 ± 7		+41	
Piperonal	98.5 ± 0.4 (3)[c]		98.9 ± 1.0[c]	188 ± 2		290 ± 11		+54
	98.7 ± 1.4 (2)	98.5 ± 1.8		208 ± 7	261 ± 12		+26	
n-Heptaldehyde	98.5 ± 0.9 (3)[c]		96.8 ± 0.7[c]	173 ± 5		233 ± 6		+35
	97.3 ± 1.8 (2)	97.5 ± 0.8		158 ± 6	237 ± 10		+50	
Acetophenone	99.5 ± 0.9 (3)[c]		96.7 ± 0.7[c]	200 ± 3		286 ± 13		+43
	96.4 ± 0.5 (3)	96.4 ± 0.3		166 ± 4	244 ± 17		+47	
Benzil	96.1 ± 1.0 (2)	96.4 ± 0.4	95.9 ± 0.5	479 ± 51	636 ± 56	812 ± 21	+33	+70
Diethylketone	101.0 ± 0.8 (3)	100.0 ± 0.4		58 ± 2 74 ± 2[d]	74 ± 2 73 ± 1[d]		+28 −1.4[d]	
	99.9 ± 0.7 (2)		99.4 ± 0.7	53 ± 1 77 ± 1[d]		95 ± 1 69 ± 4[d]		+79 −10[d]
Methylethylketone	100.0 ± 1.3 (2)	99.3 ± 1.1		51 ± 1 78 ± 1[d]	73 ± 3 86 ± 1[d]		+43 +10[d]	
	100.2 ± 1.3 (3)[c]		99.8 ± 1.3[c]	74 ± 1 76[d]		118 ± 3 76[d]		+59 0[d]

[a] These values are the averages and the relative standard deviations for each analysis. The standard deviation, r, is calculated from the blank, b, and sample, s; standard deviations from the equation $r = (b^2 + s^2)^{\frac{1}{2}}$. The numbers in parentheses are the number of analyses conducted in each case.

[b] These values are averages and average deviations.

[c] These analyses were carried out with the following quantities of reactants: hydroxylammonium acetate 5 meq, carbonyl 2.5 meq. All other analyses were conducted with 7.5 meq of hydroxylammonium acetate and 3.75 meq of carbonyl.

[d] These values represent the second end-point or ketoxime titration.

from the uncertainties of the blank determinations as well as the carbonyl-containing samples and, as a result, are somewhat larger than simple average deviations or standard deviations which may be computed without regard to the blank. When the relative standard deviations of the results in the three solvents are compared, it is noted that, except for the aromatic aldehydes, vanillin and piperonal, the values in the inert solvent-containing systems are smaller. These results further indicate that the benzene system gives results with less variation. However, *absolute* standard deviations computed for the various analyses, but not shown here, indicate that the carbon tetrachloride system is somewhat better. In neither case is there a substantial difference which would make a conclusion of solvent superiority possible. Generally, the results obtained with the mixed solvents are not greatly different from the acetic acid solvent values; but then no large changes were expected since, with the exception of the aliphatic ketones, the HIGUCHI AND BARNSTEIN[1] end-points are reasonably good.

It is possible to conclude that use of an inert solvent may lead to an improved titration curve slope, a more easily determined end-point and better analytical precision. However, an improved slope does not insure improved analytical precision, *e.g.*, the aromatic aldehydes. The safest approach appears to be the consideration of each class or each compound in order to ascertain the suitability of a solvent system.

The effect of water

The effect of water on the titration of bases in acetic acid has been studied by BRUCKENSTEIN AND KOLTHOFF[19]. Their results indicate that water exerts an effect on the system beyond the point where 95% of the base is titrated. The interference arises from the basic property of water in acetic acid. TANAKA AND NAKAGAWA[17] found that the titration error is proportional to the water content of an acetic acid system. Since water can find its way into this system if precautions are not observed, its effect on the analyses reported in this work was briefly examined.

Water may be introduced into the analytical system from different sources. Karl Fischer water determinations were done on samples of glacial acetic acid from closed bottles, on samples of acid left exposed to the atmosphere for 0.5–1 h, and on samples of perchloric acid titrant. The amount of water in the reagent acetic acid from the closed bottles was negligible as was the amount found in the titrant. The latter had been repeatedly treated with appropriate amounts of acetic anhydride in the usual manner until the water content was satisfactory[4]. However, the acid exposed to the atmosphere was found to contain about 1% (0.56 M) water, an amount which would be expected to have a definite undesirable effect.

The relative effect of water on the blank titration, *i.e.* the titration of hydroxylammonium acetate, was studied in terms of the sharpness index or titration curve slope. When titration of the blank in acetic acid solution was conducted in the presence of 0, 0.20 M and 1.18 M water, the ratio of relative slopes were 1:0.85:0.57, respectively. The blank titration in benzene–acetic acid containing the same quantities of water as in the acetic acid case yielded a very similar ratio of relative slopes, 1:0.82:0.59. As was expected, however, the blank slope in benzene–acetic acid solution was greater than that in acetic acid solution in each case. Since the slope decreases with increasing water content, the titration error is expected to increase[17] with increasing water content. It was, in fact, observed that a larger titrant volume is consumed when the water content is higher in blank titrations and in titration of residual hydroxylammonium acetate after carbonyl reaction.

Another effect of water on the analytical system must be mentioned. Since the oximation reaction produces water, it is possible that water from some other source would be sufficient to disrupt a favorable equilibrium situation. By this means the desired oxime could be hydrolyzed to a small extent, thereby affecting the analytical recovery of carbonyl compound. This is yet another undesirable possibility ascribable to the presence of water.

In summary, all observations support the fact that steps should be taken to exclude water from the system. The precautions are simple: (*1*) reduce the water content of the titrant and (*2*) keep all solutions and solvents carefully covered.

The authors wish to thank Mr. HERMAN HINITZ for carrying out the measurement of dielectric constants and for very useful discussions. Gratitude is likewise extended to the Research Council of Rutgers – The State University for financial aid.

SUMMARY

The determination of carbonyl groups with hydroxylammonium acetate in acetic acid has been re-examined. The reaction of hydroxylammonium acetate with acetic acid has been found to yield non-basic products, first acethydroxamic acid and eventually diacetylhydroxylamine, which do not interfere with the analyses. Calculations based on kinetics show that loss of the reagent is negligible in most cases, and in the extreme, involves only 0.9% of the amount originally present. Analyses in acetic acid media throughout are compared with those in which the titrations were conducted in benzene–acetic acid or carbon tetrachloride–acetic acid mixtures whose compositions were chosen to yield the most favorable titrations. The slopes of the titration curves were uniformly improved in the systems containing inert solvents, as predicted by consideration of the effect of dielectric constant change. Analytical precision was slightly improved except for aromatic aldehydes. Neither inert solvent system seemed superior to the other. The undesirable effect of small amounts of water is discussed.

RÉSUMÉ

On examine à nouveau le dosage des carbonyles au moyen d'acétate d'hydroxylammonium en milieu acide acétique. On observe que la réaction entre acétate d'hydroxylammonium et acide acétique fournit des produits non-basiques, acide acéthydroxamique et diacétylhydroxylamine éventuellement, ne gênant pas les analyses. Des calculs cinétiques montrent que la perte en réactif est négligeable dans la plupart des cas, et ne dépasse jamais 0.9% de la teneur présente à l'origine. Les analyses en milieu acétique sont comparées avec celles effectuées dans des mélanges benzène–acide acétique ou tétrachlorure de carbon–acide acétique. Les pentes des courbes de titrage sont améliorées dans des systèmes contenant des solvants inertes comme le laisse supposer l'influence du changement de constante diélectrique. La précision est légèrement meilleure sauf pour les aldéhydes aromatiques. On examine l'influence de l'eau.

ZUSAMMENFASSUNG

Die Bestimmung von Carbonyl-Gruppen mit Hydroxylammoniumacetat in Essigsäure wurde erneut geprüft. Es wurde gefunden, dass die Reaktion von Hydroxylammoniumacetat mit Essigsäure zu nichtbasischen Produkten führt, und zwar im wesentlichen zu Acethydroxamsäure und eventuell zu Diacetylhydroxylamin, welches jedoch die Analyse nicht stört. Kinetische Berechnungen zeigen, dass der Verlust des Reagenzes in den meisten Fällen vernachlässigbar ist und höchstens 0.9% des ursprünglich vorhandenen Anteils ausmacht. Die Analysen im essigsauren Medium werden mit solchen verglichen, bei denen die Titrationen in Benzol-Essigsäure oder Tetrachlorkohlenstoff-Essigsäure durchgeführt werden, und zwar mit solchen Mischungsverhältnissen, die die günstigsten Titrationen ergeben. Der Verlauf der Titrationskurven wird in den Systemen, die inerte Lösungsmittel enthalten, gleichmässig verbessert, wie es Überlegungen über den Einfluss des Wechsels der Dielektrizitätskonstanten voraussagen. Die analytische Genauigkeit wurde etwas verbessert ausser für aromatische Aldehyde. Keines der inerten Lösungsmittelsysteme scheint dem anderen überlegen zu sein. Der unerwünschte Einfluss kleiner Mengen Wasser wird diskutiert.

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THE SUBMICRO DETERMINATION OF CARBON, HYDROGEN AND NITROGEN BY A GAS-CHROMATOGRAPHIC METHOD*

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The simultaneous determination of carbon and hydrogen in organic samples weighing only *ca.* 50 µg for long proved a major obstacle in the development of the submicro technique. An accurate manometric method for this determination has been described by GOUVERNEUR *et al.*[1] and separate determinations of carbon and hydrogen for even smaller samples have been developed by TÖLG AND BALLSCHMITER[2]. The gas-chromatographic studies described in the present paper were undertaken in order to provide an alternative routine method which would also allow a simultaneous determination of nitrogen.

Many different procedures have been described for the determination of carbon, hydrogen and nitrogen by thermal conductivity methods[3]. These methods are suitable for samples weighing 0.5–5 mg; the procedures based on gas-chromatographic separation of the combustion products[4,5] appeared to be more suitable for conversion to submicro purposes than the more sophisticated apparatus based on chemical separations. The method described below involves the combustion of the sample in a helium stream, with the aid of an auxiliary oxidant as well as a layer of copper oxide. The water formed is converted to acetylene, and then nitrogen, carbon dioxide and acetylene are separated on a silica-gel column. Because of the very small sample size, there is no need to trap out the combustion products before this separation; combustion is immediate and the products emerge from the tube in a well-defined zone. BELCHER AND FLEET[6] showed that the acetylene peaks are unsuitable for quantitative measurements in the submicro range and that it is necessary to burn the acetylene to carbon dioxide before the final measurement, the water produced in this combustion being removed on a second silica-gel column. These preliminary studies[6] covered only the analysis of simple compounds without nitrogen and the precision achieved was inadequate for routine work. Extensive studies of the various parameters involved in the determination have allowed its extension to a wide variety of materials, and have improved the precision attainable to about the same level as that for other elements on the submicro scale.

STUDY OF OPTIMAL CONDITIONS

In most of the development work the main problem was the precision of the results for carbon. For the determinations of hydrogen and nitrogen, a relative error

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* This paper was read at the Symposium on Limits of Detection, Enschede, The Netherlands, April, 1968.

of 5% or even 10% can accumulate from various sources and, for most compounds, the final result will remain within the conventionally accepted limits of error on the submicro scale (±0.5% absolute). For the determination of carbon, the tolerable relative error is only slightly greater than the absolute error. Unless otherwise mentioned, all the following studies were made with samples weighing 40–80 µg.

Combustion conditions

In preliminary tests[6], the packing of the main combustion tube consisted only of copper oxide. For the simultaneous determination of nitrogen, this packing was first changed to alternate layers of copper oxide and copper (6 cm in all heated by a 12-cm furnace). Under these conditions with a helium flow of 20 ml/min, the combustion efficiency increased by 15% as the temperature of the furnace increased from 700° to 850°. The optimal temperature was 850–900°. When the temperature was further increased to 950 or 1000°, the upward baseline drift indicated evolution of oxygen from the copper oxide, which quickly lost its oxidizing power; after a few determinations at this temperature, no water was formed to react with the acetylene and a flattish peak corresponding to a mixture of carbon monoxide and dioxide emerging from the combustion tube appeared at the carbon peak position.

The best permanent tube packing was eventually shown to be a 6-cm layer of copper oxide backed by a 4–5-cm layer of electrolytic silver[7]. Platinum in the packing did not seem to have any effect on the combustion of different compounds. Some tests were made with combustion in a closed system followed by sweeping of the products through the separation and measuring system, but the peaks were badly shaped even when separation proved possible, presumably because the combustion products emerged from the tube as a rather diffuse zone.

Auxiliary oxidants

Initially, only a little copper oxide was added to the sample in the boat[6] but it was later found necessary almost to fill the small sample holder in order to improve the combustion efficiency. The copper oxide blank was then excessive, owing to adsorption of air, unless the oxide was first heated to 800° and then cooled and stored under dry helium. However, the precision of the carbon results for a range of samples remained poor (*ca.* 2%). In general, the precision achieved within a series of analyses of the same compound was better than that obtained for a series of analyses of different compounds, which indicated that the errors were arising from variations in the rates of combustion of different samples rather than from inadequate control of instrumentation parameters. Accordingly, tests were made with more powerful auxiliary oxidants.

The use of cobalto-cobaltic oxide[8] or the decomposition product of silver permanganate[9] improved the precision for carbon and it was shown by means of heating ultrapure calcium carbonate that the auxiliary oxidant did not itself affect the carbon factor. For both these oxidants, the blank values for nitrogen and carbon were found to be negligible but the blank for water corresponded to about 1 µg of hydrogen. No peak corresponding to hydrogen was obtained when no oxidant was present in the sample boat. It proved impossible to remove the last traces of water from these oxidants without destroying their oxidizing power. Heating the oxidants in a dry helium stream and storing them under helium reduced the blank; it was, however, necessary to standardize the timing between the removal of the oxidant from the helium atmosphere and the insertion of the sample holder into the main furnace.

The auxiliary oxidants were most effective when the sample was placed on top of a layer of oxidant and then covered with another layer. There was no apparent difference in the efficiencies of cobalto-cobaltic oxide and the silver permanganate decomposition product for a wide range of materials, except in the case of nitro compounds (see below).

Oxidants for acetylene

The need to convert acetylene to carbon dioxide for the final measurement was indicated previously[6]. It is well known that acetylene is difficult to burn completely and, in the present system, the problem was enhanced by the need to keep the oxidizing layer as short and compact as possible in order to prevent spreading of the peaks separated in the first gas-chromatographic column. It was confirmed that essentially no oxidation was obtained with Hopcalite or cobalto-cobaltic oxide at 600°; the cobalt oxide appeared to be efficient at 750° but after several hours at this temperature its effectiveness decreased owing to loss of oxygen, which was indicated by gradually rising base-lines. Silver orthovanadate[10] was less efficient than copper oxide at 930°. Nickel oxide at 1000° or 1100° gave very badly shaped peaks which appeared to consist of a mixture of acetylene and carbon dioxide. A quantitative indication of the relative efficiencies of the oxidants tested is shown in Table I, where the sensitivity is expressed as peak area (mm^2) per μg of hydrogen in the original sample.

TABLE I

EFFICIENCY OF OXIDANTS FOR ACETYLENE

(Sensitivity expressed as mm^2/μg H)

Oxidant	$AgVO_3$	$Co_{2,3}O_{3,4}$	CuO	CuO	CuO
Temp. (°)	700	750	850	900	930
Sensitivity	528	663	631	753	733

In all further tests, copper oxide was used at 900°. Regardless of the oxidant used for the oxidation of acetylene, the sesntivity for the carbon dioxide from the original carbon remained essentially constant at *ca.* 77 mm^2/μg C, which showed that the peak corresponding to the original carbon was unaffected by any processes occurring in the acetylene oxidation system.

Determination of nitrogen

In the first tests for this determination, the combustion tube packing consisted of alternate layers of copper oxide and copper, to reduce nitrogen oxides to nitrogen. When the main silica-gel column was maintained at about 60°, a small but well-defined peak emerged before the first carbon dioxide peak, the separation being entirely satisfactory. Despite the small size of the peak, fairly precise results were readily achieved for most compounds. However, a peculiar feature was noticed when the sample contained both nitrogen and a halogen, particularly when the nitrogen was present in nitro groups. In such cases, nitrogen values were almost invariably 2–4% high. Longer packings of silver gauze in the main combustion tube, and silver in the sample boat or at the end of the acetylene combustion system effected no improvement.

Replacement of silver by silver vanadate[11] was also unsuccessful. Compounds containing only carbon, hydrogen, oxygen and a halogen gave no peak at the nitrogen position, but when the same compounds were mixed with acetanilide, the results for nitrogen were again high.

No definite explanation of the effects noted seems available. According to the thermal conductivities[12], the formation of nitrogen dioxide should cause low rather than high results, whereas nitric oxide would cause slightly high results and nitrous oxide would create a positive relative error of some 7%. However, retention data[12] indicate that nitric oxide would elute with nitrogen while nitrous oxide would elute with carbon dioxide in the present system. The formation of a stable nitrosyl halide seems unlikely. When a layer of manganese dioxide (which is said not to absorb nitric oxide[13]) was placed at the end of the acetylene furnace, only about 50% of the orginal nitrogen appeared in the peak.

The problem was eliminated by placing a 3-cm roll of freshly reduced copper gauze between the sample holder and the main copper oxide packing. When a longer layer of reduced copper was used without copper oxide, the auxiliary oxidant in the sample boat being depended on to provide all the necessary oxygen for combustion, the nitrogen and hydrogen values came within the usual limits of error, but the carbon values were slightly low.

Chromatographic separation

Excellent separations of the nitrogen, carbon dioxide and acetylene components were obtained with a 50-cm column of activated 36–40-mesh silica gel. The optimal temperature was found to vary with the particular column packing, generally lying between 50 and 70°; once established for a column, this temperature was kept constant to ±0.5°. The second silica-gel column placed after the acetylene combustion system served simply to remove the water formed in this combustion and so could be kept short and at a higher temperature.

Thermal conductivity measurement system

In the first stages of this work[6], a specially designed thermal conductivity cell was used, because the commercially available cells were of insufficient sensitivity. Later, the GowMac thermistor micro cell became available; this was only slightly more sensitive, but was very much more stable and reliable. With this cell, the optimal filament current was about 7 mA; a current of 5 mA gave insufficient sensitivity

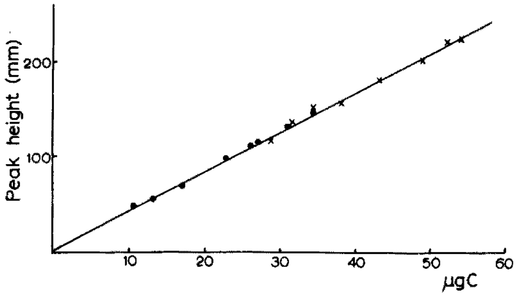

Fig. (1). (×) Dependence of cell response on amount of carbon. Benzoic acid, (●) sucrose.

whereas currents much above 8 mA caused unstable base-lines. In order to avoid damage to the thermistor, caused by the air introduced with the sample, the current was turned down during the initial sweeping out period. Errors from inaccurate resetting of the current were avoided by applying a correction based on the millivolt deflection when the *ca.* 7 mA current was applied across a 10-ohm resistor.

The cell response to carbon dioxide was checked with benzoic acid and sucrose and was found (Fig. 1) to be linear over the range 0–54 μg of carbon (the highest amount tested). For the carbon dioxide arising from the organic hydrogen, the response was also linear but the scatter was much greater and the line intercepted the peak-height axis at a value depending on the pretreatment of the auxiliary oxidant.

According to KEULEMANS[14], thermal conductivity cells should be maintained at ±0.05° at temperatures below 100° and the gas pressures on the reference and measuring channels should be equal, if maximum accuracy is to be achieved. Approximate equivalence of gas pressure was achieved by placing a dummy silica-gel column in the gas flow which passed through the reference channel. The best temperature constancy that could be achieved with the present apparatus was ±0.5°, hence it is possible that better precision could be obtained with stricter control.

With the attenuation system used, the nitrogen, carbon and hydrogen peaks were measured at attenuations of 3, 10 and 3, respectively. This ratio seemed to give the best compromise between sensitivity and base-line stability.

In comparisons of methods of peak measurement, it appeared that simple measurement of the peak heights was slightly more precise than peak-area measurements, probably because of slight fluctuations in the chart speed. Tests were made with a relatively inexpensive digital readout integrator but this was less precise than the manual methods partly because the peaks emerged too rapidly from the column and partly because the attenuation could not be changed between emergence of peaks when the integrator was in circuit.

EXPERIMENTAL

Apparatus and reagents

A line diagram of the apparatus is shown in Fig. 2. All reagents were of M.A.R.

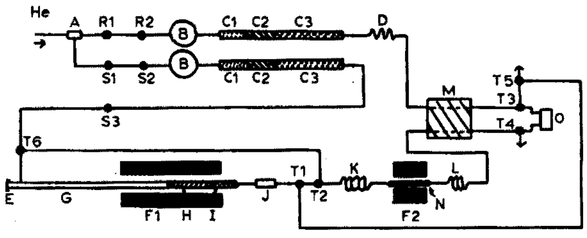

Fig. 2. Line diagram of apparatus

A.	Flow splitter made of copper	K.	Main silica gel column
B.	1-1 bulbs	L.	Secondary silica gel column
C.	Helium purification tubes	N.	Secondary combustion packing
D.	Dummy silica gel column	M.	Thermal conductivity cell in thermostatted box
E, G.	Silica tube with silica cap	O.	Bubble flowmeter
F.	Main furnace (1); secondary furnace (2)	R. S.	Needle valves
H, I.	Combustion packing	T.	3-way taps
J.	Calcium carbide chamber		

quality unless otherwise indicated.

Helium purification train. The flow from a helium cylinder (99.95% pure, British Oxygen Co., Wembley) was split at a copper T-joint and the separated streams were controlled by needle valves (R and S) placed in series. Bulbs of 1-l volume were placed in the flow to stabilize it against minor pressure fluctuations. The helium was scavenged by passage through 8 cm of molecular sieve 5A (Perkin-Elmer, Beaconsfield), 8 cm of soda asbestos and 20 cm of phosphorus pentoxide on vermiculite (G.F. Smith Chemical Company, Columbus, Ohio) contained in 15-mm bore tubes.

Combustion system. The silica tube was 45 cm long and of 7 mm or 9 mm bore (see p. 448) with a B10 male joint at the inlet end capped with a B10 cone; the outlet end was narrowed conventionally and attached by plastic tubing to the carbide chamber. The tube was packed with a 6-cm layer of wireform (1–2 mm length) copper oxide, followed by a 5-cm layer of electrolytic silver[7]. A 20-cm furnace at 850–900° was placed as shown in Fig. 2.

The platinum sample boat was 1 cm long attached by 5 cm of thick platinum wire to a sealed silica tube containing an iron bar.

Auxiliary oxidants. Cobalt oxide powder[8] was conditioned by heating for 1 h at 700° in a stream of helium. The silver permanganate decomposition product[9] was heated for 1 h at 500–550° in a stream of helium. The Model 185 oxidizing catalyst (F and M Scientific, Inc.) was conditioned in the same way as Körbl's compound and behaved in exactly the same way. All the oxidants were cooled and stored under helium.

Calcium carbide chamber. The revolving chamber (Fig. 3) was constructed from stainless steel. A new cartridge of calcium carbide was used for each determination, by slackening the nut, turning to a new contact and resealing.

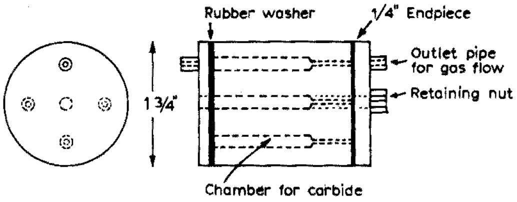

Fig. 3. Revolving chamber for calcium carbide.

Calcium carbide (Hopkin and Williams, Ltd.) was ground to 10–14 mesh and the carbide chamber was filled, both operations being carried out in a glove box in a nitrogen atmosphere with phosphorus pentoxide present.

Chromatography columns. All the chromatography columns were packed with silica gel (36–40 mesh, Perkin-Elmer, Beaconsfield) which was activated by heating in air at 400° and cooling over phosphorus pentoxide. The columns were contained in copper spirals of 2-mm bore tubing. The main column (L) was maintained at 50–70 ± 1° and was 50 cm long; the secondary column (M) was 11 cm long maintained at about 80 ± 0.5°. The actual temperatures were adjusted for each particular set of columns to give the optimum separation and peak shape.

Acetylene combustion system. The silica combustion tube was 20 cm long and of 2 mm bore, and contained a 6-cm layer of copper oxide (1–2 mm wireform) heated at 920–940° by a 9-cm furnace.

Thermal conductivity cell. A GowMac micro cell (thermistor model GM133) was housed in a thermostatted box held at 30 ±0.5°. The box walls consisted of asbestos, expanded polystyrene and metal layers and were heated by means of 65-W elements. A conventional attenuation system was used with a Honeywell-Brown Electronik recorder (1.2 sec f.s.d.; 4 in/min chart speed).

Flow meters. From the thermistor, the flow passed through a length of 0.5-mm diameter capillary tubing (to prevent back-diffusion into the cell at reduced flow rates) to a soap-bubble counter and then to the atmosphere. During actual determinations, the counter was bypassed to avoid pressure fluctuations.

Mounting of apparatus. Apart from the furnaces with the combustion systems, the chromatographic columns (L and M) and the flow counter, the whole apparatus was mounted inside a box of dimensions 80 × 40 × 25 cm, lined with 2-cm thick expanded polystyrene.

Procedure

With the flow passing through the reference and sensing channels of the thermistor to the atmosphere, the flow rates were adjusted to 20 ml/min by means of the needle valves in the two streams (R and S). Taps T6 and T2 were then adjusted so that the flow bypassed the combustion system and a fresh plug of calcium carbide was rotated into the combustion line. The sample (40–80 μg weighed on an Oertling QO1 balance) was placed on to a 2-mm layer of the auxiliary oxidant and covered with a 1–2 mm layer of the same oxidant, in the sample holder. A roll of reduced copper gauze (3 cm long) was prepared by heating in a flame, dropping into ethanol and drying *in vacuo*.

Taps T1 and T5 were adjusted so that the flow from the reference channel backswept the combustion system while the copper roll was inserted into the combustion tube up against the permanent copper oxide filling, and the sample holder was inserted just inside the combustion tube which was then recapped, before the reference flow was reverted to its normal mode. Taps T6 and T2 were then turned so that the helium flow passed through the combustion system.

After a sweeping time of 15 min, the thermistor current was switched up to its working value of 7 mA and the current was calibrated as indicated on p. 445. The sample boat was then rapidly pushed into the hot zone with a magnet. As soon as the nitrogen peak appeared and the base-line had restabilized, the attenuation was switched for the carbon peak and then again for the hydrogen peak. All the peaks emerged within 3 min of inserting the sample into the hot zone.

For optimal precision it was necessary to standardize the timing between the weighing of the sample on to the layer of oxidant and capping the combustion tube, as well as the time of sweeping the tube. The actual timing is not critical except for volatile samples. For optimal precision, the helium flow should be maintained at 20 ml/min when the apparatus is not in use.

RESULTS AND DISCUSSION

Acetanilide was used in all cases for calibration of the apparatus. It was necessary to calibrate daily, after burning off 2–3 unweighed samples, but the conversion factors obtained remained useful throughout the day.

TABLE II

CARBON, HYDROGEN AND NITROGEN RESULTS FOR SAMPLES WEIGHING 40–80 μg

Compound	*C theor. (%)*	*C found (%)*	*Error (%)*	*H theor. (%)*	*H found (%)*	*Error (%)*	*N theor. (%)*	*N found (%)*	*Error (%)*
Narrow bore tube									
Acetanilide	71.1	71.1[a]	0.31[a]	6.7	6.7[a]	0.28[a]	10.4	10.4[a]	0.11[a]
8-Hydroxyquinoline	74.5	74.6	+0.1	4.9	3.9	−1.0	9.7	10.2	+0.5
		74.6	+0.1		4.7	−0.2		10.0	+0.3
Sucrose	42.1	42.1	0.0	6.5	6.3	−0.2	—	—	—
		41.6	−0.5		5.9	−0.6	—	—	—
1-Chloro-2,4-dinitrobenzene	35.6	35.6[b]	0.0	1.5	2.0	+0.5	13.8	13.3	−0.5
		36.2	+0.6		1.9	+0.4		14.1	+0.3
Benzyl disulphide	68.3	67.8	−0.5	5.7	5.9	+0.2	—	—	—
		68.2	−0.1		6.1	+0.4	—	—	—
Diphenylsilanediol	66.6	66.4	−0.2	5.6	5.7	+0.1	—	—	—
		66.9	+0.3		6.0	+0.4	—	—	—
Wide bore tube									
Acetanilide	71.1	71.1[a]	0.53[a]	7.6	7.6[a]	0.31[a]	10.4	10.4[a]	0.22[a]
8-Hydroxyquinoline	74.5	74.2	−0.3	4.9	4.5	−0.4	9.7	9.6	−0.1
		73.6	−0.9		4.2	−0.7		10.2	+0.5
Sucrose	42.1	42.5	+0.4	6.5	6.7	+0.2	—	—	—
		42.1	0.0		6.5	0.0	—	—	—
Phenacetin	67.0	67.5	+0.5	7.3	7.5	+0.2	7.8	7.5	−0.3
		66.8	−0.2		7.9	+0.6		8.1	+0.3

[a] These results correspond to 12 random determinations for standardization purposes; the errors shown are th standard deviations found.

[b] Cobaltic oxide as auxiliary oxidant.

The standard deviations obtained for non-consecutive acetanilide samples shown in Table II, are very satisfactory considering the weight of the sample. Results for several samples which are typical of those obtained for a much wider range of compounds are also shown in Table II. Results are given for both narrow (7-mm i.d.)and wide (9-mm i.d.) combustion tubes. The use of narrow tubes allows greater precision, presumably because of the better definition of the zone of combustion products emerging from the system, but the wider tube is more convenient from the point of view of maintenance of tube packings.

The apparatus can be constructed quite cheaply and is not excessively prone to maintenance problems. The thermistor is reliable and fairly robust, despite its high sensitivity. In fact, the thermistor was not used at the limit of its sensitivity; if a very close control of physical conditions such as temperature and pressure were possible, it should be possible to analyse samples in the 10–20 μg range or even lower.

The gas-chromatographic system which is proposed, is less precise for the determinations of carbon and hydrogen than the manometric system of GOUVERNEUR *et al.*[1]. The results obtained are, however, of very reasonable accuracy for submicro work and the gas-chromatographic system has the advantage of giving a value for nitrogen which is as accurate as the results obtained by the sealed tube Kjeldahl method[15].

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SUMMARY

A method for the determination of carbon, hydrogen and nitrogen in organic samples weighing 40–80 µg is described. The sample is decomposed conventionally in a helium stream and the water formed is converted to acetylene. Nitrogen, carbon dioxide and acetylene are then separated on a silica-gel column, and the acetylene is burned to carbon dioxide by passage through copper oxide at 900° because the acetylene peak itself is not easily measured. Water from the second combustion is removed on silica gel and the three peaks emerging are measured by means of a micro thermistor cell. The standard deviations obtained for acetanilide are 0.31% for carbon, 0.28% for hydrogen and 0.11% for nitrogen. Results for other compounds are given and the parameters relevant to precision are discussed.

RÉSUMÉ

On décrit une méthode pour le dosage submicro (40 à 80 µg) du carbone, de hydrogène et de l'azote dans des substances organiques. L'échantillon est décomposé conventionnellement dans un courant d'hélium; l'eau formée est convertie en acétylène. L'azote, l'anhydride carbonique et l'acétylène sont ensuite séparés sur une colonne de gel de silice; l'acétylène est brûlé en anhydride carbonique par passage sur de l'oxyde de cuivre à 900°. L'eau de la seconde combustion est absorbée sur gel de silice. Les trois pics sont mesurés à l'aide d'une cellule microthermistor. Les déviations standards obtenues pour l'acétanilide sont 0.31% pour le carbone, 0.28% pour l'hydrogène et 0.11% pour l'azote. D'autres résultats sont donnés.

ZUSAMMENFASSUNG

Es wird eine gaschromatographische Methode zur Bestimmung von Kohlenstoff Wasserstoff und Stickstoff in organischen Proben von 40–80 µg beschrieben. Die Probe wird in überlicher Weiser unter Helium zersetzt und das gebildete Wasser zu Acetylen umgewandelt. Stickstoff, Kohlendioxid und Acetylen werden dann an einer Silicatgel-Kolonne getrennt; da der Acetylenpeak selbst nich leicht zu messen ist, wird das Acetylen bei 900° an Kupferoxid zu Kohlenstoffdioxid verbrannt. Das Wasser der zweiten Verbrennung wird auf Silicatgel zurückgehalten. Die drei auftretenden Peaks werden mit einer Mikrothermistorzelle gemessen. Die mit Acetanylid erhaltenen Standardabweichungen betragen 0.31% für Kohlenstoff, 0.28% für Wasserstoff und 0.11% für Stickstoff. Weitere Ergebnisse anderer Verbindungen werden angegeben und ihre Genauigkeit wird diskutiert.

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APPLICATION OF THE INTEGRATED ION-CURRENT TECHNIQUE TO THE STUDY OF RARE-EARTH CHELATES

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In conventional quantitative mass spectrometry, it is common practice to vaporise sample mixtures and to maintain a reservoir of sample vapour at a constant pressure while a mass spectrum is being measured or recorded. This is achieved by allowing the vapour to leak into the mass spectrometer ion source at such a rate that no perceptible change in the pressure in the reservoir is caused. The ion currents at significant m/e values may then be related to the partial pressures of the components of the sample mixture in the reservoir, provided that the sensitivity of the instrument for each component has been determined by a prior calibration with a pure sample of that component. Such a technique is wasteful since less than 1% of the total sample is consumed. Further, there is a restriction on the volatility of samples which can be analysed because it is necessary to provide a reservoir sample pressure of at least several microns in order that vapour may pass through the constriction into the ion source of the mass spectrometer.

In modern qualitative mass spectrometry, it is often necessary to study the behaviour of very small amounts of sample materials of very low volatility. Consequently, the conventional method cannot be used, and such materials are evaporated directly into the ion source from solid samples contained in a probe which can be adjusted to be close to the ionising electron beam. It is obvious that the partial pressure of the sample vapour must vary during the evaporation process and no prior calibrations of instrumental sensitivity are possible.

Recently, however, a technique was evolved[1] in which the ion current at a significant m/e value was measured before, during and after evaporation of a known weight of sample. The area under the ion-current curve, *i.e.* the integrated ion current, could then be related directly to the weight of sample evaporated. Thus, provided that no reactions took place during an evaporation process, it was possible to measure the concentrations of the components of a mixture by a series of measurements of integrated ion-current curves at several m/e values. The very high sensitivity of this method was first demonstrated using nickel dimethylglyoximate[1] but the technique was extended to studies of the oxinates of the common metals[2] and the rare earths[3]. It is the purpose of the present paper to extend the application of this technique to the chelates of holmium with a number of substituted acetylacetones, to provide a method for the estimation of these chelates and to relate their mass spectrometric behaviour to that observed in sublimation and gas chromatographic studies.

EXPERIMENTAL

General nomenclature

The following nomenclature is used throughout the text in the description of the β-diketones used. The abbreviations refer to the enolate ion used in the formation of a metal complex. Such abbreviations are only used in diagrams and tables included in the text.

Pentan-2,4-dione (acetylacetone), A*
1,1,1-Trifluoropentan-2,4-dione (trifluoroacetylacetone), TFA*
1,1,1,5,5,5-Hexafluoropentan-2,4-dione (hexafluoroacetylacetone), HFA
2,2,6,6-Tetramethylheptan-3,5-dione (dipivaloylmethane), DPM
1,1,1-Trifluoro-5,5-dimethylhexan-2,4-dione (trifluoroacetylpivaloylmethane), TPM
3-(2-Thenoyl)-1,1,1-trifluoroacetone (thenoyltrifluoroacetone), TTA*
1,1,1,2,2-Pentafluoro-6,6-dimethylheptan-3,5-dione (pentafluoropropionoylpivaloylmethane), PFM
1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctan-4,6-dione (heptafluorobutanoylpivaloylmethane), HFM
1-Phenylpentan-2,4-dione (benzoylacetone), BA*
1,1,1-Trifluoro-5-phenylpentan-2,4-dione (benzoyltrifluoroacetone), BTA*
1,5-Diphenylpentan-2,4-dione (dibenzoylmethane), DBM*

Materials

The compounds marked with an asterisk in the above list were obtained from Koch-Light Laboratories, Ltd. The other five compounds were prepared by Claisen condensation of the appropriate esters and ketones with sodium hydride as condensing agent.

Preparation of the tris chelates of holmium

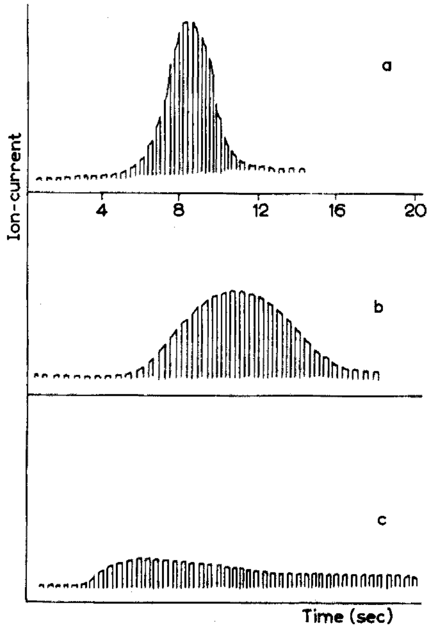
The tris chelates were prepared by dissolving holmium oxide in the minimal quantity of concentrated nitric acid and evaporating the solution to small bulk. The residue was dissolved in water and the holmium hydroxide was precipitated by the addition of 4 *M* aqueous ammonia. The precipitate was washed with water to remove the excess of ammonia, and suspended in methanol. The stoichiometric quantity of the appropriate substituted acetylacetone was dissolved in methanol and neutralised with aqueous ammonia to pH 7.5. This solution was then added slowly to the slurry of holmium hydroxide with stirring. The stirring was continued until completion of the reaction which was indicated by the disappearance of the suspended holmium hydroxide. The bulk of the methanol was removed by rotary evaporation under vacuum and the residue was poured into water to precipitate the metal chelate. The precipitate was washed, dried and purified by sublimation where possible.

Preparation of the tetrakis chelate.

The tetrakis chelate, $NaHo(TPM)_4$, was prepared by dissolving holmium oxide in concentrated nitric acid and evaporating the solution to small bulk. The residue was dissolved in water–ethanol (1:1) and the stoichiometric quantity (4 mol) of 1,1,1-trifluoro-5,5-dimethylhexan-2,4-dione was added in 1:1 water–ethanol solution with stirring under nitrogen. The alcohol was then removed by rotary evaporation under vacuum. The solution was extracted with chloroform and the extract was left in contact with an excess of anhydrous sodium carbonate overnight. The chloroform layer was separated, the chloroform evaporated and the residue purified by sublimation at 0.1 mm of mercury.

Recording of the integrated ion-current curves

The mass spectra of the chelates were first recorded by evaporating microgram quantities from the direct insertion probe of the G.E.C.-A.E.I. MS 9 mass spectrometer. On examination of the spectrum a characteristic ion was selected for the quantitative examination. The peak provided by this ion in the mass spectrum should be large in order to gain sensitivity, and be characteristic of the molecule under investigation. Theoretically, the most suitable ion to select would be the molecule ion, but this does not always carry a significant percentage of the total ion current and sometimes has an *m/e* value so high that it is not accessible with the peak-matching facilities of the instrument when heptacosafluorotri-*n*-butylamine is used as reference compound. In the present work, the ML_2^+ ion was found to be the most suitable for mass measurement because of the intensity of the spectral peak. When the appropriate ion has been selected, an ion with an *m/e* value lower but close to it in



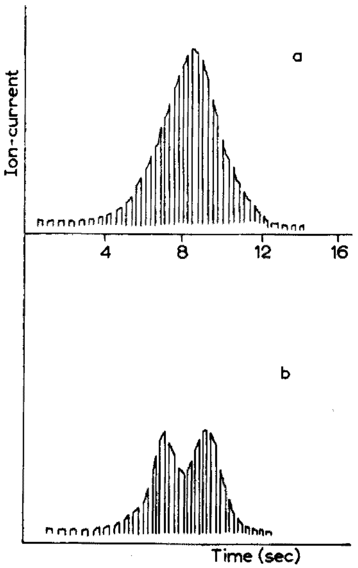
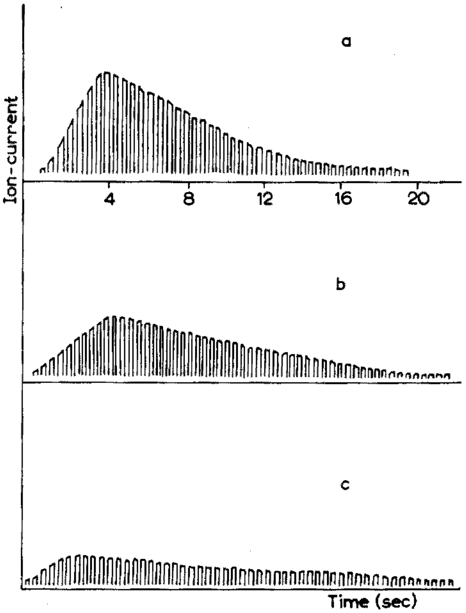


Fig. 1. Typical integrated ion-current curves for thermally stable tris chelates with symmetrical ligands. The curves shown were obtained with $Ho(DBM)_3$. (a) 420°, (b) 380°, (c) 210°.

Fig. 2. Typical integrated ion-current curves for thermally stable tris chelates with asymmetric ligands. Similar curves were found for 3 ligands, the temperatures being as follows:

	$Ho(HFM)_3$	$Ho(PFM)_3$	$Ho(TPM)_3$
Curve a	250°	240°	240°
Curve b	220°	225°	190°

the spectrum of the reference compound is chosen. A small pressure of the reference compound is admitted to the reservoir of the instrument as described previously[1] and the selected reference peak is tuned in and displayed on the oscilloscope. By means of the peak-matching facilities of the instrument, the instrument is switched to the *m/e* value of the peak to be measured. At this stage no ion current should be registered at this *m/e* value. The sample is then lowered into the heated part of the ion source and the recorder is set in operation. The ion current which can be observed as a peak on the oscilloscope rises and falls as the sample evaporates, as shown in Figs. 1–3. Finally, the area under the recorded ion-current trace, *i.e.* the integrated ion current, is measured.



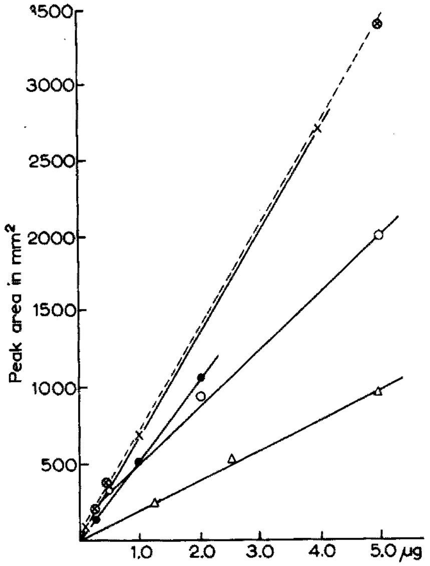


Fig. 3. Typical integrated ion-current curves for thermally unstable tris chelates. The curves shown were obtained with Ho(DPM)$_3$. (a) 240°, (b) 220°, (c) 190°.

Fig. 4. Calibration curves. ⊗ Ho(PFM)$_3$; × Ho(HFM)$_3$; ○ HoA$_3$; ⊙ Ho(TPM)$_3$; △ NaHo(TPM)$_4$.

Sublimation

Samples were sublimed on a conventional vacuum line at 0.5 mm of mercury. The chelates were heated, after desiccation over phosphorus pentoxide, in an oil bath, and the sublimates were collected on a cold finger.

Gas chromatography

Samples (10 μg) of the metal chelates as a 1% solution in chloroform were chromatographed with a Phillips PV 4000 series chromatograph with a flame ionisation detector. Nitrogen was used as a carrier gas at a flow rate of 60 ml/min and the column used was made of copper tubing (3 ft long × 0.25 in i.d.) packed with 80–100 mesh Chromosorb G (AW-DMCS) coated with 10% (w/w) Silicone Gum Rubber, SE 30. The column was silanised before use by injecting 100 μl of Silyl 8.

RESULTS AND DISCUSSION

In order that the integrated ion-current technique may be applied to the quantitative analysis of a compound, the vapour pressure of this compound and its variation with temperature must fall within clearly defined limits. At room temperature, the vapour pressure must be so low (*ca.* 10^{-8} mm Hg) that when the sample is introduced into the cold part of the vacuum system of the mass spectrometer, no detectable evaporation takes place. Evaporation must take place rapidly, however, when the sample is lowered into the heated ion source which may be raised to a maximum temperature of 500°. It has already been shown that nickel dimethylglyoximate and benzil dioximate[1] and the oxinates of a number of metals[2,3] satisfy these requirements. The acetylacetonates of some metals have, on the other hand, been found to be too volatile at room temperature to be studied by this technique. A second requirement is that the substance shall be thermally stable and not decompose during the evaporation process. Thus, the metal chelates formed from N-benzoylphenylhydroxylamine have been shown to fulfil the first but not the second requirement, and their mass spectra do not contain suitable characteristic peaks[4].

In the present study of the substituted acetylacetonates of holmium, some of the chelates fulfilled both requirements; all fulfilled the first but several did not fulfil the second requirement of thermal stability. The shape of the integrated ion-current curve provides information on 4 aspects of the metal-chelate evaporation process. The first of these is the relationship between the area under the curve, *i.e.* the integrated ion current, and the weight of metal-chelate evaporated. Although theoretically the shape of this curve, *i.e.* the proportion of height to width, should not affect this relationship, a gaussian or triangular profile is highly desirable and a long, low, flat curve is undesirable for sensitivity reasons. The selection of the m/e value at which measurements are to be made depends on purely empirical factors. The ion responsible for the mass peaks must carry a substantial percentage of the total ion current; it must be at an m/e value which does not have a contribution from the reference compound, and it must be in an accessible region of the mass spectrum. If the reference compound used is heptacosafluorotri-*n*-butylamine, then the upper limit is about 700.

Figure 4 shows a series of calibration curves for some chelates of holmium, including the tetrakis chelate, where measurements were made on two ions from the same spectrum [$Ho(TPM)_3^+$ and Na^+]. In the latter case, no suitable ion was available in the mass spectrum of the reference compound and so neon was substituted as the reference substance, the molecule ion at m/e 20 being used as the reference peak. It can be seen that there is a straight-line calibration for the ions being studied, and the slopes of the lines enable values for the sensitivity to be determined. It should be pointed out that the sensitivity values (Table I) refer to the instrument being used at its lowest sensitivity and that the values of *ca.* 500 $mm^2/\mu g$ are minimal values. An increase in sensitivity of 10^3 is easily realised, but calibration becomes increasingly unreliable. It is possible to convert salts of holmium into the chelates quantitatively by the method described and hence the integrated ion-current technique can provide a unique method which is specific for determining quantities of rare earths down to the range of 10^{-10} g.

The shape of the ion-current curve can also give information about the rate of

TABLE I

SUMMARY OF INTEGRATED ION-CURRENT DATA

Formula	*M.W.*	*Mass peak used*		*Sensitivity* $(mm^2/\mu g)$	*Peak splitting*[a]	*Comments*
		Formula	*m/e*			
$Ho(HFM)_3$	1050	$Ho(HFM)_2^+$	755	700	+	Sharp peak, no residue in probe
$Ho(PFM)_3$	900	$Ho(PFM)_2^+$	655	580	+	No residue
$Ho(TPM)_3$	750	$Ho(TPM)_2^+$	555	560	+	No residue
$Ho(DPM)_3$	714	$Ho(DPM)_2^+$	531	488	−	Slight thermal decomposition, slight residue in probe
$Ho(TFA)_3$	624	$Ho(TFA)_2^+$	471	616	+	Thermal decomposition, slight residue in probe
$Ho(TTA)_3$	828	$Ho(TTA)_2^+$	607	444	+	No residue in probe
$Ho(BTA)_3$	810	$Ho(BTA)_2^+$	595	200	+	No residue in probe
$Ho(DBM)_3$	834	$Ho(DBM)_2^+$	611	404	−	No residue in probe
HoA_3	462	HoA_2^+	363	480	−	No residue in probe
$NaHo(TPM)_4$	968	$Ho(TPM)_3^+$	750	208	+	No residue in probe
$NaHo(TPM)_4$	968	Na^+	23	517	−	No residue in probe

[a] See below

sublimation. Figure 1 shows curves typical of those obtained when thermally stable tris chelates of holmium with symmetrical ligands are evaporated at different temperatures. As indicated above, a temperature must be selected so that a satisfactory curve is obtained.

When temperature studies of this type were done with some of the metal chelates described, an interesting effect was revealed. Figure 2 shows a typical ion-current curve for various thermally stable tris chelates of holmium with asymmetric ligands recorded at different temperatures. At the higher temperatures only single peaks are observed, but as the temperatures are lowered, the peaks are split into two symmetrical portions. This effect is observed with all chelates formed from unsymmetrical ligands, and is due to the differential rates of evaporation of the two geometrical isomers of the chelate. In no case has this effect been demonstrated with a symmetrically substituted acetylacetone, so that the splitting of the peak can be considered diagnostic of the existence of isomers, and hence provides information on the configuration of the metal chelate. Chromium trifluoroacetylacetonate has two such isomeric forms, the separation of which has been previously achieved by gas chromatography[5]. Unfortunately, this chelate is too volatile for a comparative separation to be made with the present technique.

It is probable that some form of thermal decomposition takes place during the evaporation of many metal chelates, because many of these are hydrated in the solid state; however, no ions of metal chelate hydrates have been discovered. More substantial thermal decomposition involving the breaking of chemical bonds may take place during evaporation, and when this occurs there is usually a residue remaining in the probe after all the ion current has disappeared. The shape of the ion-current curve provided by the molecule ion may not be affected by such thermal decomposition, but the curves from fragment ions may be distorted in the following manner. The curve from a fragment ion derived by a purely electron-impact process will have the same shape as that of the molecule ion curve but the same ion may be produced by direct ionisation of a neutral fragment arising from the unionised molecule by

TABLE II

SUMMARY OF CHROMATOGRAPHIC AND SUBLIMATION DATA

Sample	*Sublimation*		*Comments*	*IR and mass spec. before and after sublimation*	*Chromatography peak*	*Retention time*
	Commenced (°)	*Rapid (°)*				
Ho(HFM)$_3$	135	150	No residue on sublimation	Identical	Sharp	2 min 35 sec
Ho(PFM)$_3$	135	150	No residue	Identical	Sharp	2 min 40 sec
Ho(TPM)$_3$	165	180	Sample melted. No residue	Identical	Wide	6 min 45 sec
Ho(DPM)$_3$	150	165	Residue	Identical	Wide	6 min 10 sec
Ho(TFA)$_3$	No sublimation[a]		Sample melted and charred	—	Wide	4 min
Ho(TTA)$_3$	No sublimation		Sample melted	—	None	—
Ho(BTA)$_3$	No sublimation		Sample melted	—	None	—
Ho(DBM)$_3$	No sublimation		Sample did not melt	—	None	—
HoA$_3$	No sublimation		Sample did not melt	—	None	—
NaHo(TPM)$_3$	170	185	Residue	Identical	None	—

[a] At a temperature of 230°.

thermal decomposition. Such a thermal decomposition will have an energy of activation and will be a slow process, so that the ion-current curve will have a long "tail" (Fig. 3).

There is a correlation between the result obtained in this way and the chromatographic behaviour of metal chelates. Only in the cases of the metal chelates formed with highly fluorinated acetylacetones, *viz.*, Ho(HFM)$_3$ and Ho(PFH)$_3$, were sharp peaks obtained by chromatography under the conditions described in the experimental section. Of the remainder, Ho(DPM)$_3$, Ho(TPM)$_3$ and Ho(TFA)$_3$ gave wide tailing peaks and longer retention times; none of the other chelates emerged from the column after injection.

These results are compared with the sublimation data in Table II. It proved difficult to obtain precise sublimation temperatures because of the effect of particle size and of the problem of estimating the exact temperature at which sublimation commenced, hence only a temperature range is included in the Table. In order to determine whether any change took place on sublimation, the infrared absorption spectra and mass spectra of the chelates were recorded before and after sublimation. It can be seen from Tables I and II that those compounds which sublime at low temperature without change and without leaving a residue, and which may be chromatographed satisfactorily with a short retention time, give symmetrical ion-current curves with high sensitivity and leave no residue in the probe. Thus, the two metal chelates which may be used most satisfactorily in the determination of holmium are Ho(HFM)$_3$ and Ho(PFM)$_3$.

SUMMARY

Several substituted acetylacetones have been prepared and reacted with holmium to give tris chelates of the form HoL$_3$. One of these chelates has been converted to a tetrakis chelate of the form NaHoL$_4$. The mass spectra of these compounds have been studied and the integrated ion currents at significant *m/e* values have been related to the amounts of metal chelates evaporated into the ion source of the mass spectrometer. The shape of the integrated ion-current curve is shown to give information about the nature of the evaporation process. When the β-diketone (L) is asymmetrical as in the case of 1,1,1-trifluoro-5,5-dimethylhexan-2,4-dione, the existence of geometrical isomers of the chelate, HoL_3, is reflected in the shape of the integrated ion-current curve, which shows fine structure. The results of mass spectrometric studies are compared with those of the sublimation and gas chromatographic behaviour of the metal chelates.

RÉSUMÉ

Plusieurs acétylacétones substituées ont été préparées et utilisées comme réactifs de l'holmium pour donner des chélates de la forme HoL_3. L'un d'eux est transformé en chélate "tétrakis" de forme $NaHoL_4$. On examine les spectres de masse de ces composés; la pente de la courbe courant ion intégré peut renseigner sur la nature du processus d'évaporation. Lorsque l'acétylacétone (L) est asymétrique comme dans le cas de la 1,1,1-trifluoro-5,5-diméthylhexane-2,4-dione, on peut déceler l'existence des isomères géométriques du chélate HoL_3. Les résultats des études de spectrométrie de masse sont comparés avec ceux obtenus par sublimation et chromatographie gazeuse de ces chélates métalliques.

ZUSAMMENFASSUNG

Mehrere substituierte Acetylacetonate wurden hergestellt. Sie reagierten mit Holmium zu Tris-Chelaten der Form HoL_3. Einer dieser Chelate wurde in das Tetrakis-Chelat der Form $NaHoL_4$ umgewandelt. Die Massenspektren dieser Verbindungen wurden untersucht und die integrierten Ionenströme bei bestimmten *m/e*-Werten in Verbindung gesetzt mit den Beträgen der Metallchelate, die in der Ionenquelle des Massenspektrometers verdampften. Aus den Kurven der integrierten Ionenstrom-Kurven ergaben sich Informationen über die Natur des Verdampfungsprozesses. Wenn das Acetylaceton (L) asymetrisch ist, wie im Falle des 1,1,1-Trifluoro-5,5-dimethylhexan-2,4-dion, zeigt sich die Existenz eines geometrischen Isomeren HoL_3 in dem Verlauf der integrierten Ionenstromkurven, welche eine Feinstruktur besitzen. Die Ergebnisse der massenspektrometrischen Untersuchungen werden mit denen der Sublimation und dem gaschromatographischen Verhalten der Metallchelate verglichen.

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CATION-EXCHANGE SEPARATIONS IN ORGANIC SOLVENT–DITHIZONE MEDIA*

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Recently, the use of common extractants, as used in the liquid–liquid extraction of metal ions, has been studied with respect to their applicability to ion exchange[1-5]. The strongly acidic cation-exchange resin Dowex 50 has proved highly successful. On this exchanger, several unique separations of metal ions in organic solvent–mineral acid solutions containing certain extractants have been found to be possible. For instance, the alkali metals can be selectively separated from practically all other elements on Dowex 50 when 2-thenoyltrifluoroacetone in pyridine is used as eluent[1]. Another extractant that has proved to be extremely suitable is trioctylphosphine oxide. With this extractant dissolved in tetrahydrofuran or methanol in the presence of hydrochloric acid or nitric acid, very effective cation-exchange separations of scandium from the rare earths[2], and of hafnium plus zirconium[3] and thorium[4] from accompanying metal ions can be performed. With dimethylglyoxime dissolved in tetrahydrofuran–hydrochloric acid, nickel can be separated from alkali metals, alkaline earth metals, rare earths and other elements[5].

In the present paper the applicability of organic solvent–dithizone–nitric acid systems for the separation of metal ions on Dowex 50 was investigated. As a result very effective separations of several elements have been found to be possible.

EXPERIMENTAL

Reagents

Ion-exchange resin. Air-dried Dowex 50W-X8 (100–200 mesh; hydrogen form) was used for the column separations and for the batch experiments. Before use the resin was purified by washing it successively with 6 *M* nitric acid, distilled water and methanol, whereafter it was dried in air and stored in an amber bottle. For 1 kg of resin, 2 l of 6 *M* nitric acid, 5 l of distilled water and 2 l of methanol were used.

Diphenyldithiocarbazone (dithizone). The pure reagent was obtained from Fisher Scientific Company, New York.

Organic solvents. The following reagent-grade solvents were used: tetrahydro-

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furan, acetone, methanol, methyl glycol (monomethylether of ethylene glycol) and glacial acetic acid.

Eluent solution. Freshly prepared 0.01 *M* dithizone in tetrahydrofuran–1 *M* nitric acid (19:1) was used.

Tracers. Nitric acid solutions of the following tracers were used: ^{110m}Ag(I), ^{67}Cu(II), ^{207}Bi(III), ^{210}Pb(II),^{204}Tl(I), ^{22}Na(I), ^{137}Cs(I), ^{45}Ca(II), ^{85}Sr(II), ^{46}Sc(III), ^{169}Yb(III), ^{144}Ce(III), ^{241}Am(III), ^{233}U(VI), ^{230}Th(IV), ^{239}Pu(IV), ^{44}Ti(IV), ^{181}Hf(IV), ^{54}Mn(II), ^{59}Fe(III), ^{60}Co(II), ^{63}Ni(II), ^{65}Zn(II), ^{109}Cd(II), ^{203}Hg(II), and ^{124,125}Sb(III).

The radioactive measurements were made by standard counting techniques.

Determination of distribution coefficients. The batch distribution coefficients (K_d values) of the investigated elements were determined as described earlier[6].

Working procedure

Pretreatment of resin bed. Soak the resin (1 g) for about 5 min in a few ml of tetrahydrofuran–1 *M* nitric acid (19:1) and transfer the slurry to the ion-exchange column (250 mm long, 5 mm bore). Support the resin bed by a pad of glass or quartz wool and wash with 5–10 ml of the above mixture.

Sorption. Pass a mixture of 0.5 ml of 1 *M* nitric acid containing the metal ions to be separated (plus their radioactive tracers), with 9.5 ml of tetrahydrofuran (sorption solution), through the pretreated resin bed at a flow rate corresponding to the back-pressure of the resin column (about 0.35 ml/min). Under these conditions, silver and numerous other elements, *e.g.* copper, lead, rare earths, alkaline earth metals, alkali metals, uranium, thorium, iron, cobalt, zinc and cadmium, are strongly retained by the resin while mercury and antimony pass into the effluent. Complete the elution of these two unadsorbed elements by passing (at the same flow rate) 20–30 ml of tetrahydrofuran–1 *M* nitric acid (19:1).

Elution. Elute silver, copper and bismuth quantitatively with 20 ml of the eluent solution at a flow rate of 0.35 ml/min. This volume of eluent completely elutes up to 10 mg of the elements; if larger amounts are present, either the eluent volume or its concentration in dithizone must be increased to effect quantitative elution. In the eluate, silver, copper and bismuth can be determined radiometrically or they may be recovered by wet or dry ashing of the residue which is obtained after evaporation of the eluate. In the latter case the elements can be determined by any convenient means.

The adsorbed elements (except thorium) can be eluted with 10–20 ml of 6–8 *M* hydrochloric acid after preliminary removal of residual dithizone by means of a 10–20 ml wash with tetrahydrofuran–1 *M* nitric acid (19:1). Thorium can be removed with 6 *N* sulfuric acid[4].

RESULTS AND DISCUSSION

The distribution coefficients of silver (taken as a representative of the elements forming strong dithizone complexes) were measured on Dowex 50 in mixtures consisting of 95% organic solvent and 5% 1 *M* nitric acid (v/v) (Table I). For comparison, water was included in these studies. From the data shown it is seen that silver shows the strongest affinity for the resin in the tetrahydrofuran and acetone media, while its adsorption is relatively low from the purely aqueous system. Because dithizone and dithizonates show a very high solubility in tetrahydrofuran, all further experiments were carried out with this solvent.

If in the tetrahydrofuran–1 *M* nitric acid system the silver concentration was varied, its distribution coefficient of $8 \cdot 10^3$ did not change in the concentration range from traces to 200 mg of silver per 20 ml of mixture. However, in the presence of a sufficient quantity of dithizone the distribution coefficient of silver was always less than one.

TABLE I

DISTRIBUTION COEFFICIENTS OF SILVER ON DOWEX 50 IN ORGANIC SOLVENT–1 *M* NITRIC ACID (19:1) MIXTURES

Organic solvent	*Distribution coefficient*	*Organic solvent*	*Distribution coefficient*
Tetrahydrofuran	$8 \cdot 10^3$	Methyl glycol	430
Acetone	$12 \cdot 10^3$	Acetic acid	$4 \cdot 10^3$
Methanol	$2.9 \cdot 10^3$	Water	140

An increase of the acidity in the mixture from 5% of 1 *M* nitric acid to 5% of 3, 6 or 12 *M* nitric acid caused a decrease of the distribution coefficient of silver. However, in these more acidic solutions, dithizone was more or less rapidly converted to a yellow compound which did not form dithizonates and hence was ineffective for the elution of silver, copper and bismuth. In the presence of 5% of 1 *M* nitric acid, dithizone was stable for more than 24 h. Its stability was also high in organic solvents containing pyridine but under these conditions only a few elements, which include the alkali metals, were retained by Dowex 50[7].

To investigate the effect of varying dithizone concentrations on the adsorption of 26 elements, their distribution coefficients were measured in absence of dithizone and in presence of 0.001 *M* and 0.01 *M* concentrations of this extractant (Table II). It can be seen from Table II that in the absence of dithizone only mercury and antimony had very low K_d values so that they were separable from all the other elements listed. In the presence of dithizone, silver, copper and bismuth were also not retained by Dowex 50 because they form dithizonates which are sufficiently stable to prevent their adsorption.

In the dithizone systems each of the elements with a K_d value of less than one can be separated from all the other metal ions with distribution coefficients of the order of 10^2–10^5, which are equivalent to the magnitude of their separation factors. These separations are best performed by using the working procedure described in the experimental section. Numerous experiments employing this technique have shown that in all cases absolutely complete separations of tracer and macro amounts of the elements concerned can be achieved. If the sorption solution has the same composition as the eluent solution, it is also possible to separate cobalt from many elements including manganese and nickel. Under these conditions cobalt is not retained on Dowex 50 (see footnote Table II).

Unsatisfactory results are obtained if the separations (the same applies to batch studies) are performed in the presence of chloride or other halide ions. These must be removed completely before the separations, especially when elements such as silver, zinc, cadmium and iron have to be separated. Apart from forming insoluble silver chloride, the chloride ions readily react with the latter three elements to form anionic chloride complexes which prevent their adsorption.

TABLE II

DISTRIBUTION COEFFICIENTS OF 26 ELEMENTS ON DOWEX 50 IN 95% TETRAHYDROFURAN–5% 1 *M* NITRIC ACID MEDIA CONTAINING VARYING CONCENTRATIONS OF DITHIZONE

Element	*Molarity of dithizone*			*Element*	*Molarity of dithizone*		
	0.000 M	*0.001 M*	*0.01 M*		*0.000 M*	*0.001 M*	*0.01 M*
Ag	$8\cdot 10^3$	<1	<1	Yb	$>10^4$	$>10^4$	$>10^4$
Cu	$>10^3$	<1	<1	Ce	$>10^4$	$>10^4$	$>10^4$
Bi	31	<1	<1	Am	$>10^5$	$>10^5$	$>10^5$
Tl	$>10^3$	$>10^3$	$>10^3$	U	$>10^3$	$>10^3$	$>10^3$
Hg	<1	<1	<1	Th	$>10^3$	$>10^3$	>700
Co	$>10^3$	$12(>10^3)$[a]	$<1(540)$[a]	Pu	$8\cdot 10^3$	$8\cdot 10^3$	$>10^3$
Sb	3.6	2.4	<1	Ti	$>10^3$	$>10^3$	$>10^3$
Pb	75	107	200	Hf	$2\cdot 10^4$	$>10^4$	$2\cdot 10^3$
Na	$>10^3$	$>10^3$	$>10^3$	Mn	$2\cdot 10^4$	$>10^4$	$>10^4$
Cs	$1.2\cdot 10^4$	$>10^4$	$>10^4$	Fe	$>10^3$	$>10^3$	$>10^3$
Ca	$>10^3$	$>10^3$	$>10^3$	Zn	$>10^3$	$>10^3$	$>10^3$
Sr	$>10^4$	$>10^4$	$>10^4$	Cd	$>10^3$	$>10^3$	331
Sc	$>10^4$	$>10^4$	$>10^4$	Ni	$>10^3$	$>10^3$	$>10^2$

[a] The high K_d values for cobalt were obtained after adsorption of cobalt in the absence of dithizone (conditions of working procedure). If cobalt is directly added to the dithizone solutions, low K_d values are obtained.

The elution of macro amounts of silver, or of the other metal ions that form colored dithizonates, is an excellent example for the classroom demonstration of this separation method. Silver is adsorbed as a whitish band on top of the column from 95% tetrahydrofuran–5% 1 *M* nitric acid and on subsequent passage of the deep-green eluent solution (which can also be 0.001 *M* in dithizone) this band turns red. Almost simultaneously the eluate assumes an orange color (silver dithizonate). If the elution is continued with a sufficient volume of the eluent solution, the red band disappears and the effluent acquires a deep-green color as soon as all the silver is eluted.

SUMMARY

Numerous elements can be adsorbed on a column of the strongly acidic cation-exchange resin Dowex 50 from a mixture consisting of tetrahydrofuran and 1 *M* nitric acid (19:1). These elements include Ag, Cu, Bi, Pb, rare earths, alkaline earth metals, alkali metals, U, Th, Fe, Co, Zn and Cd; Hg and Sb are not retained and so can be separated from the adsorbed elements. Fractionation of the adsorbed elements can be effected by using as eluent 0.01 *M* dithizone in tetrahydrofuran–1 *M* nitric acid (19:1); the dithizonates of silver, copper and bismuth are selectively eluted while the other adsorbed metal ions are still retained. The technique is suitable for the separation of tracer and macro amounts of elements.

RÉSUMÉ

De nombreux éléments peuvent être adsorbés sur une colonne de résine cationique, Dowex-50, fortement acide, à partir d'un mélange tétrahydrofurane–acide nitrique 1 *M* (19:1). Ces éléments comprennent: Ag, Cu, Bi, Pb, terres rares, métaux alcalino-terreux et métaux alcalins, U, Th, Fe, Co, Zn et Cd; Hg et Sb ne sont pas retenus et peuvent ainsi être séparés des éléments adsorbés. Il est possible de fractionner les éléments adsorbés en utilisant comme éluant la dithizone 0.01 *M* dans le mélange tétrahydrofurane–acide nitrique 1 *M* (19:1). Les dithizonates d'argent, de cuivre et de bismuth sont élués sélectivement, tandis que les autres métaux adsorbés sont retenus.

ZUSAMMENFASSUNG

Zahlreiche Elemente können auf einer Kolonne des stark sauren Kationenaustauschers Dowex 50 aus einer Mischung von Tetrahydrofuran und 1 *M* Salpetersäure (19:1) adsorbiert werden. Unter diesen Elementen sind Ag, Cu, Bi, Pb, Seltene Erden, Erdalkalimetalle, Alkalimetalle, U, Th, Fe, Co, Zn und Cd. Hg und Sb werden nicht zurückgehalten und können damit von den genannten Elementen abgetrennt werden. Wird mit 0.01 *M* Dithizon in dem genannten Gemisch aus Tetrahydrofuran und Salpetersäure eluiert, so werden die Elemente Hg, Cu, und Bi selektiv abgetrennt. Die Technik ist geeignet zur Trennung von Spuren und Makromengen der Elemente.

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QUANTITATIVE SEPARATION OF THE ALKALI METALS BY CATION-EXCHANGE CHROMATOGRAPHY WITH BIO-REX 40 RESIN

APPLICATION TO SILICATE ANALYSIS

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The quantitative separation of the alkali metals from each other by ion-exchange chromatography has received considerable attention during the last decade. With sulphonated polystyrene cation exchangers separation factors for the heavier alkali metals are rather low ($\alpha_K{}^{Rb} \approx 1.2$, and $\alpha_{Rb}{}^{Cs} \approx 1.3$), and very large columns and elution volumes have to be used for quantitative work[1]. Much higher separation factors can be obtained by using inorganic ion-exchange materials such as ammonium molybdophosphate[2] or tungstophosphate[3], thallous tungstophosphate[4]; hydrous zirconium phosphate[5], oxide[6], tungstate[7], molybdate[8] or antimonate[9]; the hexacyanoferrate(II) salts of titanium[10], vanadium[11] and zinc[12], and antimonic acid[13], but the exchange behaviour of these materials is seldom reproducible and varies from batch to batch. In most cases the heavier alkalies show heavy tailing and when milligram amounts are present also heading. This leads to incomplete recoveries and makes these materials less suitable for accurate quantitative analytical work.

NELSON *et al.*[14] have investigated the distribution coefficients of the alkali metals in aqueous and partly methanolic solutions of hydrochloric acid with Dowex 50-X8, a sulphonated polystyrene, and Duolite C-3, a phenolformaldehyde cation exchanger. They have shown that the phenolic resin in 1 N hydrochloric acid gives a better separation factor for the heavy alkalies ($\alpha_K{}^{Rb} = 1.9$ and $\alpha_{Rb}{}^{Cs} = 4.2$) than the polystyrene resins. Quantitative aspects do not seem to have been investigated satisfactorily, and the published elution curve for the K–Rb pair does not look very promising. A redetermination of distribution coefficients carried out in this laboratory with BIO-REX 40, an analytical equivalent of the Duolite C-3 resin, suggested that an improved separation should be obtainable by using hydrochloric acid of lower concentration (0.7 N) instead of 1.5 N as eluent for the K–Rb separation. Furthermore, 1 M hydrochloric acid in 80% methanol gave a considerably better separation of lithium from large amounts of sodium than 2.4 M hydrochloric acid in 80% methanol suggested by NELSON *et al.*[14]. From this, a procedure for the quantitative separation and the accurate determination of the five alkali metals in synthetic mixtures has been developed and applied to the determination of the alkali elements in silicate minerals, plant material and water samples.

EXPERIMENTAL

Reagents and apparatus

Analytical reagent grade chemicals were used throughout. The resin was the BIO-REX 40 condensed phenol formaldehyde with $-CH_2SO_3H$ exchange groups (BIO-RAD Laboratories, Richmond, California). A batch marked No. 3470, 6.6.1966 was used for all experimental work unless stated differently. Borosilicate glass tubes of 2–2.5 cm inner diameter fitted with B19 ground glass joints at the top and glass sinter plates of No. 2 porosity and burette taps at the bottom, were used as columns. A Perkin Elmer 303 atomic absorption spectrometer was used for the determination of small and trace amounts of the alkali metals.

Equilibrium distribution coefficients

2.500 g of BIO-REX 40 resin in the H^+ form, dried in a "Towers vacuum pistol" at 60° with phosphorus pentoxide as drying agent, were equilibrated with 3 mmol of alkali chloride in 250 ml of aqueous hydrochloric acid by shaking for 24 h at 25°. After separation of the resin from the aqueous phase, the amounts of the alkali metals in both phases were determined by a suitable analytical method. From the results the equilibrium distribution coefficients

$$D = \frac{\text{moles on resin}}{\text{moles in solution}} \times \frac{\text{ml solution}}{\text{g dry resin}}$$

were calculated. They are presented in Table I.

TABLE I

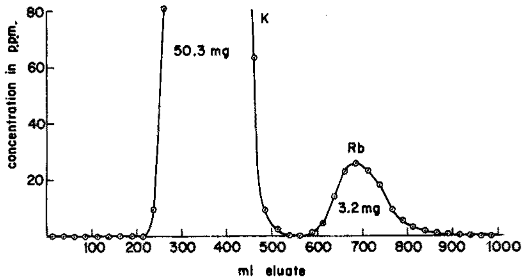
CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID WITH BIO-REX 40 RESIN

Element	*0.1 M*	*0.2 M*	*0.5 M*	*1.0 M*	*2.0 M*	*3.0 M*	*4.0 M*
Li	17.6	9.8	4.2	1.0	<0.5	<0.5	<0.5
Na	35.5	18.4	8.5	4.3	2.4	1.9	1.5
K	67	42.8	19.8	9.6	4.9	3.3	3.0
Rb	95	63	28.9	16.3	8.4	4.0	3.8
Cs	203	123	64	38.4	20.0	13.4	9.8

Elution curves

From the results in Table I, 0.70 *M* hydrochloric acid was selected as the most favourable eluent concentration for the separation of potassium and rubidium, the pair with the lowest separation factor. An elution curve was prepared with a column of 25 g (62 ml) of BIO-REX 40 resin (100–200 mesh, hydrogen form). The resin column was 18 cm in length and 2.1 cm in diameter. Potassium (50.3 mg) and rubidium (3.2 mg) as the chlorides in about 20 ml of 0.01 *M* hydrochloric acid were absorbed on the column and then eluted with 0.70 *M* hydrochloric acid at a flow rate of 2.0 ± 0.3 ml/min. Fractions of 25 ml were taken with an automatic fractionator and the amounts of potassium and rubidium in the fractions were determined by atomic absorption spectrometry; propane–butane gas, a flat water-cooled burner[15], and the 7665 Å and 7800 Å absorption lines, respectively, were used. The experimental curve is shown in Fig. 1. For comparison Fig. 2 shows a curve obtained with the same column, but with 1.50 *M* hydrochloric acid as eluent.

The separation factor for the Li–Na pair with sulphonated polystyrene[16,17] and with phenolic resins[14] is considerably enlarged by eluting with hydrochloric acid containing a large percentage of ethanol or methanol. NELSON *et al.*[14] have used 2.4 *M* hydrochloric acid in 80% methanol for the elution of lithium. The distribution coefficient for sodium is rather low under these conditions and only small amounts of sodium can be separated from lithium satisfactorily. More favourable conditions for practical separations are obtained by eluting with 1.0 *M* hydrochloric acid in 80% ethanol. An elution curve obtained with a column of 10 g (25 ml) of BIO-REX 40 resin (100–200 mesh) is shown in Fig. 3. The resin column was 8 cm in length and 1.9 cm in diameter and the flow rate was kept at 1.5 ± 0.3 ml/min.



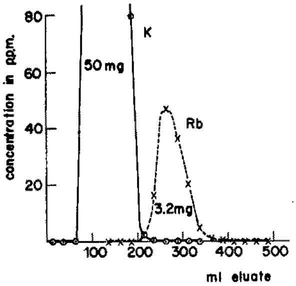
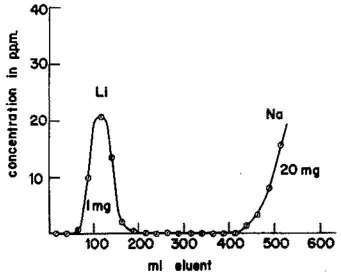


Fig. 1. Elution curve for K–Rb with 0.70 *M* HCl. Column of 25 g (62 ml) of BIO-REX 40 resin. diam. = 2.1 cm. Flow rate 2.0 ± 0.3 ml/min.

Fig. 2. Elution curve for K–Rb with 1.50 *M* HCl. Column of 25 g (62 ml) of BIO-REX 40 resin. diam. = 2.1 cm. Flow rate 2.0 ± 0.3 ml/min.



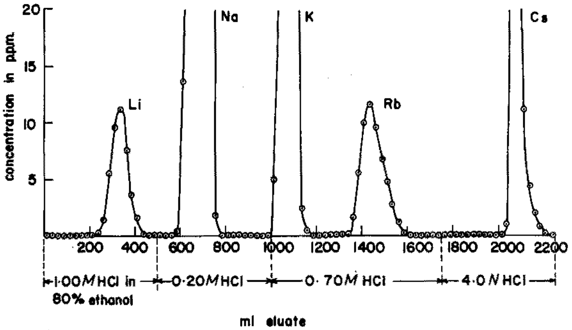


Fig. 3. Elution curve for Li–Na with 1.00 *M* HCl in 80% ethanol. Column of 10 g (25 ml) of BIO-REX 40 resin. diam. = 1.9 cm. Flow rate 1.5 ± 0.3 ml/min.

Fig. 4. Elution curve for mixture of Li, Na, K, Rb and Cs. Column of 25 g (62 ml) of BIO-REX 40 resin. diam. = 2.1 cm. 1 mg Li, 50.3 mg Na, 13.0 mg K, 1.4 mg Rb and 2.0 mg Cs.

Figure 4 shows a complete separation of a mixture containing 1.0 mg of lithium, 50.3 mg of sodium, 13.0 mg of potassium, 1.4 mg of rubidium and 2.0 mg of cesium. The elements were absorbed on a column of 25 g (62 ml) of BIO-REX 40 resin as described for the K–Rb separation, and then eluted with a sequence of 500 ml of 1.00 *M* hydrochloric acid in 80% ethanol for lithium, 500 ml of 0.20 *M* hydrochloric acid for sodium, 750 ml of 0.70 *M* hydrochloric acid for potassium, followed by rubidium, and 500 ml of 4.00 *M* hydrochloric acid for cesium. Flow rates of 1.5 ± 0.3 ml/min for the Li–Na separation and 3.0 ± 0.5 ml/min for the others were maintained throughout. The elements were determined by atomic absorption spectrometry as outlined above, the 6708 Å, 5890 Å and 8521 Å absorption lines being used for Li, Na and Cs, respectively.

Quantitative separation of synthetic mixtures

Synthetic mixtures containing two alkali metals as the chlorides in 0.01 *N* hydrochloric acid were prepared and adsorbed on columns of BIO-REX 40 resin (100–200 mesh, hydrogen form). Columns containing 20 g (50 ml) of resin were used for Li–Na and Rb–Cs, and columns of 30 g (75 ml) of resin for Na–K and K–Rb separations. The following eluents were used:

Li–Na : 400 ml 1.00 *M* hydrochloric acid in 80% ethanol for lithium, 250 ml of 0.20 *M* hydrochloric acid for sodium.
Na–K : 350 ml of 0.50 *M* hydrochloric acid for sodium, 300 ml of 2.00 *M* hydrochloric acid for potassium.
K–Rb : 625 ml of 0.70 *M* hydrochloric acid for potassium, 300 ml of 2.00 *M* hydrochloric acid for rubidium.
Rb–Cs: 400 ml of 1.50 *M* hydrochloric acid for rubidium, 500 ml of 4.0 *M* hydrochloric acid for cesium.

Finally a mixture containing all five alkaline earth elements was analysed with a column of 25 g (62.5 ml) of BIO-REX 40 resin and the eluent concentrations and volumes as given for Fig. 4. The flow rates were similar to those outlined under "elution curves". After the eluates had been evaporated to dryness, large amounts of the elements were determined gravimetrically, lithium as the sulphate, sodium as the chloride and potassium, rubidium and cesium as the tetraphenylborates. Small amounts were determined by atomic absorption spectrometry as outlined before. The results are presented in Table II.

TABLE II

QUANTITATIVE SEPARATION OF SYNTHETIC MIXTURES

mg taken				*mg found*[a]			
Li	7.06	Na	23.04	Li	7.05 ± 0.03	Na	23.06 ± 0.08
Li	0.353	Na	230.4	Li	0.353 ± 0.004	Na	230.5 ± 0.4
Li	70.6	Na	0.461	Li	70.7 ± 0.2	Na	0.462 ± 0.005
Na	23.04	K	39.62	Na	23.05 ± 0.07	K	39.60 ± 0.09
Na	0.461	K	39.62	Na	0.460 ± 0.006	K	39.61 ± 0.07
Na	23.04	K	0.396	Na	23.06 ± 0.08	K	0.395 ± 0.004
K	58.85	Rb	1.25	K	58.82 ± 0.12	Rb	1.25 ± 0.01
Rb	43.42	Cs	67.53	Rb	43.40 ± 0.11	Cs	67.53 ± 0.14
Rb	0.434	Cs	135.1	Rb	0.434 ± 0.004	Cs	135.0 ± 0.3
Rb	86.84	Cs	0.675	Rb	86.83 ± 0.21	Cs	0.673 ± 0.006
Li	1.41			Li	1.41 ± 0.01		
Na	46.08			Na	46.11 ± 0.15		
K	19.81			K	19.80 ± 0.05		
Rb	1.08			Rb	1.07 ± 0.01		
Cs	2.17			Cs	2.16 ± 0.02		

[a] The results are means of triplicate determinations.

Determination of alkali metals in silicate minerals

From the work described above, a method for the quantitative separation and accurate determination of the alkali metals in silicate minerals was elaborated and applied to the analysis of the standard granite No. W1, the potassium feldspar No. 70A and the burnt refractory No. 76 of the U.S. National Bureau of Standards.

Procedure. Dissolve the samples (1 g) in hydrofluoric–sulphuric acid mixtures in platinum dishes and heat to fumes of sulphur trioxide. Avoid prolonged fuming. (The total amount of sulphuric acid present was about 25 mmol.) Add 20 ml of 0.5 *M* oxalic acid and 10 ml of 2.5 *M* hydrochloric acid and warm gently until solids dissolve. (Silicate minerals which do not dissolve by this method have to be attacked by treatment with hydrofluoric acid alone or in mixtures with nitric or sulphuric acid in a Teflon-lined bomb at elevated temperatures (250°) and pressures.) Add another 80 ml of 0.5 *M* oxalic acid and a few drops of 30% hydrogen peroxide and dilute the solution to about 200 ml. Pass through a column of 10 g (23 ml) of AG1-X8 anion-exchange resin (100–200 mesh) which has been equilibrated with 50 ml of 0.5 *M* oxalic acid; the resin column should be 7.5 cm long and 1.9 cm in diameter. Elute alkali and alkaline earth metals plus manganese at a flow rate of 3.0±0.5 ml/min with 100 ml of 0.1 *M* hydrochloric acid containing 0.05 *M* oxalic acid. Al, Fe(III), Ti(IV), Zr, Hf, V(V), W(VI), Nb(V), Ta(V) and Mo(VI) are retained by the column as oxalato complexes. Collect the eluate from the beginning of the absorption step, mix by stirring, and pass through a column of 25 g (75 ml) of AG50W-X8 cation-exchange resin (200–400 mesh); the column should be 17.5 cm long and 2.5 cm in diameter. Remove oxalic and sulphuric acid by washing with 100 ml of 0.01 *M* hydrochloric acid. Elute lithium plus sodium with 600 ml of 0.50 *M* nitric acid at a flow rate of 3.5±0.5 ml/min; then elute potassium, rubidium and cesium with 650 ml of 0.60 *M* nitric acid at the same flow rate. The alkaline earth elements and manganese are retained by the column. Evaporate the Li–Na fraction to dryness, dissolve in 0.01 *M* hydrochloric acid and separate the two elements on a 10-g (25-ml) column of BIO-REX 40 resin as described under *Quantitative separation.* Evaporate the K–Rb–Cs fraction to dryness, dissolve in 0.01 *M* hydrochloric acid, and absorb on a column of 25 g (62 ml) of BIO-REX 40 resin of 16 cm length and 2.0 cm diameter. Elute potassium with 550 ml of 0.70 *M* hydrochloric acid, rubidium with another 500 ml of 0.70 *M* hydrochloric acid, and finally cesium with 600 ml of 4.0 *M* hydrochloric acid. Evaporate the fractions to dryness and determine the alkali metals, after dilution with a suitable volume of water, by atomic absorption spectrometry using the conditions outlined before. Large amounts can be determined gravimetrically. Blank runs were taken through the whole procedure and the results corrected accordingly. The results are presented in Table III.

Determination of alkali metals in other materials

Tobacco leaves. Ash 5-g samples of the dry leaves at 600°, dissolve the residue in 10 ml of 2.5 *M* sulphuric acid plus a few ml of hydrofluoric acid and analyse as described for silicate minerals.

Tap water. Acidify 5-l samples of tap water with 3 ml of concentration hydrochloric acid and evaporate to about 150 ml. Precipitate K, Rb and Cs quantitatively as the tetraphenylborates, the potassium serving as carrier for the two minor elements. Separate the precipitate and dissolve in acetone. After addition of an equal amount of

TABLE III

DETERMINATION OF ALKALI METALS IN SILICATES AND OTHER SAMPLES

Sample	*p.p.m. Li*	*% Na*	*% K*	*p.p.m. Rb*	*p.p.m. Cs*
Granite No. W1[a]	15.2 ± 0.2 [12.1][c]	2.19 ± 0.04 [2.09]	0.64 ± 0.02 [0.63]	22.0 ± 0.4 [22.0]	2.2 ± 0.1 [1.1]
Feldspar No. 70A[b]	2.99 ± 0.04 [not available]	2.43 ± 0.03 [2.50]	11.87 ± 0.02 [11.80]	543 ± 6 [0.06%]	12.2 ± 0.8 [not available]
Burnt refractory No. 76[b]	0.108 ± 0.001% [0.11%]	0.77 ± 0.01 [0.27 to 0.66]	1.55 ± 0.05 [1.54]	Trace [not available]	10.8 ± 0.3 [not available]
Tobacco leaves	8.7	0.0304	1.302	21.7	Trace
Pretoria tap water	Not determined	Not determined	3.03 ± 0.01 p.p.m.	2.00 ± 0.04 parts per 10^9	<1 part per 10^8

[a] Average of 6 analyses.
[b] Average of 4 analyses.
[c] [Standard values in brackets].

water, pass the solution through a column of 25 g of BIO-REX 40 resin as described. Wash the acetone through the column with 50 ml of water, elute the three heavy alkalies and determine as described for silicate analysis.

DISCUSSION

The described work provides a satisfactory method for the quantitative separation of the Group IA elements, except francium.

Optimal conditions

Li–Na. Milligram amounts can be separated very satisfactorily on a column of 10 g of BIO-REX 40 resin by eluting lithium with 1.0 *M* hydrochloric acid in 80% ethanol. Amounts up to several millimoles of each element can be separated on a 20-g column in a time of about 5 h (including elution of sodium), compared with the 30 h required for the procedure described by NEVORAL[16] with Dowex 50-X8 resin and 0.6 *M* hydrochloric acid in 60% ethanol as eluting agent for lithium, but it should be pointed out that the separation time on a column of AG50-X8 resin, an equivalent of Dowex 50-X8, can be reduced to about 3 h by using a 10-g (30-ml) resin column of 2 cm diameter and 1.0 *M* hydrochloric acid in 70% ethanol at a flow rate of about 3 ml/min as eluting agent for lithium[18].

Na–K. The best practical separation is obtained with 0.20–0.30 *M* hydrochloric acid as eluting agent. Fairly large columns (30 g) are required for the satisfactory separation of mixtures containing 1 mmol of each element. Separation on polystyrene resin[19] with 0.50 *M* hydrochloric acid or nitric acid is slightly superior because of the larger capacity of this resin and faster exchange rates. The presence of alcohol increases the separation factor D_K/D_{Na} considerably[14]. Yet actual separations with 80% alcoholic hydrochloric acid eluents are less satisfactory than those with aqueous 0.20 *M* hydrochloric acid. Exchange rates are very slow and peaks are very wide and show heavy tailing even with slow flow rates and with a resin of small particle size (200–400 mesh).

K–Rb. The best conditions for practical separation were obtained by eluting potassium with 0.70 *M* hydrochloric acid. Rubidium then can be eluted with hydrochloric acid of the same or a higher concentration. The separation factor $\alpha = D_{Rb}/D_K$ is only 1.7 (Table I). Fairly large resin columns therefore are required. On a 25-g (62-ml) column only up to about 3 mg of rubidium can be separated from 50 mg of potassium. Separation by elution with 1.50 *M* hydrochloric acid is considerably less satisfactory as shown by comparison of Figs. 1 and 2. Elution with alcoholic hydrochloric acid is impractical because the distribution coefficient of potassium is too high. Increasing the acid concentration to obtain lower distribution coefficients is unsatisfactory because the exchange rates become very slow and serious peak broadening and tailing occur. On elution with 3.0 *M* hydrochloric acid in 60% ethanol from a 30-g resin column, the potassium and rubidium peaks were extremely wide and overlapped.

Rb–Cs. A good quantitative separation is obtained by eluting rubidium with 1.50 *M* hydrochloric acid and cesium then with 4.0 *M* hydrochloric acid. This separation is attractive because the eluting agent can be removed much more easily by evaporation than the salt solutions required for the elution of cesium and rubidium from most inorganic ion-exchangers.

Behaviour of different batches of resin

An investigation showed that the distribution coefficients obtained with various batches of formaldehyde resin were far less reproducible than coefficients obtained with polystyrene resins like Dowex 50 and AG50. For three batches marked No. 3470, 6.6.1966; No. 4551, 11.4.1967 and No. 4079, 14.6.1967, the distribution coefficients for potassium and rubidium did not vary more than ±10% of their average value, but for a fourth batch marked No. 3308, 29.7.1965, the coefficients were only about 60% of the value obtained for the other batches, and about 0.4 *M* hydrochloric acid was found to be the optimum eluent concentration. Different bottles of resin within the same batch gave consistent distribution coefficient values. Furthermore the separation factor D_{Rb}/D_K seemed to be reasonably consistent for all four batches of resin. It follows from the above that the distribution coefficients and conditions for separation of the K–Rb pair presented in this paper therefore cannot be applied to other batches of resin. With an unknown batch a few distribution coefficients of potassium should be determined in the range 0.1 to 1.0 *M* hydrochloric acid. From a plot of the coefficients against acid concentration, the most favourable acid concentration can be estimated with a *D*-value of about 15 to 17. Conditions for the other ion pairs are less critical and the eluent concentration can be adjusted approximately by applying the same factor.

Conclusions

Separations are quantitative up to amounts of 1 mmol and sometimes more of each element in binary mixtures with the column dimensions described, the K–Rb pair being the only exception. The described application to silicate analysis provides accurate and reliable results down to concentrations of a few p.p.m. and should be useful for reference analysis. The danger of losing alkali metals by adsorption on, and inclusion in, bulky precipitates which leads to low results, especially when only trace amounts are present, is avoided. Table IV shows the estimated lower limits of amounts which can be determined in silicates; a final volume of 5 ml of solution and measurement of 10% absorption with 5 times scale expansion on a Perkin Elmer 303 atomic absorption spectrometer. Tetraphenylborate precipitation as a preconcentration step has been assumed for K, Rb and Cs. With care these limits are obtainable except in the case of sodium where it seems to be extremely difficult to obtain sufficiently low values for blank runs.

TABLE IV

LOWER LIMITS FOR DETERMINATIONS OF ALKALI METALS IN SILICATES BY THE DESCRIBED PROCEDURE

Element	*Sample weight (g)*	*p.p.m. alkali in sample*
Li	1	0.5
Na	1	0.05[a]
K	10	0.02
Rb	10	0.04
Cs	10	0.3

[a] Hypothetical value which is only applicable when it is possible to reduce reagent contamination to comparable values.

Although three successive ion-exchange steps may seem to be time-consuming, the actual amount of work involved is fairly small and many samples can be run at the same time.

SUMMARY

The application of BIO-REX 40, a phenolformaldehyde resin, to the quantitative separation of Li, Na, K, Rb and Cs is described. All five elements can be separated in a single procedure by using a 25-g (62-ml) resin column and eluting lithium with 500 ml of 1.00 *M* hydrochloric acid in 80% ethanol, sodium with 500 ml of 0.20 *M* hydrochloric acid, potassium with 250 ml of 0.70 *M* hydrochloric acid, rubidium with another 450 ml of 0.70 *M* hydrochloric acid and cesium with 500 ml of 4.0 *M* hydrochloric acid. Procedures are described for the accurate determination of alkali metals in silicate minerals, plant material and water. Al, Fe, Ti, Zr, V, Mo and some other elements are first separated by absorption as oxalato complexes on a column of AG1-X8 resin. The alkali metals are finally determined by gravimetry or atomic absorption spectrometry. Tables of distribution coefficients and quantitative results of analyses of synthetic mixture and standard silicate samples are presented together with typical elution curves.

RÉSUMÉ

On décrit une application du BIO-REX 40, une résine phénol-formaldéhyde, pour la séparation quantitative de Li, Na, K, Rb et Cs. Ces 5 éléments peuvent être séparés en utilisant une colonne de résine de 25 g (62 ml); on élue: le lithium avec 500 ml d'acide chlorhydrique 1 *M* dans l'éthanol à 80%; Na avec 500 ml d'acide chlorhydrique 0.2 *M*; K avec 250 ml de HCl 0.7 *M*; Rb avec une autre fraction de 450 ml de HCl 0.7 *M* et Cs avec 500 ml de HCl 4.0 *M*. Des méthodes sont décrites pour le dosage précis des métaux alcalins dans les silicates, les plantes et l'eau. Al, Fe, Ti, Zr, V, Mo et quelques autres éléments sont séparés d'abord par absorption des oxalatocomplexes sur une colonne de résine AG1-X8. Les métaux alcalins sont finalement dosés par gravimétrie ou spectrométrie par absorption atomique. Des tables de coefficients de partage et des résultats d'analyse sont donnés pour des mélanges synthétiques et des échantillons de silicates étalons, de même que des courbes d'élution typiques.

ZUSAMMENFASSUNG

Es wird die Anwendung des Phenoformaldehydharzes BIO-REX 40 zur quantitativen Trennung von Li, Na, K, Rb und Cs beschrieben. Alle 5 Elemente können in einem Schritt unter Verwendung einer 25-g-Kolonne (62 ml) getrennt werden. Lithium wird mit 500 ml 1.00 *M* Salzsäure in 80% Äthanol, Natrium mit 500 ml 0.20 *M* Salzsäure, Kalium mit 250 ml 0.70 *M* Salzsäure, Rubidium mit weiteren 450 ml 0.70 *M* Salzsäure und Cäsium mit 500 ml 4.0 *M* Salzsäure eluiert. Es wird die genaue Bestimmung der Alkalimetalle in Silikaten, Pflanzen und Wasser beschrieben. Al, Fe, Ti, Zr, V, Mo und einige andere Elemente werden vorweg durch Absorption als Oxalat-Komplexe auf einer AG1-X8-Harz-Kolonne abgetrennt. Die Alkalimetalle werden schliesslich gravimetrisch oder mit der Flammenabsorptionsspektroskopie bestimmt. Verteilungskoeffizienten, Analysenergebnisse mit synthetischen Mischungen und mit Standardgesteinen und typische Elutionskurven werden angegeben.

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A MODIFIED METHOD FOR DETERMINATION OF BORON WITH CURCUMIN AND A SIMPLIFIED WATER ELIMINATION PROCEDURE

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Because of its high sensitivity, curcumin can be used for the determination of very small amounts of boron. Several methods[1–13] are based on this reagent but most of them are rather complicated. They involve many practical difficulties and often so many precautions have to be considered that some of the possible accuracy is lost. The methods used can be divided into two groups, one using the complex rubrocurcumin and the other the complex rosocyanin. The structures of these two complexes according to ROTH AND MILLER[14] are shown in Fig. 1. The complex rubrocurcumin is formed in a reaction between boric acid, oxalic acid and curcumin in acetic acid. It is not very stable against hydrolysis, which causes lack of reproducibility in its use for the determination of boron. Accordingly, not only a strict reproducibility of the water content in the reaction solution, but also a high reproducibility of atmospheric moisture conditions are essential[1].

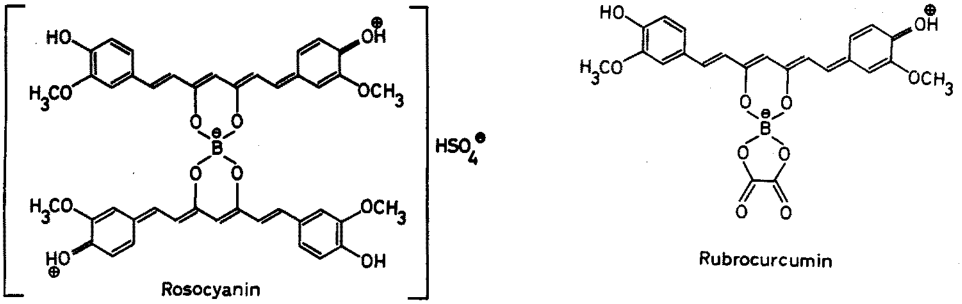

Fig. 1. Structures of rosocyanin and rubrocurcumin[14].

Rosocyanin is formed in a strongly acidic and almost water-free solution. The complex is very stable and its high extinction coefficient, about twice that for rubrocurcumin, makes it more suitable for boron analysis. One problem is, however, that the unreacted curcumin in the acidic solution forms a strongly interfering proton complex which must be destroyed before any measurements can be made. This can be performed in different ways which will be described later in this paper.

COMPARISON OF PREVIOUS METHODS

When applied to aqueous solutions, most curcumin methods include a first step to eliminate interference from water. This can be done by distillation, by evaporation of the sample, by solvent extraction, by a chemical reaction or a combination of these possibilities. In the method described by SPICER AND STRICKLAND[15] boron is distilled as methyl borate into a platinum dish containing glycerol–sodium hydroxide reagent, whereafter the distillate is evaporated to dryness. To remove the glycerol the dish must be heated to about 200° over a period of at least 10 min. The last traces of glycerol are removed by heating the dish over a Bunsen flame to a dull red-heat for about half a min. It is apparent that without a very strict control of the conditions this procedure will include many sources of error. Usually about 4% of the boron content is lost in the distillation stage. Other methods involving a preliminary separation of boron by distillation of methyl borate have been described[2-4].

In several methods the reactants are evaporated to dryness, which requires precisely controlled conditions. HAYES AND METCALFE[3] showed, however, that complex formation can take place in a non-aqueous medium without evaporation of the reactants. Furthermore, they found that small amounts of water could be permitted in a direct determination. In their "normal procedure" complex formation seemed to be unaffected by the addition of up to 0.3 ml of water. However, CRAWLEY[5] and later THIERIG AND UMLAND[6] found that the sensitivity is lowered discernibly by small amounts of water.

GREENHALGH AND RILEY[7] suggested that greater reproducibility could be obtained if the reaction proceeded in a completely liquid and homogeneous medium. They investigated organic compounds with boiling points over 120° and chose a mixture of phenol and acetic acid in which curcumin would dissolve. The water is rapidly removed from the sample when heated and the reaction between curcumin and the boric acid takes place in the homogeneous melt. They only investigated the rubrocurcumin complex but they observed the probable formation of rosocyanin when trichloroacetic acid was added instead of oxalic acid. Solvent extraction of boron from aqueous solutions combined with a direct determination by means of curcumin reagent has been given little attention. RYNASIEWICZ *et al.*[8] extracted boron with ethanol from sodium chloride made slightly acidic with hydrochloric acid, but in the further treatment the sample is evaporated to dryness.

CRAWLEY[5] investigated the use of acetic anhydride for the elimination of water by a chemical reaction catalyzed by hydrochloric acid. The reaction takes place in a platinum dish floating on a water bath at 40°. To a 1-ml sample 2 ml of acetic acid is added to obtain a controlled reaction and finally 2 drops of concentrated hydrochloric acid and 5 ml of acetic anhydride are added. In a few seconds a vigorous reaction takes place. After being cooled to room temperature the sample is treated in the same way as in the method of HAYES AND METCALFE[3]. After addition of curcumin–acetic acid and sulphuric–acetic reagents the solution is set aside for 5 min and then diluted to 100 ml with ethanol. The optical density is measured at 550 nm. The ethanol is added to the sample solution in order to remove the interference from the remaining curcumin–proton complex. Therefore the acidity must be reduced sufficiently to allow the curcumin to revert to the normal form. To ensure this it is necessary to dilute the solution to 100 ml.

In a modification of the method of HAYES AND METCALFE[3], GRINSTEAD AND SNIDER[9] replace the ethanol with an ammonium acetate buffer solution which allows the final volume to be reduced to about a fourth, thus increasing the sensitivity four times. Direct determinations can then be made on aqueous solutions for a sample volume of 0.50 ml between 0.1 and 3 mg of boron per litre, and for a sample volume of 0.25 ml between 0.1 and 5 mg of boron per litre. The method has been examined[16] in an investigation of the boron content in sea water off the Swedish west coast. It was found that on the addition of the acetate buffer solution crystallization sometimes could occur. The buffer solution was therefore diluted with redistilled water to 1.1 l instead of 1.0 l. With a sample volume of 0.200 ml determinations could be made without difficulties up to 4.0 mg of boron per litre. With the recommended sample volumes, however, a slight tendency for aggregation of the curcumin complex was observed in the analysis of higher concentrations than 4 mg of boron per litre.

For determination of boron in trace quantities HAYES AND METCALFE[3] diluted the reaction solution with water whereby the curcumin complex precipitated. The rosocyanin was then collected on an asbestos pad in a soda-glass filtration column, rinsed with water and then washed with diethyl ether until the eluate was colourless. Finally the complex was dissolved in a solution of ethanol containing 0.1% of acetic acid. A final volume of 10 ml can be obtained in this way. In a modification of this method, THIERIG AND UMLAND[6] collected the precipitated rosocyanin by solvent extraction with a methyl ethyl ketone–chloroform–phenol solution or a cyclohexanone–phenol solution.

The ranges and the precision of the different methods mentioned are summarized in Table I. Unfortunately some authors give little information about the accuracy and precision of their methods. Some sample standard deviation values given in Table I have been calculated from the few figures given in the particular paper.

From this introductory discussion the following conclusions can be drawn.

(*1*) Of the two complexes possible, rosocyanin, which is very stable against hydrolysis and has a high extinction coefficient, is to be preferred for a sensitive determination of boron.

(*2*) A method based on a reaction which proceeds directly in a completely liquid and homogeneous solution is less time-consuming and seems to be more accurate than methods which involve distillation or evaporation processes.

(*3*) For the destruction of the interfering proton complex of curcumin an acetate buffer solution instead of ethanol will keep the volume of the final solution small.

(*4*) For the measurement of very small amounts of the coloured complex solvent extraction is to be preferred to precipitation.

These requirements have all been taken into consideration in the method described in this paper.

EXPERIMENTAL

Apparatus

Measurements of spectra and absorbances were made with a Beckman DB or a Hitachi-Perkin Elmer 139 spectrophotometer using 0.5-, 1-, 4- and 5-cm cells.

TABLE I

MAIN PREVIOUS METHODS FOR THE DETERMINATION OF BORON WITH CURCUMIN

Method	*Complex used*	*Sample treatment*	*Range*	*Sample standard deviation*	*Sensitivity according to Sandell ($\mu g/cm^2$)*
SPICER AND STRICKLAND[1] procedure 1	Rubrocurcumin	Evaporation and distillation as methyl borate. Evaporation of the reactants	2–15 μg	0.10 μg	$2 \cdot 10^{-4}$ [a]
procedure 2	Rubrocurcumin	Evaporation and distillation as methyl borate. Evaporation of the reactants	0.5–4 μg	0.06 μg	
procedure 3	Rosocyanin	Evaporation and distillation as methyl borate. Evaporation of the reactants	0.005–0.2 μg	0.0015–0.011 μg	$8 \cdot 10^{-5}$ [a]
FREEGARDE AND CARTWRIGHT[2]	Rosocyanin	Distillation of methyl borate. Evaporation	~0.3 μg	0.033 μg	
HAYES AND METCALFE[3] procedure 1	Rosocyanin	As above but without evaporation	0–1.5 μg		$6.0–6.5 \cdot 10^{-5}$
procedure 2	Rosocyanin	As above but without evaporation	0–7.0 μg		
procedure 3	Rosocyanin	As under 1. Complex separation by precipitation	0–0.15 μg		
HAYES AND METCALFE[10] procedure 4	Rosocyanin	Separation as methyl borate	0.1–3.5 p.p.m.	5%	
procedure 5	Rosocyanin	Complex formed in a water solution and precipitated	~0.5 p.p.m.	6% [a]	
ELWELL AND WOOD[4]	Rosocyanin	Direct addition of reactants. Interface separation of rosocyanin formed.	0.1–0.5 p.p.m. 0.1–50 p.p.m. By variation of sample weight or volume taken.	Not given	
CRAWLEY	Rosocyanin	Water removed by acetic anhydride	Not given	Not given	

Thierig and Umland[6] procedure 1	Rosocyanin	Complex formation according to Hayes and Metcalfe[3]. Solvent extraction with methylethyl ketone, chloroform and phenol	8–100 μg B/10 ml	2.3 mg/10 ml. At the lower limit 3 ng/10 ml.	
procedure 2	Rosocyanin	Complex formation according to Hayes and Metcalfe[3]. Solvent extraction with cyclohexanone and phenol	8–1000 ng/10 ml	2.3 ng/10 ml. At the lower limit 3 ng/10 ml.	
Grinstead and Snider[9]	Rosocyanin	Direct addition of reactants	0.1–5.0 mg/l	Not given	
McIntosh and Cox[12]	Rosocyanin	Fusion with sodium carbonate	B_2O_3 26–80 p.p.m.	~5.5%[a]	
Chirnside *et al.*[11]	Rubrocurcumin	Sample dissolved by electrolysis and directly treated with the reactants	2–23 p.p.m.	7–17%[a]	
Rynasiewicz *et al.*[8]	Rubrocurcumin	Extraction and evaporation	0.1–2.0 p.p.m.	16%	
Greenhalgh and Riley[7]	Rubrocurcumin	Sample and reactants heated in a phenol–acetic acid melt	0.2–1.0 μg	0.45%	$1.3 \cdot 10^{-4}$

---

[a] Calculated from figures given in the paper.

Complex formation was carried out in polythene beakers or tubes and in some cases in teflon beakers. The use of glassware containing boron was completely avoided.

Reagents

Curcumin–acetic acid reagent. Dissolve 0.125 g of curcumin (British Drug Houses, Ltd) in 100 ml of glacial acetic acid. This reagent solution loses some of its efficiency after a few weeks.

Sulphuric–acetic acid reagent. Mix equal volumes of sulphuric acid, s.g. 1.84, and glacial acetic acid.

Buffer solution[9]. Dissolve 250 g of ammonium acetate plus 300 ml of glacial acetic acid in sufficient water to make 1 l.

Standard buffer solution. Mix 90 ml of ethanol (96%), 180 g of ammonium acetate and 135 ml of glacial acetic acid and dilute to 1 l with water.

Extraction solution. Mix 100 ml of methyl isobutyl ketone and 150 ml of chloroform plus 1 g of phenol. This solution should be stored in a dark bottle, preferably in a refrigerator.

If not otherwise stated all the reagents are of analytical grade from Merck AG, Darmstadt. Propionic anhydride (>97%; B.D.H., Ltd) and oxalyl chloride (Merck AG, Darmstadt) were used.

Procedure

To 0.50 ml of an aqueous sample containing 0–5 mg of boron per litre in a polythene beaker, add 1.0 ml of glacial acetic acid and 3.0 ml of propionic anhydride and mix by swirling. Add 0.25 ml of oxalyl chloride dropwise. Set aside for 15–30 min and cool to room temperature. Now add 3.0 ml of sulphuric acid–acetic acid solution and 3.0 ml of curcumin reagent, mix thoroughly and let the sample stand for at least 30 min. Finally add 20 ml of the standard buffer solution. Cool to room temperature. Read the absorbance at 545 nm.

TABLE II

STANDARD PROCEDURES FOR ANALYSIS

Range no.	*1*	*2*	*3*	*4*	*5*	*6*
B (mg/l)	0.0033–0.015	0.01–0.25	0.2–1.0	0.5–5.0	1–10	5–40
Sample volume (ml)	5.00	2.00	1.00	0.50	0.250	0.100
Glacial acetic acid (ml)	10.0	4.0	2.0	1.0	0.5	0.25
Propionic anhydride (ml)	25.0	10.0	5.0	3.0	2.0	1.0
Oxalyl chloride (ml)	2.0	1.0	0.50	0.25	0.10	0.10
Reaction time (min)	*30*	*30*	*30*	*30*	*30*	*30*
Sulphuric acid–acetic acid (ml)	15.0	8.0	4.0	3.0	2.0	2.0
Curcumin reagent (ml)	15.0	8.0	4.0	3.0	2.0	2.0
Reaction time (min)	*240*	*120*	*30–60*	*30–60*	*30–60*	*30–60*
Buffer (ml)	—	50	25	20	15	15
Water (ml)	100	—	—	—	—	—
Methyl isobutyl ketone–chloroform–phenol (ml)	5 or 10	—	—	—	—	—
Cell length (cm)	4–5	2–4	1	1	0.5	0.5

For trace amounts of boron (< 0.01 mg boron per litre) a solvent extraction process for concentrating the coloured complex is necessary. After the boron–curcumin reaction has taken place with sufficient volume of sample (2–10 ml), transfer the reaction solution to a 200–300 ml separatory funnel with the help of 100 ml of distilled water. Add 5 or 10 ml of methyl isobutyl ketone–chloroform–phenol solution, stopper the tube and shake carefully. Separate and if necessary centrifuge to eliminate opalescence. Pipet the coloured liquid into a suitable cell and read the absorbance at 545 nm. Standard procedures for different ranges are shown in Table II.

DISCUSSION AND RESULTS

Elimination of water

The method of GRINSTEAD AND SNIDER[9] was found to be of limited value for direct determinations of less than 0.2 mg of boron per litre or where sample quantities of more than 0.50 ml of an aqueous sample are required. Even with a 0.50-ml sample, HAYES AND METCALFE[3] found that complex formation is reduced by 20% and with a 1.0-ml sample by 70%; this was confirmed. Furthermore, the standard deviation increases considerably with the volume used. Therefore the proposal of CRAWLEY[5] that acetic anhydride could be used to remove the water was investigated. In these experiments polythene tubes were used instead of platinum dishes. The reaction repeated as described[5] was found to be too vigorous, which can cause losses of boron. After the addition of the acetic anhydride the temperature rose immediately to about 120° and the reaction was not well controlled. This can be achieved, however, by cooling the sample and keeping it in an ice-water bath at a temperature of about 0°. The reaction is then less vigorous and the maximum temperature is *ca.* 105°. However, because of the reaction between the excess of acetic anhydride in the reaction solution and the water in the GRINSTEAD–SNIDER[9] acetate buffer solution, difficulties arise in obtaining reproducible results when the excess of curcumin–proton complex has to be eliminated. Another anhydride was therefore sought and propionic anhydride, $(CH_3CH_2CO)_2O$, for which a slower and less forceful reaction could be predicted, was investigated. To dissolve the propionic anhydride in the water a certain amount of acetic acid was found to be necessary, a ternary system being established (see Table III).

The uncatalyzed reaction between propionic anhydride and water is extremely

TABLE III

INVESTIGATION OF THE TERNARY SYSTEM WATER–ACETIC ACID–PROPIONIC ANHYDRIDE

Water (ml)	*Acetic acid (ml)*	*Propionic anhydride (ml)*	*Resulting mixture*
5.0	2.5	5.0	Inhomogeneous
5.0	5.0	5.0	Becomes homogeneous on stirring
5.0	10.0	5.0	Homogeneous
5.0	10.0	10.0	Homogeneous
5.0	10.0	20.0	Homogeneous
5.0	10.0	25.0	Homogeneous

slow. The first catalyst tried was concentrated hydrochloric acid. A mixture of 1 ml of water, 2 ml of glacial acetic acid and 2 ml of propionic anhydride reached its temperature maximum after about 8 min when 0.1 ml of concentrated hydrochloric acid was used. With the same amounts of water, acetic acid and propionic anhydride and 1.0 ml of hydrochloric acid, the temperature maximum was reached in about 40 sec, but it seemed illogical to add one ml of aqueous hydrochloric acid to eliminate one ml of water. Therefore, oxalyl chloride was investigated as the catalyst. Oxalyl chloride reacts with water in two ways:

$$(COCl)_2 + H_2O \rightarrow 2HCl + CO + CO_2$$

or

$$(COCl)_2 + 2H_2O \rightarrow (COOH)_2 + 2HCl$$

the first reaction predominating in aqueous solution. Because of the hydrogen chloride formed, the work should be done in a hood. Time–temperature curves are shown in Fig. 2 for different solutions catalyzed by oxalyl chloride or hydrochloric acid. In the first experiments oxalyl chloride was added directly to the aqueous sample. The reaction started immediately and reached in a few seconds its maximum temperature of about 70°. Then the acetic acid and the propionic anhydride were added. The reaction between anhydride and water is catalyzed by the hydrochloric acid formed in the previous reaction and dissolved in the remaining water. However, there is less risk of loss of boron when acetic acid is first added to the aqueous sample, then the propionic anhydride and finally the oxalyl chloride dropwise. The reaction has a temperature maximum at about 90° and is very easily controlled.

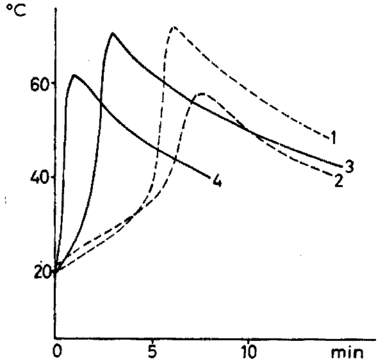

Fig. 2. Comparison of catalysts for the reaction between 1 ml of water sample and propionic anhydride.

Sample No.	*Acetic acid (ml)*	*Propionic anhydride (ml)*	*Hydrochloric acid (ml)*	*Oxalyl chloride (ml)*
1	3	5	0.1	0
2	2	2	0.1	0
3	3	5	0	0.2
4	2	2	0	0.5

Since the treatment of the sample (see *Procedure*) requires a sulphuric acid–acetic acid solution, CRAWLEY[5] tried to use this solution as a catalyst for the reaction between acetic anhydride and water. He found that only a 50% yield of the boron–curcumin complex was obtained by this procedure. This was also found to be the case with propionic anhydride (Table IV). This is probably due to the hydration of the sulphuric acid, which prevents some water from reacting with the propionic anhydride but not from later interfering with the complex formation between boron and curcumin.

TABLE IV

THE EFFECT OF OXALYL CHLORIDE ON THE ABSORBANCE WHEN WATER IS REMOVED WITH PROPIONIC ANHYDRIDE

Sample	*Treatment*	*Absorbance after colour development*
1,2	Oxalyl chloride added[a]	0.829, 0.831
3,4	Without oxalyl chloride	0.490, 0.495

[a] 0.2 ml per sample.

The remaining water content in the samples treated with oxalyl chloride was tested by the Karl Fischer method and found to be far below the maximum amount allowed for a direct determination according to HAYES AND METCALFE[3].

The buffer solution recommended by GRINSTEAD AND SNIDER[9] was modified to suit the method better. Thus the concentration of ammonium acetate and acetic acid was lowered to avoid crystallization, and some of the water was replaced by ethanol to ensure the solution of the rosocyanin formed.

Enrichment of the rosocyanin complex

For small amounts of boron, extraction with methyl isobutyl ketone was investigated. According to THIERIG AND UMLAND[6], solvents with a dielectric constant around 20, which are immiscible with water are suitable. Methyl isobutyl ketone has a dielectric constant of 12.4 at 24°. As was shown for methyl ethyl ketone and cyclohexanone the efficiency was increased by the addition of some phenol. A mixture of two parts of methyl isobutyl ketone with three parts of chloroform and 1 g of phenol is suitable for concentrations below 0.02 mg of boron per litre and the colour seems to be more stable than if cyclohexanone is used. Without further purification of the chemicals or the use of evaporation processes, a concentration of 0.0030 mg of boron per litre is the lower limit for a determination.

Stability of the coloured complex

The absorption of the developed colours was tested on different samples stored in daylight and in the dark. The colour is completely stable for about 2 h, and then a slight fading occurs which is so slow that a calibration curve can be obtained and an accurate determination can still be performed after a week. The decrease in absorbance after 5 days amounts to about 10%. There is no significant difference between samples kept in daylight and those kept in the dark.

Interferences

The only element known to interfere directly by forming a substance analogous to rosocyanin is germanium. No satisfactory method has been found for preventing the interference caused by fluoride during complex formation. When fluoride is present, the method of Gaestel and Huré[13] for the boron separation is recommended. Spicer and Strickland[1] consider that fluoride interferes at all levels but according to an investigation of Hayes and Metcalfe[3] up to 5 μg of fluoride can be present in a test solution containing 1 μg of boron without changing the absorbance. The same authors show that the interference of up to 30 mg of nitrate in samples containing 0.2–5 μg of boron can be overcome by a fuming process with aniline sulphate in a platinum dish.

Calibration curves and results

Different standard graphs obtained by procedures similar to those described in Table II are shown in Fig. 3; Beer's law is obeyed in the regions investigated. The

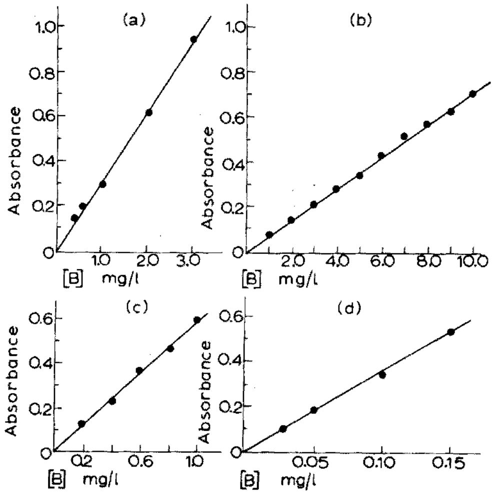

Fig. 3. Calibration curves:

Curve	*Sample volume (ml)*	*Final volume (ml)*	*Cell length (cm)*
a	0.5	26	1.0
b	0.25	30	0.5
c	2.00	37	4.0
d	3.00	82	5.0

TABLE V

REPRODUCIBILITY OF THE METHOD TESTED ON STANDARD SOLUTIONS OF BORIC ACID

Range (*cf.* Table II)	1	3	4	5
B present (mg/l)	0.01	0.50	3.0	8.0
Standard deviation (%)	4.2	0.9	1.2	1.6

TABLE VI

RECOVERY OF BORON ADDED TO SAMPLE FROM THE BALTIC SEA (BORNHOLM DEPTH)
(The chlorinity of the sample was $8.635^0/_{00}$)

Boron added (mg/l)	*Boron found*[a] *(mg/l)*	*Standard deviation (%)*	*Boron recovered (%)*
0	2.15	0.87	—
0.50	2.72	1.12	102.6
1.01	3.15	1.17	99.7
2.05	4.19	1.31	99.8

[a] Mean value of five determinations.

reproducibility of the method was tested by 10 replicate determinations carried out for different concentrations of boron, each in the middle of the range of a standard procedure described in Table II; the values are shown in Table V. The accuracy of the method was tested on Baltic sea water (Table VI); the recovery of boron is complete and thus the method is directly applicable for sea water examinations.

I am indebted to Professor DAVID DYRSSEN, head of the department, for valuable advice. Thanks are also due to Dr. R. E. CARTER for linguistic correction, and to Dr. R. GRINSTEAD for communicating his results[9] before publication.

SUMMARY

The formation of boric acid ester with curcumin is usually performed in highly acidic solution in the absence of water. Small water contents are permissible, but the efficiency is lowered. The water content of a sample can be eliminated by a reaction with propionic anhydride catalyzed by oxalyl chloride, thus avoiding methyl borate distillation or evaporation processes. An advantage is that the reaction between boron and curcumin takes place in a completely homogeneous liquid medium. The excess of protonated curcumin is best destroyed with an ammonium acetate buffer. For trace amounts of boron, extraction of the coloured complex with a mixture of methyl isobutyl ketone, chloroform and phenol is recommended. Standard procedures for aqueous solutions with boron contents between 0.0033–40.0 μg B/l are described.

RÉSUMÉ

L'ester de l'acide borique avec la curcumine s'obtient généralement en solution fortement acide, en l'absence d'eau. En présence de faibles quantités d'eau, le rendement est diminué. Les échantillons peuvent être deshydratés par l'anhydride propionique en présence de chlorure d'oxalyle comme catalyseur, ce qui permet d'éviter une distillation de méthylborate ou une évaporation. Cette réaction présente l'avantage de se produire dans un milieu liquide tout à fait homogène. L'excès de curcumine proton est détruit à l'aide d'un tampon acétate d'ammonium. Pour des traces de bore, on recommande de procéder à une extraction du complexe coloré au moyen d'un mélange méthylisobutylcétone, chloroforme et phénol. On décrit un procédé pour doser des teneurs en bore, en solutions aqueuses, allant de 0.0033 à 40.0 μg B/l.

ZUSAMMENFASSUNG

Die Bildung von Borsäureestern mit Curcumin geschieht im allgemeinen in stark saurer Lösung in Abwesenheit von Wasser. Kleine Wassergehalte sind zulässig, jedoch wird dadurch die Wirksamkeit verringert. Der Wassergehalt einer Probe kann durch die Reaktion mit Propionsäureanhydrid, welche durch Oxalylchlorid katalysiert wird, eliminiert werden. Dadurch wird die Methylboratdestillation oder der Verdampfungsprozess vermieden. Es ist ein Vorteil, dass die Reaktion zwischen Bor und Curcumin in völlig homogenen flüssigen Medien stattfindet. Ein Überschuss von Curcumin wird am besten mit einem Ammoniumacetatpuffer zerstört. Für Spuren von Bor eignet sich die Extraktion des Komplexes mit einer Mischung aus Methylisobutylketon, Chloroform und Phenol. Ein Standardverfahren zur Bestimmung von 0.0033–40.0 μg B/l in wässrigen Lösungen wird beschrieben.

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SPECIES FORMED IN THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH THORIUM OR LANTHANUM NITRATE AND FUNCTIONS SUITABLE FOR THE EVALUATION OF THE EQUIVALENCE POINTS

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Methods for the evaluation of equivalence points from potentiometric titration data are under investigation in our Department. A greater insight into a titration procedure may be obtained by using a computer to calculate the equilibrium concentrations of the species formed during the titration from information concerning total concentrations and equilibrium constants. A knowledge of these equilibrium concentrations provides all the information necessary for an appraisal of the various possible methods for evaluating the equivalence point. Furthermore, the titration errors pertaining to a particular method may be evaluated, and, since the interfering side-reactions are all known, it is often possible to refine a given titration procedure.

The potentiometric titration of fluoride with lanthanum and thorium nitrate has been studied by LINGANE[1] who used a lanthanum fluoride membrane electrode (Orion Research Inc.) to measure the fluoride ion activity. In order to illustrate how computer calculations may lead to a greater understanding of a titration problem, we have chosen four representative titrations from LINGANE's paper and have compared experimental and calculated data. The titrations have been calculated by means of the computer program HALTAFALL written by SILLÉN *et al.*[2], since this is an adequate program for the calculation of complicated chemical equilibria.

TITRATION OF FLUORIDE WITH THORIUM NITRATE IN ACID SOLUTION

Procedure[1]

An aliquot (5 ml) of 0.08000 M sodium fluoride was diluted to 100 ml and titrated with v ml of 0.0200 M thorium nitrate after the addition of 10 ml of 0.100 M hydrochloric acid.

Calculation

In order to be able to compare the calculated data with the experimental data, the theoretical log [F⁻] values were transformed into e.m.f. values according to the Nernst equation:

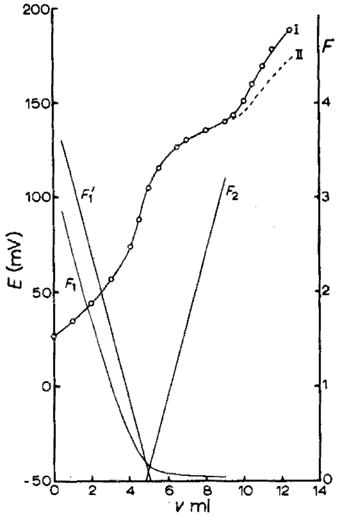
$$E = E^0 - RT \ln 10 \log [F^-]/F \qquad (1)$$

The stability and solubility constants used in the HALTAFALL calculations and specified in Table I were selected from HIETANEN AND SILLÉN[3] and from "Stability Constants"[4]. The experimental points and calculated titration curves are

TABLE I

CONSTANTS CHOSEN FOR THE CALCULATION OF THE TITRATION OF FLUORIDE WITH THORIUM AT pH 2. (cf. FIGS. 1–4)

Equilibria	*log of stab. constants*		*Choice of stability constants based on*
$2\,H_2O + Th^{4+} \rightleftharpoons Th(OH)_2^{2+} + 2H^+$	$^*\beta_{21}$	-9.1	Hietanen and Sillén[3]
$H_2O + 2Th^{4+} \rightleftharpoons Th_2OH^{7+} + H^+$	$^*\beta_{12}$	-2.65	Hietanen and Sillén[3]
$2H_2O + 2Th^{4+} \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$	$^*\beta_{22}$	-4.70	Hietanen and Sillén[3]
$3H_2O + 2Th^{4+} \rightleftharpoons Th_2(OH)_3^{5+} + 3H^+$	$^*\beta_{32}$	-8.83	Hietanen and Sillén[3]
$14H_2O + 6Th^{4+} \rightleftharpoons Th_6(OH)_{14}^{10+} + 14H^+$	$^*\beta_{6,14}$	-36.53	Hietanen and Sillén[3]
$15H_2O + 6Th^{4+} \rightleftharpoons Th_6(OH)_{15}^{9+} + 15H^+$	$^*\beta_{6,15}$	-40.37	Hietanen and Sillén[3]
$Th^{4+} + F^- \rightleftharpoons ThF^{3+}$	β_1	7.62	Initial value 7.93 from *Stab. Constants*[4]
$Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$	β_2	14.02	*Stab. Constants*[4] 49D combined with 63C
$Th^{4+} + 3F^- \rightleftharpoons ThF_3^+$	β_3	18.81	*Stab. Constants*[4] 49D combined with 63C
$H^+ + F^- \rightleftharpoons HF$	β_1	3.28	*Stab. Constants*[4] 63C
$H^+ + 2F^- \rightleftharpoons HF_2^-$	β_2	4.26	*Stab. Constants*[4] 49D combined with 63C
$ThF_4(s) \rightleftharpoons Th^{4+} + 4F^-$	K_{s0}	-27.81	*Stab. Constants*[4] 49D combined with 63C



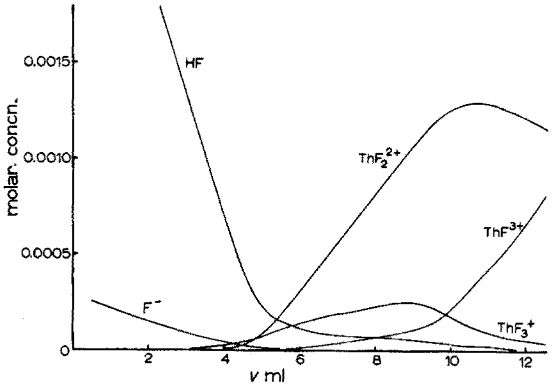


Fig. 1. Experimental points, two calculated titration curves and Gran plots $F_1 = (110 + v)[F^-]$, $F_1' = (110 + v)(1 + 1.91 \cdot 10^3[H^+])[F^-]$ and $F_2 = (110 + v)[F^-]^{-2}$ for the titration of 100 ml of 0.004 *M* fluoride + 10 ml of 0.1 *M* hydrochloric acid with *v* ml of 0.02 *M* thorium nitrate in acid solution (pH 2). Curve I was calculated using the stability constants in Table I. Curve II was calculated with the β_1 value for ThF^{3+} equal to $8.51 \cdot 10^7$ instead of $4.15 \cdot 10^7$. The functions F_1, F_1' and F_2 have been plotted on an arbitrary scale since this does not influence the point of intersection on the *v*-axis.

Fig. 2. Concentrations of the predominant species formed in the titration in acid solution (pH 2) of 100 ml of 0.004 *M* fluoride and 10 ml of 0.1 *M* hydrochloric acid with *v* ml of 0.02 *M* thorium nitrate.

shown in Fig. 1. In order to illustrate the effect which the choice of stability constant for a predominant complex has on the form of the titration curve, curves for two different values of β_1 for ThF^{3+} are shown in Fig. 1. With the set of equilibrium constants given in Table I, a perfect fit is obtained between the calculated and experimental curves. It is thus possible to use the results from the computer calculations to explain the main reactions occurring in the different parts of the titration curve. From Fig. 2, in which the different species formed during the titration have been plotted against v ml of titrant added, it is obvious that the predominant reaction for $v < v_{eq}$ ($v_{eq} = 5$ ml) is

$$Th^{4+} + 4HF \rightleftharpoons ThF_4(s) + 4H^+ \tag{2}$$

The following assumptions can thus be made for $v < v_{eq}$.

$$0.02\ (v_{eq} - v)/(v_0 + v) = 4([HF] + [F^-]) \tag{3}$$

where v_0 is the initial volume in the titration vessel and equal to 110 ml. Furthermore,

$$[HF] = 1.91 \cdot 10^3\ [H^+][F^-] \tag{4}$$

Combining eqns. (3) and (4),

$$F_1 = (v_0 + v)[F^-] = 0.005\ (v_{eq} - v)/(1 + 1.91 \cdot 10^3[H^+]) \tag{5}$$

Thus, if the function $F_1 = (v_0 + v)[F^-]$ is plotted against v ml for constant pH a straight line is obtained which, when extrapolated to $F_1 = 0$, intersects the v-axis at $v = v_{eq}$. In this particular case, however, the pH decreases with the addition of titrant causing F_1 to deviate from linearity (*cf.* Fig. 1). If the pH is measured during the titration and if β_1 for HF is known accurately the linear function

$$F_1' = (v_0 + v)(1 + \beta_1[H^+])[F^-] \tag{6}$$

should be used. This function, when extrapolated to zero, intersects the v-axis at the equivalence point, as is seen from Fig. 1. In the volume region $5 < v < 10$ ml, the main reaction is seen from Fig. 2 to be

$$ThF_4(s) + Th^{4+} \rightleftharpoons 2ThF_2^{2+} \tag{7}$$

and it can thus be assumed that

$$(v_0 + v)[ThF_2^{2+}] = 0.04\ (v - v_{eq}) \tag{8}$$

Furthermore,

$$[ThF_2^{2+}] = 1.05 \cdot 10^{14}\ [Th^{4+}][F^-]^2 \tag{9}$$

and, since solid ThF_4 is present,

$$[Th^{4+}][F^-]^4 = 1.55 \cdot 10^{-28} \tag{10}$$

Combining eqns. (8), (9) and (10)

$$(v_0 + v)[F^-]^{-2} = 2.45 \cdot 10^{12}\ (v - v_{eq}) \tag{11}$$

Thus, if $F_2 = (v_0 + v)[F^-]^{-2}$ is plotted against v ml and if no reactions other than the formation of ThF_2^{2+} occur in the volume region $5 < v < 10$ ml, F_2 will be linear and will intersect the v-axis at $v = 5$ ml when extrapolated to zero. As may be seen from Fig. 1 F_2 in fact intersects the v-axis at $v = 4.85$ ml rather than $v = 5$ ml and a systematic error can be estimated. This discrepancy may be attributed to the formation of a slight amount of ThF_3^+ in the volume region under consideration (*cf.* Fig. 2).

TABLE II

DATA TAPE FOR THE HALTAFALL PROGRAM FOR THE TITRATION OF FLUORIDE WITH THORIUM AT pH 2

Comments within parentheses are not punched on the tape

3 (No. of components)					
11 (No. of complexes)					
[complex]/[components Th^{4+} F^- H^+]					
7.940	−10	1	0	−2	($[Th(OH)_2^{2+}] = 7.94 \times 10^{-10}[Th^{4+}][H^+]^{-2}$)
2.240	−3	2	0	−1	($[Th_2OH^{7+}] = 2.24 \times 10^{-3}[Th^{4+}]^2[H^+]^{-1}$)
2.000	−5	2	0	−2	($[Th_2(OH)_2^{6+}] = 2.0 \times 10^{-5}[Th^{4+}]^2[H^+]^{-2}$)
1.480	−9	2	0	−3	($[Th_2(OH)_3^{5+}] = 1.48 \times 10^{-9}[Th^{4+}]^2[H^+]^{-3}$)
2.950	−37	6	0	−14	($[Th_6(OH)_{14}^{10+}] = 2.95 \times 10^{-37}[Th^{4+}]^6[H^+]^{-14}$)
4.270	−41	6	0	−15	($[Th_6(OH)_{15}^{9+}] = 4.27 \times 10^{-41}[Th^{4+}]^6[H^+]^{-15}$)
4.150	7	1	1	0	($[ThF^{3+}] = 4.15 \times 10^7[Th^{4+}][F^-]$)
1.047	14	1	2	0	($[ThF_2^{2+}] = 1.047 \times 10^{14}[Th^{4+}][F^-]^2$)
6.460	18	1	3	0	($[ThF_3^+] = 6.460 \times 10^{18}[Th^{4+}][F^-]^3$)
1.910	3	0	1	1	($[HF] = 1.91 \times 10^3[H^+][F^-]$)
1.820	4	0	2	1	($[HF_2^-] = 1.82 \times 10^4[H^+][F^-]^2$)
1					(No. of solid phases)
1.550	−28	1	4	0	($1.55 \times 10^{-28} = [Th^{4+}][F^-]^4$)
15					(No. of printing orders)
0	0				(print v ml titrant added)
−1	2				(print log $[Th^{4+}]$)
−2	2				(print log $[F^-]$)
−3	2				(print log $[H^+]$)
1	2				(print log $[Th(OH)_2^{2+}]$)
2	2				(print log $[Th_2(OH)^{7+}]$)
3	2				(print log $[Th_2(OH)_2^{6+}]$)
4	2				(print log $[Th_2(OH)_3^{5+}]$)
5	2				(print log $[Th_6(OH)_{14}^{10+}]$)
6	2				(print log $[Th_6(OH)_{15}^{9+}]$)
7	2				(print log $[ThF^{3+}]$)
8	2				(print log $[ThF_2^{2+}]$)
9	2				(print log $[ThF_3^+]$)
10	2				(print log $[HF]$)
11	2				(print log $[HF_2^-]$)
1					(No. of groups)
0.1					("stegbyte")
30					(No. of titration points)
4	−5	$-4_{10}-3$	0	0.02	(titration instructions[a] for component No. 1)
4	−5	$-4_{10}-3$	0.00364	0	(titration instructions[a] for component No. 2)
4	−5	$-4_{10}-3$	0.00909	0	(titration instructions[a] for component No. 3)
110					(initial volume in beaker)
0.25 0.5 1 1.5 2 2.5 3 3.5 4 4.25 4.5 4.75 5 5.25 5.5 5.75 6 6.5 7 7.5 8 8.5 9 9.5 10 10.5 11 11.5 12 12.5					(v ml titrant added)

---

[a] The instructions are: "hur"-number, guessed value for the natural logarithm of the free concentration of the component, tolerance, total concentration of the component in beaker and in buret.

It should be pointed out that all F-functions in Figs. 1, 5, 7 and 9 are calculated from the values of $[F^-]$ printed out by the computer. For solutions with unknown amounts of fluoride the F-functions are calculated from the e.m.f. data by means of eqn. (12) below.

The main advantage of using straight-line regression, a method first suggested by GRAN[5], to evaluate the equivalence point is that not only changes in the potential in the vicinity of the equivalence point but also data from a large part of the titration curve are exploited. Since F_1, F_1' and F_2 are extrapolated to zero it is sufficient to calculate values proportional to $[F^-]$ or $[F^-]^{-2}$ (or $[F^-]^{-3}$ in the titration with lanthanum below). A value proportional to $[F^-]$ is obtained from the experimental e.m.f. data by means of eqn. (1), *i.e.*

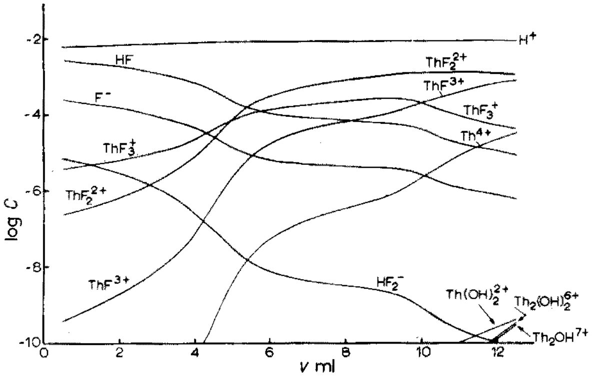


Fig. 3. The logarithmic concentrations of the different species formed in the titration in acid solution (pH 2) of 100 ml of 0.004 M fluoride and 10 ml of 0.1 M hydrochloric acid with v ml of 0.02 M thorium nitrate.

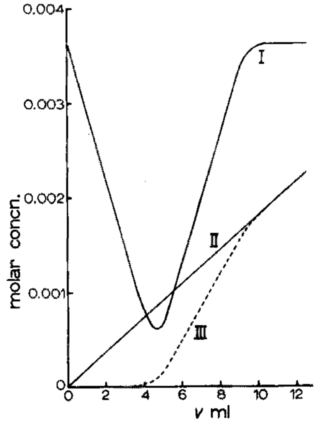


Fig. 4. Two different ways of illustrating the dissolution of the ThF_4 precipitate during the titration of an acid fluoride solution (100 ml 0.004 M NaF + 10 ml 0.1 M HCl) with v ml of 0.02 M thorium nitrate. Curve I shows the total concentration of fluoride in the solution corrected for dilution by multiplying by the factor $(110 + v)/110$. Curve II shows the total concentration of thorium as it should be if no precipitate were formed and curve III shows the actual total concentration of thorium in the solution multiplied by the dilution factor $(110 + v)/110$.

$$[F^-] \propto 10 \exp(-EF/RT \ln 10) \tag{12}$$

Only the predominating species are shown in Fig. 2. In order to obtain a survey of all complexes taken into consideration in the calculation of the titration curve a logarithmic scale must be used. Limiting the graphical representation in Fig. 3 to concentrations above 10^{-10} M, the hydroxo complexes are first visible at $v > 11$ ml, and they could therefore have been omitted in the calculation of this titration. The data tape specifying the stability constants, number of components in each complex printing orders etc., is shown in Table II. Its form is further explained by SILLÉN *et al.*[2] and in a recent textbook[6].

The HALTAFALL calculations show, furthermore, that the ThF_4 precipitate dissolves at $v = 10$ ml. This can be illustrated graphically in two ways as is shown in Fig. 4. No mention is made of this in LINGANE's paper.

TITRATION OF FLUORIDE WITH THORIUM NITRATE IN ACETATE BUFFER SOLUTION

Procedure[1]

An aliquot (5 ml) of 0.8000 *M* sodium fluoride was diluted to 100 ml and titrated with v ml of 0.0200 *M* thorium nitrate after the addition of 10 ml of 1 *M* sodium acetate–acetic acid buffer to give a pH of 4.88.

Calculation

The stability and solubility constants given in Table I have been used for the fluoride and hydroxo complexes of thorium. The additional stability constants for the acetate complexes are listed in Table III. If the titration curve is calculated from these constants, excluding those for the mixed complexes, the broken curve II shown in Fig. 5 is obtained. This curve should be compared with the experimental points shown by circles. It is obvious that the curve does not fit the e.m.f. data for $v > 5$ ml. As the calculations showed that $ThAc_3^+$ was the dominating complex after the equivalence point ($v > v_{eq} = 5$ ml) we attempted at first to increase β_3. With a value of $3.4 \cdot 10^{11}$ a good fit was, however, only obtained for $v > 10$ ml. Furthermore, this value seems to be much too high for a ligand like acetate. Since the experimental curve in the volume region $v < 10$ ml is similar in shape to the experimental curve in acidic solution (Fig. 1), the main reaction for $5 < v < 10$ ml should be the formation of a complex consisting of one thorium and two fluoride ions. The linearity of the GRAN plot $F_2 = (v_0 + v)[F^-]^{-2}$ with the experimental data confirms this assumption. In order, therefore, to obtain an apparent increase in the stability of ThF_2^{2+}, mixed complexes of the composition $ThF_2Ac_m^{(2-m)+}$ were introduced. For $v > 10$ ml the increase in slope of the experimental curve indicates the presence of slight amounts of a complex consisting of one thorium and one fluoride ion. Mixed complexes of the type $ThFAc_n^{(3-n)+}$ were therefore also introduced into the calculations. Since there are very few experimental data for $v > 10$ ml only the order of magnitude of the stability constants for $ThFAc_n^{(3-n)+}$ can be estimated. A value of $\log \beta_{13} = 13$ instead of 15.65 only decreases the curve by *ca.* 1 mV at

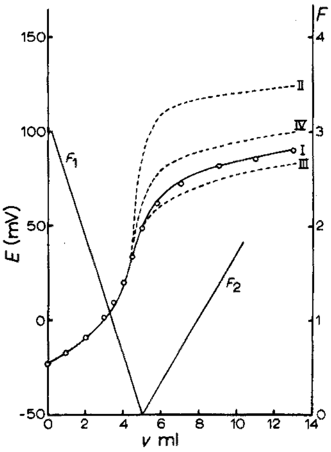
TABLE III

CONSTANTS CHOSEN FOR THE CALCULATION OF THE TITRATION OF FLUORIDE WITH THORIUM AT pH 4.88 (cf. FIGS. 5 AND 6)

Equilibria	*log of stab. constants*		*choice of stability constants based on*
$Th^{4+} + Ac^- \rightleftharpoons ThAc^{3+}$	β_1	4.20	GOLDSTEIN, MENIS AND MANNING[7]
$Th^{4+} + 2Ac^- \rightleftharpoons ThAc_2^{2+}$	β_2	5.76	$\beta_2/\beta_1 = \beta_1$ for $LaAc^{2+}$ in *Stab. Constants*[4] 58S
$Th^{4+} + 3Ac^- \rightleftharpoons ThAc_3^+$	β_3	6.68	$\beta_3/\beta_1 = \beta_2$ for $LaAc_2^+$ in *Stab. Constants*[4] 58S
$Th^{4+} + F^- + 3Ac^- \rightleftharpoons ThFAc_3$	β_{13}	15.65	estimated[a], see text
$Th^{4+} + 2F^- + 2Ac^- \rightleftharpoons ThF_2Ac_2$	β_{22}	18.70	estimated[a], see text
$H^+ + Ac^- \rightleftharpoons HAc$	K_1	4.60	

[a] These constants correspond to the equilibria
$ThF^{3+} + 3Ac^- \rightleftharpoons ThFAc_3$; $\log \beta = 15.65 - 7.62 = 8.03$
$ThF_2^{2+} + 2Ac^- \rightleftharpoons ThF_2Ac_2$; $\log \beta = 18.70 - 14.02 = 4.68$
The β's are thus overall constants for $ThFAc_n$ and ThF_2Ac_m, respectively.

$v = 13$ ml. No significance should thus be attached to our value for β_{13}, which seems to be too large in comparison with β_3 for $ThAc_3^+$. As the free concentration of acetate ions is practically constant throughout the titration (*cf.* Fig. 6) it is not possible to form any opinion as to which of the mixed complexes $ThF_2Ac_m^{(2-m)+}$ ($m = 1$ or 2) predominates. The same is true for $ThFAc_n^{(3-n)+}$ ($n = 1$, 2 or 3). In the calculations ThF_2Ac_2 and $ThFAc_3$ have been chosen as being the only mixed complexes.



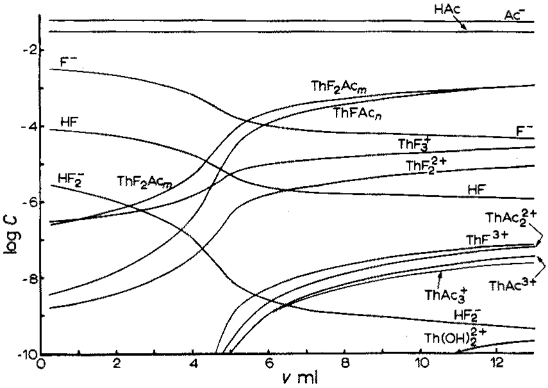


Fig. 5. Experimental points, four calculated titration curves, and GRAN plots $F_1 = (110 + v)[F^-]$ and $F_2 = (110 + v)[F^-]^{-2}$ for the titration of 100 ml of 0.004 *M* fluoride and 10 ml of 1 *M* acetate buffer (pH 4.88) with *v* ml of 0.02 *M* thorium nitrate. Curve I was calculated using the stability constants in Tables I and III and curve II with the same constants omitting the mixed complexes. In curve III the stability constants for the mixed complexes "$ThFAc_3$" and "ThF_2Ac_2" are $1.0 \cdot 10^{16}$ and $7.2 \cdot 10^{18}$, respectively, while in curve IV the corresponding constants are $2 \cdot 10^{15}$ and $1.58 \cdot 10^{17}$. The functions F_1 and F_2 have been plotted on an arbitrary scale since this does not influence the point of intersection on the *v*-axis.

Fig. 6. The logarithmic concentrations of the different species formed in the titration of 100 ml of 0.004 *M* fluoride and 10 ml of 1 *M* acetate buffer (pH 4.88) with *v* ml of 0.02 *M* thorium nitrate.

The theoretical titration curve was calculated from several sets of stability constants for ThF_2Ac_2 and $ThFAc_3$, and the results from three sets of constants are shown in Fig. 5. The values giving the best fit are those listed in Table III.

From Fig. 6, in which the logarithmic concentrations of the different species formed in the titration vessel have been plotted against *v* ml of titrant added, the main reactions in the different parts of the titration curve can be deduced. Since [HF] is much less than $[F^-]$ the dominating reaction for $v < 5$ ml is

$$Th^{4+} + 4F^- \rightleftharpoons ThF_4(s) \tag{13}$$

Consequently, the GRAN function

$$F_1 = (v_0 + v)[F^-] = (v_{eq} - v)0.02/4 \tag{14}$$

gives a straight line which when extrapolated to $F_1 = 0$ intersects the *v*-axis at $v = v_{eq}$ ($v_{eq} = 5$ ml) and the equivalence point may be obtained with a high accuracy (*cf.* Fig. 5). The GRAN plot

$$F_2 = (v_0 + v)[F^-]^{-2} = (v - v_{eq})2 \cdot 0.02/10^{18.70} \cdot 10^{-27.81} \cdot [Ac^-]^2 \tag{15}$$

has already been proposed for the volume region $5 < v < 10$ ml and from Fig. 5 it is seen that this function can also be used to evaluate v_{eq}. This equation corresponds as before (Equilibrium (7)) to the main reaction

$$ThF_4(s) + Th^{4+} + 2m\ Ac^- \rightleftharpoons 2\ ThF_2Ac_m \qquad (16)$$

In this case ThF_4(s) is not completely dissolved as in the titration in hydrochloric acid.

TITRATION OF FLUORIDE WITH LANTHANUM NITRATE IN UNBUFFERED SOLUTION

Procedure[1]

An aliquot (5 ml) of 0.08000 *M* sodium fluoride was diluted to 100 ml and titrated with v ml of 0.03189 *M* lanthanum nitrate solution.

Calculation

Suitable stability and solubility constants, selected from the literature, are specified in Table IV. The value, $7.0 \cdot 10^{-17}$, suggested by LINGANE[1] from his experimental data for the solubility product of LaF_3(s) had to be changed to $1.5 \cdot 10^{-18}$ in order to obtain a good fit. This is illustrated in Fig. 7 where the experimental values have been plotted together with calculated curves for the two values of the solubility product.

TABLE IV

CONSTANTS CHOSEN FOR THE CALCULATION OF FLUORIDE WITH LANTHANUM IN UNBUFFERED SOLUTION (cf. FIGS. 7 AND 8)

Reaction	*log of stab. constants*		*choice of stability constants based on*
$H_2O + La^{3+} \rightleftharpoons LaOH^{2+} + H^+$	$^*\beta_{11}$	-10.1	*Stab. Constants*[4] 61B
$H_2O + 2La^{3+} \rightleftharpoons La_2OH^{5+} + H^+$	$^*\beta_{12}$	-9.95	*Stab. Constants*[4] 61B
$La^{3+} + F^- \rightleftharpoons LaF^{2+}$	β_1	3.51	Estimated from *Stab. Constants*[4] by comparison with LYLE AND NAQVI[8]
$La^{3+} + 2F^- \rightleftharpoons LaF_2^+$	β_2	5.56	
$H^+ + F^- \rightleftharpoons HF$	K_1	3.28	*Stab. Constants* 63C
$H^+ + 2F^- \rightleftharpoons HF_2^-$	β_2	4.26	*Stab. Constants* 63C
$LaF_3(s) \rightleftharpoons La^{3+} + 3F^-$	K_{s0}	-17.82	LINGANE[a] (-16.15)

[a] When this work was in the form of a final manuscript LINGANE[10] published a new value for $\log K_{s0} = -17.92$, which is close to the value that we have used to fit the calculated potential curve to his data.

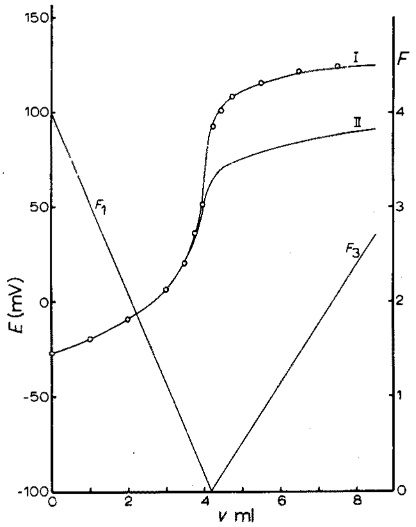
The logarithms of the concentrations of the different species in solution have been plotted in Fig. 8 as a function of v ml of titrant added. An indication as to suitable GRAN functions for evaluating the equivalence point may be otbained from this figure. Before the equivalence point ($v_{eq} = 4.18$ ml) the predominating reaction is seen to be

$$La^{3+} + 3F^- \rightleftharpoons LaF_3(s) \qquad (17)$$

The function

$$F_1 = (v_0 + v)[F^-] = (v - v_{eq})\ 0.03189/3 \qquad (18)$$

should therefore be linear and intersect the v-axis at $v = v_{eq}$ when extrapolated to



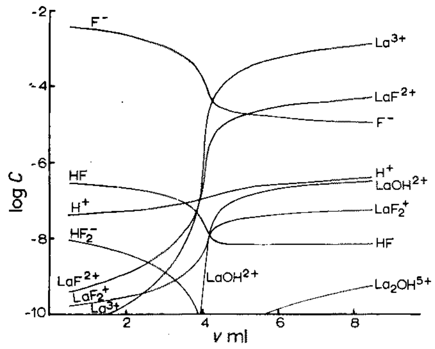


Fig. 7. Experimental points, two calculated titration curves, and GRAN plots $F_1 = (100 + v)[F^-]$ and $F_3 = (100 + v)[F^-]^{-3}$ for the titration of 100 ml of 0.004 M fluoride with v ml of 0.03189 M lanthanum nitrate in unbuffered solution. Curve I was calculated using the stability constants in Table IV. Curve II was calculated with the value of the solubility product (K_{s0}) for LaF_3 given by LINGANE[1] ($7 \cdot 10^{-17}$ instead of $1.5 \cdot 10^{-18}$). The functions F_1 and F_3 have been plotted on an arbitrary scale since this does not influence the point of intersection on the v-axis.

Fig. 8. The logarithmic concentrations of the different species formed in the titration of 100 ml of 0.004 M fluoride with v ml of 0.03189 M lanthanum nitrate in unbuffered solution.

zero. After the equivalence point, further addition of lanthanum will only increase the free lanthanum ion concentration (*cf.* Fig. 6) and, thus,

$$(v_0+v)[La^{3+}] = (v-v_{eq})0.03189 \tag{19}$$

Since the precipitate is not dissolved

$$[La^{3+}][F^-]^3 = 1.5 \cdot 10^{-18} \tag{20}$$

so that

$$F_3 = (v_0+v)[F^-]^{-3} = (v-v_{eq})0.03189/1.5 \cdot 10^{-18} \tag{21}$$

may be used as a GRAN plot. It is evident from Fig. 7 that a very high accuracy is obtained with both F_1 and F_3.

TITRATION OF FLUORIDE WITH LANTHANUM NITRATE IN ACETATE BUFFER SOLUTION

Procedure[1]

An aliquot (5 ml) of 0.08000 M sodium fluoride was diluted to 100 ml and titrated with v ml of 0.03189 M lanthanum nitrate after the addition of 10 ml 1 M sodium acetate–acetic acid buffer to give a pH of 4.88.

Calculation

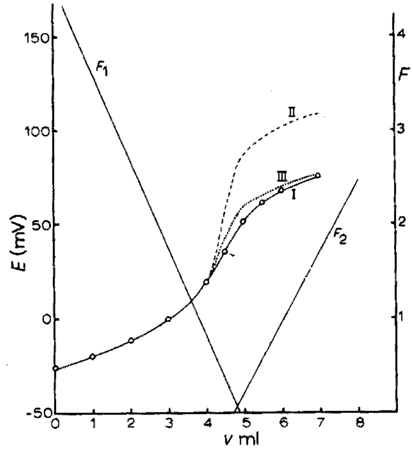
The values for the stability constants of lanthanum acetate determined by SONESSON[9] were chosen for the calculations and these constants are listed in Table V.

TABLE V

CONSTANTS CHOSEN FOR THE CALCULATION OF FLUORIDE WITH LANTHANUM AT pH 4.88 TOGETHER WITH THE CONSTANTS GIVEN IN TABLE IV (cf. FIGS. 9 AND 10)

Reaction	*log of stab. constants*		*choice of stability constants based on*
$La^{3+} + Ac^- \rightleftharpoons LaAc^{2+}$	β_1	1.56	*Stab. Constants* 58S
$La^{3+} + 2Ac^- \rightleftharpoons LaAc_2^+$	β_2	2.48	*Stab. Constants* 58S
$La^{3+} + 3Ac^- \rightleftharpoons LaAc_3$	β_3	2.98	*Stab. Constants* 58S
$H^+ + Ac^- \rightleftharpoons HAc$	K_1	4.60	
$La^{3+} + F^- + Ac^- \rightleftharpoons LaFAc^+$	β_{11}	7.87	estimated[a], see text

[a] This constant corresponds to $LaF^{2+} + Ac^- \rightleftharpoons LaFAc^+$; $\log \beta = 7.87 - 3.51 = 4.36$.



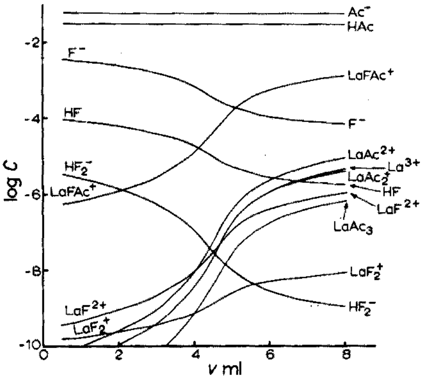


Fig. 9. Experimental points, three calculated titration curves, and GRAN plots $F_1 = (v_0 + v)[F^-]$ and $F_2 = (v_0 + v)[F^-]^{-2}$ for the titration of 100 ml of 0.004 M fluoride and 10 ml of 1 M acetate buffer (pH 4.88) with v ml of 0.03189 M lanthanum nitrate. Curve I was calculated from the stability constants in Tables IV and V. In curves II and III the mixed complex "$LaFAc^+$" has been omitted and in curve III the stability constant for $LaAc^{2+}$ has, moreover, been changed from 36.3 to 3000.

Fig. 10. The logarithmic concentrations of the different species formed in the titration of 100 ml of 0.004 M fluoride and 10 ml of 1 M acetate buffer (pH 4.88) with v ml of 0.03189 M lanthanum nitrate in acetate buffer solution.

It was not, however, possible to obtain a fit between experimental and calculated data, even for $v < v_{eq}$ ($v_{eq} = 4.18$ ml) where the formation of LaF_3(s) should be the predominating reaction. A plot of the function $F_1 = (v_0 + v)[F^-]$ with the experimental data, indicated, moreover, that the equivalence volume ought to be 4.85 ml instead of 4.18 ml (*cf.* Fig. 9). It was not, however, possible to say whether the fluoride or the lanthanum concentration was in error.

New calculations were performed with an initial fluoride concentration of 0.0930 M corresponding to an equivalence volume of 4.85 ml, and with the constants specified in Table V, that for the mixed complex being excluded. The dashed titration curve II shown in Fig. 9 was obtained. Since these constants give a far too low fluoride concentration for $v > 4$ ml, the value for the stability constant of $LaAc^{2+}$ was increased to $3 \cdot 10^3$ to give a better fit. The dotted curve III is shown in Fig. 9. It is obvious that the shape of this curve does not agree with the experimental points. If a mixed complex $LaFAc^+$ with a stability constant of $7.5 \cdot 10^7$ was introduced into the calculations the curve fitted to the experimental points as shown in Fig. 9. The logarithmic concentrations of the complexes have been plotted against v ml titrant added in Fig. 10.

For the evaluation of the equivalence point the plot $F_1 = (v_0 + v)[F^-]$ has already been suggested for $v < v_{eq}$ and it is seen from Fig. 9 that a high accuracy is obtained. After the equivalence point the main reaction is the formation of $LaFAc^+$ according to

$$LaF_3(s) + 2La^{2+} + 3Ac^- \rightleftharpoons 3LaFAc^+ \qquad (22)$$

and it can be assumed that for $v > v_{eq}$

$$3 \cdot 0.03189 \cdot (v - v_{eq})/2(v_0 + v) = [LaFAc^+] \qquad (23)$$

Furthermore,

$$[LaFAc^+] = 7.5 \cdot 10^7 \cdot 1.5 \cdot 10^{-18}[Ac^-][F^-]^{-2} \qquad (24)$$

If the free concentration of acetate ions is constant, the GRAN plot $F_2 = (v_0 + v)[F^-]^{-2}$ should be used. Since, however, a considerable amount of $LaFAc^+$ is formed before the equivalence point, the GRAN plot F_2 deviates somewhat from linearity (*cf.* Fig. 9). The plot F_1 is thus to be preferred for the titration under consideration.

LaF_3 is only partially dissolved and Fig. 7 demonstrates that LaF_3 is in fact too insoluble or the formation of LaF^{2+} too weak for the equilibrium $LaF_3(s) + 2La^{3+} \rightleftharpoons 3LaF^{2+}$ to be studied potentiometrically with a membrane electrode.

It should, however, be possible to calculate the formation constants of mixed complexes with fluoride and acetate ligands from titrations at different acetate concentrations.

It should be possible to determine the stability constants of $LaF_n^{(3-n)+}$ from a solvent extraction study of radioactive lanthanum at such low concentrations that solid LaF_3 is not formed using TTA + TBP in carbon tetrachloride as organic phase and HF + NaF solutions as aqueous phase. With this additional information a more complete interpretation of the titration curves should be possible.

OTHER TITRATIONS

When a solution of 0.004 or 0.04 *M* sodium fluoride is titrated with 0.02 *M* thorium nitrate, calculations show that considerable amounts of $Th(OH)_2^{2+}$ and polynuclear thorium hydroxide complexes are formed after the equivalence point. The calculated titration curves only approximately fit the experimental points, and as many complexes are involved no attempt was made to refine the fit. It is also questionable if equilibrium is reached during such titrations. The curve for the titration of 0.04 *M* sodium fluoride with 0.03189 *M* lanthanum nitrate was calculated with the constants in Table IV and a good fit was obtained with $K_{s0} = 1.5 \cdot 10^{-18}$.

The calculations may very well be extended to titrants containing reactants like beryllium, calcium, scandium, yttrium, europium, boric acid and aluminium. With suitable functions to evaluate the equivalence points lanthanum nitrate is, however, sufficient for the accurate determination of fluoride in aqueous solution.

We wish to thank Mrs. SUSAN JAGNER, fil.lic. and M. A. for revising the English text. We are also indebted to His Majesty the King of Sweden, who through "Statskontoret" has given us free computer time.

SUMMARY

Calculations by means of SILLÉN's HALTAFALL program have been performed on experimental curves by LINGANE for the potentiometric titration of fluoride with thorium and lanthanum in different media. After adjusting the stability constants for some of the main species formed during the titration a good fit was obtained between the experimental data and the calculated titration curves. In the cases where the solution was buffered with acetate it was necessary to consider the formation of mixed fluoride–acetate complexes. Suitable functions for the evaluation of the equivalence point could be derived from the calculations. If the functions: $F_1=(v_0+v)[F^-]$ and $F_3=(v_0+v)[F^-]^{-3}$ are used before and after the equivalence point, respectively, it ought to be possible to determine fluoride very accurately by titration with lanthanum nitrate in an unbuffered solution. A value proportional to $[F^-]$ is obtained from 10 exp $(-EF/RT \ln 10)$, the Nernst e.m.f. equation.

RÉSUMÉ

Des calculs ont été effectués par LINGANE (programme HALTAFALL de SILLÉN) pour le titrage potentiométrique du fluorure au moyen de thorium et de lanthane, dans divers milieux. Après ajustement des constantes de stabilité pour les principales particules formées au cours du titrage, les valeurs expérimentales correspondent bien au courbes calculées. Dans le cas où la solution est tamponnée à l'acétate, il est nécessaire de prendre en considération la formation de complexes mixtes fluorure–acétate. En applicant les équations: $F_1 = (v_0 + v)$ $[F^-]$ et $F_3 = (v_0 + v)$ $[F^-]^{-3}$, respectivement avant et après le point équivalent, il serait possible de doser le fluorure très exactement par titrage à l'aide de nitrate de lanthane en milieu non tamponné. Une valeur proportionnelle est obtenue pour $[F^-]$ de 10 exp $(-EF/RT \ln 10)$, équation e.m.f. de Nernst.

ZUSAMMENFASSUNG

Mit den experimentellen Kurven von Lingane für die potentiometrische Titration von Fluorid mit Thorium und Lanthan in verschiedenen Medien wurden Berechnungen unter Anwendung des HALTAFALL-Programms von Sillén durchgeführt. Nach der Anpassung der Stabilitätskonstanten für einige der Hauptspezies, die während der Titration gebildet werden, wurde eine gute Übereinstimmung zwischen den experimentellen Daten und den berechneten Titrationskurven erhalten. In den Fällen, in denen die Lösung mit Acetat gepuffert war, war es notwendig, die Bildung gemischter Fluorid–Acetat-Komplexe zu berücksichtigen. Geeignete Funktionen für die Abschätzung des Äquivalenzpunktes konnten aus den Berechnungen abgeleitet werden. Wenn die Funktionen: $F_1=(v_0+v)$ $[F^-]$ und $F_3=(v_0+v)$ $[F^-]^{-3}$ vor bzw. nach dem Äquivalenzpunkt verwendet wird, sollte es möglich sein, das Fluorid sehr genau bei der Titration mit Lanthannitrat in ungepufferter Lösung zu bestimmen. Ein Wert,

der proportional zu $[F^-]$ ist, wird aus dem Ausdruck 10 exp $(-EF/RT \ln 10)$ der Nernstschen Gleichung erhalten.

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SHORT COMMUNICATIONS

Extraction of manganese dithiocarbamate complexes for atomic absorption spectrophotometry

Dithiocarbamates are recognized as useful complexing reagents for the extraction of traces of metals, and the application of manganese dithiocarbamate complexes in atomic absorption spectrophotometry has been described[1-3]. Manganese dithiocarbamate complexes have also been investigated for absorption spectrophotometry[4,5]. However, no detailed information appears to be available about the effect of organic solvents on the stability of complexes or on the effect of buffer solutions on the extraction, particularly for atomic absorption spectrophotometry. These topics are considered in the present communication.

Apparatus

A hollow-cathode lamp (Hitachi 64608) was used with a 9-cm slot burner, a Hitachi EPU-2A monochromator and a photomultiplier tube (R-106). The manganese absorption at 2795 Å was measured in air–acetylene flame.

A Metrohm Potentiograph E336 with glass electrode was used for pH measurement. An electric shaking device (Tokiwa Seisakusho) was used in the extractions.

Reagents

Standard manganese solution (1 mg/ml). Dissolve 1 g of pure manganese metal in dilute nitric acid, boil out nitrogen oxides, and dilute to 1 l. Prepare dilute standards just before use.

Copper solution (1 mg/ml). Dissolve 1 g of pure copper metal in dilute nitric acid, boil out nitrogen oxides, and dilute to 1 l.

Tartrate (0.2 *M*) and phosphate (0.2 *M*) buffers were freshly prepared just before use. Reagent-grade organic solvents were used after being saturated with water.

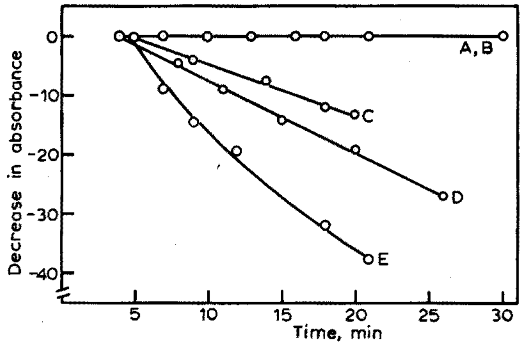
Extraction method

Place 5 ml of solution containing 51 μg of manganese in a 50-ml separatory funnel. Add 2 ml of freshly prepared aqueous 2%(w/v) sodium diethyl-dithiocarbamate solution (DDTC) or freshly prepared aqueous 5%(w/v) ammonium pyrrolidine dithiocarbamate solution (PDTC), and adjust the pH of the solution with buffer solution. Mix well and adjust the volume to 20 ml. Add exactly 10 ml of immiscible organic solvent and shake vigorously for 1 min. Drain off, discard the aqueous phase, spray the organic phase into the flame, and measure the atomic absorption of manganese.

Results and discussion

Choice of organic solvent and stability of extract. The instability of manganese complexes in organic solvents has been reported[1,3]. In the present work, various organic solvents (alcohols, ketones and esters) were tested to ascertain the effect on the stability of the complexes. The results are summarized in Fig. 1. The manganese–pyrrolidine dithiocarbamate complex was unstable in methyl isobutyl ketone (MIBK), but the manganese–pyrrolidine dithiocarbamate complex was stable in this solvent for at least 30 min. The cause of the discrepancy in the two complexes is uncertain. Both complexes were stable in esters and alcohols for 90 min.

pH range and buffer solutions. The manganese dithiocarbamate complexes were extracted from a variety of buffer solutions to ascertain the optimum pH range for extraction (Fig. 2). The data obtained showed that the optimum pH range with phosphate buffer was narrower than that with tartrate buffer. Tartrate prevented manganese from hydrolyzing at higher pH values. The DDTC complex did not differ from the PDTC complex in optimum pH for extraction. Manganese complexes were also extracted from solutions which had been adjusted with phthalate, acetate or borate buffers. The extraction of the complexes was shown to be constant over the pH range 3–11. At lower pH values, dithiocarbamic acid was also extracted into the organic phase, but this did not affect the manganese absorption.



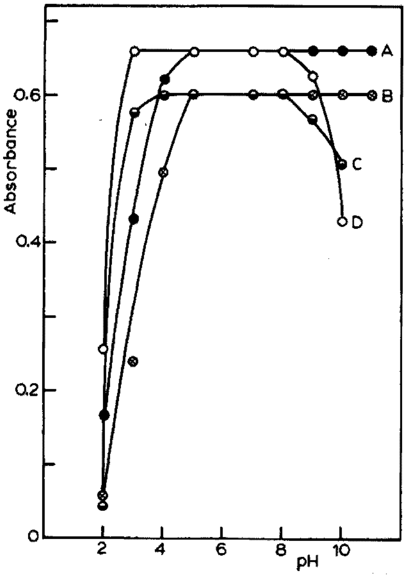


Fig. 1. Stability of extracts. (A) Mn–DDTC complex in amyl acetate and butanol, (B) Mn–PDTC complex in amyl acetate, butanol and methyl isobutyl ketone, (C) Mn–DDTC complex in cyclohexanone, (D) Mn–DDTC complex in methyl isobutyl ketone, (E) Mn–DDTC complex in methyl ethyl ketone.

Fig. 2. Effect of pH on extraction (aqueous phase 20 ml, DDTC 10 mg/20 ml or PDTC 50 mg/20 ml, organic solvent 10 ml, Mn 51.1 μg). (A) Mn–PDTC complex extracted from 0.05 *M* tartrate buffer solution with methyl isobutyl ketone; (B) Mn–DDTC complex extracted from 0.05 *M* tartrate buffer solution with amyl acetate; (C) Mn–DDTC complex extracted from 0.05 *M* phosphate buffer solution with amyl acetate; (D) Mn–PDTC complex extracted from 0.05 *M* phosphate buffer solution with methyl isobutyl ketone.

Reagent concentration. The extraction of manganese was constant when the solution contained more than 10 mg of DDTC or 50 mg of PDTC in 20 ml, irrespective of the nature of the buffer solution.

Interferences. No interference was found for the extraction of manganese complexes from solutions containing 3 g of sodium chloride in 20 ml. Reducing agents such as hydroxylamine hydrochloride had no effect, but EDTA hindered the extraction. Only a trace of manganese–DDTC complex could be extracted from 0.05 *M* pyrophosphate solution (pH 7), under which conditions no extraction of manganese–PDTC complex was observed. Hydrogen peroxide interfered with the extraction because of the decomposition of the dithiocarbamates. Various metals including copper and iron accompanied manganese into the organic phase, but these metal complexes had no effect on manganese absorption.

Composition of extracted species

Manganese is generally considered to be extracted as the manganese(III) dithiocarbamate complex[4,5], but STARY AND KRATZER[6] state that a manganese(II)–DDTC complex is extracted. To ascertain the composition of manganese dithiocarbamates in extract, the following experiment was carried out. Manganese dithiocarbamate complexes were extracted from solutions of pH 7 or 9. An aliquot of the extract was evaporated to dryness on a steam bath, the residue was dissolved in nitric acid, and manganese was measured. Another aliquot was shaken with 20 ml of solution (pH 7 or 9) which contained 250 µg of copper. After shaking for 15 min, the organic phase was measured for copper, and then the concentration of dithiocarbamate anion in the extract was calculated from the amount of copper. The exchange of manganese and copper in the extracted complexes was quantitative. The molar ratios found (Table I) indicate that manganese is present as manganese(II)–dithiocarbamate complexes in the extract.

TABLE I

COMPOSITION OF EXTRACTED SPECIES[a]

Dithiocarbamate	DDTC	PDTC
Solvent	AmOAc	MIBK
Molar ratio (Mn:DTC)	1:2.02	1:1.90

[a] At pH 7 and 9.

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A selective method for the separation of mercury(II) by chromatography on DEAE ion-exchange paper

KURODA *et al.* recently reported that mercury(II) could be selectively separated from about 40 other metal ions by chromatography on the weakly-basic cellulose exchanger DEAE in dilute thiocyanate media[1]. Conditions were described under which few other ions were significantly adsorbed. The purpose of the present work was to adapt this column method to a selective paper-chromatographic procedure for the separation of mercury(II) and to make a direct comparison between the column and paper-chromatographic techniques. Development on commercial DEAE cellulose paper with dilute thiocyanate solvents was found to give results similar to, but not identical with, those obtained with columns of DEAE cellulose.

Some previous work employing DEAE paper and thiocyanate media for the chromatography of metal ions has been reported[2,3], but neither the selective separation of mercury(II) nor a comparison with columns has been described previously.

Experimental

Diethylaminoethyl (DEAE) cellulose paper (Type DE 81, H. Reeve Angel Co., Clifton, N.J.) is an exchanger which resembles in base strength the corresponding tertiary amino anion-exchange resins and is capable of forming amino complexes with various metal ions. It is supplied with a capacity of 3.5 μeq/cm^2 in the free base form. Some comparative runs were made on Whatman No. 1 pure cellulose paper.

Chromatograms were developed by the descending flow of solvent in commercial apparatus already described[4]. For the dry-start technique, DEAE paper was washed by downward percolation of the developing solvent for 20–25 h (or soaked overnight in developer and then water[5]) and air-dried before spotting the samples. For the wet-start technique[6], the converted, dripping-wet paper was removed from the tank, lightly blotted to remove excess of liquid, spotted, replaced in the tank, and developed immediately before any appreciable drying could occur. Sheets 36 cm in length were used, and 5 μl of each test solution was applied to marked origins at 1-in intervals. Development times of 60–90 min were typical for runs of 20–25 cm with either the dry- or wet-start technique.

Except for a few cases, a solution of 0.010 *M* ammonium thiocyanate–0.10 *M* hydrochloric acid was employed as the developing solvent. KURODA *et al.*[1] determined the distribution coefficient for mercury(II) in this medium to be about $3 \cdot 10^3$, whereas the value for most other ions was approximately zero.

The ions included in this study are listed in Table I. In most cases, test solutions (0.050 *M*) were prepared by dissolving the reagent-grade chloride, oxide or oxysalt in 0.50 *M* hydrochloric acid. Solutions of samarium(III) and yttrium(III) were prepared in 0.48 *M* and 1.7 *M* nitric acid, respectively. Antimony(III) and tin(IV) were in 3 *M* hydrochloric acid. Nitrates of bismuth(III), lead(II) and thallium(I) were dissolved in 0.010 *M* ammonium thiocyanate–0.10 *M* nitric acid. Mercuric chloride was dissolved in water.

Zones containing Mn, Cr, Al, Mg, Zn and Sn were detected after drying the chromatogram by spraying with an alcoholic solution of 8-hydroxyquinoline followed by dilute ammonium hydroxide and viewing under ultraviolet light[7]. Zones containing Sm, Y, Th and Zr were placed in an ammonia atmosphere for 10 min and then sprayed

TABLE I

R_F-VALUES ON DEAE CELLULOSE PAPER WITH 0.010 M NH_4SCN–0.10 M HCl

Ion	*Dry-start technique*		*Wet-start technique*	
	R_F (rear)	*R_F (front)*	*R_F (rear)*	*R_F (front)*[a]
As(III)	0.76	1.0	0.77	0.84
Al(III)	0.88	1.0	0.80	0.99
Bi(III)	0.0	0.23	0.0	0.19
Cd(II)	0.81	0.92	0.79	0.92
Co(II)	0.85	1.0	0.80	1.0
Cr(III)	0.90	1.0	0.87	1.0
Cu(II)[b]	0.85	1.0	0.80	0.92
	0.0	0.0	0.0	0.0
Fe(III)	0.83	1.0	0.75	0.95
Ga(III)	0.95	1.0	0.78	1.0
Hg(II)	0.0	0.08	0.0	0.06
Mg(II)	0.78	1.0	0.58	0.71
Mn(II)	0.92	1.0	0.83	1.0
Ni(II)	0.77	1.0	0.81	1.0
Pb(II)	0.84	1.0	0.80	1.0
Pt(IV)	0.0	0.07	0.0	0.06
Sb(III)	0.0	0.09	0.0	0.81
Sm(III)	0.78	1.0	0.79	1.0
Sn(IV)	0.76	1.0	0.22	0.89
Th(IV)	0.75	1.0	0.85	1.0
Tl(I)	0.68	1.0	0.64	0.95
V(IV)	0.82	1.0	0.78	0.94
Y(III)	0.80	1.0	0.75	1.0
Zn(II)	0.80	1.0	0.79	0.92
Zr(IV)	0.0	1.0	0.0	0.90

[a] R_F-value relative to Cr(III) migration.

[b] Forms double zone.

with alcoholic alizarin followed by 1 N acetic acid[8]. Gallium was detected by spraying with 0.2% rhodamine B in 6 N hydrochloric acid. The rest of the metals were detected by spraying with yellow ammonium sulfide followed by dilute hydrochloric acid[7].

Results and discussion

Table I shows the R_F-values of the front and rear limits of the developed zones for each ion by the dry- and wet-start techniques. A disadvantage of the latter is that the solvent front is not visible during the chromatography. Iron(III), which forms a colored complex with thiocyanate and was found to have an R_F-value of 1.0 in the dry-start technique, was used as an approximate indicator of the movement of the solvent front. The R_F-values in Table I for the wet-start technique are relative to the migration of chromium(III), the front edge of which was taken as R_F 1.0.

These data indicate that, as on columns, only mercury and a few other ions are strongly adsorbed by the DEAE cellulose. The developed zones were in general more well-defined and compact after wet-start development, especially in regard to their widths. Because of this, and because this technique makes the column and paper methods more analogous, the wet-start technique was adopted as the method of choice.

Of the 23 representative ions studied, only Bi, Cu, Pt, Sb and Zr were not completely separated from mercury by development with 0.010 M ammonium thiocyanate–0.10 M hydrochloric acid. On columns with the same eluent, copper and zirconium were separated from mercury[1]. Zirconium forms a long streaking zone on paper that extends back to the origin and overlaps the mercury zone. Most of the copper moves in a compact zone with the solvent front, but a small, residual amount is visible at the origin. The same results were obtained when copper and zirconium were developed on Whatman No. 1 cellulose paper with this solvent, indicating that the cellulose rather than the exchange groups is responsible for these irregularities.

For the separation of bismuth(III), lead(II) or thallium(I) on columns, the sample solution and eluent were changed to 0.010 *M* ammonium thiocyanate–0.10 *M* nitric acid[1]. This solvent was not required for the separation of the latter two ions from mercury on paper (Table I). Even with this solvent, bismuth remained near the origin on DEAE paper (and Whatman No. 1) and could not be separated from mercury.

Antimony(III) was separated on columns by adding tartaric acid to the eluent[1]. Adding 1% tartaric acid to the developing solvent allowed the separation of antimony from mercury on DEAE paper as well. Platinum(IV) could not be separated from mercury either on columns[1] or on paper.

To test the separations predicted by the data of Table I, the following mixtures were resolved: As–Cd–Hg, Ni–Hg, Cd–Hg, Th–Hg, Pb–Hg and Zn–Hg. In each case, the R_F-values were the same whether the ions were alone or part of a mixture. The separation of a mixture of mercury(II): iron(III) in the proportions 1:50 was also successful.

In summary, the selective paper chromatographic separation of mercury(II) from many other ions is possible by DEAE anion-exchange paper in thiocyanate media. That these separations are due to the ion-exchange groups rather than the cellulose matrix was shown by the fact that mercury(II) was not strongly sorbed on Whatman No. 1 paper but moved near the solvent front with most of the rest of the ions. As found by a comparison of columns of polystyrene ion-exchange resins and resin-papers[5], results with DEAE cellulose paper and columns are similar but not identical, even though the paper-chromatographic technique (the wet-start method) was as similar as possible to the column technique.

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The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part II. The analysis of silica

The purity of the silica used industrially is normally controlled by determining the content of iron and aluminium. The present scheme contains methods for the determination of aluminium, iron, magnesium, calcium and titanium in silica. The scheme is probably also applicable to the analysis of other materials high in silica, *e.g.* certain glasses, quartzite, sandstone, sand, etc.

Silica yields rapidly to an attack by hydrofluoric acid; consequently, the decomposition method I (described in Part I of this series[1]), which involves simple heating in a plastic container, is normally applicable.

Reagents and solutions

The reagents and solutions required for the present determinations are listed in Part I. The composition of secondary standard solutions is given below. The detailed preparation of the primary standard solutions (designated below as metal standard I) has been described in Part I. Each of the series of standard solutions below is designed for measurement of a definite dilution of the sample solution; this dilution is indicated in each case.

Secondary standard solutions

Aluminium. (Undiluted sample solutions) Dilute aluminium standard I to a concentration of 0.05 mg Al_2O_3/ml with water. Transfer up to 40 ml, in steps of 4 ml, of this solution to plastic bottles, and add 5 ml of hydrofluoric acid, 50 ml of saturated boric acid solution and water to a final volume of 100 ml. (Range: up to 1% Al_2O_3, in steps of 0.1%.)

Iron. (Undiluted sample solutions) Dilute iron standard I to a concentration of 0.01 mg Fe_2O_3/ml with water. Transfer up to 50 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. (Range: up to 0.250% Fe_2O_3, in steps of 0.025%.)

Magnesium. (Sample solutions diluted 2 times) Dilute magnesium standard I to a concentration of 0.001 mg MgO/ml with water. Transfer up to 50 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution (10 mg K/ml) and dilute to volume with water. (Range: up to 0.050% MgO, in steps of 0.005%.)

Calcium. (Sample solutions diluted 2 times) Dilute calcium standard I to a concentration of 0.005 mg CaO/ml with water. Proceed further as in the case of magnesium. (Range: up to 0.250% CaO, in steps of 0.025%.)

Titanium. (Undiluted sample solutions) Dilute titanium standard I to a concentration of 0.02 mg TiO_2/ml with water; also prepare an aluminium standard (0.5 mg Al_2O_3/ml) from aluminium standard I by dilution with water. Transfer up to 30 ml, in steps of 5 ml, of the diluted titanium standard solution to plastic bottles, and add 5 ml of hydrofluoric acid, 50 ml of saturated boric acid solution, a volume of diluted aluminium standard corresponding approximately to the content of aluminium in the sample solution, and water to a final volume of 100 ml. (Range: up to 0.30% TiO_2, in steps of 0.05%.)

Procedure

Decompose 0.2000 g of the sample as described in decomposition method 1[1]; most samples yield to about 15 min heating on the boiling water bath. Determine aluminium, iron and titanium in the main solution. For the determination of magnesium and calcium, pipette 50 ml of the main solution into a 100-ml volumetric flask, add 10 ml of potassium reagent solution (10 mg K/ml), dilute to volume with water, and transfer at once to a plastic bottle.

All determinations, with the exception of iron, were made with acetylene–nitrous oxide flames; iron was determined with the acetylene–air flame.

The measurements and calculations were made as described in Part I.

Applications

The scheme was tested by analysing the U.S. Bureau of Standards sample No. 81 (glass sand). The analytical results and the certificate values are given in Table I.

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TABLE I

ANALYTICAL DATA FOR THE U.S. BUREAU OF STANDARDS SAMPLE NO. 81 (GLASS SAND)
(The analyses were made on an air-dried sample with a content of moisture of 0.00%)

Sample no.	*Al as Al_2O_3 (%)*	*Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Ti as TiO_2 (%)*
1	0.22	0.074	0.012	0.029	0.081
2	0.23	0.069	0.011	0.025	0.078
3	0.24	0.072	0.009	0.024	0.077
4	0.24	0.071	0.008	0.027	0.065
5	0.25	0.068	0.010	0.024	0.066
Averages	0.24	0.071	0.010[a]	0.026	0.073
Standard deviation	0.01	0.002	0.0017	0.002	0.007
Relative deviation	4.2	2.8	17	7.7	9.6
Certificate values	0.265	0.072	0.016	0.029	0.095

[a] For magnesium there is a discrepancy between the present value of 0.010% and the certificate value of 0.016%. The certificate shows that analyst No. 10 obtained a result — 0.045% — which differs markedly from those of the other nine analysts. By omitting this value the certificate average is reduced to 0.012% MgO.

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The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part III. The analysis of bauxite

In addition to being the raw material of the aluminium industry, bauxite is also used in the production of ceramics and abrasives. The quality of bauxite is normally evaluated on the basis of its content of silicon, aluminium, iron, calcium, titanium, manganese and chromium.

The determination of silicon, aluminium and titanium in bauxite by atomic absorption spectrophotometry has been described by BOWMAN AND WILLIS[1]. The present scheme comprises methods for the determination of silicon, aluminium, iron, magnesium, calcium, sodium, potassium, titanium, manganese and chromium.

Bauxite is not easily decomposed by hydrofluoric acid at the temperatures obtained on the boiling water bath. The attack should therefore be made by decomposition method 2 (described in Part I)[2].

Reagents and solutions

The reagents and solutions required for the present determinations are listed in Part I[2]. The preparation of the primary standard solutions (designated below as metal standard I) is described in Part I[2]. The composition of the secondary standard solutions is given below. Each of the series of standard solutions below is designed for measurement of a definite dilution of the sample solution; this dilution is indicated in each case.

Silicon. (Undiluted sample solutions) Transfer by plastic pipette up to 10 ml, in steps of 1 ml, of silicon standard I to plastic bottles and add water to a final volume of 100 ml. The series covers the range up to 10% SiO_2, in steps of 1%.

Aluminium. (Sample solutions diluted 10 times) Dilute aluminium standard I with water to a concentration of 0.5 mg Al_2O_3/ml. Transfer 20–28 ml, in steps of 0.8 ml, of this solution to plastic bottles, add by plastic pipette 10 ml of the combined boric acid–hydrofluoric acid reagent solution and water to a final volume of 100 ml. The series covers the range 50–70% Al_2O_3, in steps of 2%.

Iron. (Sample solutions diluted 10 times) Dilute iron standard I with water to a concentration of 0.1 mg Fe_2O_3/ml. Transfer up to 20 ml, in steps of 1 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. The series covers the range up to 10% Fe_2O_3, in steps of 0.5%.

Magnesium. (Sample solutions diluted 2 times) Dilute magnesium standard I with water to a concentration of 0.001 mg MgO/ml. Transfer up to 50 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution (10 mg K/ml) and dilute to volume with water. The series covers the range up to 0.05% MgO, in steps of 0.005%.

Calcium. (Sample solutions diluted 2 times) Dilute calcium standard I with water to give a solution containing 0.02 mg CaO/ml. Prepare the series as described for the series of magnesium solutions. The series covers the range up to 1% CaO, in steps of 0.1%.

Sodium. (Undiluted sample solutions without added caesium) Dilute sodium standard I with water to a concentration of 0.01 mg Na_2O/ml. Transfer up to 20 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. The series covers the range up to 0.1% Na_2O, in steps of 0.01%.

TABLE I

ANALYTICAL DATA FROM ANALYSIS OF THE U.S. BUREAU OF STANDARDS SAMPLE NO. 69a (BAUXITE)

Sample No.	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Na as Na_2O (%)*	*K as K_2O (%)*	*Ti as TiO_2 (%)*	*Mn as MnO (%)*	*Cr as Cr_2O_3 (%)*
1	5.82	55.02	5.94	0.020	0.34	0.037	0.0072	2.59	0.0091	0.043
2	6.00	54.81	5.92	0.018	0.24	0.038	0.0089	2.66	0.0053	0.045
3	5.76	54.97	5.88	0.022	0.33	0.037	0.0094	2.59	0.0070	0.040
4	6.17	54.75	5.84	0.019	0.31	0.040	0.0108	2.71	0.0073	0.048
5	5.96	54.83	5.80	0.018	0.29	0.034	0.0076	2.71	0.0067	0.044
Averages	5.94	54.88	5.88	0.019	0.30	0.037	0.0088	2.65	0.0071	0.044
Standard deviation	0.16	0.11	0.06	0.002	0.04	0.002	0.0014	0.06	0.0014	0.003
Relative deviation	2.7	0.20	1.0	11	13	5.4	16	2.3	19	6.8
Certificate values	6.01	55.0	5.82	0.02	0.29	<0.1	<0.1	2.78	<0.1	0.05

Potassium. (Undiluted sample solutions without added caesium) Dilute potassium standard I with water to a solution containing 0.01 mg K_2O/ml. Proceed as described above for the series of secondary sodium solutions. The series covers the range up to 0.1% K_2O, in steps of 0.01%.

Titanium. (Undiluted sample solutions) Transfer up to 10 ml, in steps of 1 ml, of titanium standard I to plastic bottles, add 50 ml of saturated boric acid solution, 5 ml of hydrofluoric acid, a volume of aluminium reagent solution (4 mg Al_2O_3/ml) corresponding approximately to the content of aluminium in the sample solution, and water to a final volume of 100 ml. The series covers the range up to 5% TiO_2, in steps of 0.5%.

Manganese. (Undiluted sample solutions) Dilute manganese standard I with water to give a solution containing 0.01 mg MnO/ml. Transfer up to 20 ml, in steps of 2 ml, of this solution to 100-ml volumetric flask and dilute to volume with water. The series covers the range up to 0.1% MnO, in steps of 0.01%.

Chromium. (Undiluted sample solutions) Dilute chromium standard I to give a concentration of 0.01 mg Cr_2O_3/ml .Transfer up to 20 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks, add a volume of iron standard I corresponding to the content of iron in the sample solution and dilute to volume with water. The series covers the range up to 0.1% Cr_2O_3, in steps of 0.01%.

Procedure

Decompose 0.2000 g of finely ground sample by decomposition method 2[2]; a temperature of about 110° and a heating time of about 30 min are normally sufficient for bauxite samples.

Determine silicon, sodium, potassium, titanium, manganese and chromium in the main solution. Determine aluminium and iron in a solution prepared by pipetting 10 ml of the main solution into a 100-ml volumetric flask and diluting to volume with water. For the determination of magnesium and calcium, pipet 50 ml of the main solution into a 100-ml volumetric flask, add 10 ml of potassium reagent solution (10 mg K/ml)[2] and dilute to the mark with water.

Silicon, aluminium, magnesium, calcium and titanium were determined with acetylene–nitrous oxide flames. Iron, sodium, potassium, manganese and chromium were determined with acetylene–air flames.

Measure and calculate results as described in Part I[2].

Applications

The suggested methods were tested by analyzing the U.S. Bureau of Standards sample no. 69a (bauxite). The analytical results and the certificate values are listed in Table I. Before analysis the sample was dried at 140° for 2 h.

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Arsenazo III as a metallochromic indicator for the direct DTPA titration of lanthanons in alumino-silicate zeolites*

Arsenazo III may be used for the spectrophotometric determination of many metals including the lanthanons[1]. Recent extensive studies of the reagent[2-5] indicate diverse analytical applications for it, but arsenazo III has served previously as a metallochromic indicator only in an EDTA titration of micro amounts of scandium(III)[6]. The present paper describes the direct titration of total lanthanons in alumino-silicate zeolites, such as molecular sieve catalysts, with diethylenetriaminepentaacetic acid. When used in the system described below, arsenazo III offers advantages over the commonly used indicators xylenol orange, methylthymol blue, or arsenazo I. Sulfosalicylic acid masks aluminum(III) and iron(III) which do not have to be removed. Large amounts of sulfate can be tolerated, and the accuracy and precision are superior to those for the classical oxalate precipitation gravimetric method. The rapidity of the titration and the superiority of arsenazo III under various conditions suggest broad applicability for the method.

Reagents

Prepare 0.025 *M* DTPA (diethylenetriaminepentaacetic acid) by dissolving 9.83 g of the reagent in 75 ml of hot 1 *M* sodium hydroxide and diluting to 1 l. Standardize the DTPA against a solution containing 5 mg of lanthanon per ml prepared from a lanthanon sesquioxide (Ln_2O_3) at least 99.9% pure. Ignite the sesquioxide at 900°C for 30 min to remove adsorbed water and carbon dioxide before dissolution in a mineral acid.

Prepare an aqueous 0.5% (w/v) solution of arsenazo III from 2,2′-[(1,8-dihydroxy-3,6-disulfo-2,7-naphthylene)bis(azo)]dibenzenearsonic acid, disodium salt (J. T. Baker Chemical Company).

Procedure

Weigh a 0.2–0.4-g sample of finely powdered, air-equilibrated zeolite into a 50-ml low-form, flat-bottom platinum crucible. Add 2 ml of water, 2 ml of sulfuric acid, and *ca.* 25 ml of 48% hydrofluoric acid. Volatilize the silicon as silicon tetrafluoride by heating nearly to dryness on a hot plate covered with a Transite plate about 1 cm thick. Finally, evaporate to dryness under an overhead infrared lamp. (In practice, either heating step may be performed overnight.) Repeat the sulfuric acid–hydrofluoric acid treatment for samples containing large amounts of silica. In this case, rinse the walls of the crucible with a minimum amount of sulfuric acid and add only 2–5 ml of hydrofluoric acid. To the dry sample residue, add 3 drops of sulfuric acid and 25 ml of water. Cover the crucible with a Teflon beaker cover and heat on the hot plate until all particles have dissolved. Cool the solution and dilute to a convenient volume.

Pipet an appropriate aliquot of the sample solution into a 150-ml beaker, adjust the volume to 50 ml with distilled water, and add 10 ml of 15% sulfosalicylic acid solution (SSA). If cerium(IV) is present, first reduce it to cerium(III) with a few mg of ascorbic acid before adding the SSA. Buffer the solution at pH 5 with

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hexamethylenetetramine. For extremely acidic solutions, first adjust to pH 2.0–2.5 by dropwise addition of 50% sodium hydroxide solution before buffering. Use a pH meter to check all adjustments. Add several drops of arsenazo III and titrate with DTPA from a 10-ml microburet to a sharp violet end-point. Performing the titration on a Thermolyne Stir-Light with all the illuminated area masked except that portion directly beneath the beaker enhances observation of the end-point. The weight-percent lanthanon on a dry basis may be found by correcting for loss on ignition at 1800°F.

Results and discussion

Table I shows the recovery data for the titration of various amounts of lanthanons in solutions prepared from pure lanthanon sesquioxides. The standard deviation at the 25-mg lanthanum level is 0.028% with 100% recovery. In comparison, the oxalate precipitation–oxide ignition method[7] for lanthanum at the same level gives only a 95.3% recovery and a standard deviation of 1.78%. Poorer recovery results from the gravimetric method at lower levels because of the solubility of the lanthanon oxalates. Lanthanon mixtures may also be titrated satisfactorily.

TABLE I

ANALYSIS OF SOME LANTHANONS BY THE DTPA–ARSENAZO III METHOD

mg Ln present	*mg Ln found*			
	La	*Sm*	*Gd*	*Dy*
2.50	2.53	2.56	2.64	2.55
5.00	5.07	5.09	5.04	5.10
10.00	10.01	10.18	10.04	10.08
15.00	15.09	14.97	15.12	15.01
25.00	25.00	25.00	24.96	24.98

TABLE II

COMPARISON OF CERIUM ANALYSES FOR SOME MOLECULAR SIEVE CATALYSTS BY THE DTPA–ARSENAZO III AND IRON(II) METHODS

Catalyst	*% Cerium*	
	Fe(II)	*DTPA*
A	1.06	1.04
B	4.27	4.43
C	6.71	6.76
D	10.20	10.15
E	10.78	10.70

Some cerium-containing molecular sieve catalysts were analyzed by the DTPA–arsenazo III and iron(II) ammonium sulfate titrimetric procedures. For the latter, cerium(III) was first oxidized to cerium(IV) with ammonium persulfate. The data in Table II show that the shorter compleximetric method gives results similar to the common iron(II) procedure. The standard deviation at the 10% cerium level is 0.07%.

Since dysprosium, gadolinium and samarium do not exhibit tetravalency and therefore cannot be titrated with iron(II), comparison analyses for zeolite catalysts containing these elements were made by the compleximetric and gravimetric techniques. The data in Table III show good agreement for the two methods, and the DTPA–arsenazo III procedure is again preferable because of its rapidity and accuracy at low levels with small sample sizes. The gravimetric technique requires preparation of recovery calibration curves and zeolite sample sizes of *ca.* 1 g when the lanthanon level is 2% or less.

TABLE III

COMPARISON OF DTPA–ARSENAZO III AND GRAVIMETRIC LANTHANON ANALYSES FOR SOME MOLECULAR SIEVE CATALYSTS

Catalyst	*Ln*	*% Ln*	
		DTPA	*Gravimetric*[a]
A	Gd	0.78	0.60
B	Gd	2.97	2.71
C	Gd	4.76	4.55
D	Gd	7.66	7.68
E	Gd	9.54	9.77
F	Sm	1.28	1.03
G	Sm	4.71	4.53
H	Sm	7.33	7.54
I	Sm	10.74	10.89
J	Sm	11.55	11.55
K	Dy	1.12	0.98
L	Dy	5.48	5.36
M	Dy	8.72	8.51
N	Dy	13.36	13.39
O	Dy	15.02	15.21

[a] Corrected by means of calibration curves to account for loss through solubility of lanthanon oxalates.

Chloride, nitrate, perchlorate and sulfate in concentrations far exceeding those found in normal samples do not interfere with the titration. For samarium(III) at the 25-mg level, 100% recovery was found for up to 100 mmol of chloride, nitrate and perchlorate present. Only when the sulfate concentration reached the 100-mmol level was there any sluggishness at the end-point, and recovery then was 98.6%. The lack of sulfate interference with the arsenazo III method is significant, since sulfate does interfere when xylenol orange and methylthymol blue are used. Sulfosalicylic acid also interferes with these sulfonphthalein dyes. Traces of fluoride cause early, fading end-points. Proper sample preparation with sulfuric acid converts the precipitated lanthanon fluorides to sulfates, eliminating fluoride as a source of error.

Iron(III) is commonly found as an impurity in zeolite catalysts at the 0.1% level or less and need not be removed. The iron(III)–SSA complex, yellow at pH 5, does not interfere with the arsenazo III end-point. No titration error is observed with 80 μg of iron(III) present and only a slight positive error at the 100-μg level. The iron(III)–SSA complex is orange at these levels. All sample aliquots contained iron(III) at only 10–20 μg levels, however. Contrary to KUTEINIKOV AND BRODSKAYA[8], the iron(III)–SSA complex does interfere with the violet to orange-red end-point color change for arsenazo I. Any ascorbic acid present to reduce cerium(IV) to cerium(III) will also reduce iron(III) to iron(II) which forms no SSA complex at pH 5, but the negligible amount normally present causes no detectable titration error.

In general, cations which normally complex with EDTA at pH 5 do likewise with DTPA. However, some cations likely to be found in lanthanon-containing catalysts were introduced into a synthetic titration mixture to determine if any cation–arsenazo III complexes interfered with the titration. Table IV shows most of the cations investigated to be tolerable at the 5-mg level. Those acceptable include Ag^+, Ca^{2+}, Cr^{3+}, Mg^{2+}, and Mn^{2+}; Mo^{2+} gave a slight positive error. Co^{2+} and Cu^{2+} strongly complex with DTPA while UO_2^{2+} forms an interfering complex with arsenazo III. Although an end-point was observed with nickel present, there is a large positive error owing to its complexing with DTPA. The disodium salt of arsenazo III was used in all experiments. One commercial lot of the free acid form of arsenazo III did not form the blue-green lanthanon complexes. Subsequent infrared analysis showed that this substance contained about 30% arsenazo I.

TABLE IV

EFFECT OF SOME CATIONS ON LANTHANON RECOVERY

Cation added[a]	*Ln present (mg)*	*Ln found (mg)*	*Recovery (%)*
Ag^+	24.12 (Dy)	24.10	99.9
Ca^{2+}	24.96 (Gd)	25.42	101.8
Co^{2+}	24.96 (Gd)	No end-point	—
Cr^{3+}	24.96 (Gd)	25.11	100.6
Cu^{2+}	24.96 (Gd)	No end-point	—
Mg^{2+}	24.96 (Gd)	25.04	100.3
Mn^{2+}	24.96 (Gd)	25.34	101.5
Mo^{2+}	24.96 (Gd)	26.10	104.6
Ni^{2+}	24.96 (Gd)	30.88	123.7
UO_2^{2+}	24.96 (Gd)	No end-point	—

[a] 5 mg of the cation were added to the titration solution containing the Ln, 25 mg Al(III), 10 μg Fe(III), and 10 ml of 15% sulfosalicylic acid.

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Non-aqueous spectrophotometric determination of carbonyl functions

Many methods are available for the determination of carbonyl compounds. One of the most useful reagents is 2,4-dinitrophenylhydrazine (DNPH), but no method based on DNPH is available for the analysis of samples which are insoluble in alcohol. In this laboratory, the analysis of some carboxy-terminated polybutadiene samples, which are not soluble in alcohol, was required. These polymers, prepared by anionic polymerization, were suspected to contain a small amount of carbonyl functional group arising during the carbonation step.

The method of LAPPIN AND CLARK[1] utilizes the reaction between DNPH and the carbonyl compound in slightly acidic methanol to yield the 2,4-dinitropheny-hydrazone (DNPHO). An alcoholic potassium hydroxide solution is then added which produces a red color that is measured spectrophotometrically. JORDAN AND VEATCH[2] used a mixed hydrocarbon–alcohol solvent and added water to ensure dissolution of inorganic chlorides. They found that after the addition of base the absorbance must be determined within the interval 8–15 min, since the color fades quite rapidly. LOHMAN[3] preferred to separate the intensely yellow DNPHO from the excess of yellow reagent by extraction with hexane and measure the absorbance of the extract; a 2:1 ethanol–hexane solvent was used and the solution was made 25% aqueous before the hexane extraction. The use of an organic system for the carbonyl–DNPH reaction precludes the use of an organic solvent for extraction unless one could be found which has a favorable distribution coefficient and is at the same time immiscible with the organic reaction phase.

In the procedure of POOL AND KLOSE[4] the DNPH reagent in benzene is absorbed on an alumina column, the sample is added and the hydrazones are eluted. SCHWARTZ AND PARKS[5] used a column impregnated with DNPH, phosphoric acid, and water to prepare carbonyl-free solvents.

Since the extraction methods were not applicable to the polymers under investigation, and since it was felt that the carboxyl-terminated polymer would not react and elute from the column in a convenient time, a modified procedure was developed. In this method, the reaction between the carbonyl compound and DNPH takes place in a chloroform solution (less than 5% ethanol present) containing methanesulfonic acid. The absorbance of the solution *vs.* a reaction blank gives the carbonyl content.

Reagents

2,4-Dinitrophenyhydrazine. Eastman White Label grade was used as received and gave the same results as the material recrystallized from purified methanol.

Chloroform. Some reagent-grade lots were observed to contain carbonyl as found from high blank values (greater than 0.4 absorbance at 400 nm *vs.* a pure chloroform blank). Such lots were purified[5].

Methanol. Spectro-grade methanol (Matheson, Coleman & Bell) was used as received. It may be necessary to purify reagent-grade methanol by addition of 1 ml of concentrated hydrochloric acid and excess of DNPH to 4 l of methanol. The mixture is allowed to reflux for 1 h and then distilled from an all-glass distillation column.

Methanesulfonic acid. Eastman White Label grade was used as received.

DNPH reagent. Dissolve 0.010 g of DNPH in chloroform. Add 12 ml of the methanol, 1 ml of methanesulfonic acid and dilute to 50 ml with chloroform.

Procedure

Weigh accurately about 150 mg of the polymer sample into a 25-ml volumetric flask and dilute to volume with chloroform. Transfer a suitable aliquot, which will yield an absorbance of 0.2–0.6, to a 10-ml volumetric flask. Pipet 2 ml of the DNPH reagent and dilute to volume with chloroform. Take a blank through the procedure. Place the flasks in a water bath at 50° for 2 h. Then allow to cool to room temperature and add additional solvent if required. Measure the absorbance *vs.* the blank in the range 350–400 nm. From a calibration curve obtained with levulinic acid, calculate the carbonyl content of the sample.

Results

The precision of the method is good, being in the range of ±5%. The accuracy of the method on polymeric samples (in which the method has its real utility) is difficult to assess for lack of samples with known carbonyl content.

TABLE I

MOLAR ABSORPTIVITIES FOR VARIOUS CARBONYL COMPOUNDS

Compound[a]	λ_{max} *(nm)*	*Molar absorptivity* $(\varepsilon \pm 300)$	
		2 h at 50°	*4 h at 50°*
Butyraldehyde	360	10,500	13,700
iso-Butyraldehyde	360	10,600	—
2-Octanone	367	14,900	—
Cyclohexanone	367	16,900	16,600
2-Pentanone	366	16,100	16,000
iso-Valeraldehyde	360	10,000	15,300
Levulinic acid	365	14,400	14,500[b]

[a] Reagent grade.
[b] After 2 h at 50° and 5 h at room temperature.

TABLE II

EQUIVALENT WEIGHTS FOR SOME BUTADIENE POLYMERS BASED ON CARBONYL CONTENT

Polymer	*Equivalent weight found*
Phillips Butarez CTL-2	38,000
Thiokol HC-434[a]	76,000
General Tire Telagen CT	47,000
3M Laboratories, Lot A	40,900
3M Laboratories, Lot B[b]	No carbonyl
3M Laboratories, Lot 5A	33,000
3M Laboratories, Lot 5B[b]	250,000

[a] A lot containing phenyl-β-naphthylamine was estimated to be low in carbonyl content. This lot containing Calco 2246, although one would expect it to be low in carbonyl, was found to have the above value.
[b] Prepared in such a manner that one would expect it to be carbonyl-free.

Table I shows the molar absorptivities (ε) of the DNPHO of several carbonyl compounds. In this solvent system, ketones appeared to react faster than aldehydes, thus there is some flexibility depending on the particular carbonyl determination. The color formed is relatively stable; heating for a further 2 h at elevated temperatures caused no change in absorbance. This stability is in contrast to procedures in which the solution is made alkaline and the determination must be completed within minutes.

The equivalent weights of several carboxy-terminated polybutadiene polymers based on carbonyl content are given in Table II. These values may not represent the true equivalent weight of the polymers since the carbonyl is not an end-group; the value is used merely as a means of reporting the low amount of carbonyl found, rather than in terms of percent. Other lots were analyzed and the data agreed with the mode of polymer preparation, *i.e.* whether one could expect keto groups to be present.

The polymer contains an anti-oxidant, generally Calco 2246 which does not interfere in the carbonyl determination. Phenyl-β-naphthylamine used in some lots interferes, and a correction for the anti-oxidant is then necessary.

Levulinic acid was chosen as the standard since both a keto and carboxyl group are present, which would be similar to the situation in the polymer sample. The use of a 2-h reaction period results in a linear calibration curve.

Discussion

The technique of making the system alkaline and determining the absorbance of the new species was investigated. In the organic system, the inorganic base was replaced (for solubility reasons) by several organic ones. Tetramethylguanidine did not form the red species while tetrabutylammonium hydroxide gave inconsistent and irreproducible results.

In the non-alkaline systems the excess of reagent and the hydrazone formed absorb within 20 nm of each other[3], so that the hydrazone cannot be determined in the presence of excess of DNPH. However, in the solvent system described here, the hydrazone can be measured in the presence of excess of reagent, because of the acid concentration employed and the low amount of alcohol present in the final color measurement.

JORDAN AND VEATCH[2] criticized LOHMAN's extraction procedure because the absorption maxima and molar absorptivities change significantly with different carbonyl compounds. The results in Table I confirm that these values are not independent of structure.

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Apparatus for the rapid degassing of liquids. Part II

In an earlier paper[1] an apparatus for the degassing of liquids was described and the criteria for determining the extent of degassing were discussed. In this communication, a more adaptable apparatus which degasses liquids more rapidly and is mechanically simpler and sturdier, is described.

Apparatus and procedure

The apparatus is shown in Fig. 1, which is drawn to scale as indicated. The principle of operation is to agitate the liquid (which fills the horizontal degassing chamber about one-half to one-third full) with the rotating paddles while the system is pumped. The horizontal orientation in combination with the rapid back-and-forth motion imparted by the paddles presents a large and constantly renewed surface to the vacuum. The condenser prevents most of the liquid being lost to the cold traps.

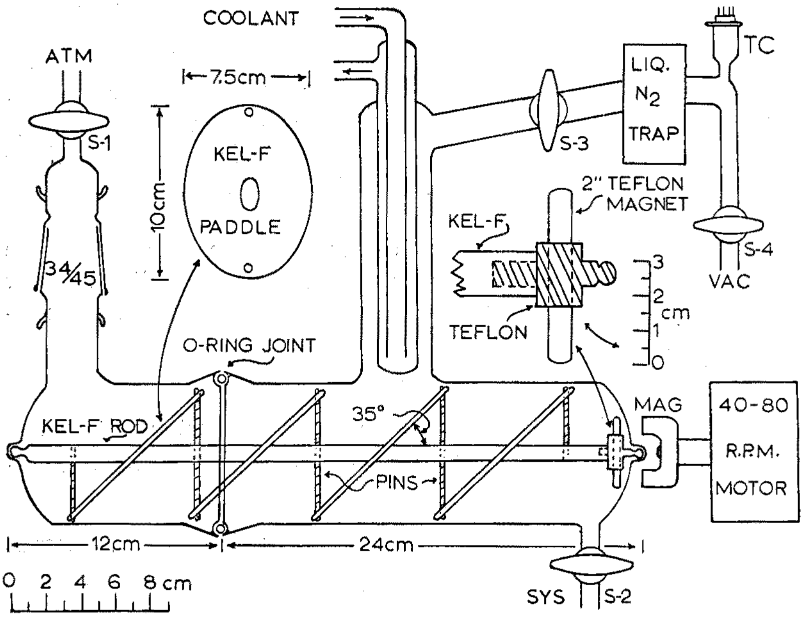

Fig. 1. Degassing apparatus.

The apparatus was fabricated from a plain 75-mm i.d. O-ring joint (Corning #6700) with a Buna-N O-ring, and was held together by a 102/75 clamp for a spherical joint. The right-hand section of the apparatus is permanently attached to a vacuum system and to the apparatus in which the degassed solvent is used. The degassing apparatus was fabricated in two sections, the left-hand side 12 cm long and the right-hand side 24 cm long. This particular size could handle up to 600 cm^3 of liquid, but the apparatus can be scaled up or down. The apparatus was made in two parts to make it easier to fit the stirrer in place after the glass parts had been annealed. It also made it easier to clean the apparatus. The O-ring joint was found to be vacuum-tight.

The stirrer was made from a 0.5-in Kel-F rod and the paddles were made from 1/16-in Kel-F sheet. The four paddles were offset at an angle of 35 degrees from the rod and were pinned in place using 1/8-in stainless steel rod. The 0.5-in Kel-F rod was necessary to maintain stiffness over the long span used. The stirrer could also be made from Teflon, but Kel-F is less expensive and is easier to machine. The stirrer was driven by a 2-in alnico magnet at either 40 or 80 r.p.m. This magnet drove a commercially available 2-in long Teflon-covered bar magnet of the type generally used for magnetic stirrers. The mounting of this magnet is shown in the detail in Fig. 1.

Solvent is loaded into the apparatus *via* the joint at J. Stopcock S-1 provides an opening to the atmosphere. Stopcock S-2 connects to the apparatus where the degassed solvent is used. Depending on what solvent is used, S-2 may be a Teflon stopcock or a greased one. The stopcock S-3 leads to a liquid nitrogen trap, a thermocouple gauge, and thence to a vacuum pump. Depending on the solvent used, either coolant from a refrigerator unit or cold water is used in the condenser C. With stopcocks S-3 open and S-4 closed, the static pressure in the system may be measured.

Comparative tests

For comparative testing, water, benzene and olive oil were used. These solvents show a great range of behavior in terms of vapor pressure, viscosity, density, and gas solubility. In all cases, degassing was more rapid with stirring than without, and increased surface area speeded up the degassing even without stirring. The comparisons were made by first determining the time necessary to reduce the permanent gas pressure above the liquid to the initial base pressure of the vacuum system with stirring of the liquid, and then to repeat the procedure without stirring. The results of this comparison are presented in Table I together with comparable data for the earlier apparatus. For benzene, the 13 sec required to attain 40 μ means that the

TABLE I

COMPARISON OF DEGASSING RATES[a] FOR THREE LIQUIDS

Liquid	*With stirring*	*Without stirring*	*With circulation*[b]
Water	70 sec for 10 μ	150 sec for 10 μ	30–40 min for 15 μ
Olive oil	33 min for 40 μ	70 min for 40 μ	2 h for 15 μ
Benzene	13 sec for 40 μ	4 min for 40 μ	5 min for 15 μ

[a] Time needed to reduce the pressure to the base pressure of the vacuum system as indicated.
[b] Degassing rates for the apparatus described in ref. 1.

system was pumped on for 13 sec with stirring, stopcock S-4 was closed, and the static pressure of the permanent gas present in the system after waiting several minutes was 40 μ. This procedure for testing was the same for all the solvents.

Conclusion

The degassing apparatus described in this paper has the same advantages as the earlier apparatus, but is more easily scaled up or down and is faster in use. The rapidity of the degassing is especially significant in the case of olive oil, a substance which has proved to be especially difficult to handle and to degass.

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Determination of nitrilotriacetic acid and ethylenediaminetetraacetic acid in granular detergent formulations

Nitrilotriacetic acid (NTA) is used in combination with triphosphates in detergents to give improved performance[1]. The usual compleximetric titrations cannot be used for NTA because both NTA and phosphates react with the metal ions used as titrant, which causes overtitration and a fading end-point. Polarographic[2,3] and electrophoretic methods[4] have been used, but their precision is usually lower than that obtained by titrimetric methods, unless very sophisticated instrumentation is used.

The method described in this paper is based on the titration of NTA with copper(II) chloride in the presence of chrome azurol S as indicator. The phosphates are removed by precipitation with tin(II). Chrome azurol S has previously been used in the titration of copper(II) with EDTA[5].

Reagents

All chemicals were of reagent-grade quality.

Procedure

Dissolve *ca.* 2 g of detergent (containing about 10% NTA) in 30 ml of distilled water in a 150-ml beaker. Add while stirring "sample weight × % sodium triphosphate × 0.25 ml" of a freshly prepared aqueous 12% solution of tin(II) chloride dihydrate, to which concentrated hydrochloric acid is added to clear the solution;

a white precipitate of tin(II) phosphate is formed. Then add 10 ml of aqueous 20% hexamethylenetetramine solution. Continue stirring for a few minutes. Adjust the pH of the mixture to 6.0 with concentrated sodium hydroxide using a pH meter. Then transfer the mixture to a centrifuge bottle and centrifuge at 3000 g. Transfer the supernate to the original beaker and rinse the bottle twice with 10 ml of water. Add 6 drops of an aqueous 0.5% solution of chrome azurol S. Titrate the yellow solution with 0.3 *M* copper(II) chloride dihydrate from a 10-ml microburette to the yellow-to-blue end-point. The milliequivalent weight of NTA is 0.257.

Accuracy and precision

The accuracy of the method was tested by adding known amounts of NTA monohydrate to detergents containing up to 55% sodium triphosphate (Table I). The assay of Detergent A before addition of standard amounts of NTA yielded 9.31% NTA. Detergent B and C were NTA-free products. From the results, it was calculated that the amount of NTA found was 98% of the theoretical amount of NTA present.

TABLE I

STANDARD ADDITION OF NTA·H_2O TO DETERGENTS WITH DIFFERENT SODIUM PHOSPHATE LEVELS

Detergent	*Phosphate level (%)*	*Wt. sample (g)*	*Wt. NTA·H_2O added (g)*	*% NTA theor.*	*% NTA found*
A	40	2.0178	0.1024	13.35	13.09
A	40	2.0060	0.2001	16.91	17.23
A	40	2.0193	0.3017	20.20	19.70
B	55	2.0047	0.2038	8.59	8.41
B	55	2.0017	0.3012	12.18	11.88
C	50	2.0065	0.2059	8.66	8.50

The precision was estimated from results obtained for Detergent A; the standard deviation calculated from the results of 5 determinations was 0.06% absolute on an average value of 9.31% NTA.

Assay after alcohol soluble–insoluble separation

For detergents containing both organic and inorganic matter, NTA may also be determined on the alcohol-insoluble part of the detergent. The end-point is sharper but the time for analysis is longer. A series of 5 analyses of Detergent A by this technique gave an average result of 9.35% NTA, which is in good agreement with the above average of the results obtained when no alcohol separation was carried out; however, the standard deviation increased to *ca.* 0.16% when the separation was used.

Interference by tin(II) chloride

NTA to which was added a ten-fold excess of tin(II) chloride was titrated with copper(II) chloride and the recovery of NTA was 100%. This proved that tin(II) ions do not displace copper from the copper–NTA complex and thus do not interfere.

Indicator

Chrome azurol S has a sharp color change from yellow to blue at the end-point. The blue color is due to a 1:1 copper–chrome azurol S complex[6] with a pK_f value of 4. The optimum pH is 6; even at pH 5.5 or 6.5, the color change is less pronounced.

Interferences

Tin(II). Tin(II) forms stable, insoluble precipitates with phosphates but only a very weak complex with NTA. Arsenic, molybdenum and tungsten cations also form weak complexes with NTA (as do antimony ions) but these ions do not mask phosphates efficiently.

EDTA. EDTA interferes with the titration. Most metal chelating agents are co-titrated with copper(II) chloride when chrome azurol S is used as indicator. The stability constants of their copper complexes are much larger than the stability constant of the copper–chrome azurol S complex; for example, pK_f for copper–EDTA[7] is 18.8 and for copper–tetraethylenepentamine, pK_f is 22.9.

The NTA content of detergents containing EDTA can however be determined by an additional titration. The detergent solution is titrated with the same copper(II) solution but with PAN [1-(2-pyridylazo)-2-naphthol] as indicator. All chelating agents with a K_f value larger than the value for the copper–PAN complex (16.0) will be titrated. NTA will not be titrated (pK_f of the copper–NTA complex is 12.6). In the "chrome azurol S titration", EDTA is completely determined; titration of 1 mmole of pure EDTA (disodium salt) showed a recovery of 100.4%. When a mixture of sodium triphosphate containing 10.0% NTA (trisodium salt) was analyzed by the "PAN titration", only 0.1% NTA was determined. Therefore, from the difference between the two titrations the amount of NTA in an EDTA-containing detergent can be calculated.

Calcium. Some detergents contain calcium salts. The difference between the calcium–NTA stability constant (pK_f = 6.4) and the copper–NTA stability constant is large enough for the titration of NTA not to be affected. Pure NTA mixed with calcium chloride at a molar ratio of 1:3.5 showed that all the NTA present could be titrated with copper(II) chloride to the chrome azurol S end-point.

Magnesium forms a complex with NTA which is about 20% less stable (pK_f = 5.4) than the calcium–NTA complex, hence no interference from magnesium would be expected. Iron(III) will probably interfere, for its NTA complex (pK_f = 15.8) is much more stable than the copper–NTA complex; however, iron is not a common impurity in these detergents.

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Simultaneous determination of rubidium and cesium in rock samples by neutron activation analysis with a lithium-drifted germanium detector after chemical group-separation

Rubidium and cesium in rocks are suited as indicator elements to elucidate the degree of geochemical fractionation. Determinations of the rare alkali metals in samples of geochemical interest have been previously reported by SMALES *et al.*[1,2] who used neutron activation analysis with time-consuming ion-exchange separations.

The recently developed high-resolution lithium-drifted germanium detector (Ge(Li) detector) has shown a high potentiality for application to non-destructive neutron activation analysis of geochemical samples[3]. Moreover, a combination of the Ge(Li) detector and chemical group-separation offers a distinct simplification in the correction of contributions from other nuclides. This technique has been successfully applied to the determination of rare-earth elements in rock samples[4,5]. In the present communication, a procedure is described for the simultaneous determination of rubidium and cesium in rock samples with a Ge(Li) detector after a simple chemical group-separation based on tetraphenylborate precipitation.

Equipment

The Ge(Li) detector used was made in this Institute; the active volume of the detector is estimated to be *ca.* 1.6 ml. The output signal from the detector was fed into an ORTEC Model 118A pre-amplifier and an ORTEC Model 410 linear amplifier. The resultant pulse was then analysed by an RCL 400-channel pulse-height analyser. Resolution for the ^{57}Co 122-keV peak was 3.4 keV.

Procedure

Rock samples (500 mg) were sealed in quartz ampoules. Aliquots (20 μl) of the reference standard solution (5.74 mg Rb/ml and 0.19 mg Cs/ml) were pipetted onto an aluminium foil, evaporated under a heat lamp and wrapped in an aluminium foil. The samples and the reference standard were irradiated in the JRR-2 reactor (Japan Atomic Energy Research Institute) at a neutron flux of $4 \cdot 10^{13}$ n/cm^2/sec for a week or in the TRIGA MARK-II reactor (Rikkyo University) at a neutron flux of $4 \cdot 10^{12}$ n/cm^2/sec intermittently for 5 days.

After cooling for a week, the irradiated samples were decomposed by sodium peroxide fusion in a nickel crucible containing rubidium (5.7 mg Rb) and cesium (0.2 mg Cs) carriers and ^{137}Cs tracer (about $2 \cdot 10^5$ counts/min). The melt was dissolved with water and minimal amounts of hydrochloric acid to ensure complete dissolution. To the clear solution was added 6 *N* sodium hydroxide solution to precipitate the hydroxides which were then discarded. The supernate was acidified with hydrochloric acid and 2 ml of iron(III) chloride solution (5 mg Fe^{3+}/ml) was added to repeat the iron(III) hydroxide scavenge. The resultant solution was neutralized with hydrochloric acid and made acid with acetic acid. The alkali metals (K, Rb, and Cs) were then precipitated with 5 ml of 2% sodium tetraphenylboron solution and mounted on aluminium trays for γ-counting.

The ^{86}Rb (18.6 d) photopeak at 1072 keV and the ^{134}Cs (2.05 y) photopeaks at 596 and 793 keV stand clearly above the background level (Fig. 1). The ^{137}Cs photopeak at 662 keV was used for the chemical yield measurement of both elements without any additional chemical treatment. The chemical yields were more than 60%.

The possible chemical fractionation of rubidium and cesium during the tetraphenylborate precipitation step and the whole procedure were examined by using ^{86}Rb and ^{134}Cs tracers. No fractionation was found under the conditions shown in Table I.

Rubidium and cesium abundances found in various geochemical standard rocks are summarized in Table II. Recommended[6] or other[3,7] values available are

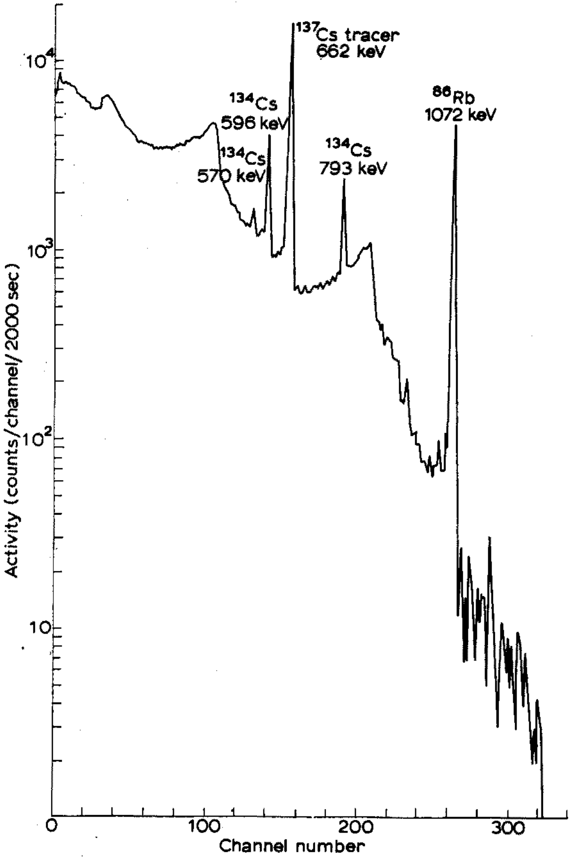

Fig. 1. The γ-ray spectrum of standard rock sample G-2 with the Ge(Li) detector 15 days after the end of irradiation.

TABLE I

TEST OF POSSIBLE CHEMICAL FRACTIONATION OF RUBIDIUM AND CESIUM DURING THE CHEMICAL PROCEDURES

(Activities taken: Rb 541±37 c/500 sec at 1072 keV, Cs 17342±167 c/500 sec at 793 keV $(Cs/Rb)_t = 32.1 \pm 2.2$)

		Rb : Cs recovered (%)	*Cs/Rb*	*(Cs/Rb)/(Cs/Rb)$_t$*
Tetraphenylborate precipitation step	1	98 : 101	33.0±2.3	1.028±0.101
	2	73 : 71	31.0±2.2	0.966±0.096
Whole procedure		66 : 66	31.9±1.7	0.994±0.087

given in the final column of the Table for comparison; these independent values agree well within the experimental errors. The agreement with previously reported values for the standard rocks also indicates that the accuracy of the determination is good.

The sensitivity for each element depends on the irradiation conditions and on the energy distribution of γ-activity induced in the samples. The ^{86}Rb (18.5 d) photopeak at 1072 keV is especially inadequate for the γ-ray detection with a Ge(Li) detector because of its very low counting efficiency for the high-energy region. In

TABLE II

CONCENTRATION OF RUBIDIUM AND CESIUM IN SEVERAL GEOCHEMICAL STANDARD ROCKS

Sample	*Values found*[a]		*Other values*	
Split/position	*Rb (p.p.m.)*	*Cs (p.p.m.)*	*Rb (p.p.m.)*	*Cs (p.p.m.)*
G-1 (Granite)	216±6[b]	1.69±0.08[b]		
	233±9[c]	1.39±0.06[c]		
	232±4[c]	1.35±0.05[c]		
	av. 228±4	av. 1.43±0.04	220[d]	1.5[d]
W-1 (Diabase)	18±2[b]	1.14±0.05[b]		
	22±1[c]	1.06±0.03[c]		
	22±1[c]	1.04±0.02[c]	< 30[e]	0.83±0.15[e]
	av. 22±1	av. 1.06±0.02	22[d]	1.1[d]
G-2 (Granite)	185±9[b]	1.26±0.05[b]		
54/10	185±4[c]	1.28±0.07[c]	129±4[e]	1.4±0.3[e]
	av. 185±4	av. 1.27±0.04	150–550[f]	—
GSP-1	273±12[b]	1.00±0.06[b]		
(Granodiorite)	271±6[c]	1.21±0.09[c]	255±10[e]	0.8±0.1[e]
13/22	av. 272±6	av. 1.07±0.05	230–800[f]	—
AGV-1	73±4[b]	1.34±0.04[b]		
(Andesite)	70±2[c]	1.21±0.01[c]	61±10[e]	1.3±0.3[e]
26/3	av. 71±2	av. 1.22±0.01	50–150[f]	—
BCR-1 (Basalt)	56±3[b]	1.10±0.07[b]		
39/20	51±2[c]	1.08±0.05[c]	< 105[e]	1.5±0.2[e]
	av. 53±2	av. 1.08±0.02	30–220[f]	—
PCC-1 (Peridotite) 52/22	< 1[b]	0.03±0.01[b]	—	—
DTS-1 (Dunite) 16/18	< 1[b]	0.02±0.01[b]	—	—
JG-1	188±4[c]	10.7±0.1[c]		
(Granodiorite)	185±4[c]	10.0±0.2[c]	—	—
9/8	av. 187±3	av. 10.6±0.1		

[a] The errors in the second and third columns were calcd. from the counting statistics. The averages were computed by suitable weighting.

[b] Irradiation in JRR-2.

[c] Irradiation in TRIGA.

[d] Recommended value[6].

[e] Neutron activation[3].

[f] Emission spectrography[7].

the non-destructive neutron activation technique with a Ge(Li) detector reported by GORDON *et al.*[3], the rubidium content in BCR-1 (basalt) could not be determined. The limits of detection for the elements are 30 p.p.m. for rubidium and 0.7 p.p.m. for cesium in the instrumental activation analysis[3]. The present combination of a simple chemical separation and a Ge(Li) detector allows lower sensitivities of 1 p.p.m. for rubidium and 0.005 p.p.m. for cesium. The proposed technique is applicable to the determination of the elements in geochemically important rocks such as basalt and diabase, but the detection of rubidium in ultramafic rocks (PCC-1 and DTS-1) is difficult and ^{86}Rb may be best determined by β-counting after the mutual separation of rubidium and cesium as reported by SMALES *et al.*[2].

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