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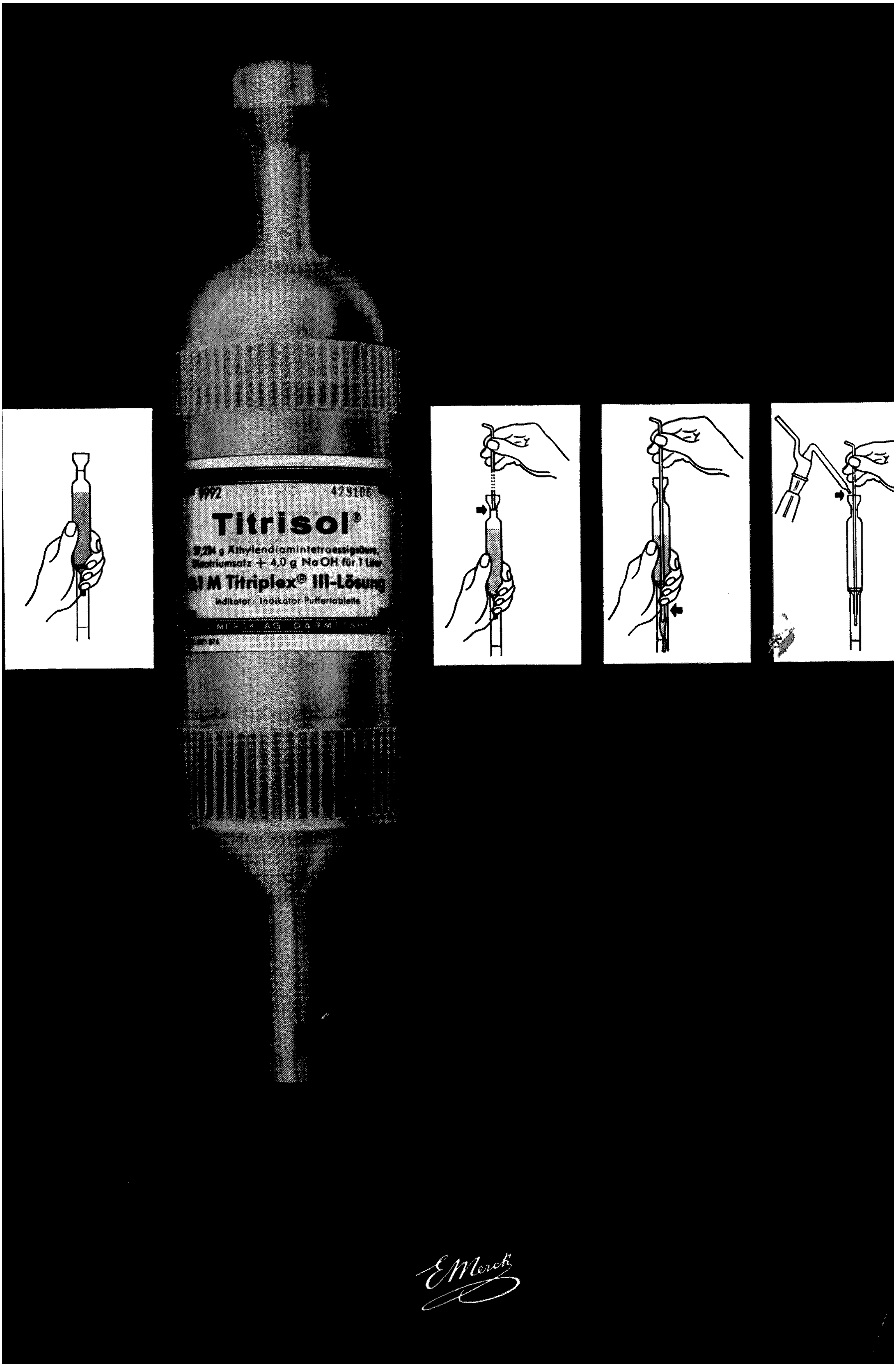
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 41, No. 2, May 1968

CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC ANALYSIS OF TRACE RARE EARTHS

PART I. QUALITATIVE STUDIES

Line emissions from f–f transitions in rare earths contained in a matrix are obtained by excitation with cathode rays. The distinctive energy of these emissions is utilized to detect the presence of trace amounts of rare earths, and non-destructive identification of such traces is carried out quickly by comparison with a derived *hauptlinien* spectrum. Matrix effects, masking interferences and the utilization of line shape are discussed.

S. LARACH,
Anal. Chim. Acta, 41 (1968) 189–195

NEUTRON ACTIVATION ANALYSIS OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART II. DETERMINATION OF MOLYBDENUM AND RHENIUM

A neutron activation analysis has been devised for the determination of traces of molybdenum and rhenium in an electrolytic zinc sulphate solution. The activities due to the daughter ^{99m}Tc and to ^{186}Re were counted. The chemical separation was performed on an anion-exchange resin. The matrix activities were separated by elution with 0.5 *N* nitric acid. The separation of technetium and rhenium was performed by an elution with 0.2 *N* perchloric acid. To avoid errors in the molybdenum determination, the uranium present in the sample was separated before the irradiation.

R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 41 (1968) 197–204

NEUTRON ACTIVATION ANALYSIS OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART III. SIMULTANEOUS DETERMINATION OF TELLURIUM, SELENIUM, ARSENIC AND ANTIMONY

A neutron activation analysis is described for the simultaneous determination of tellurium, selenium, arsenic and antimony in an electrolytic zinc sulphate solution. The activity induced in the tellurium was measured by means of its radioactive daughter ^{131}I. The chemical separation of iodine was performed by extraction into carbon tetrachloride. The interference due to the fission of uranium was minimised by a preseparation of uranium. The isotope ^{75}Se was measured by a γ,γ-coincidence technique, which allowed the determination of 0.002 μg Se/ml. Selenium was chemically separated by extraction as piazselenol. Arsenic and antimony were separated by precipitation as sulphide and distillation as chloride. The isotopes ^{76}As and ^{122}Sb were measured γ-spectrometrically, amounts of 0.02 μg/ml being determined. The method is also suitable, although not very sensitive, for the simultaneous determination of tin and germanium.

R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 41 (1968) 205–215

DETERMINATION OF RARE-EARTH ELEMENTS IN ROCK SAMPLES BY NEUTRON ACTIVATION ANALYSIS WITH A LITHIUM-DRIFTED GERMANIUM DETECTOR AFTER CHEMICAL GROUP-SEPARATION

A lithium-drifted germanium detector combined with chemical group-separation has been utilized for the determination of rare-earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu) in rock samples by neutron activation. This procedure has the advantage of a low background level which cannot be attained in the non-destructive method. The combination of the Ge(Li) detector and chemical group-separation also offers a distinct simplification in the correction of contributions from other nuclides. For optimum utility of a Ge(Li) detector in neutron activation analysis, chemical group-separations are recommended.

K. Tomura, H. Higuchi, N. Miyaji, N. Onuma and H. Hamaguchi,
Anal. Chim. Acta, 41 (1968) 217–228

THE DETERMINATION OF NEON AND ARGON IN HELIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

An atomic absorption spectrophotometric technique is described for the determination of neon and argon, respectively, in helium. The accuracies obtained for nanomoles of neon and argon, respectively, were +2.1 and −1.5%. Two Geissler-type discharge tubes containing neon and argon, respectively, were used as emission sources; the absorption source was a quartz cell which contained the sample and related standards that were excited by a high-frequency oscillator. The spectral lines that were employed were neon 6402 Å and argon 8115 Å. Because the spectral lines used had transitions to metastable energy levels, instead of ground levels, a conventional monochromator was suitable.

J. A. Goleb,
Anal. Chim. Acta, 41 (1968) 229–235

DETERMINATION OF TRACE ELEMENTS IN INORGANIC AND ORGANIC MATERIALS BY X-RAY FLUORESCENCE SPECTROSCOPY

A new, almost universally applicable method for the trace analysis of inorganic and organic materials is described. The trace element (or elements) together with a suitable coprecipitating element is isolated from interfering elements by precipitation with a suitable organic or inorganic precipitant. The precipitate is then filtered on a paper disk and the collected trace element (or elements) is determined by X-ray analysis.

C. L. Luke,
Anal. Chim. Acta, 41 (1968) 237–250

SINGLE-STEP RADIOCHEMICAL SEPARATIONS BY COLUMN PROCEDURES IN ACTIVATION ANALYSIS

Some single-step column procedures are described for both individual and group activity separations. Besides the usual ion-exchange techniques, other methods such as reverse-phase chromatography, isotopic exchange and the use of resins converted into special forms were used. Fast and simple selective separations from 2 *N* hydrochloric acid are reported for Mo(VI), Au, Cu(II), Sb(V), and for $AsO_4^{3-} + PO_4^{3-}$ from both 2 *N* hydrochloric acid and 1 *N* sulfuric acid; for Cu, Sb and As + P, the selectivity can be greatly increased by using a guard bed of resin in normal form. By combining the different techniques a single-step separation scheme for 6 elements (Mo, Au, Zn, As, Cu, Sb) in 2 *N* hydrochloric acid was developed; this allows high chemical recoveries, high cross-decontamination and very large decontamination from ^{24}Na to be reached, so that application for biological sample analysis can be envisaged. Simplified two-stage column separations for Au + Sb and Cu and Fe + Sb and Zn from concentrated hydrochloric acid (cationic and anionic resin beds coupled) are also reported.

R. MALVANO, P. GROSSO AND M. ZANARDI,
Anal. Chim. Acta, 41 (1968) 251–258

NUCLEAR MAGNETIC RESONANCE STUDIES OF PHOSPHORUS(V) PESTICIDES

PART I. CHEMICAL SHIFTS OF PROTONS AS A MEANS OF IDENTIFICATION OF PESTICIDES

Correlations of structural and proton chemical-shift data for 40 commercial phosphorus(V) pesticides are reported. Correlations of structure with the phosphorus coupling constants are discussed, and general trends are noted which aid in the use of NMR as a tool for identification and analysis of phosphorus(V) compounds.

H. BABAD, W. HERBERT AND M. C. GOLDBERG,
Anal. Chim. Acta, 41 (1968) 259–268

SPECTROFLUORIMETRIC DETERMINATION OF MALIC ACID WITH β-NAPHTHOL

A detailed study of the spectrofluorimetric determination of malic acid by reaction with β-naphthol is reported. As little as 0.1 μg of malic acid can be determined. The optimum concentration of sulfuric acid is 80% (v/v). The interferences of citric, succinic and tartaric acids are discussed.

G. D. CHRISTIAN AND J. R. MOODY,
Anal. Chim. Acta, 41 (1968) 269–274

SPECTROPHOTOMETRIC DETERMINATION OF CHLORATE ION

A simple, direct, sensitive spectrophotometric method for the determination of chlorate ion is described. The method is based upon the interference of chlorate ion on the formation of a rhenium–α-furildioxime complex, whose absorbance maximum is at 532 nm. The effect of several variables is described. The range for the method is 0–5.0 p.p.m. of chlorate ion.

N. L. TRAUTWEIN AND J. C. GUYON,
Anal. Chim. Acta, 41 (1968) 275–282

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

A direct method is presented for the spectrophotometric determination of niobium with PAR in mild and alloy steels. Interference is caused only by tantalum and large amounts of copper. A compensating solution is used to correct for coloured ions and for the copper–PAR complex. The method covers the range 0–100 μg of niobium, and Beer's law is obeyed from 0 to 2.0 μg Nb/ml. A molar absorptivity of 14,400 at 536 nm was found for the niobium–PAR complex, with a relative standard deviation of ±0.6%.

P. Pakalns,
Anal. Chim. Acta, 41 (1968) 283–292

A VOLTAMMETRIC STUDY OF AQUOZINC(II) COMPLEXES IN METHANOL

Results of chronopotentiometric and polarographic determinations of the formation constants of aquozinc(II) complexes in methanol are reported. Chronopotentiometry offers some advantages over polarographic and spectrophotometric methods for studies of this kind.

S. L. Levine and W. E. Ohnesorge,
Anal. Chim. Acta, 41 (1968) 293–301

A STUDY OF THE VOLTAMMETRIC BEHAVIOUR OF THE COUPLES Br^-/Br_2, Br^-/Br_3^-, $Br^-/HBrO$ AND Br^-/BrO^- AS A FUNCTION OF pH

The nature of the "blanks" occurring in titrations with electrically generated bromine is discussed. In acidic media such "blanks" are due to the limits of sensitivity of the experimental technique employed (mono- or biamperometric). In alkaline solutions hydrolysis of bromine plays an important role; the formation of hypobromite ion explains the very large "blanks" observed. Acid–base titrations, with bromine as indicator confirmed these findings.

F. Magno and M. Fiorani,
Anal. Chim. Acta, 41 (1968) 303–310

SOLVENT EXTRACTION OF THIODIBENZOYLMETHANE AND ITS COPPER, NICKEL AND COBALT CHELATES

(in German)

The solubility of thiodibenzoylmethane, as well as its distribution coefficients between water and organic solvents, and the enol dissociation constant were studied. The extraction of copper, nickel, and cobalt by solutions of thiodibenzoylmethane in *n*-heptane or tetrachloromethane is described; these extractions are practicable at lower pH values than for dibenzoylmethane, and only a very small excess of reagent over the stoichiometric quantity is needed.

E. Uhlemann and H. Müller,
Anal. Chim. Acta, 41 (1968) 311–318

PRECIPITATION REACTIONS OF THIOBENZOYLPHENYLHYDROXYLAMINE AND ITS USE AS A REAGENT FOR COPPER

Thiobenzoylphenylhydroxylamine (TBPHA) quantitatively precipitates copper as $Cu(C_{13}H_{10}NSO)_2$ which can be used as a weighing form for copper; the gravimetric factor is 0.12217. Iron, aluminium, chromium and commonly accompanying elements do not interfere. Quantitative precipitation and separation of several metals from highly acidic solutions is possible. The precipitation reactions of metals with TBPHA, over a wide range of acidity and in the presence of EDTA, are tabulated. TBPHA is of little value as a colorimetric reagent.

R. M. Cassidy and D. E. Ryan,
Anal. Chim. Acta, 41 (1968) 319–325

GRAVIMETRIC DETERMINATION OF GOLD WITH DI-2-THIENYLKETOXIME

Di-2-thienylketoxime may be used as a gravimetric reagent to determine gold. The error is of the order of ± 0.3%. There are few interfering ions and simple methods may be used to eliminate these.

W. J. Holland and J. Gerard,
Anal. Chim. Acta, 41 (1968) 327–330

THE USE OF QUINOXALINE-2-CARBOXYLIC ACID AND ITS DERIVATIVES AS ANALYTICAL REAGENTS

Quinoxaline-2-carboxylic acid and 3-chloro and 3-hydroxy derivatives have been studied as analytical reagents. The solubility products of the metal salts, the optimum pH range for complete precipitation and the thermal behaviours of the metal complexes have been established. Quinoxaline-2-carboxylic acid allows the gravimetric determination of Cu(II), Cd(II), Zn(II), Co(II), Ni(II) and Pd(II); with the 3-chloro and 3-hydroxy derivatives, only palladium(II) could be precipitated quantitatively.

N. K. Dutt, G. S. Sanayal and K. Nag,
Anal. Chim. Acta, 41 (1968) 331–339

COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN 1,1′-DIANTHRIMIDE AND GERMANIUM(IV) OR TELLURIUM(IV)

The complex formation in concentrated sulfuric acid between 1,1′-dianthrimide (Di) and germanium or tellurium(IV) was studied by spectrophotometry. The systems contained only one species, GeDi or TeDi; the stability constants in 93.2% sulfuric acid were calculated to be 221 and 228, respectively.

F. J. Langmyhr and G. Norheim,
Anal. Chim. Acta, 41 (1968) 341–346

THE DETERMINATION OF NICOTINE IN TOBACCO AND IN PARTICULATE MATTER OF SMOKE BY GAS CHROMATOGRAPHY

A gas chromatographic method for the determination of nicotine in tobacco and in smoke particulate matter is described. Tobacco samples are extracted with saturated barium hydroxide solution, and nicotine is then extracted with benzene–chloroform (9:1), and determined by gas chromatography. The column separates tobacco alkaloids into several fractions, giving different retention times for nicotine, nornicotine and anabasine. The results obtained by this procedure are at least as good as those obtained by other methods presently available; the method is very simple and rapid.

H. JACIN, J. M. SLANSKI AND R. J. MOSHY,
Anal. Chim. Acta, 41 (1968) 347–353

THE GAS DENSITY BALANCE IN THE QUANTITATIVE ANALYSIS OF GAS MIXTURES, WITHOUT PRIOR SEPARATION OF COMPONENTS

THE DETERMINATION OF SILICA

When a gas mixture with a major component A which has a molecular weight considerably different from those of all other components (these being close together about a molecular weight of m) is introduced into the gas density balance with a carrier gas also of molecular weight m, the integral response of the gas density balance is essentially proportional to the amount of A in the sample and independent of the concentration ratios between all other components. The applicability of this principle is demonstrated in the determination of silicon tetrafluoride in mixtures with hydrogen fluoride and water, which were formed by reactions between silica, ammonium hydrogen fluoride and sulfuric acid. A direct determination of silica in solid samples containing 10–40 mg SiO_2 is possible with a relative standard deviation of 2.5%.

J. G. M. VAN DER LINDEN AND J. J. STEGGERDA,
Anal. Chim. Acta, 41 (1968) 355–360

ANALYSIS OF MONOMERIC ALKYL- AND ARYLCHLOROSILANES

The radioisotope carbon-14 was used to study the retention of carbon in the decomposition of alkyl- and arylchlorosilanes by wet methods. Losses by sample volatilisation were overcome by preliminary cooling in dry ice. Fuming sulphuric acid alone or in mixtures with fuming nitric acid was found to be the most effective oxidant of the acids tested. Examination of the carbon-containing silica residues by X-ray powder photography indicated that amorphous carbon was present but there was no evidence of silicon carbide.

D. R. ELLIS AND R. B. HESLOP,
Anal. Chim. Acta, 41 (1968) 361–373

FLUORIMETRIC DETERMINATION OF TUNGSTEN IN ALMOST PURE TUNGSTEN, THORIATED TUNGSTEN, AND Co–Ni–Cr REFRACTORY ALLOYS

(Short Communication)

R. S. BOTTEI AND A. TRUSK,
Anal. Chim. Acta, 41 (1968) 374–377

DETERMINATION OF LANTHANUM IN TITANIA BY ACTIVATION ANALYSIS

(Short Communication)

D. L. MASSART AND J. HOSTE,
Anal. Chim. Acta, 41 (1968) 378–380

SOME PRELIMINARY STUDIES OF THE ANALYTICAL POTENTIALITIES OF THE ATOMIC-HYDROGEN PLASMA TORCH

(Short Communication)

K. M. ALDOUS, R. M. DAGNALL, K. C. THOMPSON AND T. S. WEST,
Anal. Chim. Acta, 41 (1968) 380–384

ATOMIC ABSORPTION WITH AN ELECTRODELESS HIGH-FREQUENCY PLASMA TORCH

(Short Communication)

S. GREENFIELD, P. B. SMITH, A. E. BREEZE AND N. M. D. CHILTON,
Anal. Chim. Acta, 41 (1968) 385–387

A STUDY OF THE REACTIONS OF SOME METAL IONS AND MIXTURES OF METAL IONS WITH CUPFERRON BY HIGH-FREQUENCY TITRATION

(Short Communication)

C. BERTOGLIO RIOLO, T. FULLE SOLDI AND G. SPINI,
Anal. Chim. Acta, 41 (1968) 388–391

PHOTOCHROMIC 8-QUINOLINOLS

(Short Communication)

F. PRZYSTAL, T. RUDOLPH AND J. P. PHILLIPS,
Anal. Chim. Acta, 41 (1968) 390–394

THE CONSECUTIVE TITRATION OF IODATE AND PERIODATE

(Short Communication)

R. BELCHER AND A. TOWNSHEND,
Anal. Chim. Acta, 41 (1968) 395–397

INDIUM, GALLIUM AND GERMANIUM CONCENTRATION LEVELS IN HIGH-PURITY SILICA

(Short Communication)

S. N. Tandon and J. T. Wasson,
Anal. Chim. Acta, 41 (1968) 397–399

SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF N,N′-BIS(2-SULPHOETHYL)-DITHIOOXAMIDE, N,N′-BIS(*p*-SULPHOBENZYL)-DITHIOOXAMIDE AND N,N′-BIS(*m*-SULPHOBENZYL)-DITHIOOXAMIDE

(Short Communication)

A. M. Goeminne and M. A. Herman,
Anal. Chim. Acta, 41 (1968) 400–404

SPECTROFLUORIMETRIC DETERMINATION OF TRACE AMOUNTS OF CERIUM IN YTTRIUM OXIDE

(Short Communication)

P. Cukor and R. P. Weberling,
Anal. Chim. Acta, 41 (1968) 404–407

CATEGORIZATION OF N-SUBSTITUTED THIOUREAS VIA THEIR S-METHYL DERIVATIVES

(Short Communication)

D. L. Klayman and R. J. Shine,
Anal. Chim. Acta, 41 (1968) 408–411

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CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC ANALYSIS OF TRACE RARE EARTHS

PART I. QUALITATIVE STUDIES

SIMON LARACH
RCA Laboratories, Princeton, N.J. 08540 (U.S.A.)

(Received November 2nd, 1967)

With the increasing utility of rare earths in electronically active solids and in other materials, it is important to be able to carry out non-destructive analytical procedures for traces of rare earths quickly and efficiently. While activation analysis and mass spectrometry can be utilized, these are complex techniques which are destructive, and which can be time-consuming.

In analyses for rare earths, it is useful to take advantage of the "shielded" 4f shell of the rare earth, particularly in exciting luminescence in this shell. The emission, being of the non-interacting f–f type, is essentially a line, whose energy is indicative of the particular rare earth being excited. Whereas conventional optical excitation would require detailed knowledge of the *excitation* spectrum of each rare earth, excitation with energy large enough to excite across the band gap of the matrix provides a general means of exciting f–f luminescence emission.

Cathode-ray-excited luminescence (cathodoluminescence[1])

The process of cathodoluminescence is highly complex, consisting of several sub-processes which take place between the incidence of the initial high-energy electron, and the resultant emission of luminescence photons. For example, after incidence of the primary electron, many secondary electrons can be produced, whose energy is transferred to the rare-earth ions, which emit specific energies due to their characteristic f–f transitions. The cathodoluminescence emission intensity is a function of the potential through which the primary electrons are accelerated. The specific energy loss has been derived by GARLICK[2] from Bethe's non-relativistic equation for the interaction of charged particles with matter, as being:

$$-\frac{\mathrm{d}E}{\mathrm{d}X} = \frac{2\pi NZe^4}{E}\ln\left(\frac{E}{E_i}\right) \tag{1}$$

where E is the electron energy, X is the depth of penetration measured along the electron path, N is number of bound electrons cm^{-3}, Z is the mean atomic number, e is electron charge, and E_i is the mean ionization energy for all the electrons.

At potentials higher than about 3000 eV, the Thomson–Whiddington law may be held to apply:

$$X = k(E_0{}^2 - E^2) \tag{2}$$

where E_0 is the initial electron energy, E is the energy after penetration to the distance X, and k is a constant roughly inversely proportional to the density of the material.

If cathodoluminescence emission intensity is plotted as a function of accelerating potential, a typical curve is obtained, as shown in Fig. 1. Practically all luminescent materials show a threshold when the linear portion of the curve is extrapolated to the abscissa; this threshold is often referred to as the *dead-voltage*. GERGELY[3] has proposed a mechanism to account for the *dead-voltage* which involves carrier diffusion to the surface where radiationless recombination can take place.

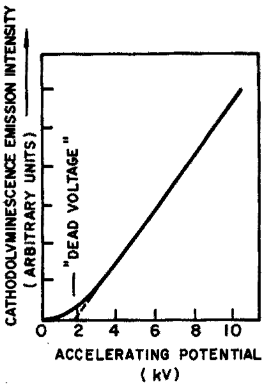

Fig. 1. Cathodoluminescence intensity as a function of accelerating potential.

In the present case, excitation with high-energy electrons creates carriers which can transfer their recombination energy to a rare-earth ion. Thus, by utilizing cathode-ray-excited emission (CREE) spectroscopy, luminescence, at room temperature, was obtained for all of the pertinent rare earths*.

EXPERIMENTAL TECHNIQUES

Materials

For the purposes of the present paper, namely the *detection* of trace amounts of rare earths, matrix materials were required which contained little or no rare-earth impurities. With the availability of ultrapure yttrium oxide (99.9999% purity with respect to rare earths; American Potash and Chemicals Co.), this material was used as the primary matrix. Series of 1, 10 and 50 p.p.m. of separate rare earths** (added as the sulfates) in Y_2O_3 were prepared by firing at 1100° in silica crucibles, in which blank charges had been fired first. Additional series of 3 rare earths together in Y_2O_3 were prepared, and finally, samples of yttria containing all of the pertinent rare earths together were prepared as standards.

The cathode-ray-excited emission spectroscopic method for detection of trace rare earths does not, however, depend on a specific matrix such as Y_2O_3. To show this, a spectrum was derived for rare earths in a zinc sulfide matrix, obtained by crystalliz-

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* La with $4f^0$ and Lu with $4f^{14}$ do not show f-f luminescence, and were not included; Pm was also omitted.

** Purity designated as 99.9%–99.99% with respect to rare earths.

ing ZnS: rare earth: lithium(I) in an inert (argon) atmosphere. The lithium is required for charge compensation reasons, and its use is treated elsewhere[4].

Measurements

A demountable cathode-ray equipment was utilized, as shown schematically in Fig. 2. In order to avoid the *dead-voltage* phenomenon, an acceleration potential of 8 kV was used, with a current of 0.7 μA. The crystallized samples were placed, as a series, on a metal disk, which could be rotated so that successive samples were excited by the electron beam. No effect due to sample geometry could be observed, and a disk containing 24 samples could be prepared in less than 1 h.

The luminescence emission from the samples was analyzed with a grating spectrometer and an RCA 1P21 multiplier phototube (S4 surface) for wavelengths from 300 nm to 700 nm, and with a cooled S1 surface multiplier (RCA 7102) for wavelengths from 700 nm to 1200 nm.

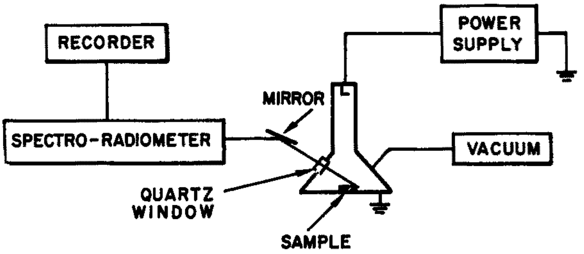

Fig. 2. Schematic representation of experimental equipment.

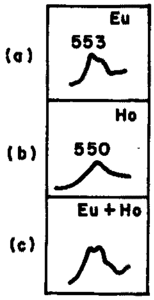

Fig. 3. Emission line shapes of (a) Eu, (b) Ho and (c) Eu+Ho in Y_2O_3 matrix.

RESULTS AND DISCUSSION

Rare-earth impurities were easily detected in Y_2O_3 by this type of spectroscopy*. At 1–50 p.p.m. concentrations of rare earths, identifying line spectra were obtained for all except cerium, which emitted in a broad band. Table I lists the lines** obtained for each rare earth, and the relative intensities. With respect to mutual interferences, between the rare earths, erbium emission is masked by terbium and holmium by europium. In the latter case, however, it is interesting to note that band *shape* can also be utilized in overcoming interference effects. Figure 3(a) shows the 553-nm emission from europium alone in Y_2O_3, and Fig. 3(b) that of holmium alone, while Fig. 3(c) shows the pair of rare earths in Y_2O_3.

Low *et al.*[5] have recently discussed the use of X-ray excitation, and this method has been utilized by LINARES *et al.*[6] for the determination of Eu, Gd, Tb and Dy, and extended by WALTERS *et al.*[7] to include Sm, Er and Tm. However, with the

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* It is interesting that this technique, utilizing Crooke's tubes, had been tried in the early 1900's by URBAIN and others. H. V. F. LITTLE has reviewed the early use of this technique as "cathodic phosphorescence analysis", to detect rare-earth impurities of the order of 1% in, mainly, pure lime. See *A Textbook of Inorganic Chemistry*, edited by J. N. FRIEND, Vol. 4, Griffin and Co., London, 1921, p. 305.

** The number of minor lines appearing is, of course, a function of the rare-earth concentration.

TABLE I

WAVELENGTHS AND INTENSITIES OF TRACE RARE EARTHS OBTAINED BY CATHODE-RAY-EXCITED EMISSION SPECTROSCOPY

(Y_2O_3 matrix)

Rare earth	λ*(nm)*	*Sensitivity* (rel. no. photons)	*Rare earth*	λ*(nm)*	*Sensitivity* (rel. no. photons)
Ce	375	(broad band)	Eu	611	54
Pr	630	27		587	18
	619	24		593	17
	635	19		582	16
	645	5		599	6
	597	5		631	3
	592	3		533	22
Nd	878	8		538	14
	893	17		553	6
	913	13		551	5
	938	8		467	19
	946	8		473	12
	1054	9		464	10
	1076	17		499	9
	1103	10		488	5
Sm	565	30		416	6
	607	28		425	5
	569	17		414	3
	576	14		427	3
	585	10	Ho	550	0.9
	617	9		536	0.3
	597	4	Er	564	1.1
	623	3		553	0.7
	556	3		539	0.5
	655	2		522	0.5
	668	1	Tm	453	1.6
Gd	631	3		460	1
	629	3		463	1
	315	3		361	0.3
Tb	543	27	Yb	950	1
	551	20		976	19
	483	11		1030	8
	492	9		1078	4
	488	9			
	501	4			
	583	2			
	596	1			
	579	1			
	588	1			
Dy	572	292			
	582	50			
	567	24			
	559	10			
	486	65			
	483	50			
	491	49			
	480	47			
	476	34			

X-ray method, sample geometry must be controlled, some rare earths do not fluoresce at room temperature, and some color center formation in the matrix was found to occur after long periods of X-irradiation. Thus, cerium and praseodymium were reported not to emit in Y_2O_3, at room temperature with X-ray excitation[7], and only a weak broad band was obtained for praseodymium in Y_2O_3 at 77°K, also with X-ray excitation[6]. However, with the cathode-ray excitation, praseodymium emitted its characteristic spectrum at 300°K, and a broad-band emission, possibly f–d in nature, was obtained for cerium.

The stick spectrum of rare-earth emission, referred to hereafter as the *hauptlinien* spectrum, is given in Fig. 4, which shows relative peak height and wavelength of the cathode-ray-excited rare-earth lines. Rare earths shown in parentheses indicate transitions of about equivalent energy which can be masked by the rare earths listed without parentheses. If the "hauptlinien" spectrum for a specific matrix is used as a

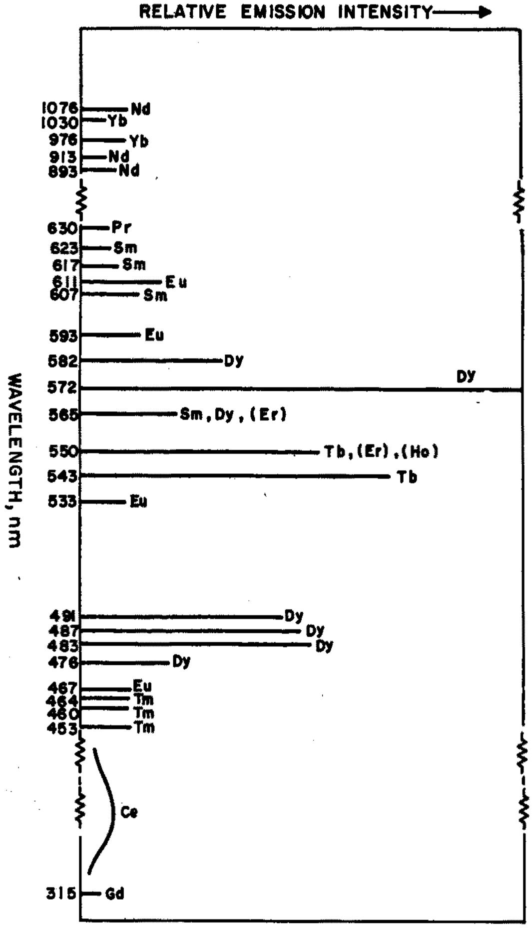

Fig. 4. Hauptlinien spectrum of trace rare earths in Y_2O_3 matrix.

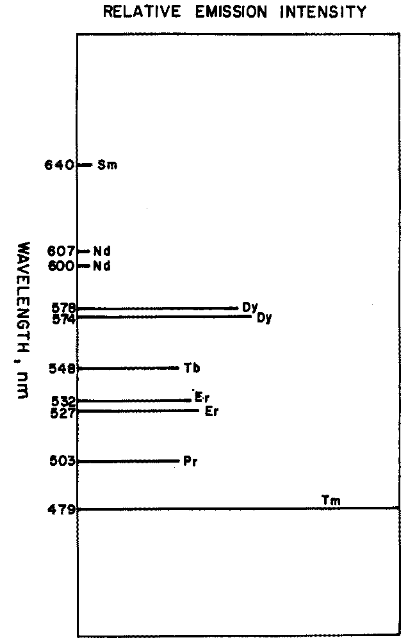

Fig. 5. Hauptlinien spectrum of trace rare earths in ZnS matrix.

standard, it is a simple matter to detect qualitatively the presence of trace amounts of rare earths. Intensification and/or poisoning effects of other ions, and concentration quenching are being studied in detail, and will be discussed in subsequent papers on the extension of this type of spectroscopy to the *quantitative* determination of rare earths.

Matrix effects

Although the major portion of this paper discusses rare earths in an yttrium oxide matrix, the method is by no means limited to this particular matrix material. Thus, cathode-ray-excited emission spectroscopy may be utilized for rare-earth analysis in any matrix which will incorporate the rare earth, and which will support cathodoluminescence. In some instances, changing the matrix can improve the sensitivity of the rare-earth emission, or even result in emission lines appearing which may not be evident in other matrices. As an example of matrix effects, Fig. 5 shows a "hauptlinien" spectrum for rare earths in a zinc sulfide matrix. Whereas neodymium in Y_2O_3 required detection at 0.9 μ, neodymium in zinc sulfide was apparent at 600 mμ and 607 mμ. It is of interest that for rare earths in the zinc sulfide matrix, Ho is masked by Tm, Eu emits in a broad band, probably as divalent Eu, and Ce and Gd also emit in broad bands.

Unknowns

Samples of "pure" yttrium oxide, obtained from two venders, were analyzed by the proposed method. A sample from vender A showed the presence of Dy, Tb, and Tm, and a sample from vender B showed the presence of Sm, Eu, Dy, Tb, Tm, and Gd.

The author wishes to thank R. A. KAUFFUNGER for assistance in materials preparation, Dr. W. FONGER for aid in measurements, and Drs. S. J. ADLER and A. L. SMITH for valuable discussions.

SUMMARY

Line emissions from f–f transitions in rare earths contained in a matrix are obtained by excitation with cathode rays. The distinctive energy of these emissions is utilized to detect the presence of trace amounts of rare earths, and non-destructive identification of such traces is carried out quickly by comparison with a derived *hauptlinien* spectrum. Matrix effects, masking interferences and the utilization of line shape are discussed.

RÉSUMÉ

Les émissions des transitions f–f dans les terres rares contenues dans une matrice sont obtenues par excitation avec rayons cathodiques. L'énergie distinctive de ces émissions est utilisée pour déceler la présence de traces de terres rares; l'identification non-destructive de ces traces est effectuée rapidement par comparaison. Divers facteurs sont examinés.

ZUSAMMENFASSUNG

Linienemissionen von f–f-Übergängen in Seltenen Erden, die in einer Matrix enthalten sind, werden durch Anregung mit Kathodenstrahlen erhalten. Die unterschiedliche Energie dieser Emissionslinien wird zum Nachweis von Spuren Seltener Erden verwendet, und eine zerstörungsfreie Bestimmung geschieht schnell durch Vergleich mit dem Hauptlinienspektrum. Matrixeffekte, verdeckte Störungen und die Verwendung der Linienform werden diskutiert.

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NEUTRON ACTIVATION ANALYSIS OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART II. DETERMINATION OF MOLYBDENUM AND RHENIUM

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In the course of an investigation on zinc sulphate solutions for the electrolytical separation of zinc, a neutron activation analysis of molybdenum and rhenium had to be devised. Neutron activation analysis of molybdenum or rhenium in zinc or zinc sulphate has not previously been described, although numerous workers have studied the determination of these elements in various other materials[1]. Molybdenum has been determined several times by means of a precipitation with α-benzoinoxime or hydrogen sulfide, or an extraction or a distillation technique. Generally β-counting or γ-spectrometry of ^{99}Mo or ^{99m}Tc is performed[2-4]. FUKAI[5] used a rather selective molybdenum determination based on the extraction of tetraphenylarsonium pertechnetate and the measurement of the daughter activity ^{101}Tc. Several authors report neutron activation analyses of rhenium based on distillation from sulphuric acid or a separation as tetraphenylarsonium perrhenate. They make use of γ-spectrometry or β-counting to measure the isotopes ^{186}Re and ^{188}Re[6-8]. A simultaneous determination of rhenium and molybdenum is difficult because of the great chemical similarity of rhenium and technetium. Also the γ-radiations and the half-lives of the respective radioisotopes, ^{99}Mo, ^{99m}Tc, ^{186}Re, are similar. In this investigation a simultaneous determination in a very complex zinc sulphate matrix[9] had to be developed.

ISHIDA AND KURODA[10] studied a neutron activation method for rhenium in molybdenites consisting of an anion-exchange separation in thiocyanate medium and an ether extraction followed by precipitation and β-counting. In the present work no reproducible results could be achieved using this method of separation. The chemical procedure finally used is based upon a specific anion-exchange separation method in nitric and in perchloric acid medium.

NUCLEAR PROPERTIES AND INTERFERENCES

Table I gives the nuclear data of the elements molybdenum and rhenium. The nuclear properties of the most important interfering elements in the zinc sulphate samples are reported in a previous paper[9]. It is clear that ^{99}Mo is the only isotope which could be used for the proposed purposes, because its half-life is long enough to permit its measurement 5 days after the irradiation, when the short-lived matrix activities have decayed to a sufficiently low level. Since the activation cross section of

TABLE I

IMPORTANT NUCLEAR DATA OF MOLYBDENUM AND RHENIUM[11]

Natural isotope	*Abundance (%)*	*Thermal cross-section (barn)*	*Isotope formed*	*Half-life*	*Gamma and X-ray energy (MeV)*
^{92}Mo	15.84	<0.006	^{93m}Mo	6.9 h	0.684; 0.148
^{98}Mo	23.78	0.51	^{99}Mo	67 h	0.181; 0.740
		Daughter	^{99m}Tc	6.0 h	0.141
^{100}Mo	9.63	0.20	^{101}Mo	14.6 m	0.191; 0.510; 0.590; 1.02
		Daughter	^{101}Tc	14.0 m	0.130; 0.186; 0.307
^{185}Re	37.07	104	^{186}Re	89 h	0.063; 0.122; 0.137; 0.769; 0.641
^{187}Re	62.93		^{188m}Re	19 m	0.064; 0.092; 0.106
		69	^{188}Re	17 h	0.063; 0.155; 0.477; 0.632

^{98}Mo is only 0.12 barns, the irradiation time and the neutron-flux must be relatively high for the determination of low amounts of molybdenum. As the isotope ^{99}Mo is a pure β-emitter in 83% of its decay mode, measurement of the shorter-lived daughter isotope ^{99m}Tc which decays entirely by an isomeric transition of 141 keV was applied. The possible interference from the threshold reaction ^{102}Ru(n,α)^{99}Mo ($\sigma = 0.0009$ mbarns)* is negligible. As the activation cross sections of ^{185}Re and ^{187}Re are very high, the isotopes ^{186}Re and ^{188}Re can be used advantageously for activation purposes. The interference from the threshold reactions ^{188}Os(n,p)^{188}Re ($\sigma = 0.025$ mbarns)* and ^{191}Ir(n,α)^{188}Re ($\alpha = 0.0009$ mbarns)* can be neglected.

The importance of the second-order interference

$$^{184}\mathrm{W}(n,\gamma)^{185}\mathrm{W} \xrightarrow{\beta^-} {}^{185}\mathrm{Re}(n,\gamma)^{186}\mathrm{Re}$$

was calculated for the present irradiation conditions (5 daily irradiations of 2 h). The ^{186}Re activity produced by 1 μg of tungsten corresponds to that produced by less than 10^{-7} μg of rhenium. As the tungsten content in the zinc sulphate solutions is low, no interference with the rhenium determination is to be expected. Three days after the end of the irradiation the most important rhenium activity consists of ^{186}Re. More than 98% of its photon emission is due to the 137-keV γ-ray and the 63-keV X-ray. Errors caused by neutron-shadowing effects in the samples or in the molybdenum and rhenium standards were avoided by an addition method of analysis. Standard solutions of both elements were added and sealed in silica tubes. As was known from a previous investigation[9], the samples contained uranium. The interference due to the fission reaction ^{235}U(n,f)^{99}Mo cannot be neglected and will be discussed in detail.

Ion-exchange separation of rhenium and technetium from interfering activities

It was shown by BUCHMAN AND FARIS[12] that on an anion-exchange resin in nitric acid medium, only very few elements are adsorbed. From dilute nitric acid (0.5 *N*), only Re(VII), Tc(VII), Pd(II) and Ru(IV) are strongly adsorbed (K_D value > 50), whereas the following ions are adsorbed to a smaller extent (K_D value < 5): Zr(IV), Pt(IV), Bi(III), Mo(VI), W(VI), Hg(II), Np(IV) and Pu(IV).

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* Estimated cross section for threshold reactions in a fission neutron spectrum (J. C. ROY AND F. J. HAWTON, *Chalk River Canada*, (1960) 1003).

Activation of the samples under investigation gives rise to important activities of ^{239}Np, ^{187}W, ^{99}Mo and ^{197}Hg. Because these isotopes also interfere γ-spectrometrically with the determination of ^{99m}Tc and ^{186}Re, decontamination factors for neptunium, tungsten, molybdenum and mercury of at least 10 must be obtained. In a series of experiments 3 ml of zinc sulphate solution was mixed with sufficient nitric acid to obtain a solution of 0.5 N nitric acid, together with tracer and carrier solutions of rhenium, molybdenum, neptunium, tungsten, mercury, sodium and zinc. The solutions were placed on the top of an anion-exchange resin column. Previously 10 mg of cerium(IV) sulphate was added to oxidize rhenium and to obtain an almost quantitative adsorption of rhenium on the resin. The results are shown in the second column of Table II.

It appears that sufficient decontamination was achieved after the elution of 75 column volumes of 0.5 N nitric acid.

TABLE II

ION-EXCHANGE SEPARATION ON DOWEX 1-X8 (100–200 mesh) COLUMN (15 cm × 0.4 cm)

Isotope added	*% Eluted*			
	75 Volumes of HNO_3 0.5N	*19 Volumes of $HClO_4$ 0.2N*	*19 Volumes of $HClO_4$ 0.2N*	*23 Volumes of $HClO_4$ 2N*
^{186}Re	0.15	0.05	96.3	3.5
^{99m}Tc	< 0.5	0.1	3.5	95.8
^{99}Mo	99.5	0.3	< 0.1	< 0.05
^{239}Np	97	< 0.1	< 0.1	0.15
^{187}W	52	0.5	0.4	1.2
^{203}Hg	95	1.7	1.5	0.8
^{22}Na	> 99.99	< 0.01	—	—
^{65}Zn	> 99.99	< 0.01	—	—

Ion-exchange separation of rhenium and technetium

The ratio of the distribution constants of rhenium and technetium on anion-exchange resin is approximately 1.8 in 0.2 M perchloric acid. SEN SARMA *et al.*[13] described a method for separating both elements in this medium, but the method is very time-consuming. More than one day is required to perform a separation with a cross-contamination of less than 0.1%. As the half-life of ^{99m}Tc is only 6 h, the method of separation used should be as fast as possible. The authors[13] claim that the length of the column should be at least 30 times the diameter of the column to obtain a useful separation.

Under the present experimental conditions the sizes of the column were reduced to 15 cm by 0.4 cm and a rather high elution rate was chosen (3 min/column volume). The first rhenium activity left the column after 19 column volumes (50 ml) of 0.2 N perchloric acid had been passed. Owing to the high elution rate, the rhenium peak showed some tailing but more than 96% could be eluted with 19 column volumes.

As the elution of the technetium activity with 0.2 N $HClO_4$ was very slow, it was hastened by elution with a stronger eluant (2 N perchloric acid). It can be seen from Fig. 1 that more than 95% of the technetium activity was recovered with 23 column volumes (60 ml) of 0.2 N and 2 N perchloric acid. The cross contamination was generally between 3 and 4%. It was determined by two activity measurements, one immediately after the elution and the other 36 h later when the technetium activity had decayed. Further elution with 4 *N* perchloric acid showed no detectable activity of rhenium or technetium. The separation of both elements thus required 3 h. Previously, attempts were made to separate these elements by elution with thiocyanate–chloride according to ISHIDA AND KURODA[10]. A lower cross-contamination was achieved but important fractions of the elements were not desorbed from the column.

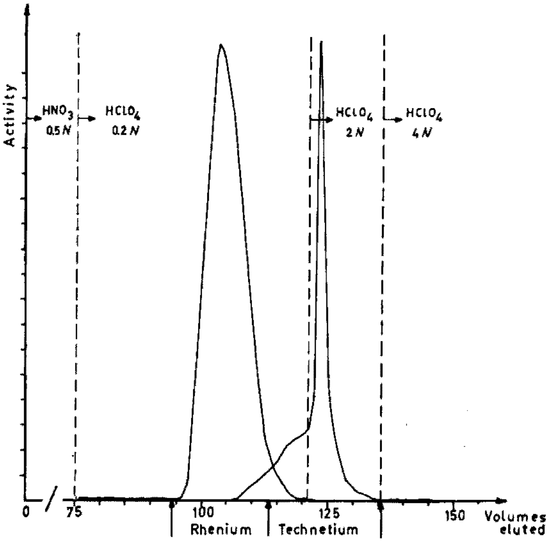
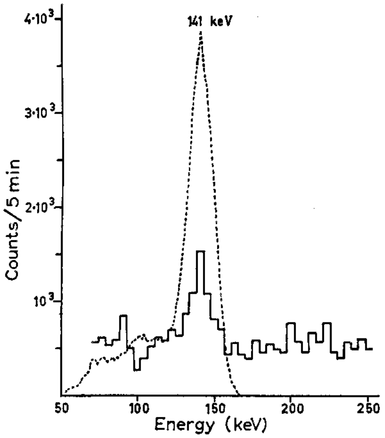


Fig. 1. Elution curve of rhenium and technetium from Dowex 1-X8 column (15 cm × 0.4 cm).

Procedure. Zinc sulphate samples are sealed in silica tubes and irradiated together with standards. The standards are identical zinc sulphate samples to which 500 μg of molybdenum and 10 μg of rhenium are added. The silica tubes are broken 3 days after the irradiation and nitrate solution is added containing the following carriers: 0.1 mg each of molybdenum, rhenium, mercury, copper and phosphorus; 10 mg of cerium(IV) sulphate are added. The acidity of the solution is adjusted to 0.5 *N* nitric acid. After 10 min the solution is placed on the top of a Dowex 1-X8 (100–200 mesh) anion-exchange resin column (15 cm × 0.4 cm) previously converted to the nitrate form. The interfering activities are eluted from the column with 75 column volumes of 0.5 *N* nitric acid. The nitrate eluant is replaced by 0.2 *N* perchloric acid. The first 19 column volumes are discarded. The rhenium activity is collected in the following 19 column volumes. The technetium activity is eluted with 23 column volumes of 2 *N* perchloric acid. The chemical treatment of standard and sample is performed simultaneously. The activity under the 141-keV photopeak due to ^{99m}Tc is measured immediately after the separation. The activity due to ^{186}Re is determined by means of its photopeaks at 63 and 137 keV. The activity due to the Compton continuum of higher-energy γ-rays of other isotopes if present is subtracted.

Determination of molybdenum and rhenium in zinc sulphate

The concentrations of molybdenum and rhenium were determined in 4 zinc sulphate solutions; 3-ml samples of zinc sulphate solution together with standard solutions containing 50 μg of molybdenum and 1 μg of rhenium in zinc sulphate were irradiated in the BR-1 reactor for 5 daily irradiations of 2 h each at a neutron flux of $5 \cdot 10^{11}$ n/cm^2/sec. After the chemical separation, the activities of the technetium and the rhenium fractions were measured for 1 h on a 3″ by 3″ NaI(Tl) crystal coupled to a multichannel pulse-height analyzer. Figures 2 and 3 show the γ-spectra of the technetium and the rhenium fractions separated from the standard and the unknown solutions. Although the neutron activation analysis devised allows the determination of *ca.* 0.1 μg of rhenium, this element could be not detected in the zinc sulphate solutions. In a previous paper[9] the concentration of uranium in the samples was determined. Approximately 0.7^5 mg of uranium per liter was found in the solutions under investigation. For an irradiation of ^{235}U with thermal neutrons, the fission yield of ^{99}Mo is 6.0% [14]. If the uranium occurring in the sample has the natural isotopic composition, the interference on the molybdenum determination can be calculated from the literature values for the cross sections of the reactions $^{98}Mo(n,\gamma)^{99}Mo$ and $^{235}U(nf)^{99}Mo$. The calculated interference is 0.85 p.p.m. molybdenum per 1.0 p.p.m. uranium. This interference was also determined experimentally. It appeared that 1 p.p.m. of uranium induced an apparent concentration of 0.58 ± 0.03 p.p.m. of molybdenum. As the molybdenum concentration is very low, the interference of uranium is too high to allow a correction and the uranium has to be removed before irradiation.



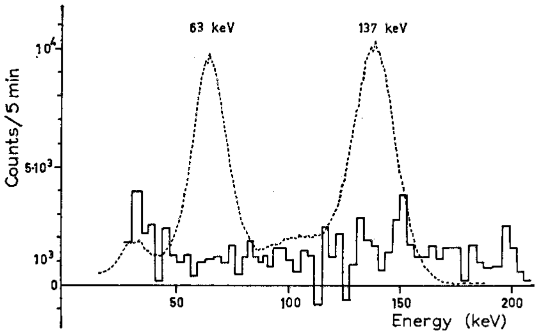


Fig. 2. γ-Spectra of ^{99m}Tc separated from the unknown sample and the standard sample. (– – –) standard; (——) sample · 100.

Fig. 3. γ-Spectra of ^{186}Re separated from the unknown sample and the standard sample. (– – –) standard; (——) sample · 1000.

Separation of uranium before irradiation

The solubility of uranyl nitrate in organic solvents is well known and the ability of ethers to extract this salt has been utilized for many years[15]. The most important advantage of this method of separation is its selectivity. The addition of nitric acid to the aqueous phase favours the extraction of uranium by preventing or decreasing the hydrolysis of the uranyl ion. Various nitrates can also be added advantageously as salting out agents. The addition of a saturated solution of a highly hydrated salt, such as aluminium nitrate, increases the extraction of uranium to a very important extent by reducing the water activity. In the present case nitric acid of a very high purity was added to the zinc sulphate solution to increase the nitrate concentration. The zinc ions present acted to a certain extent as salting agent. Further addition of a salting-out agent was unadvisable, owing to the impurities which would be introduced. Furthermore the addition of a saturated salt solution prevents the evaporation of the sample to a small volume before irradiation. Unfortunately, the presence of sulphate anions interferes strongly with the extraction of uranium. SCOTT[16] found that the extraction from a 3 *M* nitric acid–1 *M* iron(III) nitrate solution with an equal volume of ether decreases from 85% to 40% in the presence of 1.5 *M* sulphate ions. In the present investigation the extraction of uranium from the sulphate solution was increased to 68% by addition of nitric acid to obtain a solution of 8 *M* nitric acid. As nitric acid was also extracted by the organic solvent, a further addition of nitric acid before each extraction step was necessary. In the course of the investigation it appeared that isopropyl ether is a somewhat more efficient solvent than the more commonly used diethyl ether. Four subsequent extractions were performed. Further extractions did not increase the decontamination to an important extent. After the extraction, the amount of uranium still present was determined by neutron activation analysis as described previously[9]; 0.25 ml of the solution was irradiated in the BR-2 reactor at a neutron flux of $6 \cdot 10^{12}$ n/cm²/sec for 60 h and the ^{239}Np activity induced was measured. It was found that 98% ± 1% of the uranium was extracted. By means of a ^{99}Mo tracer solution, the co-extraction of molybdenum was controlled. Less than 0.2% of the molybdenum activity was co-extracted with uranium into the organic phase. Moreover, a blank determination of the molybdenum introduced by the chemical preseparation of uranium was carried out.

Procedure. To 20 ml of zinc sulphate solution, are added 28 ml of 14 *N* nitric acid. The uranium is extracted by shaking twice for 5 min with 100 ml of A.R. isopropyl ether. The phases were separated and the organic layers discarded. Then 28 ml of 14 *N* nitric acid are added and the uranium is extracted with 100 ml of isopropyl ether. Again 14 ml of nitric acid are added and shaken with 100 ml of isopropyl ether. The aqueous phase is finally washed with 20 ml of isopropyl ether and the collected organic phases are washed with 10 ml of 14 *N* nitric acid. The aqueous phase is evaporated carefully without boiling to about 40 ml and diluted to 50 ml with water.

Determination of molybdenum in zinc sulphate after uranium separation

Samples (2 ml) of the solution from which the uranium had previously been extracted, corresponding to 0.8 ml of the original sulphate solution, were evaporated almost to dryness in silica tubes. The samples were irradiated simultaneously with standards containing 1 μg of molybdenum in the BR-2 reactor for 66 h at a neutron flux of $6 \cdot 10^{12}$ n/cm²/sec. Four days after the irradiation the ^{99m}Tc activity induced in the sample was separated and measured. Since the activation cross section of ^{186}W is a 100 times higher than the cross section of ^{98}Mo, the ^{99m}Tc fraction separated was slightly contaminated with ^{187}W. This contamination was removed by a precipitation of tungsten with cinchonine[17]. The coprecipitation of technetium was less than 0.1%. Corrections were made for the apparent concentration induced by the uranium still present and for the molybdenum introduced by the preseparation of uranium. The

TABLE III

DETERMINATION OF MOLYBDENUM IN ZINC SULPHATE SOLUTIONS AFTER URANIUM EXTRACTION

Sample number	*Concentration (mg/l)*				
	Molybdenum found	*Uranium found after extraction*	*Apparent molybdenum concentration*	*Blank value molybdenum*	*Molybdenum corrected concentration*
III	0.104 ± 0.004	$0.014^{7} \pm 0.0005$	0.0085 ± 0.0005	0.086 ± 0.01	<0.01
V	0.079 ± 0.009	$0.021^{7} \pm 0.001^{1}$	$0.012^{6} \pm 0.001$	0.086 ± 0.01	<0.01

results are given in Table III. It is clear that the important blank value prevents an accurate determination of the very low amounts of molybdenum present.

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SUMMARY

A neutron activation analysis has been devised for the determination of traces of molybdenum and rhenium in an electrolytic zinc sulphate solution. The activities due to the daughter ^{99m}Tc and to ^{186}Re were counted. The chemical separation was performed on an anion-exchange resin. The matrix activities were separated by elution with 0.5 *N* nitric acid. The separation of technetium and rhenium was performed by an elution with 0.2 *N* perchloric acid. To avoid errors in the molybdenum determination, the uranium present in the sample was separated before the irradiation.

RÉSUMÉ

Une analyse par activation au moyen de neutrons est proposée pour le dosage de traces de molybdène et de rhénium dans une solution de sulfate de zinc électrolytique. Les activités dues à ^{99m}Tc et ^{186}Re sont comptées. La séparation chimique est effectuée sur résine échangeuse d'anions. Les activités de la matrice sont séparées par élution à l'aide d'acide nitrique 0.5 *N*. La séparation du technetium et du rhénium est effectuée par élution au moyen d'acide perchlorique 0.2 *N*. Afin d'éviter des erreurs dans le dosage du molybdène, l'uranium présent dans l'échantillon est séparé avant irradiation.

ZUSAMMENFASSUNG

Spuren von Molybdän und Rhenium in einer elektrolytischen Zinksulfatlösung wurden mit Hilfe der Neutronenaktivierungsanalyse bestimmt. Es wurden die Aktivitäten von ^{99m}Tc und ^{186} Re gezählt. Die chemische Trennung geschah mit einem Anionenaustauscher, von dem die Matrixaktivitäten durch Elution mit 0.5 *N* Salpeter-

säure abgetrennt wurden. Die Trennung von Technitium und Rhenium erfolgte durch Elution mit 0.2 N Perchlorsäure. Um Fehler bei der Bestimmung des Molybdäns zu vermeiden, musste Uran vor der Bestrahlung aus der Probe entfernt werden.

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NEUTRON ACTIVATION ANALYSIS OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART III. SIMULTANEOUS DETERMINATION OF TELLURIUM, SELENIUM, ARSENIC AND ANTIMONY

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It is well known that the elements germanium, arsenic, antimony, tin, tellurium and selenium inhibit the electrolytic deposition of zinc. Thus it seemed advantageous, for the zinc sulphate samples under investigation, to perform the separation and the determination of these elements before starting the systematic determination of the metals, for which an anion-exchange separation technique will be used. Because very low activities compared to the matrix activities must be measured, high decontamination factors have to be obtained in the chemical separation. According to BOCK-WERTHMANN AND SCHULZE[1] up to now no neutron activation analysis of tellurium, selenium, arsenic, germanium, antimony and tin simultaneously has been described. In the present work a method for a simultaneous determination of tellurium, selenium, arsenic and antimony is developed. For the measurement of the activities due to tellurium and selenium, separate extractions of the iodine daughter activity and of the selenium activity are carried out. Arsenic, antimony and tin are precipitated as sulfides and afterwards separated by distillation. Activation analysis of the germanium can also be performed using the same chemical procedure, as neutron irradiation of germanium gives rise to an important arsenic daughter activity. The daughter activity of ^{77}As can be measured γ-spectrometrically in presence of ^{76}As produced by neutron irradiation of arsenic. However, in the samples under investigation no tin or germanium could be detected.

NUCLEAR DATA

For the neutron activation analysis of tellurium, the isotope ^{127}Te with a half-life of 9 h is usually counted[2]. Since this isotope is a pure β-emitter and since the specific separation of tellurium is a difficult task, it is preferred in the present investigation to use the ^{131}I daughter activity of ^{131}Te. The isotope ^{131m}Te with a half-life of 30 h is formed to a very low extent owing to its very low cross section, and the isotope ^{131}Te, with a half-life of 25 min has fully decayed one day after the irradiation. Thus more than 99.5% of the total ^{131}I activity is already present when the chemical treatment is started. As the activity of ^{131}I separated from the sample is very low, a selective technique of measurement must be used. From Table I it is obvious that ^{75}Se is the only isotope of selenium formed by neutron activation analysis with a half-

TABLE I

MOST IMPORTANT NUCLEAR PROPERTIES

Natural isotope	*Abundance*	*Thermal activation cross section (barns)*	*Isotope formed*	*Half-life*	*Most important γ-energy (keV)*
^{122}Te	0.0246	1	^{123m}Te	104 d	159
^{124}Te	0.046	5	^{125m}Te	58 d	110
^{126}Te	0.187	0.8	^{127}Te	9.3 h	—
^{128}Te	0.318	0.015	^{129m}Te	33 d	1082; 1110; 145; 459; 635; 720
^{130}Te	0.345	0.22	^{131}Te	25 min	148; 450
		< 0.008	^{131m}Te	30 h	182; 780; 840; 1140
		Daughter	^{131}I	8.0 d	80; 284; 364; 638; 724
^{74}Se	0.0087	24	^{75}Se	125 d	121; 136; 265; 280; 401
^{78}Se	0.235	0.4	^{79m}Se	3.9 min	96
^{80}Se	0.498	0.50	^{81m}Se	57 min	103
		0.03	^{81}Se	17 min	276; 290; 566; 649; 828
^{82}Se	0.092	0.004	^{83}Se	25 min	225; 356; 718; 799; 837
^{75}As	1.00	4.3	^{76}As	26.5 h	559; 657; 1210; 1780
^{121}Sb	0.572	5.7	^{122}Sb	2.8 d	564; 692; 1137; 1256
^{123}Sb	0.428	3.9	^{124}Sb	61 d	603; 641; 716; 1680
^{120}Sn	0.330	0.14	^{112}Sn	27.5 h	—
^{76}Ge	0.076	0.08	^{77}Ge	12 h	215; 264; 561; 710; 1090; 1360; 1520
		Daughter	^{77}As	39 h	160; 246; 525

life of more than 1 h. The activation of ^{74}Se is not very sensitive, owing to its low natural abundance.

FINEMAN *et al.*[3] used the same isotope for activation analysis of selenium in slags and concentrates. They claim that the lower limit for the determination of selenium, after chemical separation, for an irradiation time of 30 days at a flux of $4 \cdot 10^{11}$ n/sec/cm^2 is about 0.1 μg. However, in the present investigation, with a highly sensitive counting technique and an irradiation time of 2 days at a flux of $8 \cdot 10^{12}$ n/sec/cm^2, amounts of 0.002 μg of selenium could be determined. The lower limit for the determination is in fact reduced to 0.0001 μg.

By neutron irradiation of arsenic, the isotope ^{76}As is formed in sufficiently large amounts to be used for activation purposes. Neutron activation of antimony gives rise to the isotopes ^{122}Sb and ^{124}Sb. Since the amounts to be detected are very low, it is necessary to use the dominant photopeaks of the γ-spectra. Unfortunately, the photopeaks at 559 keV due to ^{76}As and at 564 keV due to ^{122}Sb are not resolved. A separation of arsenic from antimony is thus required.

If tin must be determined, a separation of this element is also required as the isotope ^{121}Sn is a pure β-emitter. The daughter ^{77}As of the isotope ^{77}Ge formed by neutron activation analysis is radioactive. Its most important photopeak at 246 keV can be measured almost independently from the ^{76}As activity.

Radiochemical separations

As irradiations of 0.5 ml of the zinc sulphate solutions, in the BR-2 reactor at a neutron flux of $8 \cdot 10^{12}$ n/cm²/sec for 2 days, give rise to very high activities due to ^{69m}Zn (15 mC), ^{65}Zn (0.4 mC) and ^{24}Na (10 mC), efficient chemical separations are essential. The chemical treatment is started 2 or 3 days after the irradiation when the short-lived matrix activities ^{69m}Zn and ^{24}Na have decayed to a degree compatible with work in a conventional laboratory, whereas the decrease of the arsenic and tin activities to be determined is not too important.

Separation of iodine

A widely used method for direct separation of radioactive iodine from aqueous solution is carbon tetrachloride extraction of iodine in the elementary state[4]. Extensive work on the problem of isotopic exchange has shown that preliminary steps are required to insure complete isotopic exchange[5]. A successful method was elaborated by GLENDENIN *et al.*[6]; this consists of oxidation to iodate by addition of a 5% hypochlorite solution in alkaline medium, the reaction giving complete and relatively rapid exchange. The iodate is then reduced to elementary iodine by means of hydroxylamine in acid medium and extracted into carbon tetrachloride. The exchange is complete and the separation is selective, as bromine is reduced to bromide and is not extracted. A further purification is accomplished by back-extraction of the iodine, after reduction to iodide with sodium bisulphite. The iodine fraction is further purified by another carbon-tetrachloride extraction cycle. The oxidation to iodine in this step is achieved by means of sodium nitrite and nitric acid; this insures an optimal decontamination of bromine, as bromide is not oxidized by nitrite. Finally, the iodine activity is recovered by precipitation as its silver salt. The method, developed by GLENDENIN AND METCALF for separation of radiochemically pure iodine from fission products[7], does not give quantitative yields. The procedure described in the present work allows an almost quantitative separation of the iodine. From several tracer experiments it appeared that more than 98.5% of the ^{131}I activity is recovered in the precipitate. Furthermore, gravimetric determinations resulted in yields ranging from 97 to 101%. Tracer experiments showed that the decontamination factors from ^{65}Zn, ^{22}Na, ^{54}Mn, ^{75}Se, ^{76}As, ^{122}Sb, ^{64}Cu and ^{121}Sn are higher than 10,000.

Separation of selenium

Since HOSTE[8,9] proposed diaminobenzidine as a specific reagent for selenium, the formation of piazselenol compounds with several other derivatives has been described. One of the most sensitive of these reagents and one which allows quantitative extraction[10] of the piazselenol compound into toluene is 2,3-diaminonaphthalene[11]; moreover, the formation of the 4,5-benzopiazselenol can be carried out in slightly acidic medium. This is important in the present case as the zinc matrix precipitates if the pH of the solution is raised above 3. As the reaction rate is rather slow, the extraction with toluene is carried out 30 min after the addition of the reagent. Several tracer experiments showed that more than 99% of the selenium is extracted by the adopted procedure. To ensure a further decontamination of the separated selenium and to allow the preparation of a source ready for the coincidence counting, the selenium is back-extracted in hydrogen chloride and precipitated with hydroxylamine as elementary selenium. The most convenient back-extraction is obtained by the addition of 0.5 ml of hydrogen peroxide and shaking with concentrated acid. With ^{75}Se as a tracer, it was shown that a back-extraction from the toluene phase into a 5 times higher volume of 9 *N* hydrochloric acid allows the separation of *ca.* 90–95% of the selenium.

The precipitation from 6 *N* hydrochloric acid is quantitative after heating for 2 h. Gravimetric yield determinations of the entire chemical separation resulted in values varying from 87 to 93%. The separated selenium is radiochemically pure. The interference of tellurium checked with ^{123m}Te tracer is less than 0.5 %.

Separation of arsenic, antimony and tin

Tin is separated together with arsenic and antimony, thus allowing a simultaneous determination of antimony, arsenic, germanium and tin if they are present in detectable amounts. Precipitation of arsenic, antimony and tin as their sulphides from acidic medium provides a quite good separation of the matrix activities due to the isotopes of zinc and sodium. The precipitation is performed by means of thioacetamide from 1 *N* hydrochloric acid. After the filtration, the sulphides are dissolved in concentrated sulphuric acid to which some nitric acid is added. The elements arsenic, antimony and tin can then be separated by distillation from a hydrochloric acid–sulphuric acid medium[12]. The procedure as described by DEBRUYNE AND HOSTE[13] was used. From an 11 *N* hydrochloric acid solution, the arsenic is carried over quantitatively as $AsCl_3$ in a stream of carbon dioxide at 109°. Tin is complexed with phosphoric acid and antimony is carried over at 160° as $SbCl_3$ while hydrochloric acid is added dropwise into the flask. Finally, tin is distilled as a mixture of $SnCl_4$ and $SnBr_4$ by adding a mixture of hydrochloric and hydrobromic acids. In the distillates, arsenic is precipitated with hypophosphite, antimony is collected on iron powder and tin is precipitated as sulphide with thioacetamide. From tracer experiments it appears that the precipitation steps are almost quantitative, whereas the separation by distillation yields fractions with cross-contaminations of *ca.* 2–3%. The radiochemical separation of other interfering isotopes is excellent. The important matrix activities due to ^{64}Cu and ^{67}Cu produced by (n,p) reactions on zinc are precipitated together with the sulphides, but do not distil.

Measuring techniques

The activities separated from the samples were collected on a filter plate and mounted for counting. The activity due to ^{76}As and ^{122}Sb isolated from the samples was high enough to allow a direct γ-spectrometric measurement. The respective photopeaks at 559 and 564 keV were used. When the activity due to ^{76}As was contaminated to an important extent with ^{122}Sb, γ-spectrometry in two energy regions was performed[14]. The activity due to tin was measured by means of a Geiger-Muller tube as ^{121}Sn is a pure β-emitter.

The γ-activities due to ^{131}I and ^{75}Se were very low, and below the background. Since a longer irradiation or an irradiation at a higher neutron flux would give rise to a still more important matrix activity, it was preferred to elaborate a more adequate counting technique, namely coincidence counting.

As shown in Fig. 1, the decay of ^{131}I consists for 86% of a β-ray of 610 keV in cascade with a γ-ray of 364.5 keV, and to a low extent with a γ-cascade of 284.3 and 80.2 keV. In the coincidence-counting technique used, the β-ray was detected with a plastic scintillator (Fig. 2). This detector operated the gate of the coincidence circuit of the multichannel analyser and permitted the detection of the coincident γ-ray. The pulse height analyser discriminated only against the very low noise pulses. The resolving time of the system was 0.8 μsec. The distance between the two crystal surfaces was approximately 1 cm. The source placed between both detectors was on the upper side (side of the plastic scintillator) covered with a mylar foil. The plastic scintillator was screened with an aluminium foil of 4.5 mg/cm^2. The source consisting of a silver-iodide precipitate had for all the measurements the same thickness (4.8 mg/cm^2). This was important because experimentally it appeared that the coincident-counting rate was reduced by 20% if this thickness was doubled.

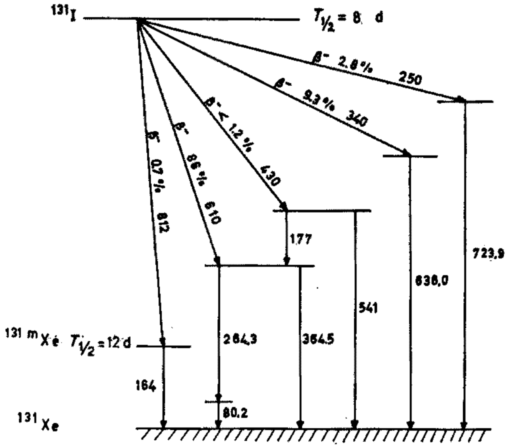


Fig. 1. Decay scheme of the isotope ^{131}I.

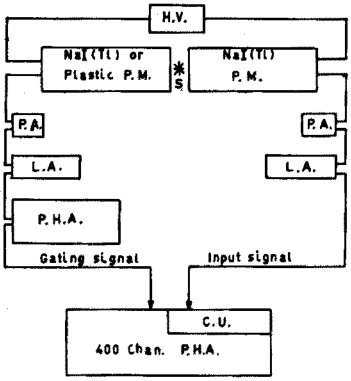
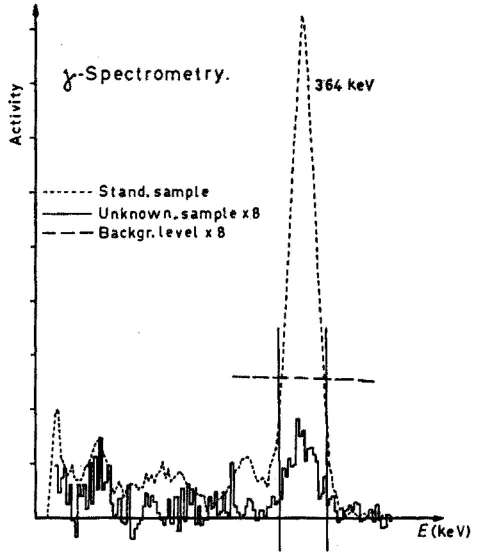


Fig. 2. Block diagram of coincidence-counting equipment. S = source; H.V. = high voltage; P.M. = photomultiplier; P.A. = preamplifier; L.A. = linear amplifier; P.H.A. = pulse height analyser; C.U. = coincidence unit.

The coincidence activity amounted to 18% of the non-coincidence count rate of the same NaI(Tl) detector in the energy region from 345 to 385 keV. The background in this energy region was decreased from 150 to 0.3 counts/min. The signal-to-background ratio was thus increased by a factor of 90. The count rate in the energy region was 2.6×10^4 counts h^{-1} for 1 μg of tellurium. Figures 3 and 4 show the γ-spectra



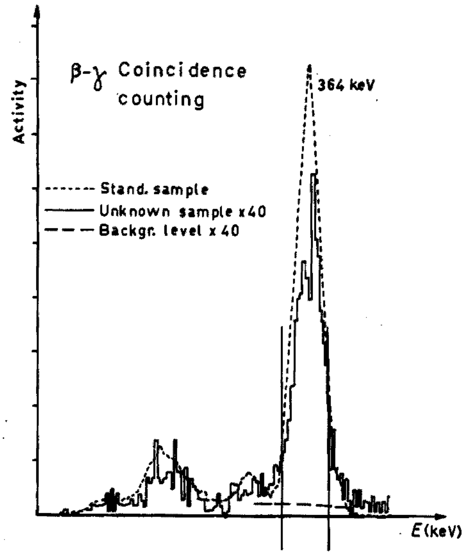
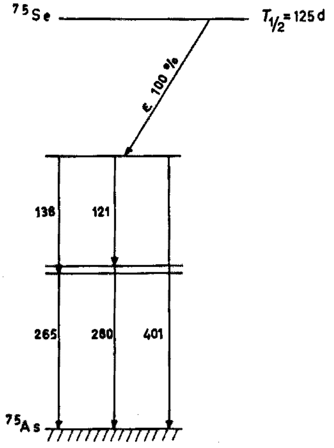


Fig. 3. γ-Spectra of separated ^{131}I fractions measured by direct γ-spectrometry.

Fig. 4. γ-Spectra of separated ^{131}I fractions measured by coincidence counting.



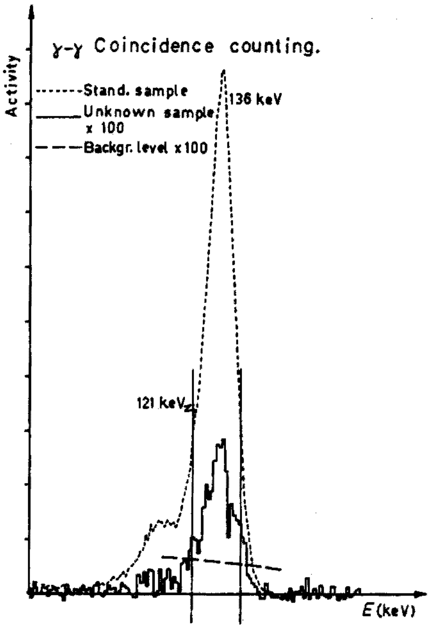


Fig. 5. Decay scheme of the isotope ^{75}Se.

Fig. 6. γ-Spectra of separated ^{75}Se fractions measured by coincidence counting.

of ^{131}I separated from a standard and an unknown sample recorded by direct γ-spectrometry and by coincidence counting. For both systems of measurement the count rate due to the background is shown. It is obvious that only the coincidence measurement allowed the determination of the separated ^{131}I activity.

A similar system of coincidence was used for the measurement of selenium-75. The plastic scintillator was replaced by a 3″×3″ NaI(Tl) detector. It is clear from the disintegration scheme of the isotope ^{75}Se (Fig. 5) that the decay of this isotope involves a γ,γ-cascade of 136 and 265 keV to the extent of 58% and a γ,γ-cascade of 121 and 280 keV to the extent of 26%. Thus a γ,γ-coincidence technique is very favourable for the measurement of this isotope. Because the two γ-cascades are so similar both cascades are detected simultaneously and 80% of the γ-activity of selenium can be used. The 265 keV and part of the 280-keV γ-ray, selected with a 10% window, was used as the gate pulse of the coincidence-counting system, and the photopeaks at 136 and 121 keV were recorded with the 400-channel pulse-height analyser. The detection efficiency of the photopeaks at 136 and 121 keV *versus* the detection efficiency for direct γ-spectrometry was 18.2%. The background in the energy region of the photopeaks in a lead castle of 50×50×50 cm was reduced from 125 counts/min to 0.12 counts/min. The signal-to-noise ratio was thus improved by a factor of 190. In a lead castle of 100×100×100 cm size and 12 cm thickness, the background was reduced from 28 counts/min to 0.035 counts/min, *i.e.* 2 counts per hour. The count rate due to ^{75}Se was 1.8×10^4 counts h^{-1} for 1 μg of selenium in the present conditions of irradiation and measurement. This measuring technique was not only very sensitive for ^{75}Se but also selective. Figure 6 shows the coincident γ-spectrum of the selenium fractions separated from the unknown and the standard sample. A measurement of 6 h was performed for the unknown sample. A direct γ-spectrometric measurement of the fraction separated from the unknown sample was impossible because the count rate in the energy region of the selenium photopeaks was approximately 15 times lower than the count rate due to the background.

EXPERIMENTAL

Instrumental

γ-Spectrometry. A 3″×3″ NaI(Tl) crystal with associated photomultiplier-tube was used with a 400-channel pulse-height analyser.

Concidence-counting unit. Two 3″×3″ NaI(Tl) crystals with associated multiplier-phototube (integral assembly) or: 44 mm diam. × 6 mm thick plastic detector (Nuclear Enterprises NE 102) with associated photomultiplier tube. Also used were a Nuclear Enterprises Amplifier NE 5256, a Nuclear Enterprises Analyser NE 5153, a Nuclear Enterprises High Voltage Supply NE 5302, and a 400-channel pulse-height analyser.

Procedure

Samples of 1 ml of zinc sulphate solution are evaporated carefully and sealed in quartz vials. They are irradiated simultaneously with standards containing 1 μg of tellurium, selenium, arsenic and antimony, tin and germanium in the BR-2 reactor for 3 days at a neutron flux of $8 \cdot 10^{12}$ n/cm²/sec. After the irradiation the samples are left to cool during 2 days to allow for the decay of the matrix activities.

The samples are dissolved in 15 ml of water and carrier solutions are added containing 5 mg each of arsenic, antimony, tin, iodine, copper and phosphorus and 10 mg of selenium. After neutralising, 10 ml of 2 *N* sodium carbonate and 6 ml of 5% sodium hypochlorite are added. The solution is boiled for 30 sec. After 40 min, 10 ml of 14 *N* nitric acid and 2 ml of 2 *M* hydroxylamine are carefully added. The iodine is extracted twice with 10 ml of carbon tetrachloride; 1 ml more of 2 *M* hydroxylamine is added and the iodine is again extracted with 10 ml and 5 ml of carbon tetrachloride.

The iodine is twice back-extracted into 10 ml of water to which 4 drops of 1 *M* sodium hydrogen sulphite have been added. The carbon tetrachloride phase is washed with 5 ml of water. The aqueous phases containing the iodine are collected and the iodine is extracted into 10 ml of carbon tetrachloride after the addition of 10 drops of 1 *M* sodium nitrite and 1 ml of 14 *N* nitric acid. The addition of sodium nitrite and the extraction with 3 ml of carbon tetrachloride are repeated. The aqueous phase is washed with 3 ml of carbon tetrachloride and the iodine is back-extracted as before. After the addition of 1 ml of 6 *N* nitric acid, the solution is boiled to expel sulfur dioxide. The iodine is finally precipitated with 1 *M* silver nitrate. After filtering, drying and weighing, the precipitate is mounted for counting. After the iodine separation 3 ml of 2.5 *M* formic acid is added to the aqueous phase and neutralised with ammonia to pH 1–2. The selenium is complexed by the addition of 20 ml of 0.2% 2,3-diaminonaphthalene in 0.2 *N* hydrochloric acid. After 45 min, selenium is extracted with 15-ml and 10-ml portions of toluene. Again 1 ml of formic acid is added, the pH adjusted to 2, and 10 ml of reagent solution added. After 15 min, the last traces of selenium are extracted twice with 10 ml of a buffer solution of pH 2 to which 1 ml of reagent solution has been added. The selenium is back-extracted, after the addition of 1 ml of 30% hydrogen peroxide, into 220 ml of 9 *N* hydrochloric acid. The organic phase is washed twice with 10 ml of 9 *N* hydrochloric acid. The selenium is precipitated with hydroxylamine in 5–6 *N* hydrochloric acid solution, filtered, dried and weighed to determine the chemical yield. After the extraction of selenium, 40 ml of 6 *N* hydrochloric acid are added to the aqueous phase and the latter is diluted to obtain a solution of 1 *N* hydrochloric acid. The concentration of nitric acid thus becomes less than 4%.

Arsenic, antimony, tin and copper are precipitated with thioacetamide. After filtration in a crucible, the precipitate is dissolved immediately in 7 ml of 35 *N* sulphuric acid, and heated with 0.5 ml of 5% hydrazine hydrate. The last traces of insoluble sulphides are dissolved with 2 ml of 14 *N* nitric acid. The nitric acid is evaporated after the addition of 3 ml of 35 *N* sulphuric acid, and then the solution is transferred quantitatively into the distillation flask by means of 100 ml of 12 *N* hydrochloric acid.

With a continuous stream of carbon dioxide bubbling through the solution, the arsenic is distilled at 109–112°. After the addition of 30 ml of 12 *N* hydrochloric acid and 0.2 ml of 85% hydrazine hydrate, the last traces of arsenic are distilled. At this point, the receiver flask is replaced and 7 ml of 85% phosphoric acid are added and the antimony is distilled at 155–165°, while hydrochloric acid is added slowly but continuously to the solution. When 125 ml of hydrochloric acid have been added, the apparatus is cooled, the receiver flask replaced and the tin distilled at 140° with 100 ml of a 3:1 mixture of concentrated hydrochloric and concentrated hydrobromic acid flowing into the distilling flask. The distillation process required *ca.* 100 min. The arsenic is precipitated from 6 *N* hydrochloric acid solution with 2 g of sodium hypophosphite. After heating for 15 min, 0.5 g more sodium hypophosphite is added. To the collected antimony fraction, 30 mg of antimony carrier is added along with 1.5 g of iron powder. The solution, which is 2 *N* in hydrochloric acid, is stirred for 1 h. The iron powder which contains the antimony activity is filtered. The tin is precipitated with thioacetamide after neutralising with ammonia to pH 0.5–1, and the precipitate is filtered, washed, dried and mounted for counting. The precipitate is ignited at 700° after the measurement and weighed to determine the chemical yield.

DETERMINATION OF TELLURIUM, SELENIUM, ARSENIC AND ANTIMONY IN ZINC SULPHATE SOLUTIONS

In several zinc sulphate solutions, which yielded either high or low electrolytic zinc deposition, the concentrations of mercury, uranium, ytterbium, molybdenum and rhenium had already been determined[15,16]. Tellurium, selenium, arsenic and antimony were determined in the same samples. It was originally intended to determine also the concentration of tin and germanium, but these determinations by activation analysis are not very sensitive, and no traces of these elements were found in the first analysis; no further attempts were made to determine them.

The reaction $^{235}U(n,f)^{131}I$ interfered strongly with the determination of tellurium by means of the isotope ^{131}I, as the fission yield of ^{131}I from ^{235}U is 3.0%. From the cross sections given in the literature, it was calculated that 1 p.p.m. of uranium gave rise to an apparent concentration of tellurium equal to 0.91 p.p.m. Experimentally, it was found that 1 p.p.m. of uranium induced an apparent concentration of 0.79 ± 0.03 p.p.m. tellurium. Since appreciable amounts of uranium were present in the samples[14], it was necessary to separate the uranium before the irradiation. This separation was performed by an ether extraction of uranium as described previously[16]. The coextrac-

TABLE II

DETERMINATIONS OF SELENIUM, ARSENIC AND ANTIMONY

Element determined	*Sample $ZnSO_4$*	*Concentration found (µg/l)*		
		I	*III*	*V*
Se	Activ. anal.	1.7 ± 0.1	2.3 ± 0.1	2.3 ± 0.2
	Indust. anal.	<20	<10	—
As	Activ. anal.	15.5 ± 0.5	18.5 ± 0.5	20.6 ± 0.3
	Indust. anal.	15	20	—
Sb	Activ. anal.	33 ± 1.0	32.7 ± 0.3	9.7 ± 1.6
	Indust. anal.	25	35	—

TABLE III

DETERMINATION OF TELLURIUM AFTER URANIUM EXTRACTION

$ZnSO_4$ sample	*Concentration (µg/l)*				
	Te found	*U found after extn.*	*Te apparent concn.*	*Blank value*	*Corrected concentration of tellurium*
III	46 ± 2^{9}	$14.^{7} \pm 0.5$	$11.^{6} \pm 0.6$	40 ± 8	<6
V	44 ± 3^{5}	$21.^{7} \pm 1.1$	$17.^{1} \pm 1.1$	40 ± 8	<3

tion of tellurium was less than 0.2%. The correction for the apparent concentration induced by the uranium still left after the separation, was calculated on the basis of the experimentally determined interference. A correction for the possible contamination induced by the preseparation of uranium was also made. The results of the determinations are summarized in Tables II and III.

All the results are mean values of at least two determinations. The results are in agreement with the results of industrial analyses. The proposed method for the determination of selenium is much more sensitive than the classical methods. The standard deviations on the results are low, considering the very small amounts to be determined. An accurate determination of the very low concentration of tellurium was impossible due to the important blank value introduced by the preseparation of uranium.

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SUMMARY

A neutron activation analysis is described for the simultaneous determination of tellurium, selenium, arsenic and antimony in an electrolytic zinc sulphate solution. The activity induced in the tellurium was measured by means of its radioactive daughter ^{131}I. The chemical separation of iodine was performed by extraction into carbon tetrachloride. The interference due to the fission of uranium was minimised by a preseparation of uranium. The isotope ^{75}Se was measured by a γ, γ-coincidence technique, which allowed the determination of 0.002 μg Se/ml. Selenium was chemically separated by extraction as piazselenol. Arsenic and antimony were separated by precipitation as sulphide and distillation as chloride. The isotopes ^{76}As and ^{122}Sb were measured γ-spectrometrically, amounts of 0.02 μg/ml being determined. The method is also suitable, although not very sensitive, for the simultaneous determination of tin and germanium.

RÉSUMÉ

Les auteurs ont mis au point une analyse par activation au moyen de neutrons pour le dosage simultané du tellure, du sélénium, de l'arsenic et de l'antimoine dans une solution de sulfate de zinc électrolytique. L'activité induite du tellure est mesurée à l'aide de sa fille radioactive ^{131}I. La séparation chimique de l'iode est effectuée par extraction dans le tétrachlorure de carbone. L'interférence due à la fission de l'uranium est réduite au minimum grâce à une préséparation de l'uranium. L'isotope ^{75}Se est mesurée par une technique de coïncidence γ, γ- permettant de doser 0.002 μg Se/ml. Le sélénium est séparé chimiquement par extraction sous forme de piazsélénol. L'arsenic et l'antimoine sont séparés par précipitation comme sulfure et distillation sous forme de chlorure. Les isotopes ^{76}As et ^{122}Sb sont mesurés par spectrométrie-γ; on peut ainsi doser des quantités de 0.02 μg/ml. Cette méthode convient également, quoique pas très sensible, pour le dosage simultané de l'étain et du germanium.

ZUSAMMENFASSUNG

Tellur, Selen, Arsen und Antimon in einer elektrolytischen Zinksulfatlösung wurden mit Hilfe der Neutronenaktivierungsanalyse bestimmt. Zur Bestimmung des Tellurs wurde ^{131}I gemessen, dessen chemische Abtrennung durch Extraktion mit Tetrachlorkohlenstoff geschah. Störungen durch das Uran wurden durch vorhergehende Abtrennung des Urans verringert. ^{75}Se wurde mit Hilfe der γ,γ-Koinzidenz-Technik gemessen, die die Bestimmung von 0.002 μg Se/ml erlaubte. Selen wurde durch Extraktion als Piazselenol abgetrennt. Arsen und Antimon wurden als Sulfid gefällt und als Chlorid destilliert und anschliessend ^{76}As und ^{122}Sb γ-spektrometrisch bis zu Gehalten von 0.02 μg/ml bestimmt. Die Methode ist ebenfalls, wenn auch nicht sehr empfindlich, für die gleichzeitige Bestimmung von Zinn und Germanium geeignet.

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DETERMINATION OF RARE-EARTH ELEMENTS IN ROCK SAMPLES BY NEUTRON ACTIVATION ANALYSIS WITH A LITHIUM-DRIFTED GERMANIUM DETECTOR AFTER CHEMICAL GROUP-SEPARATION

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In recent years, high-resolution lithium-drifted germanium detectors (Ge(Li) detector) have been applied to the non-destructive activation analysis of a wide variety of samples. PRUSSIN *et al.*[1] reported the utility of Ge(Li) detectors in non-destructive neutron activation analysis of impurities in aluminum. SCHROEDER *et al.*[2,3] demonstrated applications of these detectors in a wide variety of activation analysis and presented a method for the determination of silver in minerals and ores. COBB[4] showed that abundances of Mn, Sc, Th and several rare-earth elements in various types of rocks can be determined by non-destructive neutron activation using Ge(Li) γ-ray spectrometry. COOPER AND BROWNELL[5] constructed a large coaxial Ge(Li) detector with a plastic anti-coincidence scintillator for activation analysis and presented a γ-ray spectrum of a neutron-activated sample of blood cells. While the present work was in progress, GORDON *et al.*[6] reported on the use of high-resolution γ-ray detectors in instrumental activation analysis of standard rocks and described a scheme for the non-destructive determination of as many as 28 elements in various rocks.

Although Ge(Li) detectors have a much higher resolving power than the conventional NaI(Tl) scintillators, the photopeak efficiency of the former detectors is much lower than that of the latter. There are two ways to improve the poor sensitivity of Ge(Li) detectors in applications to neutron activation analysis; one is to make a larger-scale Ge(Li) detector, and the other is to employ chemical group-separations in order to diminish the background and eliminate spectral interferences. In the present work, the latter possibility has been studied for the determination of rare-earth elements in rock samples by neutron activation analysis. The development of a simple, convenient, and sensitive analytical method for rare-earth elements in rocks and minerals is of great interest in the geochemical field. In this paper, the results of the proposed destructive analysis with those of non-destructive analyses using Ge(Li) detectors as described by COBB[4] and by GORDON *et al.*[6] are compared.

EXPERIMENTAL

Ge(Li) detector and associated electronics

The lithium-drifted germanium detector used in this study was made in the Institute for Atomic Energy, Rikkyo University. Dimensions of the planar detector are 1.5 × 1.0 cm, with a depletion depth of 3 mm, and the active volume is estimated to be approximately 0.5 ml. The detector is operated in a vacuum at *ca.* 77°K with a bias voltage of 540 V and has a leakage current of about 10^{-9}A. The detector is mounted on an aluminum plate connecting with a copper tube that makes thermal contact with a liquid nitrogen reservoir. A Nippon Electric Co. ion pump is used to maintain a vacuum of *ca.* 10^{-7} mm Hg in the detector chamber. The front window of the detector chamber is made of aluminum foil of 0.5 mm thickness. A schematic diagram of the detector is shown in Fig. 1. The associated electronics consist of an ORTEC Model 101XL type preamplifier and an ORTEC Model 201 type main amplifier constructed at this Institute. The resultant pulses from this system are fed into an RCL 400-channel pulse-height analyzer. Resolution for the ^{57}Co 122-keV peak is 3 keV (full width at half maximum).

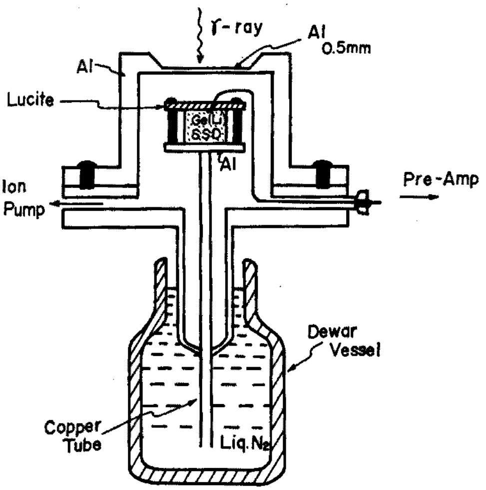

Fig. 1. Schematic diagram of Ge(Li) semiconductor detector.

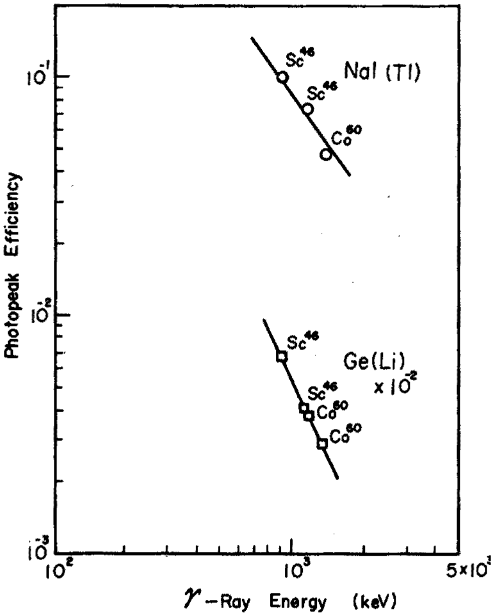

Fig. 2. Photopeak efficiency comparison of a Ge(Li) semiconductor detector (0.5 ml effective volume), and a 3 × 3 in. NaI(Tl) scintillation detector.

The energy calibration of the pulse-height scale was performed by means of the known γ-rays emitted by a set of standard nuclide samples (*i.e.*, ^{22}Na, ^{60}Co, ^{133}Ba, ^{137}Cs and ^{182}Ta). The energies of the photopeaks can easily be determined to within 2 keV and long-term gain shifts and zero drifts were generally well within 1 keV for one month.

Photopeak efficiency for the Ge(Li) detector used

The photopeak efficiency of the detector for γ-rays in the energy range around 1 MeV was obtained by ^{46}Sc and ^{60}Co sources which were standardized by a coincidence method in this Institute. The resulting experimental photopeak efficiency curve is shown in Fig. 2 along with the corresponding curve for a 3 × 3-in. NaI(Tl) scintillator.

As shown in Fig. 2, the photopeak efficiency at 1 MeV is $0.5 \cdot 10^{-4}$ for the Ge(Li) detector used in these experiments.

Sample irradiation and rare-earth group-asepartion

The samples employed in this preliminary study include the U.S. Geological Survey standard rock samples G-1 (Granite) and W-1 (Diabase). Samples (500 mg each) were sealed in polyethylene ampoules. The reference standard mixture solution which consisted of known amounts of rare-earth elements was impregnated into a filter paper, evaporated under a heat lamp, and wrapped in an aluminum foil. The samples and the reference standard were irradiated in the TRIGA MARK-II reactor of Rikkyo University for 6 h at a neutron flux of $4 \cdot 10^{12}$ n/cm^2/sec. After cooling for one day, the irradiated sample was decomposed with sodium peroxide fusion in a nickel crucible containing rare-earth carriers (4 mg each of La, Nd, Gd, Er, Lu). The rare-earth fraction was separated and purified from many activities such as ^{24}Na, ^{46}Sc, ^{56}Mn, ^{59}Fe, ^{60}Co, ^{233}Pa etc. by means of a conventional hydroxide–fluoride cycle (3 times repeated). Finally the rare-earth hydroxide fraction was centrifuged to the bottom of a 1-cm diameter polyethylene tube and transferred to the Ge(Li) detector for γ-counting. The irradiated reference standard was dissolved in a small amount of sulfuric acid containing the rare-earth carrier solutions and treated by the same chemical procedure as stated above so as to obtain the same counting geometry as the samples.

Measuring procedure

The rare-earth fractions were γ-counted at several different times after the chemical group-separation to optimize determinations for nuclides of various half-lives. γ-Spectra were taken one day after the chemical separation for lanthanum, samarium and europium; one week after for samarium and lutetium; 16 days after for terbium, ytterbium and lutetium; 50 days after for cerium, neodymium, terbium and thulium; and a few months for gadolinium, under the same counting conditions. At the end of the counting measurements, the chemical yields of the samples and reference standard were obtained by titration with EDTA in the presence of xylenol orange as indicator. The average chemical yields were greater than 85%. The content of a given element in the samples was calculated from the ratio of one or several photopeak areas in the samples to the areas of corresponding photopeaks in the reference standard spectrum for that element.

RESULTS AND DISCUSSION

Most of the γ-peaks from the rare-earth elements lie below 400 keV and the background in this region introduces serious problems in attaining good sensitivity for the non-destructive method with Ge(Li) detectors, as pointed out by COBB[4]. The high background level is largely due to Compton plateaus from higher γ-rays, so that for a highly sensitive determination of rare-earth elements in rock samples, such nuclides as ^{24}Na, ^{46}Sc, ^{56}Mn, ^{59}Fe and ^{60}Co must be excluded from the samples before direct γ-ray counting. Moreover, since the nuclides such as ^{51}Cr, ^{181}Hf, ^{182}Ta and ^{233}Pa have intense photopeaks below the 400-keV energy region, it is necessary to remove these interfering nuclides from the samples of rare-earth elements before the γ-counting.

Figures 3 and 4 illustrate the γ-ray spectra obtained from the rare-earth fractions of the U.S. Geological Survey standard rocks G-1 and W-1 respectively. As shown in these figures, most of the photopeaks stand out clearly above the general "background" level, especially in the energy region below 400 keV, so that the photopeak areas are easily determined for the group-separated rare-earth fractions.

In the following section, the counting procedure for each rare-earth element is discussed and the results are compared with those of the non-destructive analyses by COBB[4] and GORDON *et al.*[6].

Lanthanum

The γ-peaks due to ^{140}La (40 h) can be seen at energies of 328, 490, 576 (double

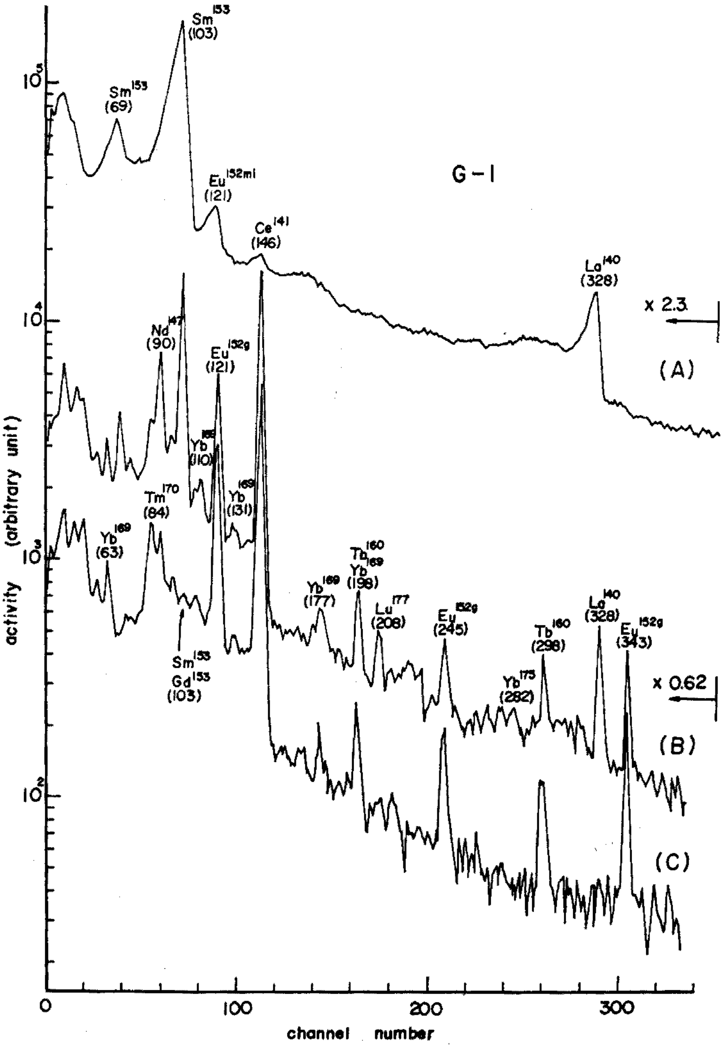

Fig. 3a. The lower-energy region γ-ray spectra of standard rock sample G-1 with the Ge(Li) detector. (A) 2 days, (B) 15 days and (C) 39 days after the end of irradiation.

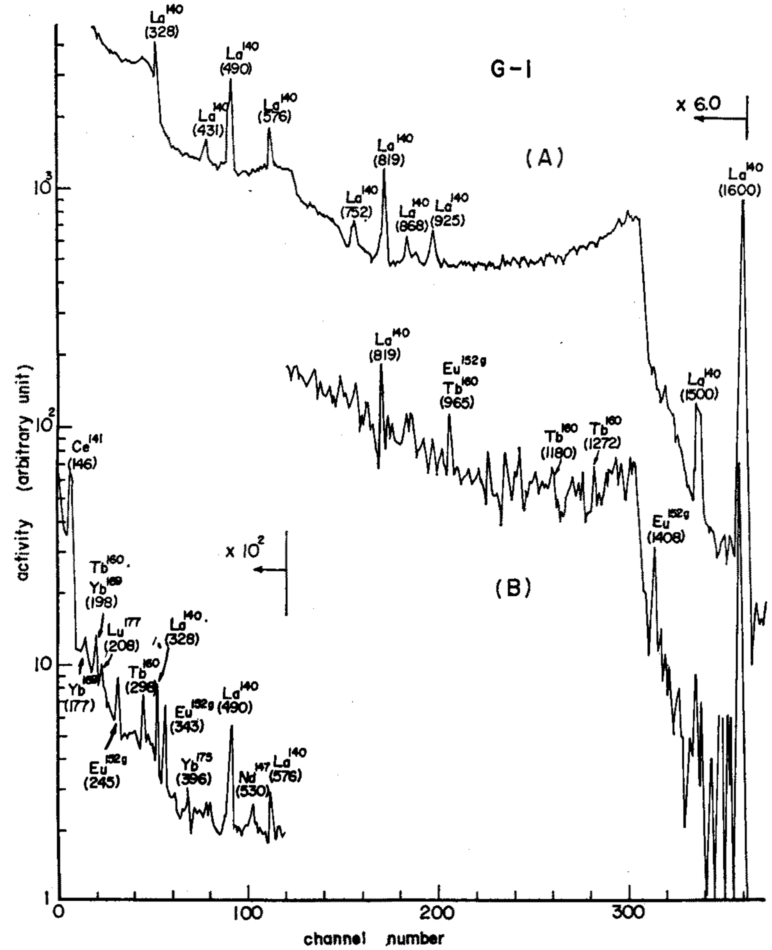

Fig. 3b. The higher-energy region γ-ray spectra of standard rock sample G-1 with the Ge(Li) detector. (A) 5 days and (B) 16 days after the end of irradiation.

escape), 819, 868, 925, 1500 (double escape), and 1600 keV in the spectra. The photopeaks at 328, 490, 819 and 1600 keV can be used in the determination of lanthanum. In non-destructive analysis, however, the presence of ^{24}Na causes considerable background problems for the use of 328-keV peak and the most prominent 490-keV peak is slightly affected by a 482-keV peak from ^{181}Hf.

Cerium

^{141}Ce (33 d) has a photopeak at 146 keV. This peak is seriously interfered with by the presence of ^{59}Fe (143 keV), as pointed out by GORDON *et al.*[6]. Furthermore, according to the results of COBB[4], the 146-keV peak of ^{141}Ce could not be detected in the case of W-1 and basalts, owing to the high background caused by ^{46}Sc. The γ-spectra obtained in the present procedure show a clear photopeak at 146 keV due to ^{141}Ce, even in the case of W-1. The contribution from the 145-keV peak of ^{175}Yb (4.21 d) to the 146-keV peak of ^{141}Ce is negligibly small because of the extremely low intensity (0.34%) of the former peak.

Neodymium

The 90-keV and 530-keV peaks of ^{147}Nd (11.1 d) show up quite well in the spectrum of G-1, while they are rather poor in that of W-1 (Fig. 3 and 4). GORDON *et al.*[6] detected the 90-keV and 530-keV peaks of ^{147}Nd using a large coaxial Ge(Li) detector (30 ml) in the spectra of silicic rocks, but they could not definitely assign the peak at 530 keV to ^{147}Nd. However, the peak can clearly be assigned to this nuclide because of the existence of this peak in the spectra from the chemically group-separated rare-earth fraction.

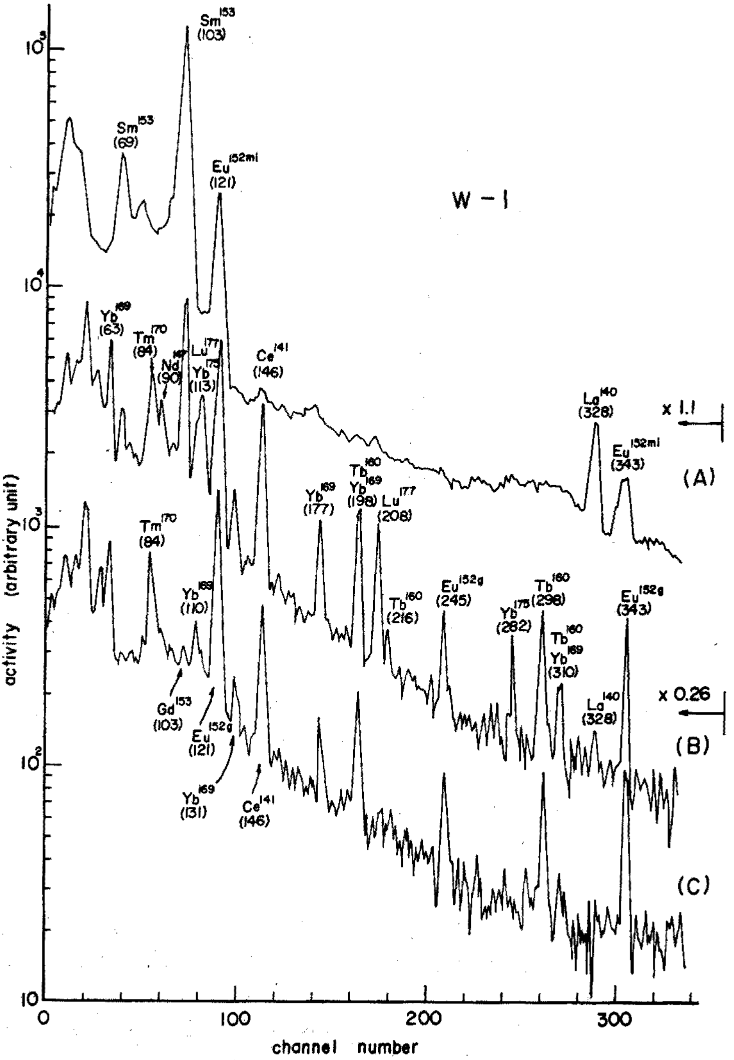

Fig. 4a. The lower-energy region γ-ray spectra of standard rock sample W-1 with the Ge(Li) detector. (A) 2 days, (B) 15 days and (C) 39 days after the end of irradiation.

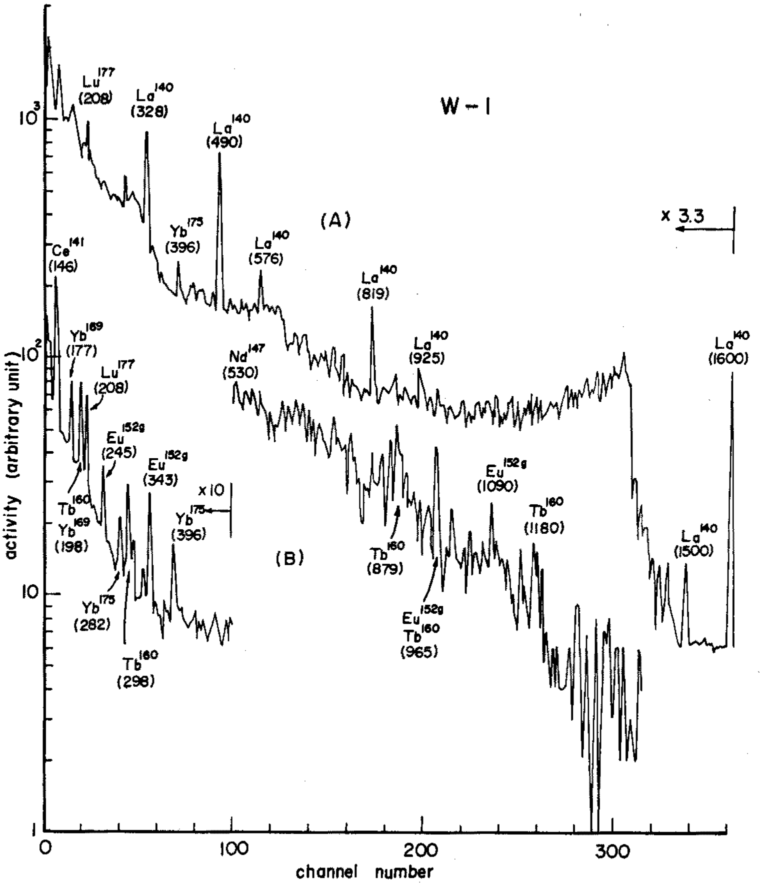

Fig. 4b. The higher-energy region γ-ray spectra of standard rock sample W-1 with the Ge(Li) detector. (A) 5 days and (B) 16 days after the end of irradiation.

Samarium

The ^{153}Sm (47 h) γ-peak at 69 keV and the intense 103-keV peak can be detected in the spectra (Fig. 3 and 4). In the non-destructive methods, the determination of samarium must be carried out within the first few days after irradiation. As pointed out by GORDON *et al.*[6], both peaks will be interfered with by the ^{153}Gd (69 keV), ^{182}Ta (68 keV), ^{153}Gd (103 keV) and ^{233}Pa (94–98 keV) photopeaks after one week. The destructive method is free from the interference of ^{182}Ta and ^{233}Pa, but cannot eliminate the contribution from ^{153}Gd (236 d; 69, 103 keV). However, one can obtain the best estimation of samarium abundance within one week after the end of irradiation.

Europium

The contents of europium in the samples can be determined quite accurately by the presented procedure. The peaks from $^{152m1}Eu$ (9.2 h; 121 and 343 keV) and ^{152g}Eu (12 y; 121, 245, 343, 965 and 1408 keV) stand out strongly and clearly above the background. The 121-, 245- and 343-keV peaks of ^{152g}Eu were used for the measurements in

TABLE I

NUCLEAR PROPERTIES OF NUCLIDES[7] AND PHOTOPEAKS USED IN THE DETERMINATION

Element	*Target nuclide*	*Isotope abundance(%)*	*Product nuclide*	*Cross section (σ_{th}: barns)*	*Photopeaks used (keV)*	*Time after irrad. for counting*
La	^{139}La	99.9	^{140}La (40.2 h)	8.9	328, 490, 819, 1600	one day–one week
Ce	^{140}Ce	88.5	^{141}Ce (33.1 d)	0.6	146	50 days
Nd	^{146}Nd	17.2	^{147}Nd (11.1 d)	2	90, 530	16–50 days
Sm	^{152}Sm	26.7	^{153}Sm (47.1 h)	210	69,103	one day–one week
Eu	^{151}Eu	47.8	^{152g}Eu (12.7 y) ^{152m1}Eu (9.2 h)	5,900 2,800	121, 245, 343 121, 343	50 days one day
Gd	^{152}Gd	0.200	^{153}Gd (236 d)	$<$125	103	a few months
Tb	^{159}Tb	100	^{160}Tb(73.0 d)	46	298	50 days
Tm	^{169}Tm	100	^{170}Tm (129 d)	125	84	50 days
Yb	^{168}Yb	0.135	^{169}Yb (31.8 d)	11,000	177	16–50 days
Lu	^{176}Lu	2.59	^{177}Lu (6.75 d)	2,100	208	one–two weeks

this study. The use of these photopeaks in the non-destructive method requires careful attention to interferences from ^{131}Ba (124 and 247 keV), ^{181}Hf (346 keV) and ^{233}Pa (340 keV). Other peaks, such as 780, 965 and 1408 keV, of ^{152g}Eu are not advisable for such determinations, since the 963- and 965-keV peaks of ^{160}Tb are superimposed on the 965-keV peak of ^{152g}Eu, and the 780- and 1408-keV peaks of ^{152g}Eu which are free from interference are less sensitive, probably because of the small effective volume of the detector used.

Gadolinium

According to the results by GORDON *et al.*[6], the 70-, 97- and 103-keV peaks from ^{153}Gd (242 d) are interfered with by ^{153}Sm (47 h; 69 and 103 keV), ^{183}Ta (118 d; 68 and 100 keV) and ^{233}Pa (27.0 d; 94–98 keV), so that gadolinium abundances in the samples cannot be determined by the non-destructive technique. On the other hand, the amounts of gadolinium in the samples can be easily determined with the group-separated rare-earth fractions after a few months when ^{153}Sm activity has decayed out completely.

Terbium

It can be seen from the figures that there are many photopeaks from ^{160}Tb (72.1 d), but most of the peaks are subject to interferences from other nuclides. Therefore, in the non-destructive method, the use of the 87-, 298-, 879- and 965-keV peaks of ^{160}Tb is permissible only when the interference contributions from ^{170}Tm (84 keV), ^{182}Ta (85 keV), ^{233}Pa (86 and 300 keV), ^{46}Sc (890 keV) and ^{152m1}Eu (965 keV) can be corrected accurately. GORDON *et al.*[6] carried out these difficult corrections successfully. The terbium abundances were determined from the area of 298-keV peak, which is free from the interference of the 300-keV peak of ^{233}Pa, in the proposed destructive method.

Thulium

The thulium abundance in W-1 can be determined from the corrected area of the 84-keV peak of ^{170}Tm (130 d) after the contribution from the 87-keV peak of ^{160}Tb has been removed, but thulium in G-1 cannot be determined because of the low abundance of the element. In the non-destructive method of GORDON *et al.*[6], it is necessary to correct for the contribution from ^{160}Tb (87 keV), ^{182}Ta (85 keV) and ^{233}Pa (87 keV) to ^{170}Tm (84 keV).

Ytterbium

γ-Peaks from ^{169}Yb (32 d) and ^{175}Yb (4.21 d) generally appear in the spectra and the ytterbium abundances in the rock samples can be determined by the use of the 177-keV peak from ^{169}Yb. This peak stands up clearly above the background and is free from the spectral interference of ^{182}Ta (179 keV) in the destructive method. In the non-destructive methods, the abundance of ytterbium is difficult to determine because of various interferences, such as ^{59}Fe, ^{131}Ba, ^{141}Ce, ^{160}Tb, ^{177}Lu and ^{233}Pa, as shown in the detailed discussion presented by GORDON *et al.*[6]. Again, they overcame this difficulty by correcting for the contributions from these various interferences.

Lutetium

The lutetium abundances are determined by means of the ^{177}Lu (6.7 d) peak at 208 keV which is free from contribution from ^{131}Ba (216 keV) and can be discriminated from the 216-keV peak of ^{160}Tb in this destructive method. The 112-keV peak of ^{177}Lu is not suitable for the lutetium abundance determination because of the various interferences from ^{169}Yb (110 keV), ^{175}Yb (114 keV) and ^{233}Pa (110–114 keV), as pointed out by GORDON *et al.*[6] and by COBB[4].

Table I summarizes the best photopeaks used in the determination of rare-earth elements in the rock samples along with the nuclear properties. In Table II, the rare-earth abundances found in the samples G-1 and W-1 are summarized along with the data previously reported.

TABLE II

DETERMINATIONS OF RARE-EARTH ELEMENTS IN G-1 AND W-1 (in p.p.m.) BY NEUTRON ACTIVATION ANALYSIS

	Element	*This work*[a]	*Cobb*[4] *(1967)*[b]	*Gordon et al.*[6] *(1967)*[c]	*Haskin and Gehl*[8] *(1963)*[d]	*Towell et al.*[9] *(1965)*[e]
G-1	La	109	85	—	102	92
	Ce	156	157	—	134	150
	Nd	44	—	—	55	55
	Sm	7.52	7.6	—	8.6	8.3
	Eu	1.04	1.3	—	1.04	1.36
	Gd	4.8	—	—	4.9	—
	Tb	0.40	—	—	0.50	0.64
	Tm	—	—	—	0.20	0.16
	Yb	0.63	—	—	0.63	0.94
	Lu	0.13	0.12	—	0.17	0.12
W-1	La	13.9	9.6	12	11.7	9.3
	Ce	24	—	21	24	15
	Nd	21	—	—	15	20
	Sm	3.78	3.4	2.8	3.8	3.5
	Eu	1.04	1.2	1.08	1.09	1.29
	Gd	3.4	—	—	4.2	—
	Tb	0.60	—	0.57	0.75	0.81
	Tm	0.30	—	0.3	0.36	0.33
	Yb	1.9	2.1	2.2	2.1	2.2
	Lu	0.35	0.35	0.44	0.33	0.35

[a] Chemical group-separation and Ge(Li) detector (0.5 ml).
[b] Non-destructive using Ge(Li) detector (1.6 ml).
[c] Non-destructive using Ge(Li) detector (30 ml).
[d] Ion-exchange separation.
[f] Reversed-phase chromatographic separation.

As shown in Table II, the results obtained in this work agree well with those obtained by various workers using neutron activation analysis, with Ge(Li) detectors or with elaborate chemical separations. The results obtained show that the sensitivity is improved compared to the non-destructive analyses presented by COBB[4] and GORDON *et al.*[6]. In the non-destructive method by COBB[4], the determinations of neodymium, gadolinium, terbium and thulium in both G-1 and W-1, ytterbium in G-1, and cerium in W-1 were not performed because of the high background level and the spectral interferences due to the presence of many other interfering nuclides. Even in the technique which employed a large coaxial Ge(Li) detector[6], the serious spectral interferences for gadolinium, terbium, thulium, ytterbium and lutetium give rise to difficulties for the determination of these elements, as stated above. On the other hand, the present procedure involving chemical group-separations coupled with a Ge(Li) detector allows a low background level to be achieved and is free from spectral interferences due to ^{24}Na, ^{46}Sc, ^{56}Mn, ^{59}Fe, ^{60}Co, ^{181}Hf, ^{182}Ta and ^{233}Pa. Table II indicates that the sensitivity of the small Ge(Li) detector (effective volume 0.5 ml) used is comparable with that of the large coaxial type Ge(Li) detector (effective volume 30 ml), when a simple group-separation of rare-earth elements is applied. Of course, the tedious and elaborate mutual separations of rare-earth elements by ion-exchange or reversed-phase chromatography can be excluded in this procedure.

It may be said that more effective utility of a Ge(Li) detector for applications to neutron activation analysis can be attained when one introduces a chemical group-separation without any fractionation of all elements of interest.

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SUMMARY

A lithium-drifted germanium detector combined with chemical group-separation has been utilized for the determination of rare-earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu) in rock samples by neutron activation. This procedure has the advantage of a low background level which cannot be attained in the non-destructive method. The combination of the Ge(Li) detector and chemical group-separation also offers a distinct simplification in the correction of contributions from other nuclides. For optimum utility of a Ge(Li) detector in neutron activation analysis, chemical group-separations are recommended.

RÉSUMÉ

On propose l'utilisation d'un détecteur lithium–germanium après séparation chimique pour le dosage des terres rares (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb et Lu) dans des échantillons de roches par activation au moyen de neutrons. Ce procédé présente l'avantage d'un faible fond ce qui n'est pas possible avec la méthode non-destructive.

ZUSAMMENFASSUNG

In Gesteinsproben werden die Seltenen Erden (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb und Lu) mit der Neutronenaktivierungsanalyse bestimmt. Dabei wird eine chemische Gruppentrennung vorgenommen und das γ-Spektrum mit einem lithium-gedrifteten Germanium-Detektor analysiert. Dieses Verfahren besitzt den Vorteil eines niedrigen Untergrundes und bietet eine einfache Korrektur des Anteils anderer Nuklide im γ-Spektrum.

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THE DETERMINATION OF NEON AND ARGON IN HELIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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The absorption of incident monochromatic radiation from a noble gas by excited atoms of the same gas in an absorption source is known in the field of spectroscopy. However, little work has been reported in which this method is utilized for the determination of noble gases, even though analytical methods are presently needed for the determination of noble gases in noble gas mixtures that are used for laser experiments, in new noble gas compounds, and in stones and minerals that are used for chronological dating investigations.

Recent investigations[1] performed at the Argonne National Laboratory, showed that approximately 10 μmoles of helium, neon, argon, krypton and xenon, respectively, were easily detected by atomic absorption techniques. The pure gas samples were excited in a hollow-cathode discharge tube that was used as an absorption source. Many spectral lines of the noble gases that were investigated in the near ultraviolet–visible region were strongly absorbed. From this evidence it was decided to employ a somewhat similar absorption technique for the analysis of binary mixtures of noble gases since a conventional monochromator was employed for this work. Earlier, it was thought that expensive vacuum ultraviolet equipment would be needed to analyze noble gases by atomic absorption methods because their resonance lines are located in the vacuum ultraviolet region.

Other investigators[2] have analyzed a number of binary mixtures of noble gases with atomic absorption techniques. In this work incident radiation was absorbed by excited noble gas atoms in the absorption source also. However, an indirect method was employed. That is, a minor gas was determined in a major gas by absorbing a spectral line of the major gas instead of a line of a minor gas. This technique was possible for the conditions used because the concentration of excited atoms of the major gas was reduced by a change in concentration of the minor gas. The work done with this technique was limited, and it is not clear, for example, what effects trace impurities have on the concentration of excited atoms of the major gas, or that the method is applicable to binary noble gases of interest. Thus, to determine neon and argon, respectively, in helium it was decided to determine the gases of interest directly, that is, by absorbing a spectral line of the gas sought.

EXPERIMENTAL

Emission tubes

Figure 1 shows the optical arrangement that was used for this work. Two

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

commercial Geissler-type discharge tubes (Pen Ray, Models 11SC-1) containing neon and argon, respectively, were employed as emission sources. A commercial transformer (Pen Ray, Model SCT-2) was employed to drive the tubes. It was operated at 110 V and a frequency of 150 c.p.s. The modulated light from the emission tube filled the absorption tube, and the light coming out of the absorption tube was focussed on a 20-μ slit of the modified Jarrell-Ash monochromator, Model 82-000, equipped with two photomultiplier tubes (R.C.A. 1P 21 and Hamamatsu – R 196).

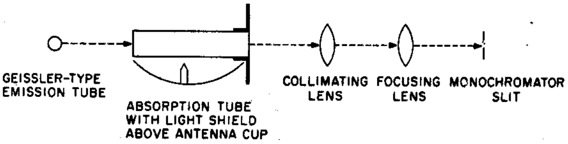

Fig. 1. Optical arrangement.

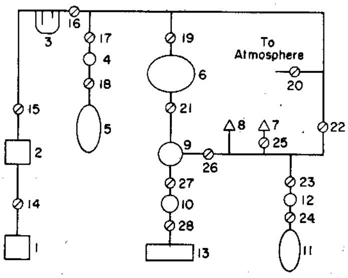

Fig. 2. Vacuum system. (1) Forepump. (2) Mercury diffusion pump. (3) Liquid nitrogen cold trap. (4), (9), (10), (12) Calibrated volumes. (5) Minor gas. (6) Calibrated volume for mixing gases. (7) McLeod gauge. (8) Pirani-type gauge tube. (11) Major gas. (13) Absorption cell. (14)–(27) Vacuum stopcocks greased with Apiezon T. (28) Metal vacuum stopcock.

Since the incident light coming from the emission tubes was intense, and it was simple to fill the absorption tube with incident light, as illustrated in Fig. 1, a focussing lens that is normally used in atomic absorption methods to focus incident light on the absorption source was not needed.

Absorption tube and related vacuum system

A diagram of the absorption tube and related vacuum line, used for convenience, is shown in Fig. 2. The quartz tube was about 10 cm long and had a diameter of 2 cm. This size of tube was chosen so that it would just fit above a Raytheon Antenna Cup, having a diameter of about 10 cm, that was powered by a 2450 megacycle Raytheon Oscillator Model No. PGM-10X. With this arrangement, gas in all parts of the absorption tube was excited when radiation was emitted from the antenna, and maximum light from the emission tube was absorbed by the excited atoms in the absorption tube. For example, virtually 100% of incident light, He 3888 Å, was absorbed when pure helium, covering a pressure range of 0.1–5.0 torr, was excited in the absorption tube by the Raytheon Oscillator operated at 40 W. For this work, helium was employed at a pressure of about 1 torr, *i.e.* some 2 μmoles, since it was easy to excite the gas. All noble gases used in this experiment were Linde spectrographically pure noble gases.

To determine the volume of the absorption tube and other volumes of interest on the vacuum line, a gas expansion method was used; a Texas Instrument, Fused Quartz Precision Pressure Gauge, Model No. 141, was used to measure gas pressures. To test the accuracy of this method, several bulbs were calculated independently, using a liquid method for determining volumes, before they were attached on the vacuum line. The results obtained by the two methods were essentially the same; thus it was concluded that the volumes shown in Fig. 2, calibrated by the gas expansion method, were accurate.

For the results reported in this paper, an Autovac Pressure Gauge, Type 3294B, and a conventional 10-mm tilting McLeod Gauge were employed for convenience. The latter was used to measure noble gas pressures accurately in the range of about one torr, and the former to measure noble gas pressures roughly and to test the stability of the vacuum line at a gas pressure of about $1 \cdot 10^{-3}$ torr or lower.

Except for a metal stopcock that connects the absorption tube to the vacuum line, all the other stopcocks were conventional vacuum-type stopcocks that were made of pyrex glass. The grease used was Apiezon T. After the stopcocks were greased and the vacuum line was pumped out for some 3 days, a vacuum of $1 \cdot 10^{3-}$ torr or better was obtained in the absorption tube, and this vacuum could be maintained for hours. To clean the inside of the absorption tube of surface contamination, *e.g.* mercury, several loadings of helium at a pressure of about 2 torr were excited, consecutively, in the tube by a Raytheon Oscillator that was operating at 80 W. This cleaning treatment was effective since only a few very weak impurity spectral lines, due to mercury, and no molecular bands were observed with a hand spectroscope when a subsequent noble gas was excited in the absorption tube.

To cover a concentration range of interest for neon and argon, respectively, in helium a conventional technique was employed for mixing gases. For example, the vacuum system in Fig. 2 was evacuated to a pressure of $1 \cdot 10^{-3}$ torr or less. Subsequently, a minor gas from bulb 4 was expanded into (bulb 9 and) bulb 10, with a volume of about 1 ml, and the gas pressure was measured with the McLeod Gauge. Bulb 9 was evacuated and then the minor gas was expanded into bulb 9 and a relatively large bulb 6, of volume about 1 l. The major gas was transferred from bulb 12 to the evacuated bulb 9, which had a volume of *ca.* 24 ml, and the pressure was measured with the McLeod Gauge. The major gas was mixed with the minor gas by expanding the former to bulb 6. After evacuation of bulbs 9 and 10, the mixture of gases from bulb 6 was introduced into the absorption tube by opening and closing stopcock 28. By repeating this technique for mixing gases, essentially the same pressure of a given gas mixture was obtained in the absorption tube without the use of a McLeod Gauge. The reason for this was that a very small volume (*ca.* 1 ml) of a noble gas was taken from a relatively large container (*ca.* 1 l) for use in the absorption tube. The advantage of this technique was that mercury from the McLeod Gauge was kept out of the absorption tube. Results for this work were obtained with the McLeod Gauge closed to the vacuum line.

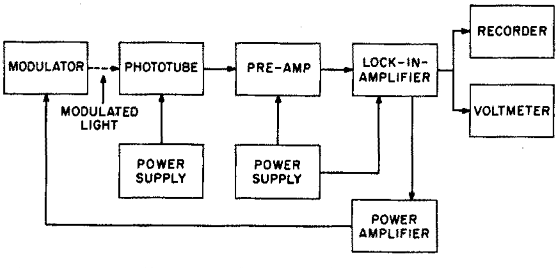

Fig. 3. Block diagram of electronic system.

Readout system

A block diagram of the readout system that was used for this work is shown in Fig. 3. It consisted essentially of commercial equipment that was assembled at the Argonne National Laboratory. This system was useful because the incident light was modulated at a tuned frequency, 150 c.p.s., that gave a better signal-to-noise ratio than other frequencies for the experimental conditions used. Since the emission tube emitted an a.c. signal, a light chopper was eliminated; thus maximum incident intensity was obtained from the emission source.

RESULTS

Analytical curves

Analytical curves for neon and argon are shown in Fig. 4. Each point on the curve is an average of a number of absorption readings that were obtained for a standard mixture. To obtain an absorption reading, the following technique was employed. The emission tube was switched on for several minutes to obtain a steady signal. An absorption reading was then obtained by exciting a gas mixture in the absorption tube by turning on the power (40 W) of the Raytheon Oscillator for about 1 min. Subsequently, more absorption readings were obtained of the same mixture by turning the oscillator power on and then off for 1 min without waiting for the absorption tube to cool. For the analytical curves depicted, a straight line can be drawn covering a concentration range of about 1–10 nanomoles. The reason why the curves are not linear beyond a concentration of 10 nanomoles is not readily apparent.

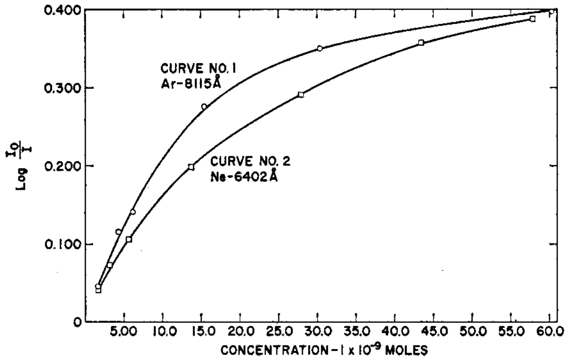

Fig. 4. Analytical curves for neon and argon.

Precision and accuracy

To test the precision and accuracy of this atomic absorption technique, known amounts of neon and helium, taken from the liter bulbs on the vacuum line were mixed and introduced into the absorption tube as previously described. Subsequently, the absorption tracings were obtained for this sample and the results obtained from the previously prepared analytical curve. The precision (Table I) was ± 2.4% and the accuracy for this method (Table II) was essentially the same (±2.1%). A similar test

TABLE I

PRECISION FOR NEON

Tracing no.	*Neon ($1 \cdot 10^{-9}$ moles)*	*Deviation from mean*
1	6.00	+0.24
2	6.00	+0.24
3	5.80	+0.04
4	5.80	+0.04
5	5.80	+0.04
6	5.65	−0.11
7	5.65	−0.11
8	5.65	−0.11
9	5.65	−0.11
10	5.65	−0.11
	Mean 5.76	

Std. dev.: ±0.14. Rel. std. dev.: ±2.4%.

TABLE II

ACCURACY FOR NEON AND ARGON

Sample	*Major gas*	*Minor gas*		*Rel. error (%)*
1	Helium	Neon		
		Moles added	Moles found	
		$5.64 \cdot 10^{-9}$	$5.76 \cdot 10^{-9}$	+2.1
2	Helium	Argon		
		Moles added	Moles found	
		$6.15 \cdot 10^{-9}$	$6.06 \cdot 10^{-9}$	−1.5

was performed for a sample containing argon in helium. The precision obtained for argon was better than that obtained for neon, and the accuracy for argon (Table II) was −1.5%.

Comparison of sensitivities with the absorption tube as emission source and absorption source, respectively

A comparison of sensitivities for a number of metals with a conventional flame as an absorption source for routine atomic absorption work and as an emission source for routine atomic emission work[3], indicates that atomic absorption techniques are more sensitive. This is because many more atoms in the flame are in the ground state than in excited states. However, for the techniques described in this paper, atoms in the metastable states instead of the ground state are employed in the absorption tube to absorb incident light. Thus, to see if the absorption tube (Fig. 2) was a better absorber than an emitter, the following test was employed. An absorption tracing was obtained for a sample consisting of about 1 nanomole of neon in helium by the method described above. Subsequently, the emission tube was switched off and an emission tracing of the same excited sample in the absorption tube was obtained by merely placing a mechanical chopper, operating at 150 c.p.s. in front of the slit of the monochromator. The chopper blocked off some 50% of incident light. Results of this test showed that the signal obtained for the absorption method was about a factor of 20 times greater than the signal obtained by the emission method.

Determination of neon and argon, respectively, in helium by an indirect method

Under the conditions employed in this work, the indirect method mentioned earlier, could not be used for the determination of neon and argon, respectively, in helium, because practically the same percentage, about 100% of incident light, He 3888 Å, that was obtained from a Pen Ray tube, Model No. 11SC-1, was absorbed when the absorption tube contained pure helium and the high standard mixture of neon and argon in helium, respectively (see Fig. 4), at a pressure of about one torr. The techniques that were used to plot the analytical curves were also employed to obtain the results for this test.

DISCUSSION AND CONCLUSIONS

The results shown in Table II indicate that neon and argon, respectively, can be determined in helium by atomic absorption spectrophotometric techniques. A direct method for measuring the minor gas was employed. The accuracy of the atomic absorption method is comparable to that of the mass spectrometric[4] and gas chromatographic[5] methods that are used routinely for the determination of noble gases. Further, the minimum measurable amount of minor gas is smaller in the case of the atomic absorption method. On the other hand, the lower limit of concentration (p.p.m.) is not nearly as good as in the case of the mass spectrometric and especially the gas chromatographic method. Also, it has been shown that the absorption tube used for this work was a better absorber than emitter. Hence, a relatively large number of metastable atoms, capable of absorbing incident light were present when a noble gas was excited. However, it should be pointed out that the value reported in this work applies to our particular experimental conditions.

Trace amounts of mercury in the absorption tube decreased the sensitivity of this method, probably because metastable atoms of the noble gases are destroyed by mercury atoms, so that the population of metastable atoms is reduced. Mercury contamination, however, was minimized since the absorption tube was thoroughly cleaned by the discharge process mentioned earlier.

Since a minor gas has been excited and determined in an electrodeless discharge tube containing a major gas, having a higher excitation potential, this method of excitation is useful not only for atomic absorption work, but also for atomic emission work. For instance, samples that are too small to maintain a discharge in a electrodeless tube can be excited by adding another gas to the tube to help sustain a discharge. Maximum excitation of a small sample can be obtained by using a suitable major gas.

The author acknowledges helpful assistance from a number of our staff members: H. H. Claassen for consultations regarding the work described, J. Bobis and R. George for arranging the readout system, and E. Rauh for discussions regarding vacuum techniques.

SUMMARY

An atomic absorption spectrophotometric technique is described for the determination of neon and argon, respectively, in helium. The accuracies obtained for

nanomoles of neon and argon, respectively, were +2.1 and −1.5%. Two Geissler-type discharge tubes containing neon and argon, respectively, were used as emission sources; the absorption source was a quartz cell which contained the sample and related standards that were excited by a high-frequency oscillator. The spectral lines that were employed were neon 6402 Å and argon 8115 Å. Because the spectral lines used had transitions to metastable energy levels, instead of ground levels, a conventional monochromator was suitable.

RÉSUMÉ

Une technique spectrophotométrique par absorption atomique est décrite pour le dosage du néon et de l'argon dans l'hélium. Les précisions obtenues pour des nanomoles de néon et d'argon sont respectivement +2.1 et −1.5%. Les tubes de décharge du type Geissler remplis de néon et d'argon sont utilisés comme sources d'émission, la source d'absorption est une cellule de quartz contenant l'échantillon et les standards relatifs excités par un oscillateur à haute fréquence. Les lignes spectrales utilisées sont néon 6402 Å et argon 8115 Å. Un monochromateur conventionnel peut convenir.

ZUSAMMENFASSUNG

Die Bestimmung von Neon bzw. Argon in Helium mit Hilfe der Flammenabsorptionsspektralanalyse wird beschrieben. Nanomole können mit einer Genauigkeit von etwa 2% bestimmt werden. Geisslersche Entladungsröhren, die Neon bzw. Argon enthielten, wurden als Emissionsquellen benutzt. Die Absorption geschah in einer Quarzzelle, in der die Probe und Vergleichsstandards mit einem Hochfrequenzoszillator angeregt wurden. Die verwendeten Spektrallinien lagen für Neon bei 6402 Å und für Argon bei 8115 Å.

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DETERMINATION OF TRACE ELEMENTS IN INORGANIC AND ORGANIC MATERIALS BY X-RAY FLUORESCENCE SPECTROSCOPY

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Several workers have attempted to develop a suitable X-ray method for trace analysis[1-4]. Some of the proposed methods are capable of high accuracy and sensitivity when matrix elements are absent, but they do not provide a means of isolating the trace elements before the X-ray analysis and hence are of limited value. In view of this, a new method has been developed in which the trace elements to be determined are isolated before the X-ray analysis is made[5,6].

The proposed method involves obtaining the sample, free from organic material, in dilute acid solution, and if necessary, making preliminary chemical separations to remove interfering elements. Then 50–200 μg of a suitable element is added to act as a coprecipitant, the solution is adjusted to the proper acidity or alkalinity, and the trace element or elements are precipitated with a suitable organic or inorganic precipitant. The precipitate is filtered on a small paper disk, washed and dried, and finally the intensity of the characteristic X-radiation of the elements in the precipitate is measured on a conventional X-ray spectrograph.

The method is rapid, sensitive, accurate and almost universally applicable. Suitable procedures have been developed for the determination of microgram amounts of 69 of the 72 elements that are customarily determined with an X-ray spectrograph. The only ones for which procedures are, at present, lacking are Pa, Pm and Kr. As little as 20 ng of Ni, Ti and Sc, 0.1 μg of Ca, Cu, Fe, Co and Zn and 1 μg of most of the other elements can be separated and determined. A complete analysis can be made in less than 15 min.

The three main features that have made the method so successful are: first, by the use of preliminary separations or a selective precipitant or both, it is possible to isolate the trace elements from matrix elements or from elements which will cause line interference; second, by the use of a coprecipitating element and a suitable precipitating reagent it is possible to precipitate the trace elements quantitatively; and third, by arranging to isolate the trace elements, uniformly dispersed in a low atomic number matrix of relatively large area, interelement absorption and enhancement is virtually nil and hence the accuracy and sensitivity of analysis is high.

The method has proved to be very useful in the trace analysis of metals and alloys used in industrial development and pure research and will be equally useful in organic and biological work. In addition to the use of the method for the determination of a single element, it seems likely that by using one or more wide-spectrum precipitating reagents, it will be possible to determine several trace elements in such materials as blood, serum, urine, fresh or salt water, air, etc. on a single paper disk.

Incidentally, it is precisely this specific nature of X-ray analysis that makes it possible to use a coprecipitant in the method. It also simplifies the task of determining individual elements, since it is seldom necessary completely to isolate the element to be determined.

Because of the comprehensive nature of the present work it has been limited, for the most part, to a semiquantitative investigation. However, the data obtained have yielded valuable information on selectivity and sensitivity and will serve as a preliminary guide for future quantitative work.

PRELIMINARY CHEMICAL SEPARATIONS

If a direct precipitation of the trace element to be determined is impractical, it will be necessary to make a preliminary separation to remove interfering elements. This separation will take the form of one or more of such classical methods as precipitation, coprecipitation, reduction to the elemental state, adsorption on MnO_2, ion exchange, electrodeposition, distillation or solvent extraction. In such separations it will occasionally be necessary to change the valence of an element or elements before the separation, or to use a complexing agent.

PRECIPITANTS AND COPRECIPITANTS

By the proper choice of precipitant and working conditions, the trace element to be determined can often be precipitated and determined without resorting to a preliminary separation. This will be particularly true, of course, when a specific reagent is available. However, the number of specific reagents available is limited and hence it will usually be necessary to use a less specific reagent. Such a reagent can be used, provided that the sample to be analyzed contains little or no interfering elements or that such elements can be made harmless by complexing, changing the valence state, or by precipitating in strong acid solution. Among the most useful of the less selective reagents that have been investigated are sodium diethyldithiocarbamate (carbamate), cupferron, ammonia and hydrogen sulfide. In addition, it has been shown that phenylfluorone is a valuable reagent, especially in the determination of germanium, molybdenum and tungsten. The use of oxine as a precipitant has, so far, been disappointing.

It is sometimes possible, in those instances where it is desirable to gather a large number of elements, to use two wide-spectrum precipitants in the same solution. Thus, one can precipitate hydroxide elements by neutralizing the solution with ammonia solution and then gather these along with carbamate elements by precipitating with carbamate. When, however, both precipitants are organic compounds, the multiple precipitation may not be possible because the first precipitant may complex some of the elements and prevent their precipitation by the second precipitant. This has been shown to be true in the case of cupferron and phenylfluorone.

Since most precipitates, no matter how insoluble they are, have a certain solubility and sometimes also exhibit supersaturation, it is necessary to use 50–200 μg of a suitable coprecipitating element to insure quantitative recovery of trace elements. Even when a coprecipitant is used, recovery of certain trace elements by a particular precipitant may not be quantitative, but as long as the loss is not more than about 10%, it is still possible to make a reasonably good analysis, since this loss will be compensated for in the calibration. Thus, the precipitation of a few elements has been labeled quantitative in some of the subsequent figures, even though recovery appears to be only about 90%. In this respect it should be emphasized that in the present semiquantitative investigation, no rigorous attempt has been made to determine the completeness of precipitation of the various elements. It has been assumed that, if a reasonably high X-ray count was obtained, and especially if the same count was obtained, using two or more different precipitants, quantitative precipitation is indicated.

The phenomenon of coprecipitation appears to be very complicated[7] and hence no attempt has been made to study it in detail in the present work. However, experience indicates that, up to a point, the coprecipitation of an element is more effective, the larger the ratio of coprecipitant to trace element present. This suggests that when a trace element precipitate is very insoluble, it should be possible to recover nanogram quantities of such an element by using a suitable coprecipitant. Data supporting this view will be given subsequently.

In most instances, the precipitation of a trace element will be complete shortly after the addition of the precipitant. However, since this is not always true, the practice, in the present work, has been to allow the solution to stand for 5 min before the filtration. Exceptions to this rule occur in certain of the precipitations with hydrogen sulfide or gathering of elements with iron(III) hydroxide. In such cases immediate filtration is required to prevent agglomeration of the precipitate.

INTERFERENCE OF ANIONS

Anions which complex elements to such an extent that they are incompletely precipitated by a particular reagent must be absent. Tests with such commonly encountered anions as cyanide, fluoride, phosphate, tartrate, citrate and oxalate have shown that the extent of the interference of the anion depends on the amount of anion present and the strength of the complex or the solubility of the compound formed by the element with the particular precipitant. Thus, it has been shown that the precipitation of cobalt and 25 or more other elements as carbamate and hydroxide at pH 9 is quantitative in the presence of 0.1 g of sodium cyanide; copper, mercury, palladium and several other elements can be precipitated in the presence of 0.2 g of EDTA or ammonium citrate.

The behavior of phosphate is important in the analysis of such materials as gallium phosphide and urine. Tests have shown that as much as 25 mg of phosphorus as diammonium hydrogen phosphate causes no interference in any of the carbamate or cupferron precipitations. The same will probably be found to be true with the hydrogen sulfide precipitations. However, when the elements are to be precipitated with ammonia solution, most of them will precipitate as crystalline phosphates rather than as hydroxides and will hence provide very little coprecipitating ability. Fortunately, this difficulty can be overcome by using beryllium as the coprecipitant, provided that the neutralization is carried just barely to the purple color of *m*-cresol purple. The use of beryllium has the additional advantage that it exhibits only weak X-ray absorption and hence assures high sensitivity in the X-ray analysis of the light elements. It should not be forgotten that, in the presence of an excess of phosphate, traces of barium, strontium and calcium, but strangely not magnesium, will be quantitatively precipitated along with the hydroxide elements.

Whenever possible, interfering anions should be removed before the precipitation of trace elements. This is usually easy to do. Thus, organic anions can be destroyed by wet oxidation and fluoride or cyanide can be expelled by evaporation with sulfuric acid.

FILTRATION OF PRECIPITATES

The filter equipment used in the present work is shown in Fig. 1. It consists of a Pyrex filter holder supplied by the Millipore Corporation of Bedford, Mass. and includes a reservoir, a 17-mm circular fritted glass support and a metal clamp. The filter paper disks used are white or black 25-mm Millipore paper disks of 0.8-μ or 5-μ pore size, depending on the precipitate to be filtered. After inserting the disk and clamping on the reservoir, the solution is filtered, using adequate suction and the reservoir and disk are washed with 2 or 3 ml of water. The disk is dried, with gentle heat if desired. Then an aluminum mask which has a circular hole, just slightly larger than the spot of precipitate on the paper disk, is smeared lightly with stopcock grease and pressed onto the disk so that the precipitate is completely exposed through the hole. The mask is then inserted in the X-ray spectrograph and the intensity of the characteristic X-radiation of the element being determined is measured.

The stopcock grease should be sufficiently viscous so that it will keep the disk attached to the mask, even when the latter heats up in the X-ray spectrograph, but

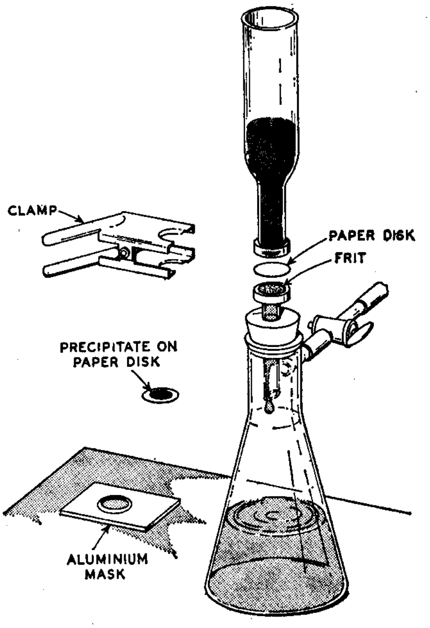

Fig. 1.

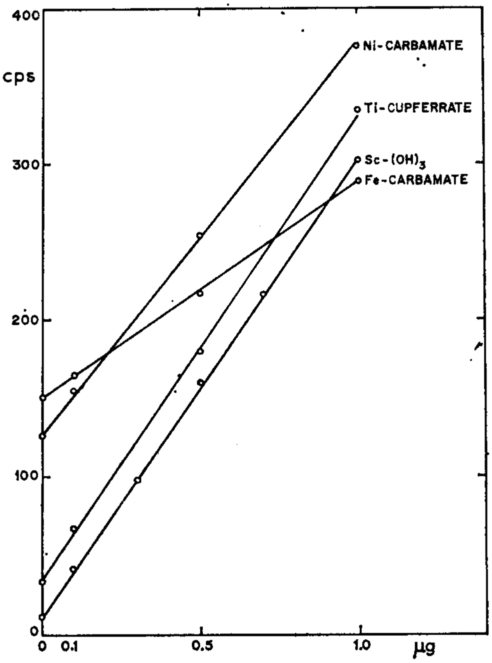

Fig. 2. Calibration graphs for Ni, Ti, Sc and Fe.

it should be soft enough to permit sliding the mask back or forth in order to adjust the position of the circle of precipitate over the hole in the mask. Sisco 300 stopcock grease (Swedish Iron and Steel Corporation of Elizabeth, New Jersey) was used in the present work. Phenylfluorone precipitates tend to cause the paper disks to curl up on drying. In such cases it may be desirable to use a mask supplied with a circular clamping ring to hold the disk flat.

X-RAY ANALYSIS OF TRACE ELEMENTS

In most of the present work a General Electric XRD 6 X-ray spectrograph with a W target, a LiF crystal, a 10-mil Soller slit and a dual counter made up of a SPG-7 flow proportional counter backed up by a scintillation counter was used. However, in the determination of a few of the elements, it was necessary to use a chromium (or titanium) target and an appropriate crystal. In order to obtain high sensitivity, the X-ray spectrograph was operated at maximum power and helium was used in all the analyses.

In most instances, of course, the K line of an element should be used in preference to an L line. However, where the K radiation of a metal is very hard, higher counts can be obtained if an L line is used, and a further 4- or 5-fold increase in sensitivity can be had by measuring this same L line in conjunction with a chromium (or titanium) target. In fact, when the wavelength of the X-ray line used in the determination of an element, be it the K line or an L line, exceeds 2.5 Å, the Cr (or Ti) target should usually be used. The elements which should be determined with a Cr (or Ti) target are shown in Table I.

TABLE I

ELEMENTS THAT SHOULD BE DETERMINED WITH A CHROMIUM TARGET

LiF			*EDT or PET*	*ADP*
Ti(Kα)	Ba(Lα)	Sb(Lα)	Cl(Kα)	Mg(Kα)
Sc(Kα)	Cs(Lα)	Sn(Lα)	S(Kα)	
Ca(Kα)	I(Lα)	In(Lα)	P(Kα)	*NaCl*
K(Kα)	Te(Lα)	Cd(Lβ)	Si(Kα)	Cl(Kα)
	Xe(Lα)		Al(Kα)	S(Kα)

The sensitivity in the X-ray analysis varies from a low of about 2 net counts per sec per μg for magnesium to a high of about 300 net counts/sec/μg for such elements as nickel, titanium and scandium. Most of the elements yield 20–100 net counts/sec/μg.

The present work has been limited, for the most part, to the determination of 50-μg quantities of the various elements. However, the precipitation of submicrogram amounts of such elements as Ni, Fe, Ti and Sc has been studied, in order to determine the effectiveness of coprecipitation and the ultimate sensitivity of the X-ray method. Calibration graphs covering the range 0–1 μg of these elements are shown in Fig. 2. In this work, nickel was precipitated at pH 9 with carbamate, titanium was precipitated in 1%(v/v) sulfuric acid solution with cupferron, scandium was precipitated as hydroxide and iron(III) was precipitated at pH 2 with carbamate, using, in all cases, 50 μg of a suitable coprecipitant. From Fig. 2 it is seen that the graphs obtained are linear, which suggests that the precipitation of the 4 elements is quantitative and that as little as 20 ng of nickel, titanium and scandium can be separated and determined.

PREPARATION OF CALIBRATION GRAPHS

Calibration graphs are made by precipitating and determining known quantities of the trace elements in the manner to be used in an actual analysis. The prepared standard disks are reasonably permanent. Blank disks, containing only the co-precipitating element, must also be prepared for use in obtaining the net counts in the calibration and analyses. The scattered background for a blank disk usually amounts to about 10–300 counts/sec, depending on the element being determined. Of course, the background counts obtained at the wavelengths of elements present in the X-ray target tube will be much higher. Hence, when tungsten is to be determined, it will be desirable to use a Cr, Mo or Pt target in place of a tungsten target. And, of course, the tungsten target should be used to determine chromium. Furthermore, it is advisable, when aluminum is to be determined, to use a brass mask in place of the usual aluminum mask in order to keep the scattered background to the minimum.

The calibration graphs obtained for most of the elements will be linear up to at least 200 or 300 µg of the element. However, if the measured X-radiation, be it from a K line or an L line of an element, is of long wavelength, infinite thickness will be more quickly attained with an increase in element concentration and hence linearity may not extend much beyond 100 µg of the element.

In order to obtain accurate and reproducible results it will be necessary to limit the amount of an element taken for analysis so that the precipitate obtained will not agglomerate before the filtration and will not crack, peel off or become powdery on drying.

PRECIPITATION OF ELEMENTS WITH CARBAMATE AND AMMONIUM HYDROXIDE

The elements that are quantitatively precipitated with carbamate and ammonia

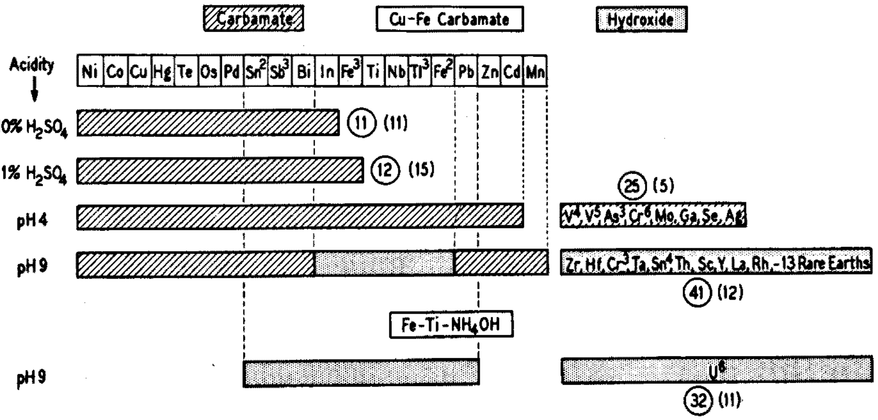

Fig. 3. Precipitation with carbamate and ammonia.

solution are shown in Fig. 3. Precipitation was made as follows. Aliquots containing 50 μg of the various elements were added to 25 ml of 10% or 1% (v/v) sulfuric acid or a mixture of 15 ml of water plus 10 ml of pH 4 buffer solution (37 g of anhydrous sodium acetate in 500 ml of water, add 143 ml of glacial acetic acid and dilute to 1 l). Then 50 μg of copper(II) was added to act as a coprecipitant and the trace elements were precipitated by adding 5 ml of a freshly prepared and filtered aqueous 2% carbamate solution. The solution was allowed to stand for 5 min and then filtered through the paper disk. If desired, hydrochloric acid can be used in place of sulfuric acid, in the above procedure.

When precipitation was to be made at pH 9, the elements plus 50 μg of iron(III) and copper(II), to act as coprecipitants, were added to 15 ml of water containing 2 drops of hydrochloric acid. The solution was neutralized to the purple color of *m*-cresol purple with ammonia solution and the carbamate elements were then precipitated. When precipitation of only the hydroxide elements was desired, 100 μg of iron(III) was used as the coprecipitant and the solution was filtered immediately after neutralization to pH 9.

In general, it is best to add an extra drop (or more with La or Th) of ammonia solution after the color of the solution turns purple, in order to assure complete precipitation of the hydroxide elements. However, when working with such amphoteric elements as zinc (and probably others), the excess of ammonia should not be added, otherwise incomplete recovery will result.

In the figure and in some of the subsequent figures the recommended coprecipitating elements are shown in clear blocks. The first element shown should be used to gather all the elements except, of course, itself. The second should be used when the first one is to be determined. The chemical symbols refer to the elements present in their normal valence states. Exceptions to this rule are indicated. If an element is missing it means that it does not precipitate, or only precipitates in part.

In order to avoid confusion, the elements that are partially precipitated with carbamate and ammonia solution have not been listed in the figure. Instead, the number that are quantitatively precipitated are indicated in circles and the number that are partially precipitated are indicated in parentheses after or beside the various blocks. In general, if an element is listed as quantitatively precipitated at one acidity and is unlisted at the next higher acidity, the element will usually be found to be partially precipitated at the higher acidity.

In addition to the elements that are only partially precipitated by a particular reagent there are many, which by themselves will not precipitate, but which will tend to accompany other precipitated elements by adsorption, occlusion or by forming an insoluble compound with these elements. This is particularly true when precipitation is made with ammonia. Moreover, when an organic precipitant is used, small amounts of gold and some of the platinum metals will be reduced to the elemental state, and will be found in the precipitates if these noble metals are present in the solution.

Before considering the figure in detail it is important to insert a word of caution. In order to save time the data shown in the figure were obtained by analyzing groups of 5 elements each. This may turn out to have been an important factor in determining which elements are quantitatively precipitated, if it is true that the effectiveness of coprecipitation is greater, the larger the ratio of coprecipitant to trace element.

From Fig. 3 it is seen that the selectivity of carbamate increases with an increase in the acidity at the time of precipitation. This makes it possible to separate the first 11 elements listed from many elements whose carbamate complexes are weaker and, of course, from the hydroxide elements, the alkalis, the alkaline earths, gold and most of the platinum metals. Thus, for example, it has been shown that in 1% sulfuric acid solution, traces of any of the 11 elements can be recovered from as much as 1 g of manganese.

Contrary to the data shown in Fig. 3, Os does not precipitate with carbamate. Both tin(II) and antimony(III) are quantitatively precipitated as carbamate from solutions of pH 9 to 10% sulfuric acid but recovery of arsenic(III) as carbamate[8] is quantitative only at pH 4. At pH 9, tin(IV) is quantitatively precipitated as hydroxide but the precipitation of tin(IV) as carbamate is increasingly incomplete as the acidity increases. Recoveries of arsenic(V) and antimony(V) are incomplete or nil at pH 9 or in acid solution. Iron(III) is only partially precipitated from 10% sulfuric acid solution but recovery is virtually complete from 1% sulfuric acid solution. Precipitation of traces of thallium(I) by carbamate is incomplete, but quantitative precipitation of thallium(III) is possible at pH 4 provided that iron(III) or copper(II) is used as the coprecipitant. Strangely, if cobalt is used as the coprecipitant, the recovery of thallium(III) is very low. At pH 9, thallium(III) precipitates quantitatively as hydroxide. Manganese is quantitatively precipitated as carbamate at pH 9, but at pH 4 the carbamate precipitate formed redissolves very rapidly on standing and at higher acidities no precipitation occurs. Even if the filtration is made immediately, the recovery of manganese at pH 4 tends to be low. It is seen that chromium(VI) precipitates at pH 4 as carbamate, whereas chromium(III) precipitates at pH 9 as hydroxide. At pH 4, gallium but not aluminum is precipitated as carbamate, but at pH 9 the recovery of these two metals as hydroxide is nil because of their amphoteric nature. Even when the solution is controlled at pH 6, precipitation of their hydroxides is highly incomplete. The precipitation of uranium(VI) as hydroxide is quantitative

TABLE II

THE USE OF EDTA AND CITRATE AS COMPLEXING AGENTS IN THE CARBAMATE METHOD

Cu–Co–Carbamate

EDTA		*Citrate*
pH 4	*pH* 9	*pH* 9
Cu	Cu	Cu
Hg	Hg	Hg
Pd	Pd	Pd
Co	—	Co
Bi	Bi	—
Cr^{6+}	Te	Fe^{2+}
As^{3+}	—	Ni
Se	—	Zn
(12)	(2)	(10)

when 100 μg of iron(III) is used as the coprecipitant, but strangely, it is somewhat incomplete in the copper–pH 9–carbamate method.

The selectivity of precipitation by carbamate and ammonia can be markedly altered by the use of certain complexing agents. The elements that are quantitatively precipitated in the presence of 0.2 g of EDTA or ammonium citrate are shown in Table II. It can be seen that the carbamate complexes of copper, mercury and palladium must be very strong since they resist the complexing action of both EDTA and citrate. Moreover, it is seen that cobalt is complexed by EDTA at pH 9 but not at pH 4 and that, while iron(III) is partially complexed by citrate, iron(II) is not. The information in the Table should be useful in the determination of the elements shown.

An investigation of the use of sodium hydroxide as a precipitant has not yet been made but, without doubt, several interesting applications of this reagent will eventually be found.

PRECIPITATION WITH CUPFERRON AND PHENYLFLUORONE

The elements that are quantitatively precipitated with cupferron and phenylfluorone are shown in Fig. 4. They were precipitated in 50 ml of 10% or 1% (v/v) sulfuric acid or in 15 ml of water plus 10 ml of pH 4 buffer solution by the addition of 5 ml of a freshly prepared aqueous 1% solution of cupferron; or in 25 ml of 1% sulfuric acid or in 15 ml of water plus 10 ml of pH 4 solution with 10 ml of phenylfluorone solution[9]. When precipitating from 1% sulfuric acid solution with phenylfluorone, the solution was allowed to stand for 10 min before filtration.

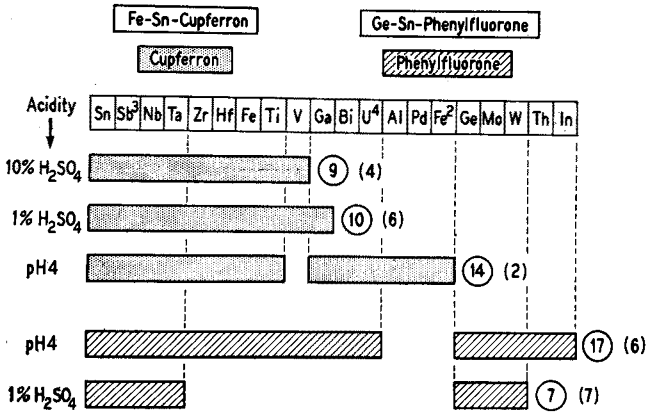

Fig. 4. Precipitation with cupferron and phenylfluorone.

The data in the figure were obtained with sulfuric acid as the acid. However, 1% hydrochloric acid can be used in place of 1% sulfuric acid, if desired. On the other hand, recovery of some of the elements is low when 10% hydrochloric acid is used. In fact, the precipitation of certain elements such as iron and vanadium tends to be slightly incomplete even in 10% sulfuric acid solution. In general, it will be best to precipitate in 1% acid solution wherever possible. Under certain conditions, recovery of iron and vanadium may be quite low when precipitation is done in 10% sulfuric acid in the presence of tantalum. However, more work on this needs to be done.

From Fig. 4, it can be seen that, here again, the precipitants become increasingly specific as the acidity at the time of precipitation increases. This is especially true with phenylfluorone. It is also seen that the behavior of the two reagents is remarkably similar, especially at pH 4. However, there are some striking differences. Thus, molybdenum and tungsten, which are normally included in the cupferron group of elements cannot, in trace quantities, be quantitatively precipitated with cupferron, whereas they can be with phenylfluorone. In addition, such elements as germanium, thorium and indium can also be precipitated with phenylfluorone. On the other hand, cupferron precipitates aluminum, palladium and iron(II). Surprisingly, vanadium(V) does not precipitate at pH 4 with cupferron, but does so with phenylfluorone. As expected, uranium(IV) but not uranium(VI) is precipitated with cupferron or phenylfluorone at pH 4. In order to prevent reoxidation of the uranium(IV) before its precipitation by cupferron, titanium(IV) should be used as the coprecipitant in place of iron(III).

Except for the fact that it will precipitate germanium, molybdenum and tungsten, the phenylfluorone reagent is inferior to cupferron as a wide-spectrum precipitant because the amount of element that can be handled is limited, owing to the limited solubility of the reagent itself in water.

Tests on the use of complexing agents in the precipitation with cupferron and phenylfluorone at pH 4 have yielded no practical results but it has been established that in 1% sulfuric or hydrochloric acid solution containing hydrogen peroxide the precipitation of germanium and tin is quantitative while that of the other five elements that normally precipitate in 1% acid is largely suppressed. Moreover, if both hydrogen peroxide and EDTA are present, germanium alone precipitates quantitatively.

PRECIPITATION WITH HYDROGEN SULFIDE

Thirty-three elements form insoluble sulfides that are of use in analytical chemistry. Twenty-two of these form insoluble sulfides in fairly strong acid solution (*ca.* 0.3 *N*) and of these about 10 can be quantitatively precipitated in 1:1 sulfuric acid solution. Certain of the elements require special conditions for precipitation. In the present work it has been shown that traces of such elements as Pt, Pd, Re and Au can be quantitatively precipitated from hot 20% sulfuric acid solution provided that 200 μg of tellurium is used as a coprecipitant; and that traces of Pb, Cd and Zn can be recovered from pH 4 solution or traces of Ru from hot 5% HCl solution if bismuth is used as the coprecipitant. In general, it is best to use the minimum amount of coprecipitant and to avoid standing or warming in order to prevent agglomeration.

MISCELLANEOUS ANALYSES

Cesium, rubidium and potassium with tetraphenylboron

The solubility of the tetraphenylboron compounds of the alkalis increases in the order Cs, Rb and K. To determine these elements, precipitate rubidium or potassium plus 200 μg of cesium as a coprecipitant in 15 ml of 1% hydrochloric acid with 1 ml of 2% tetraphenylboron solution. Allow to stand for 5 min and filter on black paper. Proceed in the same manner for determination of cesium but use 200 µg of rubidium as the coprecipitant.

Palladium with dimethylglyoxime

Precipitate the palladium, without the use of a coprecipitant, in 15 ml of 1% hydrochloric acid solution with 1 ml of ethanolic 1% solution of dimethylglyoxime. Allow to stand for 10 min and filter.

Nickel with α-benzildioxime

Microgram quantities of nickel cannot be quantitatively precipitated with dimethylglyoxime. However, the solubility of the α-benzildioxime compound is much less and the precipitation of nickel with this reagent is quantitative in ammoniacal solution. Obtain the nickel in 15 ml of dilute hydrochloric acid solution, neutralize to the purple color of *m*-cresol purple with ammonia solution and precipitate by the addition of 2 ml of a 0.05% solution of α-benzildioxime in acetone.

Citrate cannot be used to prevent the precipitation of the hydroxide elements since it tends to complex the nickel and prevent its quantitative precipitation. Fortunately, tartrate does not complex nickel. The only elements that will interfere are copper and cobalt. They can be removed on a Dowex-1 anion-exchange column in 8 *N* hydrochloric acid solution. Such a separation will, of course, remove 25 or more other elements.

Barium, strontium and calcium as phosphate

Obtain the barium, strontium or calcium in 15 ml of water. Add 1 ml of 10% diammonium hydrogen phosphate solution plus 100 µg of beryllium and 2 drops of hydrochloric acid. Neutralize just barely to the purple color of *m*-cresol purple. Filter immediately on black paper and wash.

Barium as chromate

Dilute the barium solution plus 500 µg of lead as a coprecipitant to 15 ml, neutralize to pH 9 with ammonia solution, add potassium chromate, allow to stand for 5 min and filter. Precipitation of lead, with barium as the coprecipitant, is incomplete.

Strontium and calcium as carbonate

Obtain the calcium or strontium plus 2 mg of barium as the coprecipitant in 15 ml of neutral solution, add 3 ml of 1% sodium carbonate solution, allow to stand for 5 min, and filter on black paper. Precipitation of barium, with Sr or Ca as the coprecipitant, is incomplete. Traces of the alkaline earths cannot be quantitatively precipitated with sodium rhodizonate.

Magnesium as hydroxide

The absorption of magnesium radiation by heavy elements is severe. Hence, the use of a coprecipitant should be avoided if possible. In the absence of other hydroxide elements, obtain the magnesium in 5 ml of dilute hydrochloric acid solution, neutralize to the purple color of *m*-cresol purple with 4% sodium hydroxide solution, add 2 drops in excess and filter immediately. This is not an ideal way to determine magnesium because when a calibration graph covering the range 0–100 μg Mg is obtained, it is seen that the precipitation is progressively incomplete as the amount of magnesium decreases. However, in the absence of a better precipitant, the method is reasonably satisfactory.

Xenon as barium perxenate

Tests have been made on the precipitation of xenon from a solution of xenon fluoride dissolved in water. Obtain 25–200 μg of xenon plus 500 μg of silver as the coprecipitant in 5 ml of water, add 1 ml of barium hydroxide solution (5 mg Ba/ml) and filter immediately on 0.8-μ paper with gentle suction. Measure the wet disk immediately on the X-ray spectrograph. The counts obtained decrease on repeated X-ray measurement. The calibration graph obtained over the range of 25–200 μg Xe is reasonably linear.

Silver and thallium(I) as iodide

Precipitate silver as iodide from 15 ml of 1% sulfuric acid solution with 200 μg of thallium(I) as the coprecipitant; or precipitate thallium(I) in the same manner with 200 μg of silver as the coprecipitant.

Iridium as hydrated dioxide

Oxidize the Ir to the quadrivalent state in 1% HCl solution by boiling with an excess of $NaBrO_3$. Neutralize the boiling solution to pH 8 with 10% $NaHCO_3$ solution and then cool before the filtration.

Tellurium, selenium, mercury, gold, platinum and palladium by reduction to the element

Obtain 50 μg of the element plus 100 μg of tellurium as the coprecipitant in 25 ml of 35% hydrochloric acid solution. Add 1 ml of hypophosphorous acid solution (50%) and heat to 80°. Cool to 30° and filter on a 0.8-μ white paper. Do not wash. When tellurium is to be determined, use 100 μg of gold as the coprecipitant. Precipitation of silver and rhodium is incomplete.

Phosphorus by precipitation as beryllium phosphate

Convert the phosphorus to orthophosphate. Dissolve in 15 ml of water containing 2 drops of concentrated hydrochloric acid. Add 200 μg of beryllium as a salt. Neutralize just barely to the purple color of *m*-cresol purple with ammonia solution. Filter immediately on black paper and wash.

Silicon by dehydration to silicon dioxide

Transfer the silicic acid to a platinum dish. Add 200 μg of chromium(III) as a salt plus 10 drops of concentrated sulfuric acid and evaporate to copious white fumes. Cool, add 15 ml of water, police the platinum dish and stir to mix; filter on 0.8-μ white paper and wash with 3 ml of water and then with 0.5 ml of aqueous 0.01% solution of *m*-cresol purple to color the precipitate on the disk.

Iodide, bromide and chloride by precipitation with silver

Precipitate bromide or chloride with silver using 50 μg of iodide as the coprecipitant; or precipitate iodide in the same manner with bromide as the coprecipitant. In order to keep interelement interference to the minimum, the excess of silver used for the precipitation should not be too great and the precipitate on the paper disk should be washed relatively free of silver. In the determination of chloride, the line interference of the LL line of silver is negligible when no silver other than that associated with the halide precipitate is present. Greater sensitivity can be obtained in the X-ray analysis of chloride if a sodium chloride crystal is used in place of a PET or EDT crystal.

Sulfur by precipitation as barium sulfate

Oxidize the sulfur to sulfate. Obtain the sulfate sample in 8 ml of neutral or dilute hydrochloric acid solution. Add 8 ml of ethanol and mix well. Add 200 μg of selenium as sodium selenate and then, if necessary, neutralize just to the yellow color of methyl red. Add 2 mg of barium as barium chloride, allow to stand for 5 min, filter on low-sulfur white (or preferably black) paper and measure on the X-ray spectrograph using a chromium target and a sodium chloride crystal.

Selenium by precipitation as barium selenate

Oxidize to the selenium(VI) state and then proceed as directed above but use 200 μg of sulfur as sulfate to act as the coprecipitant and measure with a tungsten target and a lithium fluoride crystal.

APPLICATIONS OF THE METHOD

The method has been extensively used in these laboratories for the determination of trace elements in pure metals and alloys. Another useful application has been in the determination of traces of zinc in gallium phosphide. The zinc is precipitated as carbamate from a pH 9 solution containing enough citrate to prevent precipitation of the gallium. The high accuracy and sensitivity of the method has also made it possible to obtain a complete analysis of tiny ferromagnetic bits used in memory devices. In addition, the method has been used to help solve the difficult problem of the determination of traces of Hf in Zr metal or Zr in Hf metal[10]. Preliminary tests have also shown that if a Selas Flotronic disk of porous silver (Selas Flotronics, Spring House, Pennsylvania) is used in place of a paper disk in the filtration of trace elements, they can be determined with a solid mass spectrograph instead of an X-ray spectrograph. This should be a very useful form of analysis in view of the extremely high sensitivity available and the fact that the light elements can be determined. It is evident, also, that the coprecipitation separation technique can be used to concentrate trace elements in spectrophotometric, emission spectrographic and atomic absorption analyses.

To date, the method has not been used in organic, biological, water or air pollution analyses but it is obvious that it will prove to be very useful in these fields.

The present paper is meant to serve only as an introduction to the new technique of coprecipitation–X-ray ("coprex") analysis. Further work will be required to put the method on a sound quantitative basis, to provide methods of analysis for the elements for which methods are lacking and to explore the use of other precipitants.

It is obvious that this method will find wide application throughout the field of trace analysis and may eventually replace a large number of the emission spectrographic, spectrophotometric, atomic absorption and polarographic methods in current use.

SUMMARY

A new, almost universally applicable method for the trace analysis of inorganic and organic materials is described. The trace element (or elements) together with a suitable coprecipitating element is isolated from interfering elements by precipitation with a suitable organic or inorganic precipitant. The precipitate is then filtered on a paper disk and the collected trace element (or elements) is determined by X-ray analysis.

RÉSUMÉ

On décrit une méthode quasi universelle pour l'analyse de traces de substances inorganiques et organiques. Le ou les éléments, en trace, sont isolés au moyen d'un élément de coprécipitation d'avec les éléments gênants par précipitation avec un réactif organique ou inorganique. Le précipité est ensuite filtré sur un disque de papier; le ou les éléments recueillis sont dosés par analyse aux rayons-X.

ZUSAMMENFASSUNG

Zur Bestimmung von Spurenelementen werden diese zusammen mit einem anderen Element durch Mitfällung abgetrennt und der abfiltrierte Niederschlag mit Hilfe der Röntgenspektralanalyse untersucht.

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SINGLE-STEP RADIOCHEMICAL SEPARATIONS BY COLUMN PROCEDURES IN ACTIVATION ANALYSIS

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Besides the usual ion-exchange methods, other column procedures such as isotopic exchange, reverse-phase chromatography and the use of resins converted into particular forms, can be regarded as attractive techniques in order to increase the possibility of selective retention of given activities. Moreover, a combination of the different techniques allows fast and simple single-step group separations by successive trapping of each activity on a suitable bed from the same medium.

In this paper, some single-step radiochemical separations are described. These procedures, for both individual and group activity separations, were successfully employed particularly for biological problems.

High chemical recoveries and cross-decontaminations must be obtained, while a moderate selectivity may still be adequate, as the interfering activities can be retained on another resin bed in a preliminary step; moreover, the number of elements to be separated is generally not large, since a first group subdivision is normally founded on the half-life characteristics of the activities produced.

Normal ion-exchange resins, of both anionic and cationic type, were of course useful for developing a separation scheme, but less usual techniques were also considered:

(*1*) Reverse-phase chromatography, which is widely used in radiochemistry (see, e.g., refs. 1, 2), but not particularly for activation analysis[3], despite its attractive features of selectivity and flexibility.

(*2*) Isotopic exchange, which offers remarkable advantages such as operative simplicity and rapidity, but has not been widely adopted for problems in activation analysis[4–9].

(*3*) Use of exchange resins in special forms, which can be used in order to improve the possibility of retention by including a number of different reaction mechanisms such as complex formation, oxidation–reduction, isotopic exchange and possibly precipitation reactions.

SEPARATION OF SINGLE ACTIVITIES

Some selective separations were developed for individual elements from strong acid solutions, which are generally obtained after the sample dissolution step. In particular, a 2 *N* hydrochloric acid medium was adopted and tested for single activity separations to be combined in a group separation scheme.

Molybdenum

The highly selective extraction of the α-benzoinoxime complex of molybdenum(VI) formed the basis of a reverse-phase chromatography procedure. A 2 *N* hydrochloric acid solution containing 10–50 μg of molybdenum carrier was passed through a column (0.5 cm diameter and 7 cm height) of powdered polytetrafluoroethylene (Algoflon "F", Montecatini) supporting α-benzoinoxime, at a rate of 0.5–1 ml/min.

The columns were prepared before use by mixing 1 g of Algoflon with 1 ml of an acetone solution of α-benzoinoxime (0.5 g/ml), drying at 70° and thoroughly mixing with 1 ml of chloroform.

Quantitative recoveries for molybdenum were constantly obtained with washing volumes up to 30 ml (see Table I). The only serious interference was found to be tungsten(VI), which is retained quantitatively on the column, at least when diluted tungstate solutions are used (about 1 μg W/ml). Because of the much higher tungsten sensitivity, the presence of tungsten sets a severe limitation to the analysis for molybdenum; however, when normal techniques are used, *e.g.*, suitable waiting periods and correction with standard spectra, both elements can be determined without further separations, in the range of Mo/W concentration 1700 to 0.3.

TABLE I

SEPARATION OF INDIVIDUAL ELEMENTS BY COLUMN PROCEDURE

(2 *N* HCl, 25 ml washing, 1 ml/min, 10–100 μg carrier)

Column (diam. × height in cm)	*Element (% retention)*	*Elements removed*[a]
α-Benzoinoxime in $CHCl_3$ on Algoflon (0.5×7)	Mo(VI) (96±2)	Alkali metals, alkaline earths, R.E., As, Au[b], Br^-, Co, Cr^{3+}, Cu, Fe, Mn, PO_4^{3-}, Sb, Tc, Zn
Precipitated Au on quartz powder (0.5 × 10)	(99±1)	Alkali metals, alkaline earths, R.E., As, Br^-, Co, Cr^{3+}, Cu, Fe, Mn, Mo, PO_4^{3-}, Sb, W, Zn
Dowex 50-X4 resin, 20° (0.5×30)	Au (96±2)	
40° (0.5×15)	(97±1)	
60° (0.5×10)	(95±1)	

[a] Generally more than 99% removed.
[b] Partial retention (10%), possibly due to reduction.

Gold

A selective separation by isotopic exchange is easily made from hydrochloric acid media on precipitated metallic gold: quantitative yields were found from a 2 *N* hydrochloric acid solution (10–50 μg Au carrier) passed through a 0.5 × 10 cm column of 0.5 g of precipitated gold mixed with inert materials such as powdered quartz or asbestos at a flow-rate of 1 ml/min. The gold was precipitated by addition of hydrogen peroxide to $HAuCl_4$ solutions, after which the mixture was made alkaline and boiled and the precipitate was washed with acid.

Similar results were obtained with gold reduced after adsorption from 8 *N* hydrochloric acid on cationic resin (Dowex 50-X4, 50–100 mesh, about 0.85 meq Au/g wet resin; batchwise reduction as indicated above). Under these conditions, highly selective in 2 *N* hydrochloric acid media, quantitative recoveries were obtained when a 0.5 × 30 cm column was used; shorter columns were satisfactory at higher temperatures (see Table I).

Copper

A complete retention of the ^{64}Cu activity from hydrochloric acid media by anion exchange is difficult, owing to the rather low distribution coefficients for the copper(II) species normally existing in solution[9]. As the copper(I) chlorocomplexes are strongly adsorbed on anionic resins at moderately low hydrochloric acid normalities[9], a quantitative separation can be accomplished by isotopic exchange between copper(II) in 2 *N* hydrochloric acid solution and copper(I) fixed on an anionic resin.

The resin (Dowex 1-X10, 50–100 mesh) is prepared by adsorbing copper(I) from 1–2 *N* hydrochloric acid solution (about 0.2 meq/g wet resin); the resin is then washed and stored in distilled water. The copper(I) solution is prepared by bubbling sulfur dioxide through a copper(II) solution. A 0.5 × 7 cm column was found to retain quantitatively the ^{64}Cu activity (5–100 μg carrier), from a 2 *N* hydrochloric acid solution passed at a rate of 0.5–1.5 ml/min (see Table II).

TABLE II

SEPARATION OF INDIVIDUAL ELEMENTS BY DOUBLE STAGE COLUMN PROCEDURE

(40 ml washing, 1 ml/min, 5–100 μg carrier)

Column (diam. × height in cm)	*Medium*	*Element (% retention)*	*Guard bed*	*Elements removed*[a]	
				Guard bed adsorption	*Washing*
Dowex 1-X10 resin in Cu^+ form (0.5 × 7)	2 *N* HCl	Cu (99.5 ± 0.5)	Dowex 1-X10 resin in Cl^-form	Au, Cd, Hg, Sb(III), Zn	Alkali metals, alkaline earths, R.E., As, Co, Cr^{3+}, Mn, PO_4^{3-}, Sb(V)
Dowex 1-X10 resin in I^- form (0.5 × 10)	2 *N* HCl	Sb(V) (98.5 ± 1.5)	Dowex 1-X10 resin in Cl^-form	Au, Cd, Hg, Sb(III), Zn	Alkali metals, alkaline earths, R.E., As, Co, Cr^{3+}, Cu, Mn, PO_4^{3-}
Dowex 1-X8 resin in Mo(VI) form (0.5 × 5)	1 *N* H_2SO_4	As(V) (99.9 ± 0.1) PO_4^{3-} (99.3 ± 0.3)	Dowex 1-X8 resin in SO_4^{2-} form	Au[b], Hg[c], Mo(VI), Tc(VII), W(VI) (90%)	Alkali metals, alkaline earths, R.E., Co, Cr^{3+}, Cu, Fe^{3+}, Hg (95%), Mn, Sb, Zn

[a] Generally more than 99% removed.
[b] Little amounts of HCl present in the sample solution (0.01 *N* HCl).
[c] From 1 *N* H_2SO_4–0.1 *N* HCl solutions.

Antimony

Antimony(V) is not adsorbed on anionic resins at hydrochloric acid concentrations of less than 2 *N*, whereas for antimony(III), an adsorption maximum has been reported for 2 *N* hydrochloric acid[9]. The antimony(V) activity can therefore be separated on an anionic exchanger from 2 *N* hydrochloric acid only after a reduction process:

the reduction and adsorption may be simultaneously obtained by using a resin supporting a reducing agent such as iodide.

A 0.5 × 10 cm column of Dowex 1-X10, 50–100 mesh, partially in the iodide form (about 0.4 meq I/g wet resin), was used to separate quantitatively antimony(V) (10–50 μg carrier) from 2 *N* hydrochloric acid, at a rate of 0.5–1.5 ml/min (see Table II). A partial iodide oxidation to iodine, observed during the operation, did not affect the efficiency of the separation. The resin was prepared by passing an iodide solution in water through the column: the resin was then washed and stored in the dark under deionized water.

Arsenic and phosphate

Phosphate ions cannot be separated by the usual column procedure from strong acid at moderate and high concentrations. Rather low distribution coefficients for anion-exchange resins have been reported for arsenic(V) and very low ones for arsenic(III) from hydrochloric acid media[9] as well as for both valence states from sulfuric acid media[10,11], so that a separation of this element seems difficult. Quantitative separation for both arsenic(V) and phosphate can, however, be achieved from strong acid media, by using an anion-exchange resin in the molybdate form, as heteropolycomplexes are formed on the bed.

From 1 *N* sulfuric acid media, quantitative retentions for both elements (100–200 μg carrier) were found when a 0.5 × 5 cm column of Dowex 1-X8 resin (100–200 mesh, molybdate form at about 0.25 meq/g) was used at a flow-rate of 1 ml/min (see Table II). Since molybdate is slowly eluted from an anionic column with 2 *N* hydrochloric acid, low arsenic and phosphate recoveries were expected from this medium; however, considerable retentions were found even after prolonged washing, which were correlated to the partial reduction of molybdate on the resin to a more strongly adsorbed blue molybdenum complex. Actually when the resin was previously submitted to a reduction process with hydrazine, quantitative separations were obtained (see Table III).

TABLE III

SEPARATION OF ARSENIC(V) ON RESIN IN MOLYBDATE FORM FROM 2 *N* HYDROCHLORIC ACID

(0.5 × 5 cm column, 1 ml/min, 100 μg carrier)

Columns pre-treatment	*% As retention*		
	20-ml washing	*40-ml washing*	*80-ml washing*
None	97 ± 2	77 ± 6	41 ± 7
Hydrazine reduction	99.9 ± 0.1	99.5 ± 0.3	99.0 ± 0.5

Because of the difference in half-lives, the ^{76}As and ^{32}P activities do not interfere reciprocally in many cases, so that the method can then be employed for the determination of arsenic or phosphorus depending on the irradiation and decay programme.

The resin was prepared by passing molybdate solutions in 1 *N* sulfuric acid through the resin in the sulfate form; for the separation from 2 *N* hydrochloric acid media, a reduction with hydrazine and thorough washing was carried out.

The methods developed for molybdenum and gold allow a fast separation from most foreign activities, and can be considered more selective than the usual anion exchange from hydrochloric acid media. It must also be noted that the methods for copper, antimony, and arsenic with phosphate can be made highly selective, by simply placing a "guard" bed of the same resin in its normal form before the main resin bed. The few activities that show large adsorption coefficients for the selected acidity conditions are retained in the preliminary bed, the activity to be measured is adsorbed on the second one, and the other activities are removed by washing (see Table II).

SEPARATION OF ACTIVITY GROUPS

By combining the techniques reported above, it is possible to set up some separations of activity groups with a single passage on a composite column. In Table IV a separation scheme for 6 elements from 2 *N* hydrochloric acid media is illustrated.

TABLE IV

GROUP SEPARATION BY SINGLE-STEP COLUMN PROCEDURE

(2 *N* HCl–0.1 *N* Na^+, 40 ml washing, 1 ml/min, 50–100 μg carrier)

Element	*% retention*					
	1	*2*	*3*	*4*	*5*	*6*
Mo(VI)[a]	91.5±3.5	3	5	0.5	0.0	0.0
Au	11	88.5±2.5	0.5	0.0	0.0	0.0
Zn	0.3	0.5	98±2	0.5	0.0	0.0
As(V)	2	1.5	1	99.5±1.5	0.0	0.0
Cu	0.3	1	0.5	2.5	97.0±0.5	0.2
Sb(V)	0.3	1	0.5	3	0.3	95.5±1.5
Na	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$

1 = α-Benzoinoxime on Algoflon, 0.5 × 7 cm column.
2 = Precipitated Au on quartz powder, 0.5 × 10 cm column.
3 = Dowex 1-X10 resin in Cl^- form, 0.5 × 12 cm column.
4 = Dowex 1-X10 resin in MoO_3^{2-} form, reduced with hydrazine, 0.5 × 7 cm column.
5 = Dowex 1-X10 resin in Cu^+ form 0.5 × 7 cm.
6 = Dowex 1-X10 resin in I^- form, 0.5 × 10 cm.

[a] The daughter Tc activity is recovered on stage 3 along with zinc; interference on the latter element is generally negligible, owing to the differences in both half-life and γ-energy for ^{99m}Tc and ^{69m}Zn.

Since the method was used sometimes for the analysis of biological samples, the decontamination from the prevailing ^{24}Na is shown as well, when an acid medium containing some sodium is used; when more prolonged washing (60 ml) is employed, the decontamination factors for ^{24}Na are 2–5 times higher, while the yields for the activities separated remain practically unchanged. As the ^{32}P activity is retained together with ^{76}As, when biological samples are analysed, this stage was omitted and arsenic determined by other methods in the washing solution. The decontamination from ^{32}P was quite adequate for the other stages.

Glass columns (0.5 cm internal diameter and 60 cm in height) are used, the different beds being separated by an inert material such as 1-cm layers of quartz powder. A complete separation of the 6 elements from one another and from sodium-24 activities can be carried out in less than 1 h, and several samples can be simultaneously processed on different columns by the same operator. The column is then cut and each bed directly counted by γ-spectrometry.

Since in irradiated biological samples, such as plasma, the ^{198}Au and ^{122}Sb activities were found not to interfere mutually for γ-spectrometry measurements, and zinc was mostly determined through ^{65}Zn in a longer-lived activity group, a simplified separation method was adopted for gold, copper and antimony. A similar technique was also used for iron, zinc, as well as antimony on samples irradiated and cooled for longer periods. Both methods are based on the fact that iron(III), antimony(V) and gold are strongly adsorbed on cation-exchange resin, such as Dowex 50, from concentrated hydrochloric acid[12]. A double-stage column containing 0.5 × 10 cm of Dowex 50-X4 (100–200 mesh) and 0.5 × 20 cm of Dowex 1-X16 (50–100 mesh) was used for the shorter-lived ^{198}Au, ^{122}Sb and ^{64}Cu activities; for ^{59}Fe, ^{124}Sb and ^{65}Zn the same cation-exchange bed coupled with a 0.5 × 15 cm bed of Dowex 1-X10 (50–100 mesh) was employed. On the cation exchanger gold is quantitatively adsorbed from 8 *N* hydrochloric acid together with about 90% of the antimony(V): for the latter element quantitative recoveries were obtained from 10 *N* hydrochloric acid, as reported by NELSON *et al.*[12], but an 8 *N* concentration was found to represent the most favourable adsorption conditions for copper on the cation-exchange resin. The ^{64}Cu activity was found to be retained to a sufficient and constant extent for prolonged washing condi-

TABLE V

SEPARATION OF SHORT-LIVED ACTIVITIES BY DOUBLE-STAGE COLUMN PROCEDURE

(8 *N* HCl, 50 ml washing, 1 ml/min, 10–500 μg carrier)

Stage (diam. × height in cm)	*Activity*	*% retention*	*Further separation by elution (10 ml) (% retention)*
			12 N HCl–0.05 N NH_4I
Dowex 50-X4 resin	^{122}Sb(V)	90±2	3±2
(0.5 × 10)	^{198}Au	95±3	100±0.0
Dowex 1-X16 resin	^{64}Cu	66±2	
(0.5 × 20)			

TABLE VI

SEPARATION OF LONG-LIVED ACTIVITIES BY DOUBLE-STAGE COLUMN PROCEDURE

(8 *N* HCl, 50 ml washing, 1 ml/min, 100 μg carrier)

Stage (diam. × height in cm)	*Activity*	*% retention*	*Further separation by elution (10 ml) (% retention)*
			5 N HCl
Dowex 50-X4 resin	^{124}Sb(V)	95±2	99.5±0.2
(0.5 × 10)	^{59}Fe(III)	93±0.5	4±2
			2 N HCl
Dowex 1-X10 resin	^{65}Zn	99.9±0.1	100±0.0
(0.5 × 15)	^{60}Co	99.6±0.2	3.5±0.5

tions, only when resins with a high degree of cross-linking were used ($92 \pm 2\%$ for 20 ml of washing, and $66 \pm 2\%$ for 50 ml).

For the longer-lived activity group, ^{124}Sb and ^{59}Fe are adsorbed together on the cation-exchange stage and ^{65}Zn on the anion-exchange stage. In Tables V and VI the procedures are summarised, and the possibility of further separations for pairs of elements is reported as well. Actually, for a number of different cases, the activities separated together cannot be resolved simply by γ-spectrometry, and also for plasma samples, when cobalt has to be measured in the longer-lived activity group, the ^{60}Co activity is submerged by the predominant ^{65}Zn activity in the anion-exchange bed. In these instances a simple and fast 10-ml elution of the single beds allows a good separation with high yields.

Very high decontamination factors for ^{24}Na and ^{32}P are obtained by these methods, which are, however, not highly selective towards a number of activities that are adsorbed on the anion-exchange resin[9]; in the case of plasma analysis these activities do not interfere.

CONCLUSION

Some column procedures which are rather unusual in activation analysis, *e.g.* reverse-phase chromatography, isotopic exchange and the use of exchange resins converted into suitable forms, can be coupled with the ion-exchange methods widely employed, in order to have available selective and flexible techniques for developing simple and fast radiochemical separations by a single passage from the same selected medium. Such procedures could be readily automated, since no variation of the type and concentration of the eluting medium is required.

The techniques reported can be regarded as an example of the wide possibilities offered by the combination of the different column procedures for some analytical problems. Retention of individual elements which are not adsorbed on normal ion exchangers is possible, as well as selective separation of single elements and single-step separation of a number of elements.

SUMMARY

Some single-step column procedures are described for both individual and group activity separations. Besides the usual ion-exchange techniques, other methods such as reverse-phase chromatography, isotopic exchange and the use of resins converted into special forms were used. Fast and simple selective separations from 2 *N* hydrochloric acid are reported for Mo(VI), Cu(II), Sb(V), and for $AsO_4^{3-} + PO_4^{3-}$ from both 2 *N* hydrochloric acid and 1 *N* sulfuric acid; for Cu, Sb and As + P, the selectivity can be greatly increased by using a guard bed of resin in normal form. By combining the different techniques a single-step separation scheme for 6 elements (Mo, Au, Zn, As, Cu, Sb) in 2 *N* hydrochloric acid was developed; this allows high chemical recoveries, high cross-decontamination and very large decontamination from ^{24}Na to be reached, so that application for biological sample analysis can be envisaged. Simplified two-stage column separations for Au + Sb and Cu and Fe + Sb and Zn from concentrated hydrochloric acid (cationic and anionic resin beds coupled) are also reported.

RÉSUMÉ

Quelques procédés avec colonne à un palier sont décrits pour les séparations d'activités individuelles ou par groupes. En plus des techniques usuelles par échange d'ions, d'autres méthodes sont utilisées: chromatographie à phase réversible, échange isotopique et utilisation de résines sous des formes spéciales. Des séparations sélectives rapides et simples en milieu acide chlorhydrique 2 *N* sont proposées pour Mo(VI), Au, Cu(II), Sb(V), et pour $AsO_4^{3-} + PO_4^{3-}$ en milieu acide chlorhydrique 2 *N* et sulfurique *N*. On peut envisager une application pour des échantillons d'analyse biologique. Des séparations sur des colonnes simplifiées à deux étages sont décrites également pour Au + Sb et Cu, ainsi que Fe + Sb et Zn en milieu acide chlorhydrique conc. (lits de résine cationique et anionique couplés).

ZUSAMMENFASSUNG

Einige Kolonnenverfahren mit nur einem Schritt werden sowohl zur Trennung von Einzel- als auch Gruppen-Aktivitäten beschrieben. Neben den üblichen Ionenaustauschermethoden werden andere spezielle Verfahren verwendet. Schnelle und einfache selektive Trennungen aus 2 *N* HCl für Mo(VI), Au, Cu(II), Sb(V) und AsO_4^{3-} und PO_4^{3-} (diese auch aus 1 *N* H_2SO_4) werden beschrieben. Trennungsschemata für die 6 Elemente Mo, Au, Zn, As, Cu und Sb wurden entwickelt, die eine hohe chemische Rückgewinnung und eine sehr grosse Dekontamination von ^{24}Na erzielen, so dass eine Anwendung für die Analyse biologischer Proben erwogen werden kann. Vereinfachte 2-Stufen-Trennungen für Au + Sb und Cu und Fe + Sb und Zn aus konzentrierter Salzsäure werden ebenfalls angegeben.

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NUCLEAR MAGNETIC RESONANCE STUDIES OF PHOSPHORUS(V) PESTICIDES*

PART I. CHEMICAL SHIFTS OF PROTONS AS A MEANS OF IDENTIFICATION OF PESTICIDES

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As part of a study of the usefulness of NMR for determining the rates and product compositions in the aqueous hydrolysis of some of the more common pesticides containing a pentavalent phosphorus atom, the NMR spectra of some 40 compounds were gathered and interpreted. The detailed spectra of these materials are reported below along with some general observations that aid in the interpretation of the spectra of phosphorus(V) compounds.

Many publications both on ^{31}P resonance and on the proton resonance of phosphorus-containing compounds have appeared in the literature since KNIGHT's historic paper in 1949[1]. A recent review of ^{31}P resonance has been written by JONES AND KATRITZKY[2], and certain other references are pertinent[3-6]. This paper is concerned with proton magnetic resonance, since the instrumentation for such measurements is readily accessible to most research groups.

The use of proton magnetic resonance (NMR) for the elucidation of structures of organic molecules is dependent on the recognition and interpretation of certain characteristics of NMR spectra, chemical shift and spin-coupling. First, the chemical shift (signal position) can be related, often quantitatively[7], to the molecular environment of any particular homogeneous fragment or functional group, and second, the signals of a homogeneous group of protons are often complicated by spin–spin interactions due to perturbations of the resonance signal by neighboring protons. Since the signal strength in a spectrum is directly proportional to the number of protons causing it, this factor results in spectra containing recognizable patterns, which often can be easily correlated with molecular structure, a topic reviewed recently by DYER[8]. In this paper, the overall changes in pattern brought about in the NMR spectrum of an organic molecule by the presence of a pentavalent phosphoric ester group are discussed.

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EXPERIMENTAL

Spectra were measured with a Varian A-60 NMR spectrometer calibrated with TMS as zero in carbon tetrachloride or deuteriochloroform as solvent. Chemical shifts were measured in parts per million (p.p.m.) downfield from internal TMS and coupling constants were measured in cycles per second (c.p.s.) on expanded spectra taken at a sweep width of 100 c.p.s. at a sweep rate of 250 sec. In situations where multiplets could not be analyzed easily, a range is reported for the value of the chemical shift. The materials used in this study were industrial analytical standards and were used without further purification. The details of the spectra for the model compounds are listed below.

Abate (I)

Doublet (12H) at 3.85 p.p.m. (OCH_3), $J_{PH}=14$ c.p.s.; Quartet (4H) at 7.18 p.p.m. (aromatic).

Aspon (II)

Triplet (12H) at 1.0 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Sextet (8H) at 1.73 p.p.m. (CH_2), $J_{CH}=7$ c.p.s.; Sextet (8H) at 4.10 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.

Azodrin (III) ($DCCl_3$)

Singlet (3H) at 2.53 p.p.m. ($CH_3C=C$); Doublet (3H) at 2.80 p.p.m. (CH_3N), $J_{CH}=5$ c.p.s.; Doublet (6H) at 3.83 p.p.m. (OCH_3), $J_{PH}=11$ c.p.s.; Singlet (1H) at 5.89 p.p.m. ($HC=C$); Broad Singlet (1H) at 7.1 p.p.m. (NH).

Baytex (IV)

Singlet (3H) at 2.30 p.p.m. ($ArCH_3$); Singlet (3H) at 2.83 p.p.m. (CH_3S); Doublet (6H) at 3.75 p.p.m. (OCH_3), $J_{PH}=14$ c.p.s.; Multiplet (3H) at 6.9 p.p.m. (Ar–H).

Betasan (V)

Quartet (12H) at 1.3 p.p.m. (CH_3), $J_{PH}=2$ c.p.s., $J_{CH}=6$ c.p.s.; Broad Multiplet (4H) at 2.7–3.3 p.p.m. (NCH_2CH_2S); Septet (2H) at 4.75 p.p.m. (OC–H), $J_{CH}=6$ c.p.s., $J_{PH}=6.5$ c.p.s.; Broad Singlet (1H) at 5.85 p.p.m. (NH); Multiplet (5H) at 7.4–8.0 p.p.m. (Ar–H).

Bidrin (VI)

Singlet (3H) at 2.19 p.p.m. ($CH_3C=C$); Doublet (6H) at 2.97 p.p.m. ($N–CH_3$), $\delta=7$ c.p.s.; Doublet (6H) at 3.82 p.p.m. (OCH_3), $J_{PH}=12$ c.p.s.; Quartet (1H) at 6.08 p.p.m. ($H–C=C$), $J_{CH}=1$ c.p.s.

Ciodrin (VII)

Doublet (3H) at 1.50 p.p.m. (CH_3), $J_{CH}=6$ c.p.s.; Singlet (3H) at 2.35 p.p.m. ($CH_3C=C$); Doublet (6H) at 3.72 p.p.m. (OCH_3), $J_{PH}=11$ c.p.s.; Quartet (1H) at 5.83 p.p.m. ($CH_3–C–\underline{H}$), $J_{CH}=6$ c.p.s.; Singlet (1H) at 5.78 p.p.m. ($C=C–H$).

Compound 4072 (Shell) (VIII) 91% β-isomer

Double Triplet (6H) at 1.25 p.p.m. (CH_3), $J_{CH}=7$ c.p.s., $\delta=1.5$ c.p.s.; Pentet

(4H) at 4.1 p.p.m. (OCH_2), $J_{PH}=9$ c.p.s., $J_{CH}=7$ c.p.s.; Doublet (.9H) at 5.9 p.p.m. ($HC=C$), $J_{PH}=1.5$ c.p.s.; Doublet (.1H) at 6.54 p.p.m. ($HC=C$), $J_{PH}=3.0$ c.p.s.; Multiplet (3H) at 7.38 p.p.m. (Ar–H).

Co-Ral ($DCCl_3$) (IX)

Triplet (6H) at 1.4 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Singlet (3H) at 2.6 p.p.m. ($ArCH_3$); Octet (4H) at 4.3 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=10$ c.p.s.; Multiplet (3H) at 7.2–7.8 p.p.m. (Ar–H).

Diazinon ($DCCl_3$) (X)

Triplet (6H) at 1.4 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Doublet (6H) at 1.46 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Singlet (3H) at 2.46 p.p.m. ($ArCH_3$); Sextet (1H) at 3.1 p.p.m. ($C\underline{H}$–Me_2), $J_{CH}=7$ c.p.s.; Octet (4H) at 4.35 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s.; $J_{PH}=11$ c.p.s.; Singlet (1H) at 6.6 p.p.m. (Ar–H).

Dicapthion (XI)

Doublet (6H) at 3.9 p.p.m. (OCH_3); Multiplet (3H) at 7.4–8.4 p.p.m. (Ar–H).

Dimethoate (XII)

Doublet (3H) at 2.85 p.p.m. (NCH_3), $J_{CH}=5$ c.p.s.; Doublet (2H) at 3.53 p.p.m. (SCH_2CO), $J_{PH}=18$ c.p.s.; Doublet (6H) at 3.80 p.p.m. (OCH_3), $J_{PH}=15$ c.p.s.

Dioxathion (XIII) ($DCCl_3$)

Triplet (12H) at 1.35 p.p.m. (CH_3), $J_{CH}=6$ c.p.s.; Multiplet (12H) at 3.7–4.4 p.p.m. (OCH_2); Quartet (2H) at 5.5 p.p.m. (OCH), $J_{PH}=14$ c.p.s., $\delta=9$ c.p.s.

Disyston (XIV)

Triplet (3H) at 1.28 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Triplet (6H) at 1.40 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Multiplet (6H) at 2.4–3.4 p.p.m. (SCH_2); Octet (4H) at 4.15 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=10.5$ c.p.s.

Dursban (XV)

Triplet (6H) at 1.5 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Octet (4H) at 4.38 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.; Singlet (1H) at 7.85 p.p.m. (Ar–H).

Dyfonate (XVI)

Multiplet (6H) at 0.8–1.5 p.p.m. (CH_3); Sextet (2H) at 1.95 p.p.m. (PCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.; Multiplet (2H) at 3.9–4.5 p.p.m. (OCH_2), $J_{PH}=9$ c.p.s., peaks doubled[9]; Singlet (5H) at 7.35 p.p.m. (Ar–H).

EPN (XVII)

Triplet (3H) at 1.33 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Octet (2H) at 4.24 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.; Multiplet (9H) at 7.1–8.2 p.p.m. (Ar–H).

Ethion (XVIII)

Triplet (12H) at 1.38 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Multiplet (10H) at 3.95–4.5 p.p.m. (SCH_2S+OCH_2)*.

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* A detailed analysis of the nine line pattern shows a typical oxymethylene octet superimposed on a methylene (SCH_2S) doublet; J_{CH} = 7.0 c.p.s., J_{PH} = 10 c.p.s. and J_{PH} = 16 c.p.s.

GS-13005 (Geigy) (XVIX)

Doublet (6H) at 3.75 p.p.m. (OCH_3), $J_{PH}=15$ c.p.s.; Singlet (3H) at 4.02 p.p.m. (OCH_3); Doublet (2H) at 5.13 p.p.m. (NCH_2S), $J_{PH}=15$ c.p.s.

Ethyl Guthion (XX)

Triplet (6H) at 1.35 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Double Octet (4H) at 4.17 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s., $\delta=2$ c.p.s.[9,10]; Doublet (2H) at 5.7 p.p.m. (SCH_2N), $J_{PH}=15$ c.p.s.; Multiplet (4H) at 7.7–8.4 p.p.m. (Ar–H).

Methyl Guthion (XXI)

Doublet (6H) at 3.75 p.p.m. (OCH_3), $J_{PH}=15.5$ c.p.s.; Doublet (2H) at 5.7 p.p.m. (SCH_2N), $J_{PH}=15$ c.p.s.; Multiplet (4H) at 7.7–8.5 p.p.m. (Ar–H).

Imidan (XXII) ($DCCl_3$)

Doublet (6H) at 3.0 p.p.m. (OCH_3), $J_{PH}=15$ c.p.s.; Doublet (2H) at 5.05 p.p.m. (SCH_2N), $J_{PH}=14$ c.p.s.; Doublet (4H) at 7.84 p.p.m. (Ar–H).

Malathion (XXIII)

Double Triplet (6H) at 1.28 p.p.m. (CH_3), $J_{CH}=7$ c.p.s., $\delta=3$ c.p.s.; Unsymmetrical Triplet (2H) at 2.85 p.p.m. ($CH_2C=O$); Doublet (6.5H) at 3.78 p.p.m. (OCH_3), $J_{PH}=15.5$ c.p.s.*; Septet (4.5H) at 4.18 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $\delta=4$ c.p.s.*

Meta-Systox-R (XXIV)

Triplet (3H) at 1.31 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Multiplet (6H) at 2.6–3.3 p.p.m. ($SCH_2+CH_2S=O$); Doublet (6H) at 3.8 p.p.m. (OCH_3), $J_{PH}=11.5$ c.p.s.

Naled (XXV)

Doublet (6H) at 3.9 p.p.m. (OCH_3), $J_{PH}=12$ c.p.s.; Doublet (1H) at 6.8 p.p.m. (OCHBr), $J_{PH}=9$ c.p.s.

Nellite (XXVI)

Doublet (6H) at 2.64 p.p.m. (NCH_3), $J_{PH}=12$ c.p.s.; Broad Singlet (2H) at 3.1 p.p.m. (N–H); Singlet (5H) at 7.2 p.p.m. (Ar–H).

Parathion (XXVII)

Triplet (6H) at 1.42 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Octet (4H) at 4.25 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.; A_2M_2 Quartet (4H) at 7.75 p.p.m. (Ar–H).

Methyl Parathion (XXVIII)

Doublet (6H) at 3.9 p.p.m. (OCH_3), $J_{PH}=14$ c.p.s.; A_2M_2 Quartet at 7.85 p.p.m. (Ar–H).

Phosdrin (62% α-isomer) (XXIX)[11]

Multiplet (1H) at 2.15 p.p.m. ($CH_3C=C$); Doublet (2H) at 2.38 p.p.m.

---

* The region between 3.85 and 4.4 p.p.m. contains 11 protons, so the methine proton (SCH–C=O) must have the same chemical shift as the oxymethylene octet.

($CH_3C=C$), $J_{CH}=0.8$ c.p.s.; Unsymmetrical Sextet (9H) at 3.6–3.96 p.p.m. (OCH_3); Quartet (0.3H) at 5.23 p.p.m. ($HC=C$), $J_{CH}=1$ c.p.s.; Quartet (0.7H) at 5.82 p.p.m. ($HC=C$), $J_{CH}=0.8$ c.p.s.

Ronnel (XXX)

Doublet (6H) at 3.9 p.p.m. (OCH_3), $J_{PH}=14$ c.p.s.; Multiplet (2H) at 7.45 p.p.m. (Ar–H).

Ruelene (XXXI)

Singlet (9H) at 1.32 p.p.m. (*t*-Bu); Quartet (3H) at 2.60 p.p.m. ($N–CH_3$), $J_{CH}=6$ c.p.s., $J_{PH}=12.5$ c.p.s.; Doublet (3H) at 3.75 p.p.m. (OCH_3), $J_{PH}=11.5$ c.p.s.; Multiplet (1H) at 4.7–5.2 p.p.m. (N–H); Multiplet (3H) at 7.1–7.55 p.p.m. (Ar–H).

Schradran (OMPA) (XXXII)

Doublet (24H) at 2.65 p.p.m. (NCH_3), $J_{PH}=11.5$ c.p.s.

Sulfotepp (XXXIII)

Triplet (12H) at 1.42 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Octet (8H) at 4.30 p.p.m. (OCH_2), $J_{CH}=7$ c.p.s., $J_{PH}=11$ c.p.s.

Systox (1:1 mixture) (XXXIV)

Multiplet (9H) at 1.18–1.50 p.p.m. (CH_3); Multiplet (5H) at 2.40–3.30 p.p.m. (SCH_2); Multiplet (5H) at 3.80–4.35 p.p.m. (OCH_2).

Thimet (XXXV)

Multiplet (9H) at 1.16–1.47 p.p.m. (CH_3), 6 lines; Quartet (2H) at 2.7 p.p.m. (SCH_2), $J_{CH}=7$ c.p.s.; Multiplet (6H) at 3.9–4.4 p.p.m. (OCH_2+SCH_2S), 8 lines, $J_{PH}=14.5$ c.p.s., $J'_{PH}=10.5$ c.p.s., $J_{CH}=7$ c.p.s.

Trichlorofon (XXXVI) ($DCCl_3$)

Doublet (6H) at 3.9 p.p.m. (OCH_3), $J_{PH}=11$ c.p.s.; Doublet (1H) at 4.55 p.p.m. (O–C–H), $J_{PH}=11$ c.p.s.; Singlet (1H) at 5.95 p.p.m. (OH).

Trithion (XXXVII)

Triplet (6H) at 1.33 p.p.m. (CH_3), $J_{CH}=7$ c.p.s.; Multiplet (6H) at 3.85–4.40 p.p.m. (OCH_2+SCH_2S); Singlet (4H) at 7.32 p.p.m. (Ar–H).

Methyl Trithion (XXXVIII)

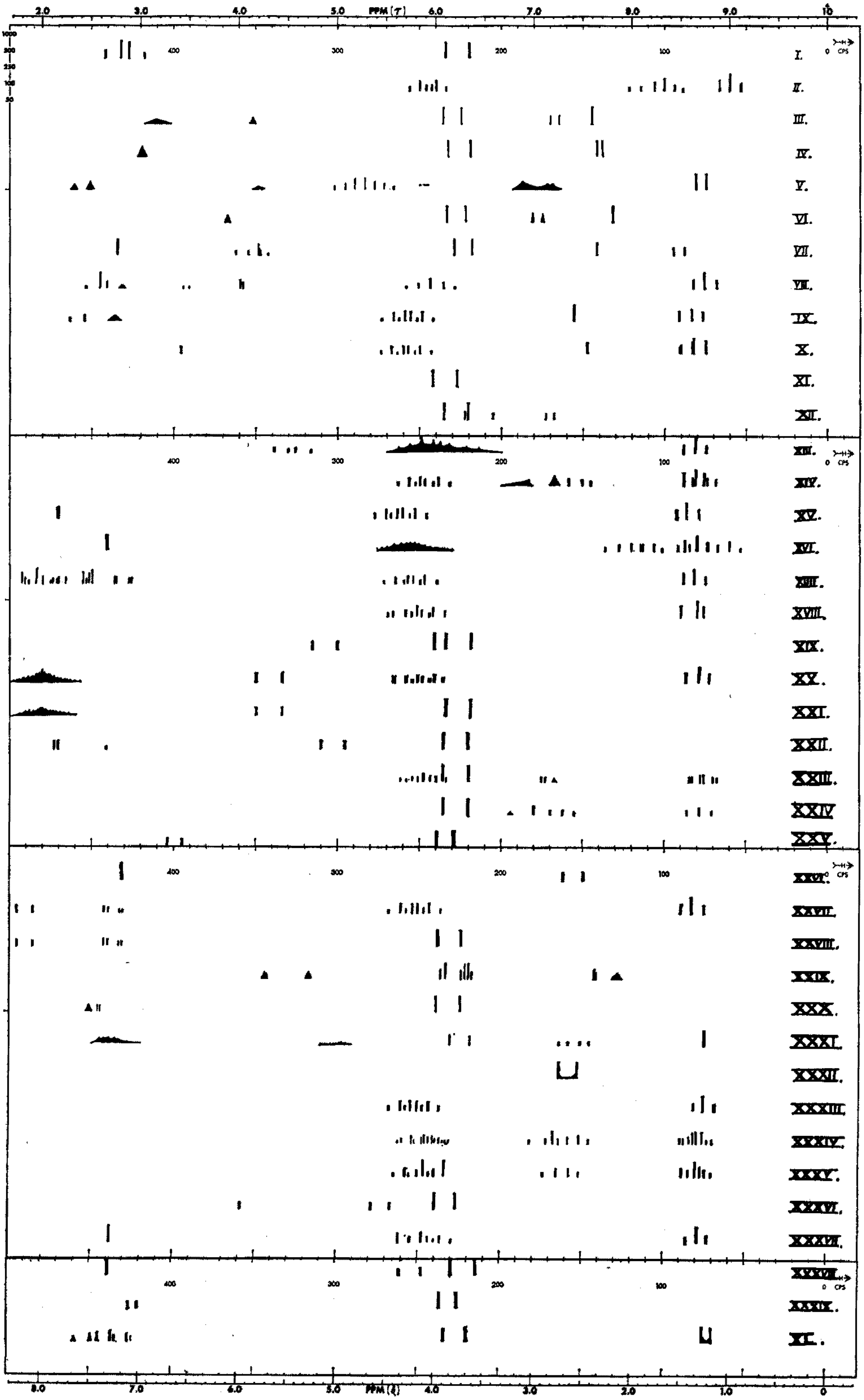
Doublet (6H) at 3.70 p.p.m. (OCH_3), $J_{PH}=14.5$ c.p.s.; Doublet (2H) at 4.25 p.p.m. (SCH_2S), $J_{PH}=14.5$ c.p.s.; Singlet (4H) at 7.32 p.p.m. (Ar–H).

Vapona-R (XXXIX)

Doublet (6H) at 3.83 p.p.m. (OCH_3), $J_{PH}=11.5$ c.p.s.; Doublet (1H) at 7.0 p.p.m. ($C=C–H$), $J_{PH}=6$ c.p.s.

Zytron (XL)

Doublet (6H) at 1.12 p.p.m. (*i*-propyl), $J_{CH}=6$ c.p.s.; Doublet (3H) at 3.80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p.p.m. (OCH_3), $J_{PH} = 14$ c.p.s.; Multiplet (2H) at 3.1–3.8 p.p.m. (NH + CH); Multiplet (3H) at 7.1–7.4 p.p.m. (Ar–H).

DISCUSSION

The spectra of the pesticides examined in this study are summarized in Fig. I and are reported in detail in the experimental section. In general, there is only a negligible change in chemical shift values of protons bound to a phosphoric ester linkage and so the chemical shifts reported in Fig. 1 approximate those reported in the literature for ethers, thioethers, amines and other organic functional groups or radicals, in the absence of a phosphorus atom[8]. On the other hand alkyl groups attached directly to a phosphorus atom have been reported to undergo resonance in the 2.0–3.5 p.p.m. region[9,12,13].

TABLE I

PHOSPHORUS–HYDROGEN COUPLING CONSTANTS FOR PESTICIDE STRUCTURES

Structure	*Substituent (J_{PH} in c.p.s.)*				
	$POCH_3$	*POEt*	*PO-i-Pr*	*$PSCH_2$*	*$PNCH_3$*
$O_2(P{=}O)O$	11–11.5	9	6–7		
$O_2(P{=}O)S$	11.5	9		9	
$O_2(P{=}O)N$	11.5				11.5–12
$O_2(P{=}O)C$	11+				
$O(P{=}O)N_2$					11.5–12
$O_2(P{=}S)O$	14–14.5	10–11.5			
$O_2(P{=}S)S$	15.5–16	10–10.5	6–7	14.5–15.5	
$O_2(P{=}S)C$		10.5			

The major effect which complicates NMR spectra of organic molecules containing a pentavalent phosphorus atom results from the spin states ($I = \frac{1}{2}$) of ^{31}P. This can be illustrated by the change in intensity and multiplicity of spectral lines caused by single homogeneous groups due to interaction of the C–H bonds with ^{31}P atom. Coupling (J_{PH}) of the phosphorus nucleus with a proton causes the signal to be split into two lines of equal intensity. These signals can be further complicated by coupling with adjacent protons to give signals which appear as two doublets or triplets, that may not be completely resolved, as is illustrated in Fig. 2 for the oxymethylene octet ($CH_3\underline{CH_2}OP$). This coupling, as measured by the coupling constant, falls off rapidly with the distance of the proton from the phosphorus atom. Some average values for J_{PH} are given on the following page[14]:

Fig. 1. NMR spectra of compounds tested. I = Abate, II = Aspon, III = Azodrin, IV = Baytex, V = Betasan, VI = Bidrin, VII = Ciodrin, VIII = Compound 4072, IX = Co-Ral, X = Diazinon, XI = Dicapthion, XII = Dimethoate, XIII = Dioxathion, XIV = Disyston, XV = Dursban, XVI = Dyfonate, XVII = EPN, XVIII = Ethion, XVIV = GS-13005, XX = Ethyl Guthion, XXI = Methyl Guthion, XXII = Imidan, XXIII = Malathion, XXIV = Meta-Systox-R, XXV = Naled, XXVI = Nellite, XXVII = Parathion, XXVIII = Methyl Parathion, XXIX = Phosdrin, XXX = Ronnel, XXXI = Ruelene, XXXII = Schradran (OMPA), XXXIII = Sulfotepp, XXXIV = Systox, XXXV = Thimet, XXXVI = Trichlorofon, XXXVII = Trithion, XXXVIII = Methyl Trithion, XXXIX = Vapona-R and XL = Zytron.

P–H	P–O–H	P–O–C–H	P–O–C–C–H	
470–80	250	7–16	0–3	c.p.s.

The coupling constants (J_{PH}) for the compounds included in this study vary between 0 and 25 c.p.s. The magnitude of the coupling constant can be shown to depend on two factors. First, the value of J_{PH} increases as one goes from a methine, to a methylene to a methyl group in a comparable environment. Second, in phosphoric(V) esters of the type studied here, the magnitude of the coupling constant is almost independent of the atom linking the proton-bearing carbon to phosphorus atom (P–O–CH$_3$, P–N–CH$_3$ and P–S–CH$_3$) but highly dependent on the nature of the atom coordinately bound to the phosphorus atom[15] (P=S, P=O). These results are summarized in Table I.

One additional factor causes complications in the spectra of pentavalent phosphorus compounds. In certain rare instances, the signal due to an alkyl or alkoxy group in an aromatic pesticide is doubled because of hindered rotation in these molecules leading to unequal conformation populations[9,10]. The NMR spectrum of Dyfonate (XVI) is typical of such phenomenon.

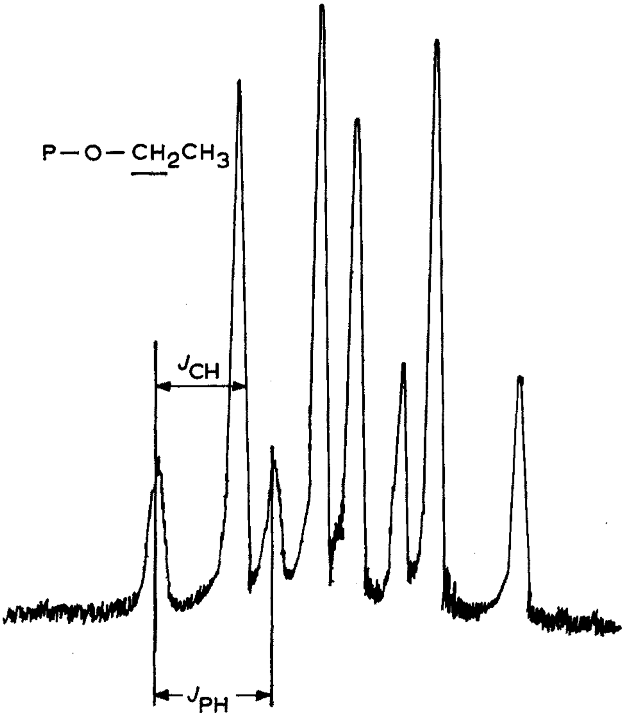

Fig. 2. Oxymethylene octet.

CONCLUSION

The characteristic patterns (multiplicity and chemical shift) contained in the NMR spectra of pentavalent phosphorus pesticides, coupled with information obtained by integrating the peak areas and by measuring various coupling constants directly from the spectrum, enables one to make an accurate rapid first order identification of the aliphatic portion of most phosphorus pesticides. This technique constitutes a rapid method of distinguishing between the phosphate [$O_2(P=O)O$] and thioate [$O_2(P=S)O$] structures that characterize most of these compounds.

The authors express their thanks to Dr. A. L. SCHALGE of the Marathon Oil Company, Denver Research Center, for allowing access to the A-60 Spectrometer, to R. WILLIAMS for assistance in the preparation of samples, to the Trona division of American Potash and Chemical Corporation, and to the Agricultural Divisions of the Monsanto Company, Stauffer Chemical Company, Geigy Chemical Corporation, American Cyanamid Company, Shell Chemical Company, E.I. du Pont De Nemours and Company, Dow Chemical Corporation, and the Chemargo Corporation for supplying analytical standards of the pesticides used.

SUMMARY

Correlations of structural and proton chemical-shift data for 40 commercial phosphorus(V) pesticides are reported. Correlations of structure with the phosphorus coupling constants are discussed, and general trends are noted which aid in the use of NMR as a tool for identification and analysis of phosphorus(V) compounds.

RÉSUMÉ

Un rapport est présenté sur la corrélation des valeurs structurelles et de transferts chimiques de protons pour 40 pesticides phophorés du commerce. Une discussion est faite et les tendances générales sont notées, aidant l'emploi de la résonance magnétique nucléaire pour l'identification et l'analyse des composés de phosphore(V).

ZUSAMMENFASSUNG

Es werden für 40 kommerzielle Phosphor(V)-Pestizide die Zusammenhänge der chemischen Verschiebung beschrieben, die durch die Struktur und durch Protonen hervorgerufen wird. Die Beziehungen zwischen der Struktur und der Phosphorkopplungskonstanten werden diskutiert, und es wird die allgemeine Entwicklung bei der Verwendung der KMR als Hilfsmittel zur Identifizierung und Analyse von Phosphor(V)-Verbindungen aufgezeigt.

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SPECTROFLUORIMETRIC DETERMINATION OF MALIC ACID WITH β-NAPHTHOL

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(Received November 1st, 1967)

In 1932, EEGRIWE[1] developed a fluorimetric qualitative test for malic acid based upon its reaction with β-naphthol in concentrated sulfuric acid. LEININGER AND KATZ[2] later reported a quantitative method for malic acid based upon this fluorescence which eliminated the interference of citric acid found when resorcinol is used as the reagent[3]. They were able to determine 1–30 μg of malic acid in apple juice. Citric and succinic acids did not interfere and tartaric acid showed a small interference when present in amounts equal to the malic acid present.

The present paper reports a detailed investigation of the optimum conditions for this reaction and for measuring the fluorescence intensity employing a spectrophotofluorimeter. As little as 0.1 μg or 0.002 p.p.m. of malic acid can be determined.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used without further purification. Malic acid solutions were prepared from Calbiochem DL-malic acid, A grade. β-Naphthol solutions were prepared by grinding crystals to a fine powder and dissolving this in sulfuric acid solution. A solution of 93% of concentrated sulfuric acid was prepared by adding 92 ml of concentrated sulfuric acid (s.g. 1.8407–1.8437) to 10 ml of water and then cooling in an ice bath. The final volume was about 99 ml. An 80% solution was prepared by adding 400 ml of acid to 128 ml of water.

Apparatus

Fluorimetric measurements were made with an Aminco-Bowman spectrophotofluorimeter. Fluorescence readings are reported in arbitrary units. Colorimetric measurements were made with a Bausch & Lomb Model 340 spectrophotometer.

Micropipettes were prepared and calibrated as previously described[4].

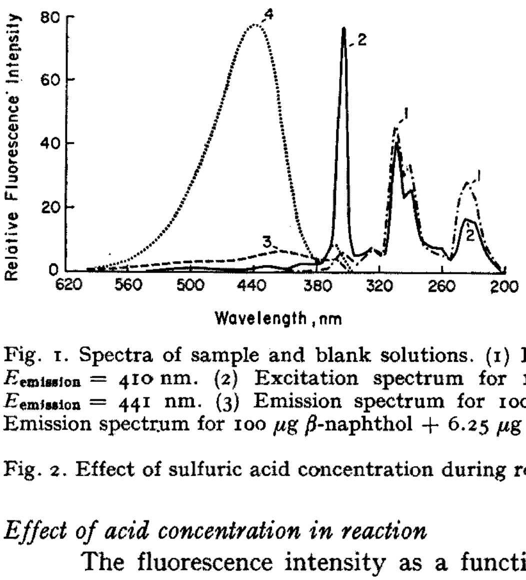
Procedure

Malic acid solution (5–30 μl) was added to clean dry 50-ml volumetric flasks. The required volume of β-naphthol dissolved in various concentrations of sulfuric acid was added. The flask was stoppered to prevent evaporation of water and was heated on a steam bath for the required time. The flask was then cooled in an ice bath and the solution was diluted to 50 ml with sulfuric acid of the desired concentration.

RESULTS AND DISCUSSION

Optimum wavelength settings

The excitation spectra of β-naphthol and malic acid–β-naphthol solutions are shown in Fig. 1. All the excitation peaks were investigated; the sample fluorescence was the greatest and the blank fluorescence the smallest at an exciting wavelength of 357 nm; this excitation wavelength was therefore used in all other measurements. The maximum sample fluorescence under these conditions occurred at 441 nm. It should be noted that if a filter instrument is used which allows wavelengths shorter than 357 nm to excite the sample, the blank fluorescence will increase markedly relative to the sample fluorescence. This is especially true if 310 nm or shorter is passed by the filter (see Fig. 1).



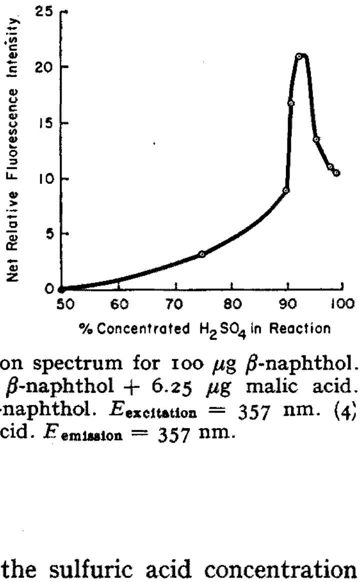


Fig. 1. Spectra of sample and blank solutions. (1) Excitation spectrum for 100 μg β-naphthol. E_{emission} = 410 nm. (2) Excitation spectrum for 100 μg β-naphthol + 6.25 μg malic acid. E_{emission} = 441 nm. (3) Emission spectrum for 100 μg β-naphthol. $E_{\text{excitation}}$ = 357 nm. (4) Emission spectrum for 100 μg β-naphthol + 6.25 μg malic acid. E_{emission} = 357 nm.

Fig. 2. Effect of sulfuric acid concentration during reaction.

Effect of acid concentration in reaction

The fluorescence intensity as a function of the sulfuric acid concentration during the reaction of the malic acid and β-naphthol is shown in Fig. 2. The percent of acid refers to the final volume percent of concentrated sulfuric acid (s.g. 1.8407–1.8437). The maximum occurred at about 93% (or 90% H_2SO_4). This is in close agreement with the results of LEININGER AND KATZ[2] who obtained maximum fluorescence at 92% sulfuric acid. It is important that the sulfuric acid used to dissolve the naphthol be prepared in the same manner at all times or else a new calibration curve be prepared with each new reagent solution. This latter procedure is recommended.

Effect of total acid in reaction

It appears that the smaller the total volume of acid during the reaction, the greater the fluorescence intensity (Fig. 3). It is convenient to use 1 ml of β-naphthol reagent in 93% sulfuric acid and since this gives sufficiently great fluorescence, lesser amounts are not necessary unless maximum sensitivity is desired. It is important that the reactant vessel be dry before adding the reagent.

Effect of final acid concentration

LEININGER AND KATZ diluted their samples with water to a final acid concentration of less than 1%. Figure 4 illustrates that the fluorescence intensity increased as the final acid concentration was increased. While a maximum was obtained at about 90% sulfuric acid, the sample-to-blank ratio decreased at greater than 80% acid. Therefore, a final acid concentration of 80% is recommended.

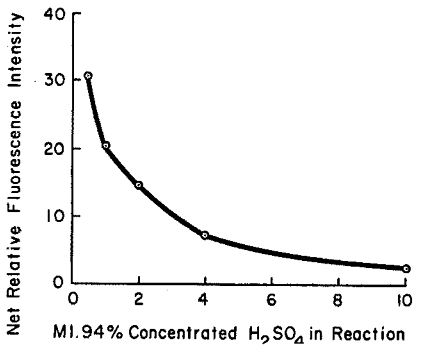


Fig. 3. Effect of amount of sulfuric acid during reaction.

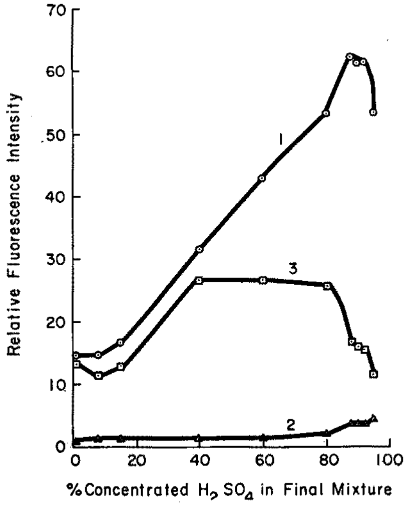


Fig. 4. Effect of final sulfuric acid concentration. (1) Sample + blank fluorescence readings. (2) Blank fluorescence readings. (3) Ratio of net sample reading to blank reading.

Effect of time of heating

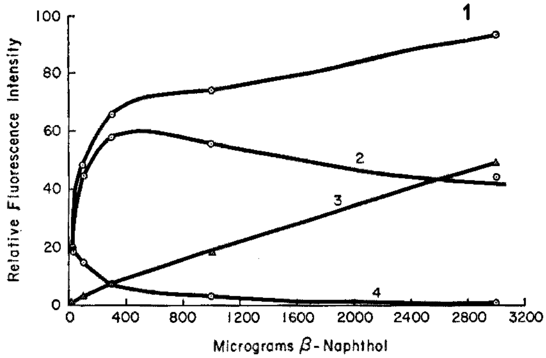
The reaction appears to be complete after heating for 30 min on a steam bath for a wide range of malic acid concentrations. This is in agreement with previous results[2]. Further heating up to at least 60 min does not affect the results.

Stability of solutions

The malic acid solution is stable for at least two weeks. The β-naphthol solution in sulfuric acid is stable for two weeks if kept refrigerated in the dark. The solution is yellow when immediately prepared but becomes very pale or nearly colorless after about an hour. The same results were obtained when a freshly prepared solution or one several hours old was used. It is important that care be taken to prevent contamination of the β-naphthol solution with malic acid. A very small amount will cause rapid decomposition of the naphthol. Prepared samples and blanks are stable for at least 24 h.

Effect of excess β-naphthol

The effect of excess β-naphthol on the fluorescence intensity is illustrated in Fig. 5 for 12.5 μg of malic acid. The intensity increased markedly with increasing amounts of naphthol up to about 400 μg and then increased only gradually (curve 1). One would expect a leveling off in fluorescence intensity as the naphthol concentration exceeded the malic acid concentration (see below for continuous variations study).



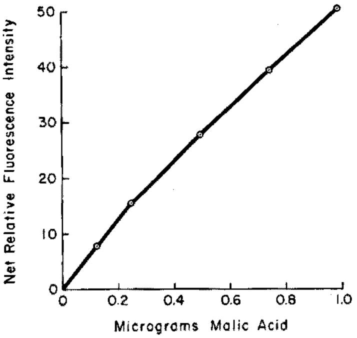


Fig. 5. Effect of amount of excess β-naphthol on fluorescence intensity. (1) Sample + blank fluorescence readings. (2) Net sample fluorescence readings. (3) Blank fluorescence readings. (4) Ratio of net sample readings to blank readings.

Fig. 6. Calibration curve with 10 μg of β-naphthol in 1 ml of 93% sulfuric acid as reagent. Final concentration of acid 80% and final volume 50 ml. All points corrected for a blank reading of 11.3.

The observed results would indicate a complex or other reaction product whose formation constant is not very large. KIRKBRIGHT, WEST AND WOODWARD[5], for example, have observed a similar phenomenon for aluminum and beryllium complexes with 2-hydroxy-3-naphthoic acid. The sample-to-blank signal decreased as the naphthol was increased. One would expect from these results to obtain a high degree of curvature of the calibration curves when a constant amount of naphthol is used, because the naphthol/malic acid ratio increases as the malic acid is decreased. However, such was not the case (see below) and the amount of fluorescent product produced appeared to depend only on the total amount of naphthol (and malic acid) and not on the ratio of these two. A 10–100 fold excess of naphthol was chosen to give a linear calibration curve for a 10-fold range of malic acid concentrations with a sufficiently small blank reading. It is important to add the same amount of naphthol reproducibly to all samples.

Preparation of calibration curves

A nearly linear calibration curve was obtained over a 10-fold range of malic acid concentrations with a 10-fold excess of β-naphthol over the highest malic acid concentration. The blank reading became significant when the weight of malic acid was less than about 1% that of β-naphthol. With 100 μg of naphthol, the blank reading (relative) was 6.1 while the net reading for 1.26 μg of malic acid was 16.0. A 0.1-μg sample of malic acid in a final volume of 50 ml (2 p.p.b.) could be determined using 10 μg of β-naphthol (see Fig. 6). A slight curvature of the calibration curve was obtained under these conditions. The relative blank reading was 11.3.

Continuous variations plot

A plot of mole fraction of malic acid *vs.* fluorescence intensity (Job's method)[6] resulted in a maximum at a 1:1 mole ratio. This would agree with the evidence[7,8] that the fluorescing product is 5,6-benzocoumarin which is formed by condensation of the intermediate, formyl acetic acid, with β-naphthol.

Interferences

The effect of citric, succinic, and tartaric (added as Rochelle salt) acids on the fluorescence intensity was investigated. Results are summarized in Table I. Citric and succinic acids caused no apparent effect up to an 80-fold excess. This is in agreement with results of LEININGER AND KATZ. Tartaric acid, however, caused a negative error at these larger amounts. At 10 and 50 μg, no appreciable net effect was apparent.

TABLE I

EFFECT OF OTHER ACIDS ON FLUORESCENCE INTENSITY

(All solutions contained 100 μg of β-naphthol. The blank reading was 6.1)

Malic acid (μg)	*Added compound (μg)*		*Net fluorescence reading*
6.25			67.0
6.25	Citric acid	500	67.8
6.25	Succinic acid	500	66.8
6.25	Tartaric acid	10	66
6.25	Tartaric acid	50	66
6.25	Tartaric acid	500	49
0	Tartaric acid	50	2.8
0	Tartaric acid	500	13.9

However, in the absence of malic acid, tartaric acid produced a net fluorescence. The solutions containing tartaric acid were blue-green in color and exhibited some absorbance at 441 nm. There were 3 possible contributions to the observed results with tartaric acid. With solutions containing higher concentrations of tartaric acid, self-absorption could occur which more than offsets the fluorescence due to the tartaric acid. At lower concentrations, the two effects would be either negligible or else would compensate each other. A second possibility is that the high concentrations of tartaric acid competitively reacted with most of the naphthol reagent, leaving less to react with the malic acid. Thirdly, a malic acid–tartaric acid complex might form. DAMANSKI *et al.*[9] have isolated an equimolar complex of D-tartaric acid and L-malic acid from green apple juice.

An experiment was run to determine the effect of increasing the concentration of naphthol on the tartaric acid interference; 5 μg of malic acid plus 200 μg of β-naphthol were reacted in the presence of 50 μg and 500 μg of tartaric acid. The color intensity of the solutions (due to tartaric acid) was greater than when 100 μg of naphthol was used. The net fluorescence readings were 83.5 and 82.8, respectively, for the solutions containing 50 and 500 μg of tartaric acid. The absorbance of the solutions at 441 nm was 0.00 and 0.022, respectively; the same solutions, but with only 100 μg of naphthol, gave absorbance readings of 0.00 and 0.002. Thus, the absorbance by these solutions at 441 nm was small. It appears that the interference was due mainly to reaction of the tartaric acid with the reagent.

Samples were also run using 400 μg of naphthol (5 μg of malic acid). The net fluorescence readings for solutions containing 0, 50 and 500 μg of tartaric acid were: 80.6, 88.2, and 107.5. Therefore, when larger concentrations of naphthol are used to prevent reaction of a majority of the reagent with tartaric acid, the fluorescence of the tartaric acid causes positive results. There is a competition between the two effects and results will depend on the amount of tartaric acid and/or β-naphthol present, and their ratios.

Reproducibility

A series of 7 samples (6.25 μg malic acid and 100 μg β-naphthol) were reacted in 1 ml of 93% sulfuric acid and then diluted to 50 ml with 80% sulfuric acid. The range of fluorescence readings was 62.6 to 64.2 with a mean of 63.7 and a standard deviation of ±0.52. Results were corrected for instrument variations by comparing to the reading of a quinine sulfate solution (1 p.p.m.) obtained at the same wavelength settings as used for samples.

SUMMARY

A detailed study of the spectrofluorimetric determination of malic acid by reaction with β-naphthol is reported. As little as 0.1 μg of malic acid can be determined. The optimum concentration of sulfuric acid is 80% (v/v). The interferences of citric, succinic and tartaric acids are discussed.

RÉSUMÉ

On décrit une étude détaillée sur le dosage spectrofluorimétrique de l'acide malique au moyen de β-naphtol. On peut doser ainsi jusqu'à 0.1 μg d'acide malique. La concentration optimum d'acide sulfurique est de 80% (v/v). L'influence des acides citrique, succinique et tartrique est examinée.

ZUSAMMENFASSUNG

Es wird über eine spektralfluorimetrische Bestimmung von Äpfelsäure durch Reaktion mit β-Naphthol berichtet. Gehalte bis hinab zu 0.1 μg können bestimmt werden. Die optimale Konzentration der Schwefelsäure beträgt 80 Vol.-%. Störungen durch Citronen-, Bernstein- und Weinsäure werden diskutiert.

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SPECTROPHOTOMETRIC DETERMINATION OF CHLORATE ION

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Spectrophotometric methods for the determination of chlorate ion are rare. FRUMINA[1] determined chlorate with N,N'-bis(*o*-carboxyphenyl)tolidine. JORDANOV AND DAIEV[2] used N,N,N',N'-tetramethyl-*o*-tolidine (tetron) to measure chlorate. URONE AND BONDE[3] utilized a prior reduction of chlorate to chlorine and subsequent reaction with *o*-tolidine. BURNS[4] also used a reduction technique and reacted the produced chlorine with benzidine to form a yellow haloquinone. PRINCE[5] and CHEN[6] determined chlorate by the oxidation of iron(II) to iron(III) and the subsequent measurement of iron(III).

This paper presents a new approach to the determination of the chlorate ion. The method, based on the interference of chlorate ion with the formation of the color of the rhenium–α-furildioxime complex[7], is simple, and subject to few interferences. This technique is considerably more sensitive than existing methods, except for that of URONE AND BONDE, in which case it is only slightly more sensitive.

EXPERIMENTAL

Apparatus

All spectral measurements were made with a Cary Model 12 or 15 recording spectrophotometer, or a Beckman DU spectrophotometer. Matched 1.000 ± 0.002-cm quartz cells were used. Temperatures were controlled to within ± 0.3° by means of a water bath in conjunction with a Sargent Model 3554 thermoregulating unit.

Reagents

Potassium perrhenate (obtained from University of Tennessee) was used without further purification. A stock solution was prepared by dissolution in deionized water.

Tin(II) chloride solution. An 8.5% solution was prepared by dissolving 100 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid and diluting to 1 l with deionized water.

α-Furildioxime (Eastman Kodak Company) was used without further purification. A solution was prepared by dissolution of 7.0000 g in methanol and dilution to 1 l with methanol.

Recommended procedure

Prepare a calibration curve by adding up to 0.25 mg of chlorate ion to 50-ml volumetric flasks and bringing to a total volume of 10 ml with deionized water. To

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each flask add 5.00 ml of aqueous potassium perrhenate solution (0.090 g/l), 13.00 ml of methanol, 4.70 ml of 1:1 hydrochloric acid, and lastly, 5.90 ml of 8.5% tin(II) chloride. Mix and place each flask into a 25° constant temperature water bath for exactly 15 min. Add 5.00 ml of the α-furildioxime solution, dilute to 50 ml with deionized water, and return each flask to the 25° water bath. After exactly 15 min, read the absorbance at 532 nm.

A sample containing chlorate may be analyzed by placing a solution containing the ion in a 50-ml volumetric flask, adjusting the volume to 10 ml, and proceeding as above.

STUDY OF VARIABLES

Studies were made on the effect of time and reagent concentrations on the color formed in the presence and absence of chlorate ion.

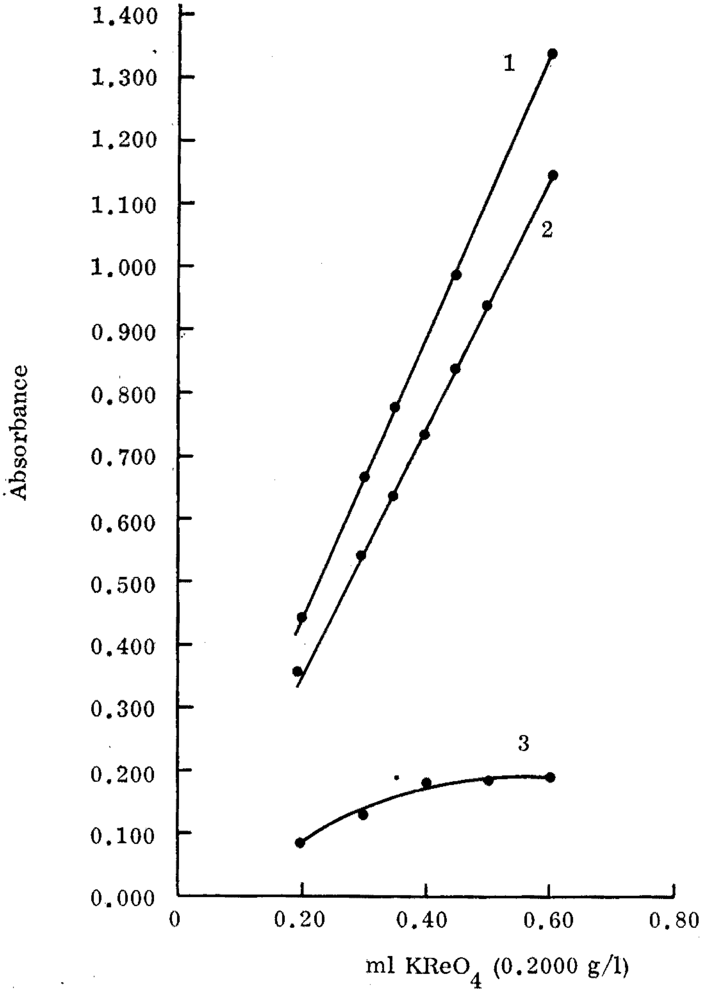

Fig. 1. Effect of potassium perrhenate concentration. (1) No added chlorate. (2) 0.6 p.p.m. chlorate. (3) Δ Absorbance (1 − 2).

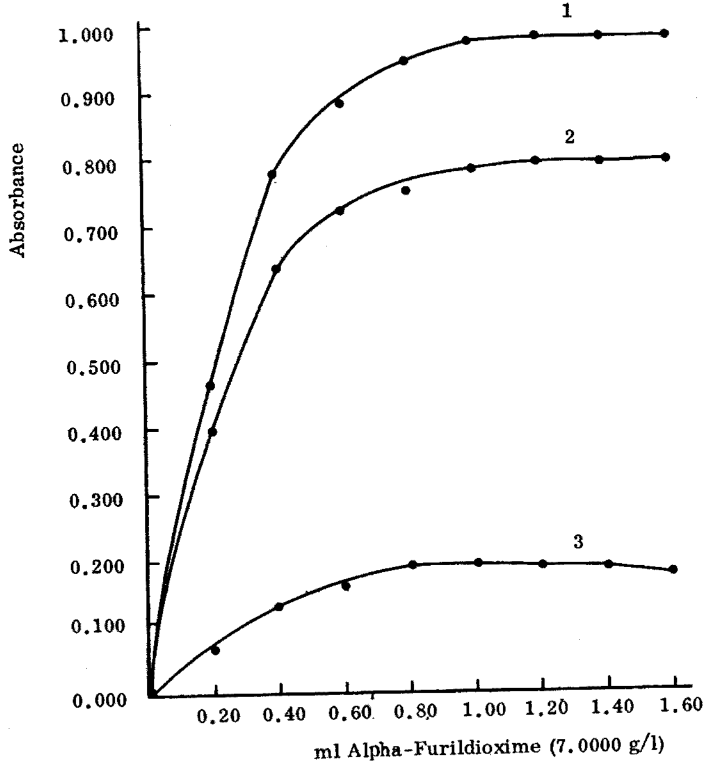

Fig. 2. Effect of α-furildioxime concentration. Lines 1–3 as in Fig. 1.

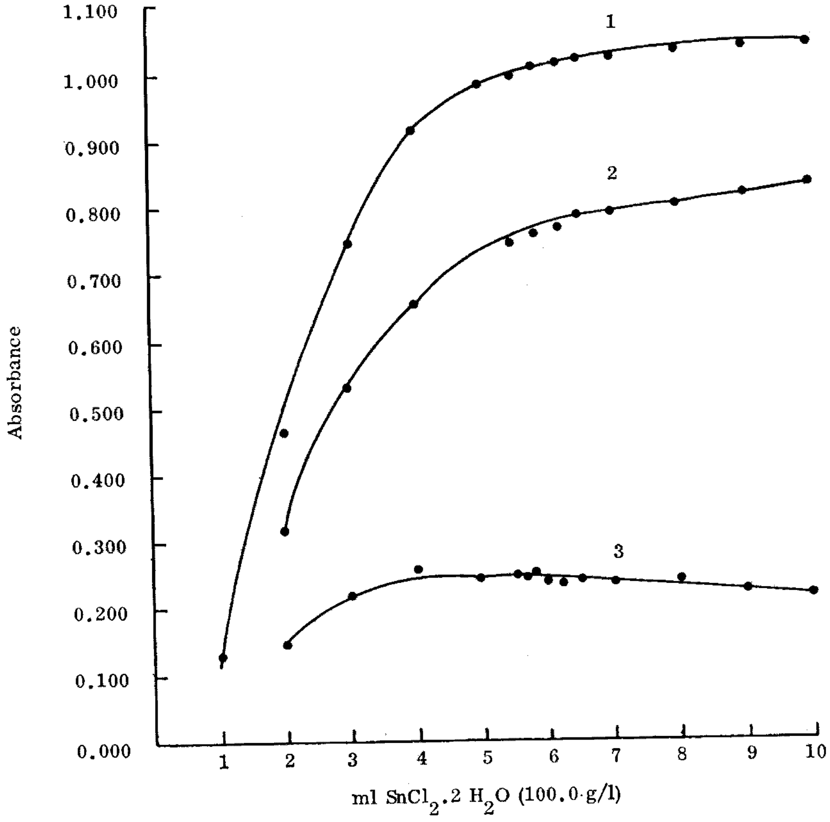

Fig. 3. Effect of tin(II) concentration. Lines 1–3 as in Fig. 1.

Effect of reagent concentrations

The effect of the potassium perrhenate concentration is illustrated in Fig. 1. A concentration of potassium perrhenate corresponding to 0.45 ml of a 0.2000 g/l potassium perrhenate solution was chosen for use in 10-ml volumetric flasks. This gave a reasonable absorbance value and a good chlorate bleaching effect. For convenience this solution was diluted, and 5.00 ml of a 0.0900 g/l solution was used in 50-ml volumetric flasks in the recommended procedure.

The effect of ligand concentration is shown in Fig. 2. Maximum color development and chlorate interference occurred at 1.00 ml of the 7.0000 g/l α-furildioxime solution in 10-ml volumetric flasks. A volume of 5.00 ml was used for the 50-ml volumetric flasks as in the recommended procedure, and was also used in subsequent studies.

Various reductants for the potassium perrhenate were considered. Hydrazine hydrochloride, ascorbic acid, hydroxylamine hydrochloride, and iron(II) failed to produce any color. Tin(II) proved to be the only effective reductant. The effect of tin(II) concentration is shown in Fig. 3. A volume of 5.90 ml of the 100 g/l solution gave a strong interference by the chlorate ion, and exellent color stability.

Studies showed hydrochloric acid to be the only effective acid. Figure 4 shows the effect of the hydrochloric acid concentration; a volume of 4.70 ml of 1:1 hydro-

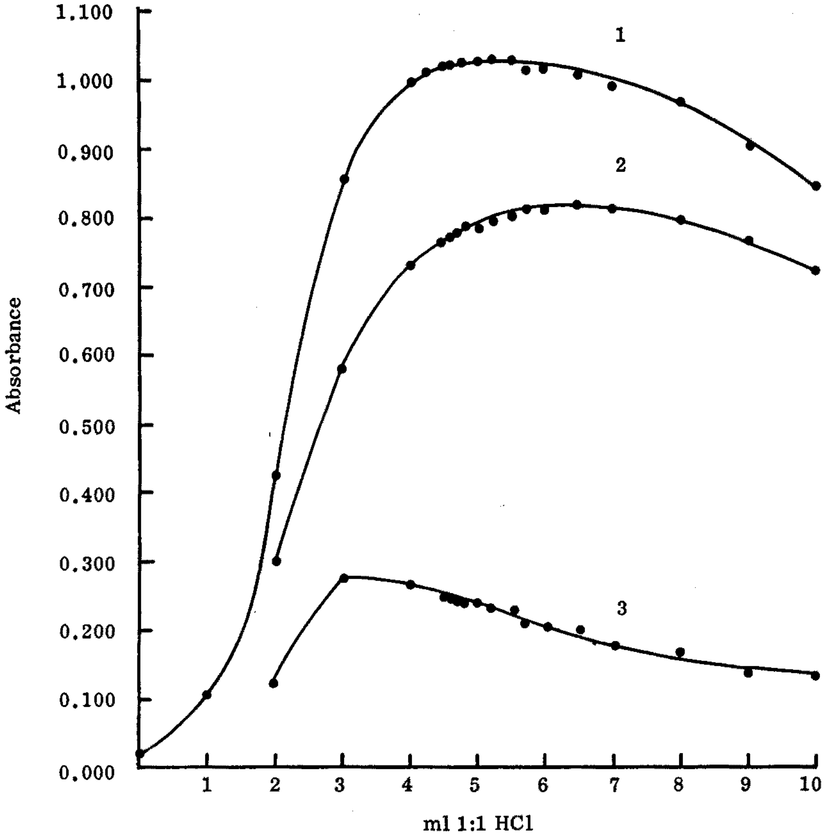

Fig. 4. Effect of 1:1 hydrochloric acid concentration. Lines 1–3 as in Fig. 1.

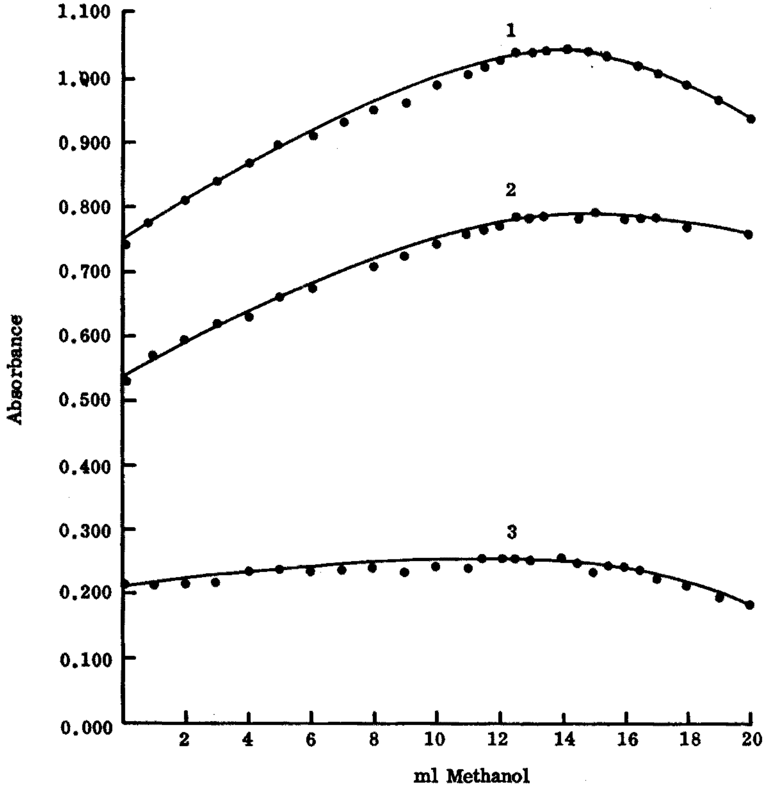

Fig. 5. Effect of methanol concentration. Lines 1–3 as in Fig. 1.

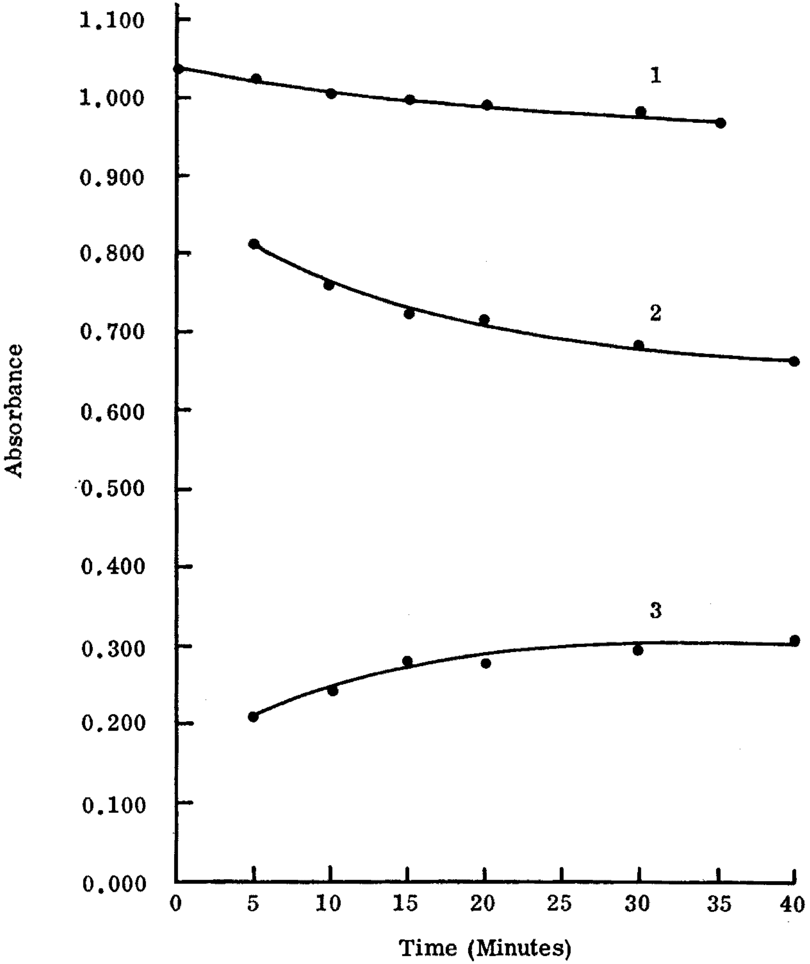

Fig. 6. Effect of time between tin(II) and α-furildioxime additions. Lines 1–3 as in Fig. 1.

chloric acid provided a significant chlorate interference, and allowed sufficient color development in the blank solutions.

Early studies indicated that the system would require methanol for color development. Figure 5 shows the results of a study to determine the optimum methanol concentration; a volume of 13.00 ml was selected.

Temperature

Temperature did not appear to be critical in this system. When the effect of temperature was studied, it was observed that temperature control to within a few degrees was adequate. A temperature bath is recommended but only for gross control.

Time

The reduction of perrhenate ion by tin(II) must occur in the presence of chlorate ion and in the absence of α-furildioxime. This effect is shown in Fig. 6. A period of 15 min provided nearly maximum, blank color development, significant chlorate interference, and a rapid analysis time.

The chlorate interference in the color development of the system is diminished with

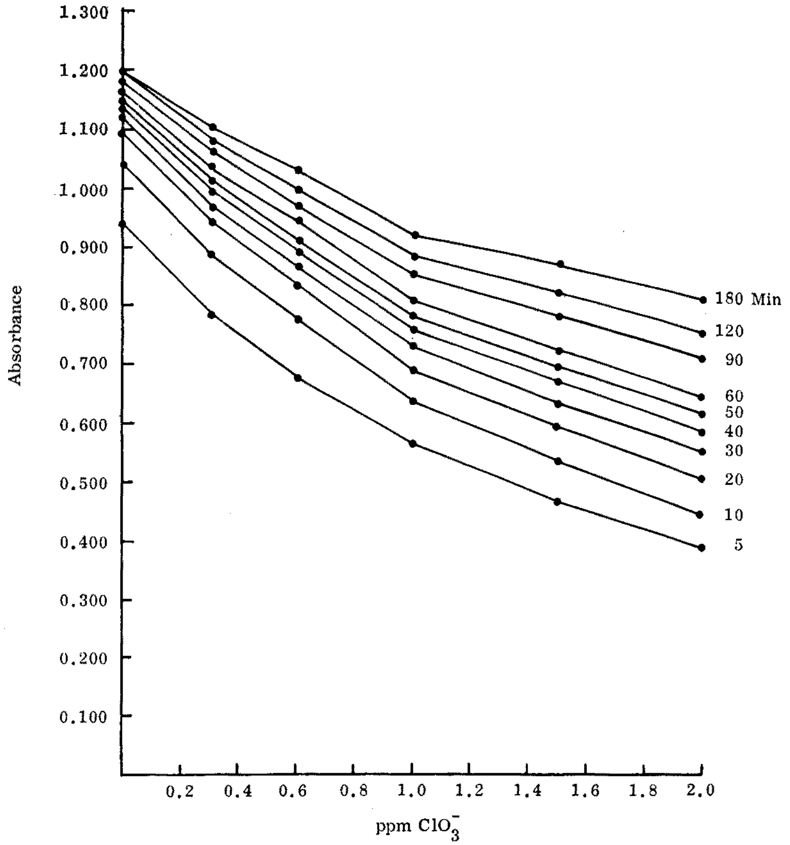

Fig. 7. Effect of time between α-furildioxime addition and absorbance reading.

time (Fig. 7); 15 min was chosen as the optimum time. This allows up to 6 simultaneous samples to be analyzed while maintaining a reasonably rapid analysis time.

Diverse ions

A variety of ions were added to the system in order to study interferences. The results of this investigation are shown in Table I. The principal interferences are copper(II), thiocyanate, tungstate and uranyl ions. Copper(II) and uranium(VI) increase the absorbance and diminish the interference of the chlorate ion. Thiocyanate ion produces a yellow color with perrhenate in the presence of tin(II) chloride. Tungstate forms a precipitate on the addition of tin(II) chloride.

TABLE I

STUDY OF DIVERSE IONS

Ions[a]	*Amount permitted*[b] *(p.p.m.)*	*Ions*	*Amount permitted (p.p.m.)*
$C_2H_3O_2^-$	100	Mg^{2+}	100
V^{5+}	9	Fe^{3+}	9
SO_4^{2-}	100	$S_2O_8^{2-}$	100
Fe^{2+}	15	UO_2^{2+}	CI[c]
Br^-	100	Zr^{4+}	38
IO_3^-	100	WO_4^{2-}	CI
NH_4^+	100	SiO_3^{2-}	100
Tartrate	100	Citrate	100
BrO_3^-	100	IO_4^-	100
Ni^{2+}	37	ClO_4^-	30
$C_2O_4^{2-}$	100	IO_3^-	100
Mn^{2+}	42	F^-	100
I^-	37	Pb^{2+}	100
Cu^{2+}	CI	$Cr_2O_7^{2-}$	38
SCN^-	CI	NO_3^-	CI

[a] 100 p.p.m.
[b] 2% error considered tolerable.
[c] CI = Complete interference.

SUMMARY

A simple, direct, sensitive spectrophotometric method for the determination of chlorate ion is described. The method is based upon the interference of chlorate ion on the formation of a rhenium–α-furildioxime complex, whose absorbance maximum is at 532 nm. The effect of several variables is described. The range for the method is 0–5.0 p.p.m. of chlorate ion.

RÉSUMÉ

On décrit une méthode spectrophotométrique pour le dosage simple, direct et sensible des chlorates. Ce procédé est basé sur l'interférence des chlorates sur la formation du complexe rhénium–α-furildioxime, dont l'absorption maximum est à 532 nm. On décrit l'influence de plusieurs variables. Cette méthode convient pour des concentrations en chlorate comprises entre 0 et 50 p.p.m.

ZUSAMMENFASSUNG

Es wird eine einfache direkte und empfindliche spektralphotometrische Methode zur Bestimmung des Chlorat-Ions beschrieben. Die Methode beruht auf der Störung des Chlorat-Ions auf die Bildung des Rhenium–α-furildioxim-Komplexes, dessen Absorptionsmaximum bei 532 nm liegt. Mit der Methode können 0–5.0 p.p.m Chlorat bestimmt werden.

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

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ELWELL AND WOOD[1] and COCKBILL[2] have reviewed methods used for the spectrophotometric determination of niobium in steels. The most widely used procedures are the peroxide, thiocyanate, and pyrogallol methods. WHITE AND SCHOLES[3] have separated niobium with phenylarsonic acid, but titanium coprecipitated to such an extent that the titanium had to be determined separately to correct for its interference. WILLIAMS[4] separated niobium from the matrix elements by absorption of niobium on anion-exchange resin from a hydrofluoric–nitric acid solution, and determined niobium spectrophotometrically with bromopyrogallol red.

THE NIOBIUM ANALYSIS PANEL[5], after a critical assessment of numerous procedures, selected a spectrophotometric thiocyanate–oxalate method. It is based on the bleaching effect of ammonium oxalate on the coloured niobium thiocyanate, which can be determined in the presence of other coloured thiocyanates by difference. This method is applicable only to mild or low alloy steels, and is limited to steels containing not more than 0.6% molybdenum, 0.25% tungsten, 1% titanium or 0.1% vanadium, the last element forming a very strong colour with thiocyanate. In addition, the sensitivity of this modified thiocyanate method is only one half of that of the normal thiocyanate procedure[6].

BELCHER *et al.*[7] have reported a selective method for the determination of niobium with 4-(2-pyridylazo)-resorcinol, disodium salt (PAR) in an acetate–tartrate medium at pH 5.8, but even milligram amounts of iron(III) caused serious interference. JENKINS[8] determined niobium in mild steels with PAR, at pH 6.0 after separating the niobium with a controlled amount of cupferron. ELINSON *et al.*[9] showed that niobium can be determined with PAR in 0.75 *N* hydrochloric acid medium, thus overcoming the interference of a large number of cations, but even then the amount of iron(III) that can be tolerated is limited to few milligrams.

The present paper describes a direct spectrophotometric method for the determination of niobium in mild, low alloy and high alloy steels with PAR. The interference of large amounts of iron is overcome by reduction of iron(III) to iron(II). A compensating solution is used to correct for the colour of some metal ions and for the absorbance of the copper–PAR complex. The niobium–PAR complex is formed in 1 *N* hydrochloric–0.2 *N* perchloric acid medium, where the only serious interference is tantalum. This method, although slightly less sensitive than the thiocyanate extraction procedure, is simpler and faster than other methods, and permits the determination of niobium in all types of steels. Milligram amounts of molybdenum, tungsten, titanium, and vanadium do not interfere with the colour development.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 4-cm glass cuvettes was used.

Standard niobium(V) solutions (100 µg/ml and 10 µg/ml). Prepare a stock solution containing 100 µg Nb/ml by fusing 0.1431 g of Nb_2O_5 with 3.5 g of potassium hydrogen sulphate. Extract the melt with 20 ml of 20% tartaric acid and add another 80 ml of tartaric acid solution. Dilute to 1 l with water. To obtain 10 µg Nb/ml solution, take 25 ml of the 100 µg/ml solution, add 22.5 ml of 20% tartaric acid and dilute to 250 ml with water.

Iron(III) chloride solutions (100 mg Fe/ml and 2 mg Fe/ml). Dilute 50 ml of iron(III) chloride solution ("Analar", s.g. 1.45) to 100 ml. Transfer 1 ml of this 100 mg Fe/ml solution to a 100-ml volumetric flask, add 1 ml of 10 *M* HCl and dilute to volume, to prepare a 2 mg Fe/ml solution.

Aluminium chloride solution. Dissolve 27 g of $AlCl_3 \cdot 6H_2O$ in 80 ml of water and dilute to 100 ml.

PAR solution (0.1%). Dissolve 0.1 g of PAR, "Merck", in water, add 0.5 ml of 10% sodium hydroxide and dilute to 100 ml.

Recommended procedures

Method A (low niobium steel, less than 0.2% Nb). Weigh 1.0 g of sample into a 250-ml beaker, add 7 ml of water, 7 ml of 10 *M* hydrochloric acid, 7 ml of 15 *M* nitric acid and 0.5 ml of 40% hydrofluoric acid. After dissolution, add 13 ml of 72% perchloric acid and heat until perchloric acid refluxes on the sides of the beaker. Cool, adjust the volume to 10 ml with 72% perchloric acid, add 30 ml of water and 1 ml of 40% hydrofluoric acid, and transfer the contents to a Teflon beaker. Heat the solution at 85° for 15 min. Cool, transfer to a 100-ml volumetric flask containing 10 ml of 20% tartaric acid, and dilute to volume.

Pipette two aliquots of equal volume (containing 0–100 µg Nb and not more than 100 mg Fe) into 250-ml beakers. Add 20% tartaric acid solution, to increase the total amount of tartaric acid to 200 mg, iron(III) chloride solution, to bring the total iron to 100 mg, and 72% perchloric acid and 4% hydrofluoric acid to bring the total amount of each to 1.0 ml. Add 0.5 ml of 10 *M* hydrochloric acid and dilute to 35 ml with water. Add 3 ml of 10% anhydrous sodium sulphite, bring to the boil, add 1 ml of 3% ascorbic acid and boil for 2.5 min. Cool and transfer to 50-ml volumetric flasks, one flask containing 4.5 ml of 10 *M* hydrochloric acid and 3 ml of aluminium chloride solution, and the other flask containing 4.5 ml of 10 *M* hydrochloric acid only. Add 4.00 ml of 0.1% PAR solution, dilute to the mark and mix. Measure the absorbance after 15–20 min at 536 nm against a blank. Use 4-cm cells for 0–50 µg of Nb and 2-cm cells for 50–100 µg of Nb. Calculate the amount of niobium from the difference in absorbances of the two aliquots.

Prepare a blank and standard, which contains the same amount of tartaric acid, iron(III), perchloric acid, hydrofluoric acid and hydrochloric acid as the sample before the reduction step.

For samples containing small amounts of niobium and large amounts of chromium see *Study of interferences*.

Method B (high niobium alloy steels). Weigh 0.2 g of sample into a 250-ml beaker and add acids as in Method A. After dissolution, add 23 ml of 72% perchloric acid and heat until perchloric acid refluxes on the sides of the beaker. Cool, adjust the volume to 20 ml with 72% perchloric acid, add 40 ml of water and 5.0 ml of hydrofluoric acid and transfer the contents to a Teflon beaker. Heat the solution at 85° for 15 min. Cool, transfer to a volumetric flask so as to obtain a solution containing approximately 10 μg of Nb per ml, and add 20% tartaric acid to obtain a solution of 20 mg of tartaric acid per ml.

Pipette two aliquots of equal volume (containing 0–100 μg Nb and not more than 2 mg Fe) into 250-ml beakers. Adjust all reagents as in Method A, except for the iron(III) chloride, which is adjusted to 2 mg of iron using the 2 mg Fe/ml solution. Dilute to 37 ml with water. Add 1 ml of 10% anhydrous sodium sulphite, bring the solution to the boil and continue as in Method A.

DISCUSSION

Dissolution of the sample

The samples are dissolved in a dilute nitric–hydrochloric acid mixture containing 0.5 ml of 40% hydrofluoric acid. Hydrofluoric acid is used to volatilize silicon and to prevent the precipitation of tungsten, niobium and other oxides during the initial dissolution step. All samples are fumed with perchloric acid to oxidize acid insoluble carbides, leaving at the end of the dissolution, precipitated tungsten and niobium oxides in the solution. Treatment with hydrofluoric acid for 15 min at 85° renders these oxides soluble.

Sensitivity and stability of the method

The niobium–PAR complex, when measured against the blank, has maximum absorbance at 536 nm. The molar absorptivity of the complex is $1.44 \cdot 10^4$ for Method B (2 mg of Fe) and $1.32 \cdot 10^4$ for Method A (100 mg of Fe), corresponding to 0.0065 μg Nb/cm^2 and 0.007 μg Nb/cm^2 on the Sandell scale respectively. Beer's law is obeyed up to 2.0 μg Nb/ml.

It has been reported[9] that the colour of the niobium–PAR complex develops gradually and the absorbance must be read after 50–60 min. The incorporation of aluminium ion accelerates the colour development and the full colour of the complex develops in 15 min. Standard solutions are stable for at least 1 h, but the absorbance of steel solutions must be read between 15 and 20 min after mixing, because of the drop in the absorbance caused by some ions, *e.g.* copper and molybdenum, on standing.

The absorbance of the niobium–PAR complex does not change in the temperature range 19°–25°.

Choice of acidity and the effect of varying reagent concentrations

ELINSON *et al.*[9] showed that the absorbance of the niobium–PAR complex changes little over the range 0.5–1.0 *M* hydrochloric acid. We tried to develop the colour in 0.5 *M* hydrochloric acid, but copper interfered badly. With increasing acid concentration the interference by copper decreased rapidly, and a final acidity of 1 *M* hydrochloric acid was selected. In addition, the solution is 0.2 *M* in perchloric acid, which is introduced with the sample aliquot.

It is recommended that 20 mg of tartaric acid per ml be present in the solution containing niobium to prevent hydrolysis. A total amount of 200 mg of tartaric acid per determination was selected to give more flexibility with sample dilution and the selection of aliquots for analysis. Any other level of tartaric acid above 50 mg can be used. The effect of tartaric acid on the absorbance is given in Fig. 1.

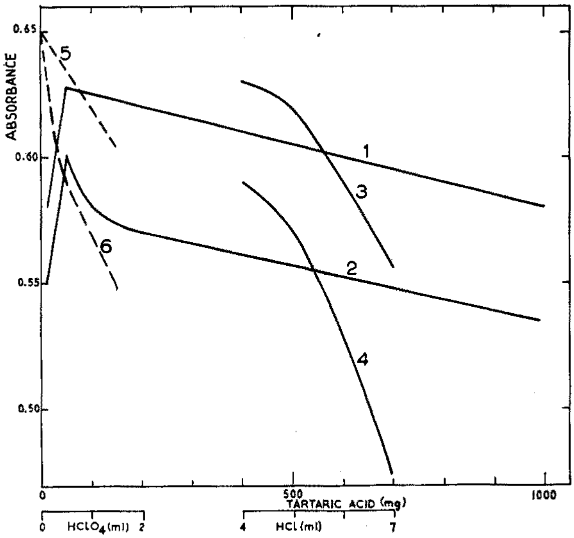

Fig. 1. The effect of tartaric, hydrochloric and perchloric acids on the absorbance (50 μg Nb/50 ml; 1 ml 4% HF; 90 mg Al; 4-cm cells). (1) Tartaric acid (2 mg Fe; 5 ml HCl; 1 ml $HClO_4$). (2) Tartaric acid (100 mg Fe; 5 ml HCl; 1 ml $HClO_4$). (3) HCl (2 mg Fe, 1 ml $HClO_4$, 200 mg tartaric acid). (4) HCl (100 mg Fe, 1 ml $HClO_4$, 200 mg tartaric acid). (5) $HClO_4$ (2 mg Fe, 5 ml HCl, 200 mg tartaric acid). (6) $HClO_4$ (100 mg Fe, 5 ml HCl, 200 mg tartaric acid).

The colour development step is governed by the method of dissolution and it is important that the amounts of iron, and hydrofluoric, tartaric, perchloric and hydrochloric acids be strictly controlled. The effect of variation in the reagent concentrations is shown in Fig. 1. It is possible to select a sample aliquot containing any amount of iron up to 100 mg, as long as the blank and standard contain the same amount of iron.

Reagent blank

The absorbance of the reagent blank is relatively high (0.920 *vs.* water in 4-cm cells) and therefore it is important that the reagent solution be pipetted as accurately as possible. The largest volume of reagent which could be added to a 50-ml flask containing the sample solution was 4 ml.

Reducing agents

Sodium sulphite and ascorbic acid are used for the reduction of iron. It was found that sodium sulphite did not completely reduce iron(III) to iron(II) and that small amounts of ascorbic acid were required for complete reduction. An amount of 3 ml of 10% sodium sulphite is sufficient for 100 mg of iron and only 1 ml of reducing solution is needed for 2 mg of iron. Hydrochloric acid (0.5 ml) is added to the sample aliquot because it assists with the reduction, and also gives an indication when all the iron has been reduced by the disappearance of the yellow iron(III) chloride colour. An excess of sulphite does not interfere with the spectrophotometric procedure, but solutions must be boiled for 2.5 min to destroy ascorbic acid which interferes with the colour development.

Compensating solution and demasking of niobium

A compensating solution was used to correct for the effect of coloured ions and metal–PAR complexes in the solution. Fluoride forms complexes with niobium and tantalum and prevents the formation of coloured niobium and tantalum–PAR complexes, but does not interfere with the formation of other metal–PAR complexes or change colour of other metal ions.

Aluminium(III) was used as a demasking agent to form the fluoride complex, thus releasing niobium and tantalum to react with PAR. It was found that 0.5 ml and 1.0 ml of 4% hydrofluoric acid could be masked with 60 mg and 80 mg of aluminium respectively. Taking into account the variations in purity of aluminium chloride reagents, 90 mg of aluminium was chosen as a suitable amount. The sample and the compensating solutions must be measured together.

TABLE I

EFFECT OF VARIOUS ELEMENTS

(50 µg Nb/50 ml, 100 mg Fe, 1 ml 4% HF and 90 mg Al)

Foreign ion added	*Amount taken (mg)*	*Niobium found (µg)*	*Relative[a] error (%)*
Co^{2+}	10	55.7	11
Cr^{3+}	5	56.0	12
Cu^{2+}	0.25	55.7	11[c]
Cu^{2+}	0.5	61.4	23[b,c]
Mn^{2+}	5	50.0	0
Mo(VI)	2	50.0	0
Mo(VI)	4	50.0	0[b,d]
Ni^{2+}	10	51.3	3
PO_4^{3-}	3	50.0	0
Pb^{2+}	1	50.0	0
Ta^{5+}	0.050	59.0	18
Ta^{5+}	0.100	65.0	30
Ti^{4+}	5	50.0	0
U(VI)	5	50.0	0
V^{5+}	5	50.0	0
W(VI)	1	50.0	0
W(VI)	2	50.5	1
W(VI)	5	51.5	3
W(VI)	5	50.0	0[e]
Na_2SO_4	142	47.4	−5

[a] All interferences, except for Ta, are removed by the use of a compensating solution.
[b] Maximum permissible amount.
[c] Absorbance drops after 15 min standing time.
[d] Absorbance drops after 20 min standing time with 100 mg Fe, but not with 2 mg Fe.
[e] 2 mg Fe.

Study of interferences

Of the various elements examined, only copper and tantalum formed coloured complexes with PAR under the experimental conditions. The compensating solution corrects for all coloured ions and the copper–PAR complex, and the only remaining interference is tantalum. The effect of various elements on the absorbance when measured against a blank is given in Table I.

Sulphate ion decreases the absorbance and therefore sulphuric acid cannot be used for sample dissolution. Sulphate is introduced into the solution by the oxidation of sulphite to sulphate in the reduction step. As the amount of sulphate introduced depends on the concentration of iron(III), the amount of iron must be the same in all solutions.

Chromium produces a large absorbance in the compensating solution and therefore chromium should be volatilized as chromyl chloride with hydrochloric acid. This procedure can be applied when small amounts of niobium are determined in chromium steels. It is important to adjust the amount of perchloric acid to 10 ml after fuming.

Copper forms a colour with PAR and 15 min after mixing slowly reduces the absorbance of the colour and compensating solution by the same extent. No error is introduced provided the absorbances of these two solutions are read together within the specified time.

Molybdenum can be present in amounts up to 4 mg. However, in solutions containing 100 mg of iron, there is a slow drop in absorbance 20 min after mixing if more than 2 mg of molybdenum is present.

Tantalum cannot be masked or compensated, and therefore interferes in the procedure. Amounts of 50 μg and 100 μg of tantalum will produce an absorbance equivalent to 9 μg and 15 μg of niobium, respectively.

Aluminium even at the 2% level produces a negative error of only 1% (2 mg of Al increases the absorbance of compensating solution by 0.005).

Reproducibility of the method

Readings on a series of 10 standards showed the relative standard deviation at the 1.0 μg Nb/ml level to be ± 0.6%.

The reproducibility of the method at the 50 μg of niobium level in steel samples using a compensating solution is ±1.5%, which will increase at the 25 μg niobium level to ±3%.

APPLICATIONS

Recovery of niobium from dissolution solutions, prepared either in tartaric acid or tartaric–perchloric acid media, decreased on standing when hydrofluoric acid was added to dissolve the precipitated oxides. Spectrophotometric measurements must therefore be carried out the same day as sample preparation, or alternatively the sample may be left standing after fuming with perchloric acid and prepared for spectrophotometric measurement when required.

Method A has been written primarily for niobium determination in structural steels where the range of niobium is between 0.010 and 0.060%. A 10-ml aliquot can be taken for the analysis without requiring any further adjustment of reagents. For niobium contents between 0.060 and 0.12% and between 0.12 and 0.18%, samples of 0.5 g and 0.3 g, respectively, should be taken.

Stainless steel samples (NBS 845–850) containing niobium between 0.05 and 0.60% were dissolved and analysed according to Method A. The details are given in Table II.

TABLE II

ANALYTICAL PROCEDURE USED FOR NBS 845–850 STAINLESS STEELS

NBS^{a} *sample no.*	*Chromium (%)*	*Sample taken (g)*	*After fuming with* $HClO_4$^{b}		*Aliquot taken (ml)*	*Reagents added*	
			40% HF added (ml)	*Diluted to (ml)*		$HClO_4$ *(ml)*	*Fe (mg)*
845	13.31	0.5^{c}	1	100^{d}	10	—	56
846	18.35	0.2	2.5	250^{e}	10	0.6	94
847	23.72	1.0^{c}	1	100^{d}	10	—	37
848	9.09	0.25	2.5	250^{e}	10	0.6	90
849	5.48	0.4	2.5	25c^{e}	10	0.6	85
850	2.99	1.0	1	100^{d}	10	—	28

[a] For Nb content see Table III.
[b] All samples contain 10 ml of $HClO_4$.
[c] 16 ml of $HClO_4$ added, chromium volatilized as CrO_2Cl_2, $HClO_4$ adjusted to 10 ml.
[d] Contains 10 ml of 20% tartaric acid.
[e] Contains 25 ml of 20% tartaric acid.

The sample solution after fuming must contain at least 1 ml of 40% hydrofluoric acid for low niobium steels, and 2.5 ml of hydrofluoric acid when high niobium steels are analysed, otherwise insoluble oxides may not be rendered soluble. The compensating solution must contain 1 ml of 4% hydrofluoric acid to form the niobium and tantalum complexes and, when smaller aliquots are taken for the colorimetric procedure, additional amounts of hydrofluoric acid must be added to the solution. Deficiency in fluoride will lead to high absorbance readings for the compensating solution.

Correction for tantalum

Tantalum interferes with this method, but in amounts up to 50 µg of tantalum, the tantalum–PAR colour is only 18% as sensitive as the niobium–PAR colour. The niobium/tantalum ratio in stainless steels is usually about 4, hence tantalum gives a positive error of 5% in the niobium determination. Recently, high-alloy steels or "superalloys" containing 0.44–4% niobium have been prepared and also tungsten alloys (turbine steel) containing 2.5–10% niobium have found application in industry. This method makes available a fast and simple procedure for the determination of niobium in steels containing tungsten and other metal carbides, which are not soluble in sulphuric–nitric acid media.

If the Nb+Ta content is known, then the spectrophotometric results for aliquots containing up to 50 µg of tantalum can be corrected for tantalum interference by the formula:

$$Nb_T = \frac{Nb_S - 0.21\ Nb_G}{0.79}$$

and tantalum calculated as

$$Ta = 1.17\ (Nb_G - Nb_T),$$

where Nb_T = true % niobium, Nb_S = % niobium by spectrophotometry, Nb_G = % niobium by gravimetric procedure, where oxides of Nb and Ta are expressed as % niobium, and Ta = % tantalum.

Comparison with standard samples

The results obtained for a variety of materials are shown in Table III. Few standard samples containing niobium only were available, so that standard samples containing niobium and tantalum had to be used and appropriate corrections made for tantalum interference. The main aim was to test this procedure in steels containing varying amounts of diverse ions usually encountered in different types of steels. The results obtained were in good agreement with certified values, with the exception of one sample (BCS 312).

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM IN VARIOUS MATERIALS

Sample	*Certified*		*Nb found (%)*	*Corrected for Ta Nb (%)*
	Nb (%)	*Ta (%)*		
BCS 275 (mild steel)	0.035	0.003	0.0347	0.0342
BCS 277 (mild steel)	0.021	0.0006	0.0206	0.0205
BCS 225/2 (Ni–Cr–Mo steel)	0.003[a]	0.001	0.0042	0.0040
NBS 1161 (low alloy steel)	0.011	0.002	0.0119	0.0115
NBS 1162 (low alloy steel)	0.096	0.036	0.102	0.096
NBS 1163 (low alloy steel)	0.195	0.15	0.228	0.201
NBS 1164 (low alloy steel)	0.037	0.069[b]	0.0475	0.0372
NBS 1165 (ingot iron)	(0.001)	0.001	0.0013	0.0011
NBS 1166 (ingot iron)	0.005	0.002	0.0072	0.0068
NBS 1167 (low alloy steel)	0.29	0.23	0.347	0.304
NBS 1168 (low alloy steel)	0.006	0.005	0.0068	0.0059
NBS 845	0.11[a]	(0.002)	0.108	0.108
NBS 846	0.60	(0.030)	0.604	0.598
NBS 847 (stainless steel)	0.03[a]	(0.002)	0.0335	0.0331
NBS 848	0.49	(0.026)	0.488	0.483
NBS 849	0.31	(0.021)	0.312	0.308
NBS 850	0.05	(0.002)	0.0482	0.0478
BCS 312 (permanent magnet)	1.33[c]	0.13	1.10	1.04
			1.11[d]	1.05
SAA 125 (turbine steel)	—	—	2.48	2.41
(13 Ni–13 Cr–12 Co–3 Mo–6 W–3 Nb)			2.49[e]	2.42[f]

[a] Chromium volatilized as CrO_2Cl_2.
[b] Correction for Ta: $0.069 \times 0.15 = 0.0103$.
[c] Nb (+Ta).
[d] Analysed to ASTM E 30–56 para 153 (1956), oxides fused with $NaHSO_4$ dissolved in 20% tartaric acid, determined to Method B.
[e] Analysed to ASTM E 30–56 para 154 (1956), continued as for d.
[f] Nb (+Ta) 2.76%, Nb 2.42%, Ta 0.40%.

Permanent magnet alloy (BCS 312) was analysed by Method B giving a result of 1.10% Nb. The certified value for Nb (+Ta) is given as 1.33%, with one value for tantalum of 0.13%, which would give the true value for niobium of 1.22%. WILLIAMS[4] has reported the niobium content of BCS 312 as 1.19%. In the present work, a number of gravimetric analyses were made by the ASTM E 30-56 para 153 (1956) method and the result for Nb (+Ta) was 1.32%. Some of the combined oxides were fused with 5 g of sodium hydrogen sulphate, dissolved in 20% tartaric acid, and the niobium determined spectrophotometrically by Method B. In this case the absorbance of the compensating solution was zero and the value for niobium was 1.11%, which would give the true value for niobium as 1.05% and for tantalum as 0.33%.

It is a pleasure to acknowledge the assistance given by Mrs. B. McALLISTER with the experimental work.

SUMMARY

A direct method is presented for the spectrophotometric determination of niobium with PAR in mild and alloy steels. Interference is caused only by tantalum and large amounts of copper. A compensating solution is used to correct for coloured ions and for the copper–PAR complex. The method covers the range 0–100 µg of niobium, and Beer's law is obeyed from 0 to 2.0 µg Nb/ml. A molar absorptivity of 14,400 at 536 nm was found for the niobium–PAR complex, with a relative standard deviation of ±0.6%.

RÉSUMÉ

Une méthode directe est présentée pour le dosage spectrophotométrique du niobium au moyen de PAR (4-(2-pyridylazo)-résorcinol) dans divers aciers. Seul le tantale peut gêner ainsi que de grandes quantités de cuivre. Une solution de compensation est utilisée pour corriger l'influence d'ions colorés et du complexe cuivre–PAR. Cette méthode permet de doser de 0–100 µg de niobium; la loi de Beer s'applique de 0–2.0 µg Nb/ml. Coefficient d'extinction molaire: 14,400 à 536 nm pour le complexe niobium–PAR avec une déviation standard relative de ±0.6%.

ZUSAMMENFASSUNG

Es wird eine direkte Methode zur spektralphotometrischen Bestimmung von Niob mit 4-(2-Pyridylazo)-resorcinol (PAR) in kohlenstoffarmen und legierten Stählen beschrieben. Nur Tantal und grössere Mengen Kupfer stören. Eine Vergleichslösung wird für gefärbte Ionen und für den Kupfer–PAR-Komplex verwendet. Die Methode eignet sich für den Bereich von 0–100 µg Nb; das Beersche Gesetz wird von 0–2.0 µg Nb/ml befolgt. Die molare Absorption bei 536 nm beträgt 14400, die relative Standardabweichung ±0.6%.

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A VOLTAMMETRIC STUDY OF AQUOZINC(II) COMPLEXES IN METHANOL*

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Chemical studies in nonaqueous solvents have received considerable attention in recent years. Water is a common impurity in nonaqueous solvents and even small amounts may drastically alter the nature, structure, and behavior of the species present. The water concentration in a typical nonaqueous solvent containing 0.02% water is approximately 10 mM, a value that often exceeds the concentration of added solutes. Water has a relatively high solvating energy and can replace one or more nonaqueous solvent molecules (SH) from the inner coordination sphere of a metal ion:

$$M(SH)_m{}^{n+} + j\ H_2O = [M(SH)_{m-j}(H_2O)_j]^{n+} + j\ SH \tag{1}$$

where m is the maximum coordination number of the metal ion, M^{n+}. The stepwise formation constant for the jth aquo complex is given by:

$$K_j = \frac{[M(SH)_{m-j}(H_2O)_j]^{n+}}{[M(SH)_{m-j+1}(H_2O)_{j-1}]^{n+}[H_2O]} \tag{2}$$

Two techniques are commonly used to determine the formation constants of aquo–metal complexes in nonaqueous solvents. One method relies on optical measurements[1-3] and the other uses polarographic data[1]. The optical technique is useful only when there is appreciable complexation; it requires the solution of a series of simultaneous equations and becomes increasingly tedious as the coordination number increases. The determination of polarographic half-wave potentials is also a time-consuming process; recorded current–voltage curves must be corrected for the residual current determined from another polarogram[4]. A plot of E *vs.* log $[(i_d-i)/i]$ is required for each $E_{\frac{1}{2}}$ determined.

By using chronopotentiometry with its relatively simple apparatus, one can avoid some of these disadvantages[5]. This method offers an advantage over polarography because of the relative ease with which $E_{\tau/4}$ (the chronopotentiometric analog of the polarographic $E_{\frac{1}{2}}$) can be determined[6]. It has been shown in a chronopotentiometric study of europium(III) acetate complexes, that $E_{\tau/4}$ will shift toward more negative potentials, as does $E_{\frac{1}{2}}$, when the ligand concentration is increased and complexation occurs[7].

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The equation for the chronopotentiometric determination of formation constants of aquo–metal complexes in nonaqueous solvents is similar to the analogous equation using polarographic data. It is easily derived from the Nernst equation. For the reversible reduction:

$$M(SH)_m{}^{n+} + n\ e^- = M + m\ SH \tag{3}$$

the Nernst equation (written as it applies at the working electrode surface, *i.e.* at $x=0$) at 25° is:

$$E = E^{\circ\prime} - \frac{0.059}{n} \log \left\{\frac{M}{[M(SH)_m{}^{n+}]}\right\}_{x=0} \tag{4}$$

where $E^{\circ\prime}$ is the formal potential for the redox system (3).

When water is present in the solution the fraction of the metal ion which exists as $M(SH)_m{}^{n+}$ is given by*:

$$f_{M(SH)_m^{n+}} = \left\{\frac{[M(SH)_m{}^{n+}]}{C_M}\right\} \tag{5}$$

$$f_{M(SH)_m^{n+}} = \frac{[M(SH)_m{}^{n+}]}{[M(SH)_m{}^{n+}] + [M(H_2O)(SH)_{m-1}{}^{n+}] + \ldots + [M(H_2O)_j(SH)_{m-j}{}^{n+}] + \ldots + [M(H_2O)_m{}^{n+}]} \tag{6}$$

Taking the formation constants, K_j, for the aquo complexes (eqn. (2)) and simplifying:

$$f_{M(SH)_m^{n+}} = \frac{1}{1 + [K_1(H_2O) + \ldots + [K_1 \ldots K_j(H_2O)^j] + \ldots + [K_1 \ldots K_m(H_2O)^m]} \tag{7}$$

At the quarter-wave potential, $E_{\tau/4}$, which is identical to the polarographic half-wave potential[8], the concentration of the metal ion at the working electrode surface, $(C_M{}^{n+})_{x=0}$, is equal to one-half the bulk concentration of the metal ion, $C_M{}^*$ [9], thus from eqns. (4), (5), and (7):

$$E_{\tau/4} = E^{\circ\prime} - \frac{0.059}{n} \log \left[\frac{2}{C_M{}^*}\right] - \frac{0.059}{n} \log\{1 + [K_1(H_2O)] + \ldots + [K_1 \ldots K_j(H_2O)^j] + \ldots + [K_1 \ldots K_m(H_2O)^m]\} \tag{8}$$

Equation (8) should yield a composite curve of straight line sections intersecting at pH_2O ($= -\log [H_2O]$) values corresponding to pK_j when $E_{\tau/4}$ is plotted as a function of pH_2O. If pK_1 is unobtainable from this plot, it can easily be calculated from eqn. (4) given by LARSON AND IWAMOTO[1], $E_{\tau/4}$ being substituted for $E_{\frac{1}{2}}$.

EXPERIMENTAL

Apparatus

The polarographic electrolysis cell (a 50-ml beaker) was thermostated at 25 ± 0.5°. Polarograms were recorded using a Sargent Model XV Polarograph equipped with the Sargent Model A IR-Compensator. The instrument was calibrated with a

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* The water concentration in these solutions is sufficiently large that the additional amount released from the coordination sphere upon reduction of an aquated metal ion is negligible.

Leeds and Northrup Student's Model Potentiometer and the dropping mercury electrode potentials were measured *versus* an aqueous saturated calomel electrode (SCE). A stopper in the beaker was provided with inlets for the electrodes and a dispersion tube for deaeration with nitrogen.

The current source for the chronopotentiometer was a Hewlett-Packard Model 721A transistorized power supply. A 5-megohm resistor was placed in series with the output to stabilize the current which was read on a milliammeter. A Leeds and Northrup Model 7401 pH meter provided the readout which was recorded with a Sargent Model SR recorder at a chart speed of 3 in./min. The instrument was calibrated with a potentiometer and could follow potentials up to about 2.1 V.

The chronopotentiometric electrolysis cell was a 60-ml separatory funnel which was thermostated, stoppered, and provided with inlets to admit the electrodes and nitrogen dispersion tube. The working electrode was a mercury pool ranging in size from approximately 2.8 cm² to about 7.1 cm² for currents ranging from 1.00 to 2.75 mA. The reference electrode was an aqueous SCE; a platinum foil, isolated from the bulk of the solution by means of a fritted disc, served as the auxiliary electrode. This compartment contained a solution identical to that in the cell compartment, but with no added zinc(II).

Reagents

Analytical reagent-grade chemicals were used as obtained. Bottles of methanol (Fisher Scientific, "Suitable for Karl Fischer Reagent"), selected at random, were found to contain 0.051 ± 0.0015% of water, based on the average of 8 Karl Fischer titrations[10,11].

The supporting electrolyte, tetraethylammonium perchlorate, was prepared as described by KOLTHOFF AND COETZEE[12] from tetraethylammonium bromide (Eastman, White Label) and perchloric acid (Mallinkrodt, 70%). A negligible amount of water (less than 0.01%) remained after drying. This quarternary ammonium salt minimized competition between the ions of the supporting electrolyte and the metal ions for the water. Variations from several to a hundred millivolts in the $E_{\frac{1}{2}}$ of similar solutions were noted when acetate or chloride supporting electrolytes were used. Perchlorate ion forms relatively weak complexes with only a few metal ions[13-15]; there is no evidence for zinc(II)-perchlorate complexes[14,16]. Zinc perchlorate hexahydrate (K and K Laboratories) was dried in a continuously drawn vacuum at 50° and stored at room temperature *in vacuo* over P_2O_5. The average of 5 Karl Fischer titrations showed the presence of 8.52 ± 0.03 % water.

Stock methanol solutions (50 mM in zinc perchlorate) and aqueous solutions (10 mM in zinc perchlorate) were prepared and stored in a nitrogen atmosphere. Test solutions were prepared by adding measured amounts of water and methanol and sufficient tetraethylammonium perchlorate to make the solution 0.1 M in this salt. Twenty ml of test solution (0.909 mM in zinc(II)) were used for each polarogram and chronopotentiogram; all data were corrected for the water introduced with the methanol and the zinc perchlorate.

Procedures

Both the polarograph and the chronopotentiometer were tested periodically by electrolyzing aqueous cadmium(II) in 0.1 M potassium chloride; the $E_{\frac{1}{2}}$ was

-600 ± 2 mV *vs.* SCE and $E_{\tau/4}$, -598 ± 4 mV *vs.* SCE throughout the study. These values corresponded closely with the literature values[17,18]. The linear log plots corresponded to a 2-electron electrolysis.

Polarographic half-wave potentials were taken as the point where the linear plot E_{DME} *vs.* log $[(i_d - i)/i]$ (after correction for the residual current) crossed the zero axis[19]. The IR Compensator eliminated the need to correct for the iR drop and the $E_{\frac{1}{2}}$ values represent the average of 6 determinations on at least 3 separate solutions.

Transition times and quarter-wave potentials were determined as described by DELAHAY AND BERZINS[20] with measurements made to the nearest 1/40 in. (1 in. = 20 sec). No additional accuracy was gained from $E_{\tau/4}$ *vs.* log $[(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}]$ plots. The values are the average of 8 determinations on at least 3 separate solutions. No correction for iR drop was necessary; the highest resistance (measured with an a.c. galvanometer and resistance box) was about 7000 ohms; the pH meter drew a maximum of $1 \cdot 10^{-12}$ A [21].

Rejection or retention of data was based on the normal error curve using a 95% confidence limit. A deaeration time of 20 min proved sufficient for methanolic solutions; 10 min sufficed for the aqueous solutions. The nitrogen was first bubbled through a solution similar in composition to the test solution but without zinc(II), to saturate the gas with the vapor and minimize evaporation. Karl Fischer titrations showed that water introduced by the nitrogen was negligible.

RESULTS

Table I shows the variation and shift to more cathodic values of half-wave and quarter-wave potentials with increased water concentration experimentally determined in this study. About 70% of the replicate values agree to within ±10 mV. The mean per cent error in $E_{\frac{1}{2}}$ was 1.15%; in $E_{\tau/4}$, it was 1.20%. An F-test[22] showed that there was no significant difference between the mean per cent errors in the potentials at a 1% level of significance.

Only small differences between successive half-wave and quarter-wave potentials exist for solutions with low water content, a phenomenon that has been previously observed. The half-wave potentials of various metal ions were almost unaffected by the addition of up to 1% water in "water-like" solvents[23].

A few irregularities in the shifts to more negative potentials as the water content increases were found in the solutions containing low water concentrations. This may be due to the reported slow response of the SCE in solutions of this kind[24].

Plots of E_{DME} *vs.* log $[(i_d - i)/i]$ indicate that zinc(II) is reversibly reduced in 0.1 *M* tetraethylammonium perchlorate. The slopes of the linear plots (25 mV) were somewhat less than the theoretical value for a 2-electron process. Constant-potential coulometric data on various solutions using known weights of zinc(II) as well as the oxidation potential of zinc amalgams at 0.222 τ', corresponding to the cathodic $E_{\tau/4}$ [25], proved that the reversible reduction was: $\mathrm{Zn(II)} + 2\,e^- = \mathrm{Zn} \cdot (\mathrm{Hg})$.

Figures 1 and 2 show typical $E_{\frac{1}{2}}$ and the $E_{\tau/4}$ *vs.* pH_2O curves; Table II shows the pK_j values determined for the aquozinc(II) complexes in methanol. Except for pK_1 these were determined from the intersections of the tangents drawn to the E *vs.* pH_2O curves with slopes of $(0.059/2) \cdot n_{H_2O}$. Within the limits of error the slopes of straight line segments of these curves could indicate a coordination number of 4 or 5

TABLE I

HALF-WAVE AND QUARTER-WAVE POTENTIALS

(25°; 0.909 m*M* Zn(II))

H_2O (*M*)	pH_2O	$-E_{1/2}$ (*mV vs. SCE*)	$-E_{\tau/4}$ (*mV vs. SCE*)
0.0235	1.63	1061	1027
0.0297	1.57	1077	1090
0.0471	1.33	1041	1047
0.0754	1.24	1046	1060
0.0952	1.02	1050	1073
0.148	0.830	1064	1060
0.199	0.702	1078	1104
0.274	0.563	1069	1069
0.510	0.292	1089	1084
0.768	0.115	1114	1069
1.001	−0.0041	1138	1148
2.42	−0.0384	1152	1161
3.55	−0.550	1165	1166
4.60	−0.662	1189	1188
6.59	−0.819	1193	1185
7.52	−0.876	1207	1218
8.41	−0.925	1220	1212
12.63	−1.10	1218	1215
13.04	−1.12	1230	1237
13.74	−1.14	1237	1248
25.17	−1.40	1237	1238
37.73	−1.57	1315	1288
47.17	−1.66	1368	1341
54.11	−1.73	1367	1366
55.5	—	1401	1400

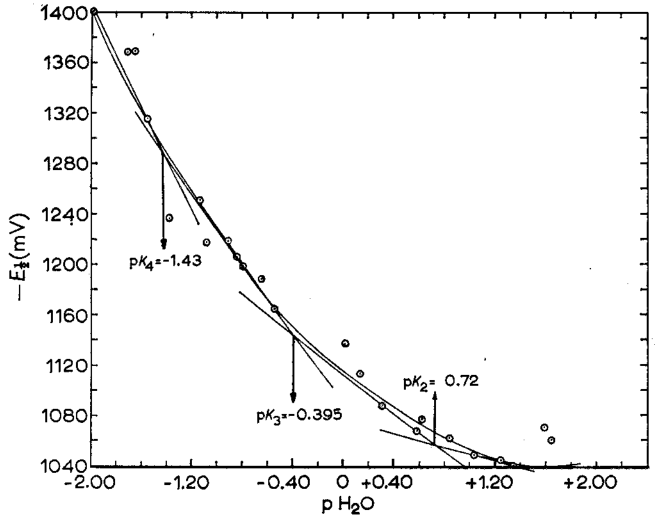

Fig. 1. $E_{1/2}$ (mV *vs.* SCE) *vs.* pH_2O (25°; 0.909 m*M* Zn(II)).

for zinc(II). Because this metal ion is rarely 5-coordinate and most often has a coordination number of four[26], the latter value was used when interpreting these data.

The values determined by polarography are used as the "true" values for comparison purposes because no other reliable values have been reported; the polarographic method has been shown to give reliable results[1,27]. MIGAL AND GRINBERG[28] determined the instability constants of the aquo-complexes of cadmium(II), lead(II), and zinc(II) in methanol using ammonium perchlorate as a supporting electrolyte. Because the ammine complexes of zinc(II) are quite stable[29], it is very possible that their values are for mixed aquo–ammine complexes as the water competes with NH_3 for the zinc ions.

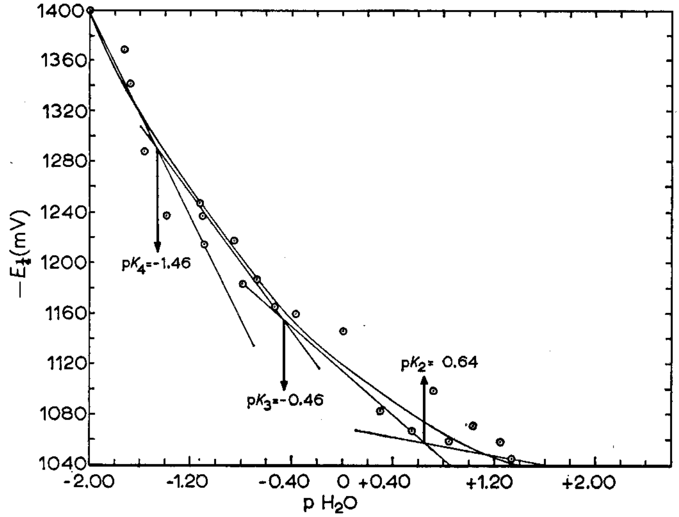

Fig. 2. $E_{\tau/4}$ (mV *vs.* SCE) *vs.* pH_2O (25°; 0.909 m*M* Zn(II)).

TABLE II

FORMATION CONSTANTS OF THE AQUOZINC(II) COMPLEXES FROM POLAROGRAPHIC AND CHRONOPOTENTIOMETRIC DATA[a]

K_j	pK_j *Polarography*	pK_j *Chronopotentiometry*	*No. of bound H_2O molecules*
1	1.29[b]	1.07[b]	1
2	0.720	0.640	2
3	−0.395	−0.460	3
4	−1.43	−1.42	4

[a] Precision of data by each method is *ca.* 10%.
[b] Calculated using eqn. (4) from ref. 1.

The formation constants determined from chronopotentiometric data are in good agreement with those from the polarographic data. The pK_4 values agree with the similar value determined by a Ringbom–Eriksson approach[30] and the average formation constant (2) calculated from data of both techniques shows a good agreement: K_{av} (polarography) is 0.29 and is 0.25 from chronopotentiometric data. These values are of the same order of magnitude as the aquocopper(II) and aquonickel(II) complexes in ethanol[3].

The possibility of polymerization of the complex ions in this system cannot be discounted, especially in solutions of high methanol content. Although this phenomenon is more prevalent in systems containing ions of higher charge than zinc(II) [31], this ion was found to form a polynuclear complex in an acidified solvent of low dielectric constant (ethanol)[32].

Data were also obtained on solutions containing 0.566 mM zinc(II) by chronopotentiometry and 5.38 mM zinc(II) by polarography; pK_4 values were -1.52 and -1.46 for these concentrations, respectively. These are in agreement with the pK_4 determined on solutions 0.909 mM in zinc(II). These data neither prove nor disprove the presence of polynuclear complexes; they do show that if polymerization occurs, it does so to the same extent over the range (0.566 to 5.38 mM) of zinc(II) concentrations used.

Ion-association has been neglected in these considerations. This complication should be considered in solutions where the dielectric constant is less than 40 [33]. Theoretical considerations show that K_d, the ion-pair dissociation constant, increases as the ionic radius increases from 2 Å to 3 Å[34]. Because zinc(II) has an ionic radius of 7 Å[35] and it is known that ionic compounds are almost completely dissociated in methanol[36], it would seem that ion-association has little or no effect in this study. However, the small effect it may have could account for the anomalies noted in the potential data of Table I for the first few solutions.

The magnitudes of the shifts in the half-wave or quarter-wave potentials could be influenced by the liquid junction potential at the boundary of the test solution and aqueous SCE reference electrode. This factor has been neglected because of the difficulty in measuring or estimating its value (4 different ions are involved). In the 0.1 M lithium perchlorate solution, the junction potential between methanol and the SCE is +60 mV [37]; because the tetraethylammonium ion is larger than lithium(I) and, therefore, less mobile, the junction potential in this study is probably greater than 60 mV. As the water content increases, E_{JCT} will gradually decrease, but no information is available for the aqueous $(C_2H_5)_4NClO_4$(0.1 M)–KCl (3.5 M) junction potential. If all the junction potentials are positive, correction for this value would shift the $E_{\frac{1}{2}}$ and $E_{\tau/4}$ values to less negative potentials, but the effect on Figs. 1 and 2 would remain unchanged. The orders of magnitude of the formation constants would probably not be changed.

The results of this study indicate that chronopotentiometry can be used with confidence to determine the formation constants of aquo–metal complexes and for the study of other complex equilibria in nonaqueous solvents. The method has the advantage of being less time-consuming than polarography and still allows for relatively easy graphical interpretation of results. The use of derivative chronopotentiometry[6] would apparently simplify the operation and improve the accuracy and precision of locating the transition times.

SUMMARY

Results of chronopotentiometric and polarographic determinations of the formation constants of aquozinc(II) complexes in methanol are reported. Chrono-

potentiometry offers some advantages over polarographic and spectrophotometric methods for studies of this kind.

RÉSUMÉ

Des résultats de déterminations chronopotentiométriques et polarographiques de constantes de formation des complexes aquozinc(II) dans le méthanol sont donnés. Pour de telles études la chronopotentiométrie offre quelques avantages sur les méthodes polarographiques et spectrophotométriques.

ZUSAMMENFASSUNG

Die Ergebnisse von chronopotentiometrischen und polarographischen Bestimmungen von Bildungskonstanten des Aquozink(II)-Komplexes in Methanol werden angegeben. Die Chronopotentiometrie bietet einige Vorteile gegenüber der Polarographie und spectralphotometrischen Methoden für Untersuchungen dieser Art.

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A STUDY OF THE VOLTAMMETRIC BEHAVIOUR OF THE COUPLES Br^-/Br_2, Br^-/Br_3^-, $Br^-/HBrO$ AND Br^-/BrO^- AS A FUNCTION OF pH

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The coulometric production of bromine has often been applied to the titration of oxidizable compounds, both in acidic and alkaline media[1]. It is a common experience to encounter significant "blanks" in such titrations. The "blanks" have been ascribed to the presence in solution of reducing impurities[2,3], but we have found that the magnitude of these "blanks" is larger than the content of impurities in the reagents employed, and that the "blanks" are higher in solutions of higher pH, so that other causes must be sought. The present paper deals with the hydrolysis of bromine in alkaline media, and shows that this hydrolysis, together with the different voltammetric behaviour of the various couples which are produced, is responsible for the observed "blank".

EXPERIMENTAL

Materials

All materials were reagent grade (Merck p.a.). Before use, potassium bromide and sodium tetraborate were stored for some hours with liquid bromine in order to destroy possible reducing impurities[4]. Double-distilled water was used in the preparation of all solutions. Nitrogen (99.99%) was further purified from oxygen by passing it through a chromium(II) solution in sulphuric acid[5].

Apparatus

The H-cell which was used for current–voltage measurements and for the mono- and biamperometric experiments has already been described[6]. The electrical apparatus consisted of the following: a constant-current electronic generator, whose stability was better than 0.1%, a Leeds and Northrup model K-3 potentiometer, a standard Siemens 1000-ohm resistor, a Sefram Verispot galvanometer, a Solartron model LM 1420 electrometer and a 100-ohm Metrohm potentiometer. An electrical contact chronometer was used as a switch.

Procedures

Current–voltage curves were plotted for sulphuric acid (1 *M*), sodium bicarbonate (0.24 *M*), sodium tetraborate (10^{-2} *M*) and potassium hydroxide (10^{-2} *M*) media. The oxidized species were either electrically generated *in situ* (from 1 *M* potassium bromide) or were added from a burette (standard solution of hypobromite[7])

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to the potassium bromide solution. The volume of the solution in the cell was about 80 ml. The potential was varied from positive to negative values with reference to a S.C.E. The current was measured after 5 min.

The mono- and biamperometric techniques were employed to measure the "blanks". In each experiment the "blank" was taken as the time required for the current to begin to increase in the absence of oxidizable substances. These tests were carried out in sulphuric acid solution (1 *M*), in acetate buffer (0.1 *M*), in tetraborate buffer ($10^{-2}M$) and in potassium hydroxide (10^{-2} *M*). The potassium bromide concentration was either 1 *M* or 0.1 *M*. In the mono-amperometric tests the rotating platinum disk electrode was polarized at +200 mV *vs.* S.C.E.[8]. In the biamperometric tests a potential difference of 200 mV was applied to the two platinum wire electrodes. Such values ensured diffusion currents that were proportional to the concentration of the oxidized species.

Acid–base titrations were carried out by employing bromine as the indicator. The apparatus was the usual one for biamperometric titrations, and, again, a potential difference of 200 mV was applied to the platinum wire electrodes. The technique was checked by titrations of potassium hydroxide with perchloric acid and of acetic acid with potassium hydroxide. The concentration of potassium bromide required was a function of the strength of the acid. This point is discussed below. The half-current point in the curve of current against volume of added reagent was taken as the end-point of the titration.

RESULTS AND DISCUSSION

Figures 1–4 show a series of polarization curves at pH values of zero (1 *M* sulphuric acid), 8.3 (0.24 *M* sodium bicarbonate), 9.2 (10^{-2} *M* borax) and 12 (10^{-2} *M* potassium hydroxide). The concentration of bromide was 1 *M* in the first, third and fourth experiments and about 10^{-3} *M* in the second one. As can be seen from the curve in Fig. 1, the Br^-/Br_3^- couple is highly reversible, hence a very small concentration of the oxidized species is sufficient to produce a rise in the indicating current when the biamperometric technique is used. At pH 9.2, the current–voltage curves show different degrees of reversibility depending on the total concentration of oxidized species. However, at pH 12, a remarkable irreversibility is always noted, independent of concentration. The different character of the current–voltage curves at different pH values can be explained by the competition of various equilibria. In fact the following equilibria are well known:

$Br_2+Br^- \leftrightarrows Br_3^-$ $K=16$ (see ref. 9) (1)

$Br_2+H_2O \leftrightarrows H^++Br^-+HBrO$ $K=5.8\cdot 10^{-9}$ (see ref. 9) (2)

$HBrO \leftrightarrows H^++BrO^-$ $K=10^{-8.6}$ (see ref. 10) (3)

We have neglected the equilibrium

$Br_3^-+2\ Br^- \leftrightarrows Br_5^{3-}$

because of its small constant value. If Br^-/Br_3^- and Br^-/Br_2 are the only reversible couples* in the different solutions, the "blank" must be attributed to the presence

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* It was also possible to check the reversibility of the Br^-/Br_2 couple by working with a low concentration of potassium bromide (10^{-3} *M*).

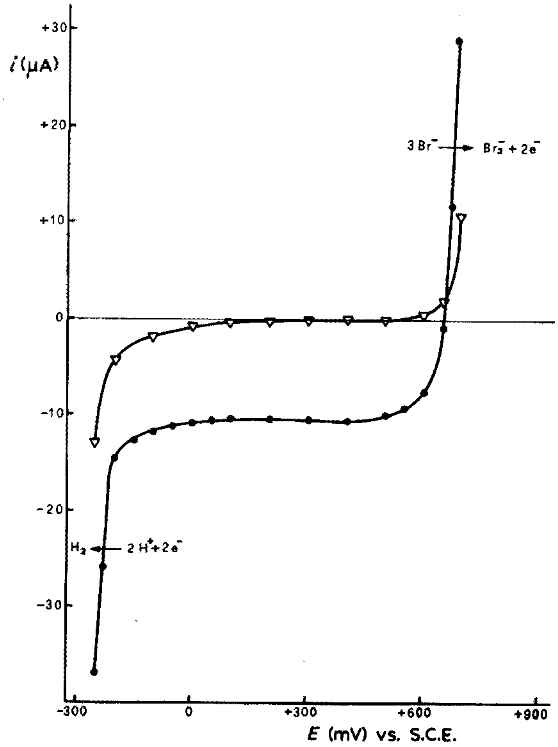

Fig. 1. Polarization curves in 1 M potassium bromide and 1 M sulphuric acid. ▽ supporting electrolyte; ● $8 \cdot 10^{-5}$ M Br_3^-.

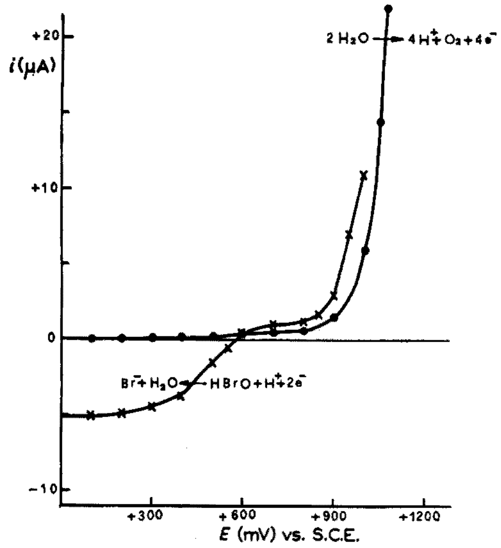

Fig. 2. Polarization curves in 10^{-3} M potassium bromide and 0.24 M sodium hydrogen carbonate. ● supporting electrolyte; × about $4 \cdot 10^{-5}$ M HBrO.

of the non-electroactive species hypobromous acid and hypobromite. The irreversibility of the Br^-/HBrO couple was checked in two ways. First, a current–voltage curve was plotted at pH 8.3 (Fig. 2) for a low concentration of potassium bromide (10^{-3} *M*), and then a biamperometric test was carried out in the same solution; no indicating

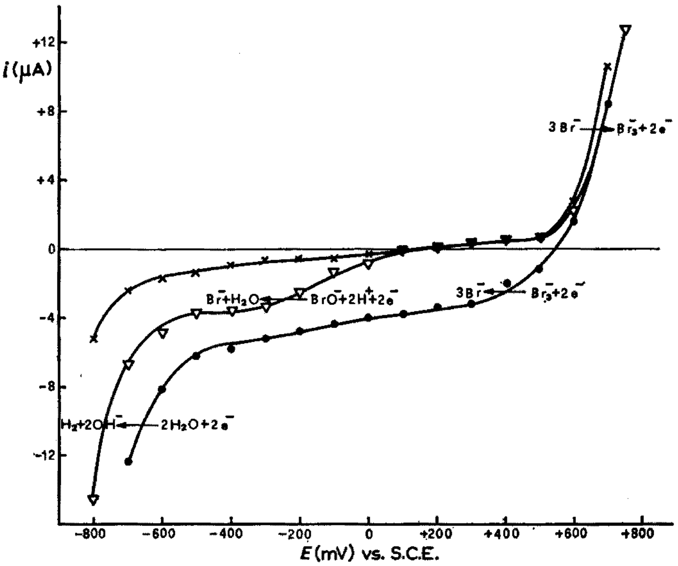

Fig. 3. Polarization curves in 1 *M* potassium bromide and 10^{-2} *M* sodium tetraborate. × supporting electrolyte; ▽ $0.9 \cdot 10^{-5}$ *M* of oxidized species; ● $2.7 \cdot 10^{-5}$ *M* of oxidized species.

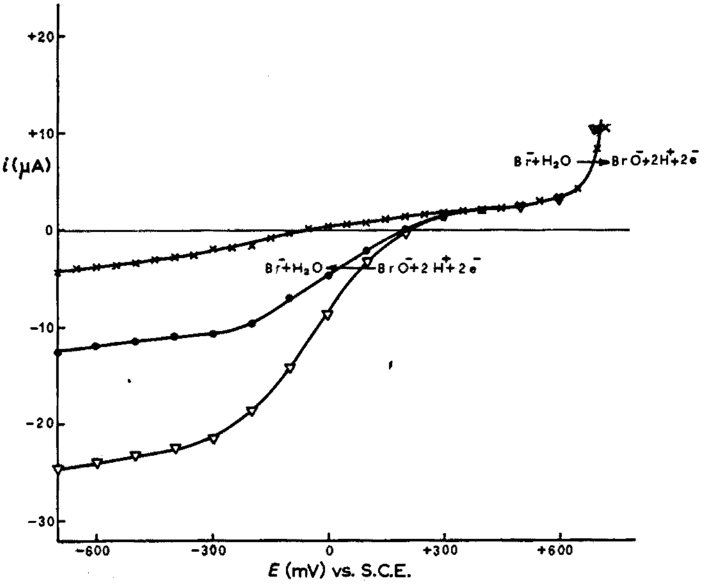

Fig. 4. Polarization curves in 1 *M* potassium hydroxide. × supporting electrolyte; ● $8 \cdot 10^{-5}$ *M* BrO^-; ▽ $1.6 \cdot 10^{-4}$ *M* BrO^-.

current was observed at pH 8.3, but when sulfuric acid was added, the current increased immediately because of the transformation of hypobromous acid to bromine.

Table I shows the "blank" values obtained biamperometrically at different pH values. The very small "blank" at pH *ca.* 0 is considered to be due to a definite limit of sensitivity ($1.7 \cdot 10^{-6}$ *M* tribromide) of the indicating system; no appreciable decrease in the "blanks" was noted when the potassium bromide concentration was changed from 1 *M* to 0.1 *M*. The "blank" in acetate buffer was also very small; this agrees with calculations based on the equilibrium constants in eqns. (1), (2) and (3). The "blank" obtained in sulphuric acid and in acetate buffer was independent of the technique employed (mono- or biamperometric). In 1 *M* potassium bromide solution, at both pH values, the tribromide ion was the only species which was oxidized. Therefore the tribromide ion could be detected by both mono- and biamperometric measurements when its concentration exceeded the sensitivity limit of the particular technique employed.

TABLE I

"BLANKS" AT DIFFERENT pH VALUES

(Electrolysis current: 0.5 mA)

pH	*0*	*0*	*4.8*	*9.2*	*9.2*[a]	*12*
KBr conc. (*M*)	1	0.1	1	1	1	1
"Blank" av. (min.)	1.07	1.05	1.53	6.96	6.77	∞

[a] Monoamperometric test.

The "blank" in the tetraborate solutions was large, and was almost without limit in hydroxide solutions. These results were in agreement with the current–voltage curves shown in Figs. 3 and 4. In 10^{-2} *M* hydroxide the hypobromite ion is the only species which is oxidized; it is reduced only at very low potentials, hence neither a rotating platinum disk electrode (at +200 mV *vs.* S.C.E.), nor two platinum wires with an applied potential difference of 200 mV could detect it. An increase in the current with increasing hypobromite concentration could be detected when the potential of the rotating electrode was −400 mV *vs.* S.C.E.

A calculation of the concentrations of all of the oxidized species at pH 9.2 (when the current rose) is given below for a total bromine concentration of $1.1 \cdot 10^{-5}$ *M*.

$$1.1 \cdot 10^{-5} = [\mathrm{HBrO}] + [\mathrm{BrO^-}] + [\mathrm{Br_3^-}] + [\mathrm{Br_2}];$$

$$[\mathrm{Br^-}] = 1$$

$$[\mathrm{H^+}] \cdot [\mathrm{BrO^-}]/[\mathrm{HBrO}] = 10^{-8.6}$$

$$[\mathrm{H^+}] \cdot [\mathrm{Br^-}] \cdot [\mathrm{HBrO}]/[\mathrm{Br_2}] = 5.8 \cdot 10^{-9}$$

$$[\mathrm{Br_3^-}]/[\mathrm{Br_2}] \cdot [\mathrm{Br^-}] = 16$$

The following concentrations result from the calculations: $[\mathrm{Br_3^-}] = 2.8 \cdot 10^{-6}$ *M*; $[\mathrm{Br_2}] = 1.8 \cdot 10^{-7}$ *M*; $[\mathrm{HBrO}] = 1.6 \cdot 10^{-6}$ *M*; $[\mathrm{BrO^-}] = 6.4 \cdot 10^{-6}$ *M*.

The value of $2.8 \cdot 10^{-6}$ for the tribromide ion agrees rather well with the value which was considered to represent the limit of sensitivity of the technique, if one takes into account the fact that 3 different equilibrium constants were used in the calculations and that concentrations were employed instead of activities. The agreement between calculated and found values would be even better if the claim of LIBERTI AND LAZZARI[11] that at pH values greater than 7 the current efficiency is less than unity, were taken into account. However, this is contrary to the findings of other workers[2,3,12].

It can be concluded that the "blanks" in tetraborate solutions were essentially a consequence of the fact that only a small amount of the electrically generated bromine was electroactive because of hydrolysis. It is, therefore, not correct to ascribe the "blanks" to impurities, particularly since the "blank" increased when the potassium bromide concentration was changed from 1 M to 0.1 M. Furthermore, when the solution was acidified, the "blank" disappeared; that is, the current rose immediately after acidification.

TABLE II

RESULTS OF ACID–BASE TITRATIONS

Eq. taken	*Eq. found*	*Error (%)*
Titration of $1.8 \cdot 10^{-2}$ M potassium hydroxide with perchloric acid ($[Br^-] = 8.2 \cdot 10^{-3}$ M)		
$142.00 \cdot 10^{-5}$	$142.06 \cdot 10^{-5}$	+0.04
$142.00 \cdot 10^{-5}$	$142.36 \cdot 10^{-5}$	+0.25
$142.00 \cdot 10^{-5}$	$141.60 \cdot 10^{-5}$	−0.28
Titration of 10^{-3} M acetic acid with potassium hydroxide ($[Br^-] = 0.12$ M)		
$9.58 \cdot 10^{-5}$	$9.58 \cdot 10^{-5}$	0.00
$9.58 \cdot 10^{-5}$	$9.64 \cdot 10^{-5}$	+0.61
$9.58 \cdot 10^{-5}$	$9.62 \cdot 10^{-5}$	+0.42

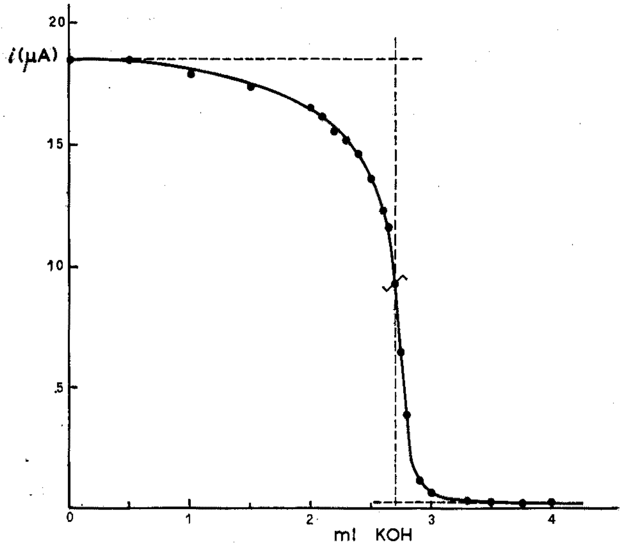

Fig. 5. Titration curves of 10^{-3} M acetic acid with potassium hydroxide.

Table II shows the results of acid–base titrations with bromine as indicator. According to eqns. (1) and (2), the ratio $[HBrO]/[Br_2]+[Br_3^-]$ may become unity at different pH values, depending on the potassium bromide concentration. Accordingly, the pH at the equivalence point of the acid–base titration was calculated, and a suitable concentration of potassium bromide was chosen so that the ratio $[HBrO]/[Br_2]+[Br_3^-]$ became unity at the equivalence point. Figure 5 shows a curve of the titration of acetic acid with potassium hydroxide. The curve may be divided into 3 parts: in the first part the current is nearly constant, the oxidized forms of bromine being almost entirely Br_2 and Br_3^-, because of the low pH. In the second part the current quickly decreases because of the increase in pH. In the third part the current is nearly zero, as bromine is almost entirely in the hypobromite form. Thus, the equivalence point is placed at the point when the current is half the initial value. It is obvious that by varying the bromide concentration, acids of different strengths can be titrated.

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SUMMARY

The nature of the "blanks" occurring in titrations with electrically generated bromine is discussed. In acidic media such "blanks" are due to the limits of sensitivity of the experimental technique employed (mono- or biamperometric). In alkaline solutions hydrolysis of bromine plays an important role; the formation of hypobromite ion explains the very large "blanks" observed. Acid–base titrations, with bromine as indicator confirmed these findings.

RÉSUMÉ

La nature des valeurs "à blanc" observées dans les titrages au brome, électriquement formé est examinée. En milieu acide, elles sont dues aux limites de sensibilité de la technique expérimentale utilisée (mono ou biampérométrique). En solution alcaline, l'hydrolyse du brome joue un rôle important; la formation d'hypobromite explique les grandes valeurs "à blanc" observées. Ce qui est confirmé par les titrations acide–base, utilisant le brome comme indicateur.

ZUSAMMENFASSUNG

Das voltametrische Verhalten der Paare Br^-/Br_2, Br^-/Br_3^-, $Br^-/HBrO$ und Br^-/BrO^- wird in Abhängigkeit vom pH-Wert untersucht. Die Grösse der Blindwerte, welche bei der Titration von elektrisch erzeugtem Brom auftreten, werden diskutiert. Im sauren Medium werden die Blindwerte von den Empfindlichkeitsgrenzen der experimentellen Technik (mono- oder biamperometrisch) bestimmt. In alkalischer Lösung spielt die Hydrolyse des Broms eine wichtige Rolle. Die Bildung von Hypobromitionen erklärt die sehr grossen Blindwerte, welche beobachtet wurden. Säure–Basen-Titrationen mit Brom als Indikator bestätigen diese Ergebnisse.

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CHELATE VON β-DIKETONDERIVATEN[1]

TEIL X. ZWEIPHASENVERTEILUNG VON THIODIBENZOYLMETHAN UND SEINEN KUPFER-, NICKEL- UND KOBALTCHELATEN

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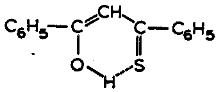
Thioderivate von β-Diketonen sind in letzter Zeit leicht zugänglich geworden[2,3]. In Analogie zu den β-Diketonen wird das chemische Verhalten dieser Substanzen durch die vorliegende Keto–Enol-Tautomerie[4] und die Tendenz zur Bildung von Metallchelaten bestimmt. Die Farbigkeit zahlreicher Metallchelate, ihre in Wasser sehr geringe, jedoch in organischen Lösungsmitteln gute Löslichkeit, sowie die grosse Stabilität der Chelate ermöglichen die Verwendung solcher β-Thioxoketone als extraktionsanalytische Reagenzien. Die vorliegenden Untersuchungen wurden mit dem sehr beständigen Thiodibenzoylmethan durchgeführt:



Reagenzien und Apparate

Thiodibenzoylmethan wurde nach den Angaben der Literatur[3] dargestellt und zeigte nach zweimaligem Umkristallisieren einen Schmelzpunkt von 83–84°.

Die verwendeten organischen Lösungsmittel waren durch Destillation gereinigt. Für die Bereitung der wässrigen Lösungen kam demineralisiertes Wasser zum Einsatz. Natronlauge und Kaliumchloridlösungen wurden durch Ionenaustausch an einem Dowex-Chelatharz von Schwermetallspuren befreit.

Die Absorptionsspektren wurden mit einem Spectrophotometer Beckman DK-2 aufgenommen, für alle übrigen spektrophotometrischen Untersuchungen diente das Spektralkolorimeter Spekol des VEB Carl Zeiss Jena mit Zusatzverstärker.

Für die Untersuchung der Extraktionsgleichgewichte wurde die Apparatur zur analytischen Flüssig–Flüssig-Trennung des VEB Glaswerke Stützerbach verwendet, die pH-Messungen erfolgten über eine Einstabmesskette mit dem pH-Messverstärker MV 11 der Fa. Clamann und Grahnert, Dresden.

DISSOZIATIONSKONSTANTE, VERTEILUNGSKOEFFIZIENT UND LÖSLICHKEIT VON THIODIBENZOYLMETHAN

Für die Untersuchung der Extraktion von Metallen wurden zunächst die Enoldissoziationskonstante von Thiodibenzoylmethan und der Verteilungskoeffizient zwischen verschiedenen organischen Lösungsmitteln und wässriger 0.1 *N* Kaliumchloridlösung ermittelt.

Versuchsausführung und Messergebnisse

Die spektrophotometrische Bestimmung der Dissoziationskonstanten beruht auf der Beziehung

$$pK_{\mathrm{HA}} = \mathrm{pH} - \log\left([\mathrm{A}^-]/[\mathrm{HA}]\right)$$

Durch die Substitutionen $[\mathrm{A}^-] = \varepsilon - \varepsilon_{\mathrm{HA}}$ und $[\mathrm{HA}] = \varepsilon_{\mathrm{A}} - \varepsilon$ ergibt sich

$$pK_{\mathrm{HA}} = \mathrm{pH} - \log(\varepsilon - \varepsilon_{\mathrm{HA}})/(\varepsilon_{\mathrm{A}} - \varepsilon).$$

Darin bedeutet ε den bei dem entsprechenden pH-Wert gemessenen molaren Extinktionskoeffizienten, $\varepsilon_{\mathrm{HA}}$ den molaren Extinktionskoeffizienten der Lösung, in der der gesamte Ligand in undissoziierter Form vorliegt und ε_{A} den molaren Extinktionskoeffizienten der Lösung, die den Liganden in Form seines Anions enthält.

Zur Durchführung der Messung wurden 4-ml Anteile einer 10^{-4} *M* Lösung von Thiodibenzoylmethan in reinstem absoluten Alkohol abgemessen und in einem 50-ml Masskolben mit Pufferlösung bis zur Eichmarke aufgefüllt. Die Pufferlösungen bestanden aus 0.025 *M* NaH_2PO_4 und 0.025 *M* Na_2HPO_4 und waren mit Kaliumchlorid auf die Ionenstärke $J = 0.1$ korrigiert. Zur Bestimmung von $\varepsilon_{\mathrm{HA}}$ bzw. ε_{A} wurde im Masskolben mit 0.1 *N* HCl bzw. 0.1 *N* NaOH bis zur Eichmarke aufgefüllt. Die Absorptionsmessungen wurden bei 390 nm und einer Schichtdicke von $d = 5.00$ cm vorgenommen. Die Bezugslösungen setzten sich aus 4-ml Portionen Alkohol und entsprechenden Mengen des Puffers zusammen.

Über die erhaltenen Ergebnisse informiert Tabelle I.

Eine weitere Möglichkeit zur Bestimmung der Säuredissoziationskonstanten beruht auf der Bestimmung von Verteilungsgleichgewichten des Reagenzes zwischen einem organischen Lösungsmittel und wässerigen Lösungen bei verschiedenen pH-Werten[5]. Dabei wird vorausgesetzt, dass nur die undissoziierte Form des Reagenzes in der organischen Phase löslich ist, nicht aber ionische Assoziate oder Polymerisationsprodukte extrahiert werden. Der Verteilungskoeffizient wird dann durch den Ausdruck

$$[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{w}} = p$$

beschrieben.

TABELLE I

BESTIMMUNG DER DISSOZIATIONSKONSTANTEN VON THIODIBENZOYLMETHAN

pH	ε	*log* $(\varepsilon - \varepsilon_{\mathrm{HA}})/(\varepsilon_{\mathrm{A}} - \varepsilon)$	*pK-Wert*	
0.1 *N* HCl	7250	—	—	
5.53	9375	−0.61	6.14	6.28 ± 0.07
6.10	11425	−0.20	6.30	
6.69	14525	0.32	6.37	
7.05	16000	0.64	6.31	
0.1 *N* NaOH	18000	—		

In der wässrigen Phase ist die Dissoziation der Substanz zu berücksichtigen:

$$[H^+]\,[A^-]_w/[HA]_w = K$$

Die Kombination dieser beiden Beziehungen liefert den Extraktionskoeffizienten E, der die Verteilung des Reagenzes in dissoziierter und undissoziierter Form zwischen Wasser und organischer Phase bei bestimmtem pH-Wert wiedergibt:

$$E = \frac{[HA]_{org}}{[HA]_w + [A^-]_w} = \frac{[H^+]\cdot p}{[H^+] + K}$$

Ist $[H^+]$ klein gegen K, so folgt:

$$E = [H^+]\cdot p/K$$

und daraus

$$\log (K/p) = \log [A^-]_w - \mathrm{pH} - \log [HA]_{org}$$

Diese Beziehungen gestatten die Berechnung der Dissoziationskonstanten aus den experimentell bestimmten Werten für Extraktionskoeffizient und Verteilungskoeffizient.

TABELLE II

BESTIMMUNG VON EXTRAKTIONSKENNGRÖSSEN FÜR THIODIBENZOYLMETHAN

pH	*log K/p*	*log K/p (Mittelwert)*
8.23	−11.93	
8.61	−12.16	−12.09±0.07
8.95	−12.10	
9.23	−12.16	

Zur Berechnung des pK-Wertes von Thiodibenzoylmethan wurde der Extraktionskoeffizient zwischen einer 0.05 M Lösung des Chelatbildners in *n*-Heptan und Pufferlösungen der konstanten Ionenstärke $J=0.1$ bei einer Temperatur von 25° bestimmt. Die Messergebnisse sind in Tabelle II zusammengestellt. Für den Verteilungskoeffizienten von Thiodibenzoylmethan zwischen *n*-Heptan und 0.1 N Kaliumchloridlösung vom pH-Wert 2 ergab sich

$$\log p = 5.61 \pm 0.08$$

daraus errechnet sich ein pK-Wert von

$$\mathrm{p}K = 6.48 \pm 0.15$$

Dieser Wert steht in guter Übereinstimmung mit der auf spektralphotometrischem Wege erhaltenen Grösse. Für Dioxan–Wasser-Mischungen wurden die pK-Werte des Thiodibenzoylmethans bereits auf potentiometrischem Wege bestimmt[6,7].

Die Verteilungskoeffizienten von Monothiodibenzoylmethan zwischen organischen Lösungsmitteln und 0.1 N Kaliumchloridlösung vom pH-Wert 2 wurden ebenfalls spektrophotometrisch mit Hilfe von Eichkurven bei einer Wellenlänge $\lambda = 410$ nm bestimmt. Die Werte für die Löslichkeiten und die Verteilungskoeffizienten sind in Tabelle III zusammengefasst.

Bei der Verwendung von Thiodibenzoylmethan zur Extraktion und Bestimmung von Metallen muss der nichtumgesetzte Komplexbildner mit Alkali aus der organischen Phase entfernt werden. Dabei ist der Grad der Rückextraktion der Löslichkeit von Thiodibenzoylmethan in den untersuchten Lösungsmitteln umgekehrt proportional. Die erhaltenen Ergebnisse sind in Fig. 1 graphisch dargestellt. Es zeigt sich, dass der Chelatbildner aus seinen Lösungen in *n*-Heptan mit Alkali weitaus besser reextrahiert werden kann als aus den anderen untersuchten Lösungsmitteln. Deshalb wurde *n*-Heptan auch als Lösungsmittel für die Metallextraktion eingesetzt.

TABELLE III

LÖSLICHKEITEN UND VERTEILUNGSKOEFFIZIENTEN VON MONOTHIODIBENZOYLMETHAN BEI 25°

Lösungsmittel	*Löslichkeit (Mol/l)*	*Logarithmus des Verteilungs-koeffizienten*
Wasser (0.1 *N* KCl)	$7.5 \cdot 10^{-6}$	—
n-Heptan	0.01	5.61
Tetrachlorkohlenstoff	0.84	5.8
Benzol	1.3	6.1
Chloroform	2.0	6.3

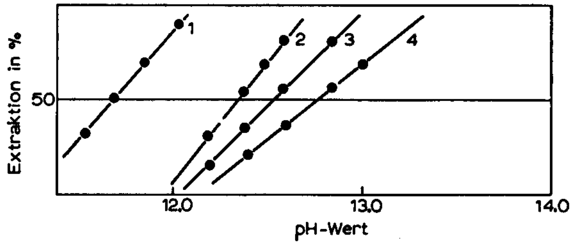


Fig. 1. Rückextraktion von Thiodibenzoylmethan aus 10^{-2} molaren Lösungen in organischen Lösungsmitteln in Abhängigkeit vom pH-Wert. (1) *n*-Heptan. (2) CCl_4. (3) Benzol. (4) Chloroform.

DIE EXTRAKTION VON KUPFER, NICKEL UND KOBALT MIT MONOTHIODIBENZOYLMETHAN

Die Absorptionsspektren der Thiodibenzoylmethanchelate von Kupfer, Nickel und Kobalt (Fig. 2) sind durch intensive Absorptionsbanden charakterisiert, die eine photometrische Bestimmung der Metalle gestatten.

Will man die Absorptionsmaxima der Metallchelate bei 410 nm bw. 430 nm für die photometrische Analyse ausnutzen, so stört die hohe Eigenabsorption des Komplexbildners in diesem Bereich. Eine extraktionsphotometrische Bestimmung ist deshalb nur möglich, wenn es gelingt, überschüssigen Komplexbildner vollständig und reproduzierbar aus der organischen Phase zu entfernen. Bei Verwendung von *n*-Heptan als Lösungsmittel ist diese Bedingung erfüllt.

Versuchsausführung und Messergebnisse

Zur Aufnahme der Extraktionskurve des Kupfers wurden 1-ml Anteile einer 10^{-3} molaren Kupfersulfatlösung mit 0.1 *N*, 1 *N* bzw. 2 *N* Salzsäure auf 10 ml aufgefüllt und zur Einstellung der Extraktionsgleichgewichte mit 10 ml 10^{-3} *M* Lösung von Thiodibenzoylmethan in *n*-Heptan 12 Stunden geschüttelt. Nach der Phasentrennung wurde die Wasserstoffionenkonzentration in der wässrigen Phase durch Titration mit 0.1 *N* Natronlauge ermittelt; aus der organischen Phase wurde überschüssiger Ligand mit 0.1 *N* Natronlauge entfernt und das zurückbleibende Kupferchelat photometrisch ($\lambda = 410$ nm) bestimmt.

Zur Untersuchung der Extraktion von Nickel und Kobalt wurden 1-ml Anteile von 10^{-3} *M* Nickelsulfat- bzw. $5.7 \cdot 10^{-4}$ *M* Kobaltnitratlösung in 0.1 *N* Kaliumchlorid mit Pufferlösungen (Natriumacetat/Essigsäure) der Ionenstärke $J = 0.1$ auf 10 ml aufgefüllt und mit 10 ml 10^{-3} *M* Thiodibenzoylmethanlösung 12 Stunden geschüttelt. Die Analyse der Phasen erfolgte wie bei der Extraktion des Kupfers. Nickel und Kobalt in der organischen Phase wurden in Form ihrer Metallchelate photometrisch bestimmt.

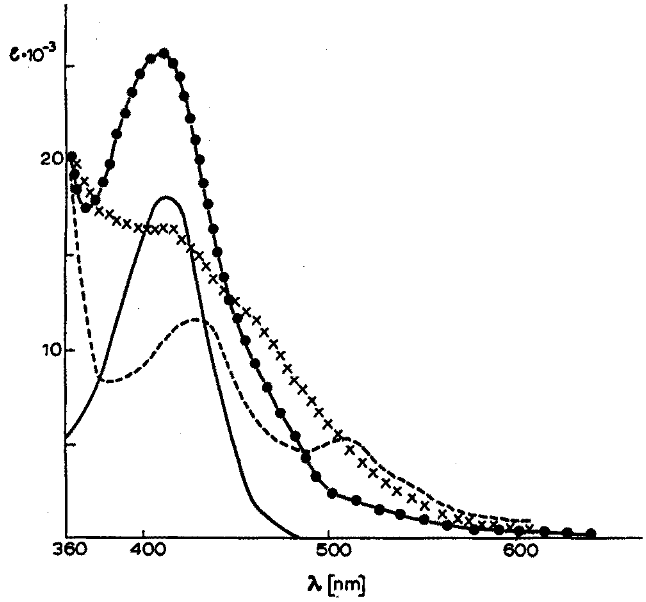
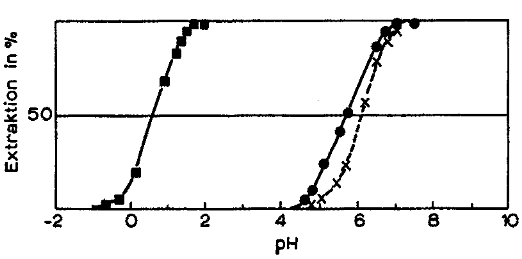


Fig. 2. Absorptionsspektren einiger Thiodibenzoylmethan-Chelate. — Thiodibenzoylmethan ($CHCl_3$). –●–●–Kupfer(II)-Chelat (*n*-Heptan). –×–×– Kobalt(III)-Chelat (CCl_4.). – – – Nickel(II)-Chelat (*n*-Heptan.)



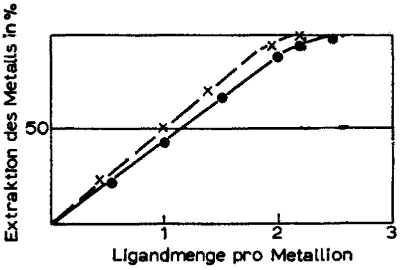


Fig. 3. Extraktion von Metallen mit Thiodibenzoylmethan –■–■– Cu, –●–●– Ni, –×–×– Co.

Fig. 4. Abhängigkeit der Extraktion von Kupfer und Nickel mit Thiodibenzoylmethan von der Ligandkonzentration.–●–●– Ni, –×–×– Cu.

In Übereinstimmung mit den analytischen Befunden der festen Komplexe werden Kupfer und Nickel als Bisligand-Komplexe extrahiert.

Kobalt wird unter diesen Versuchsbedingungen als Tris-Chelat extrahiert, selbst in Gegenwart von Ascorbinsäure.

Die erhaltenen Extraktionskurven sind in Fig. 3 wiedergegeben.

Thiodibenzoylmethan ermöglicht eine Extraktion der Metalle aus stärker saurer Lösung, als dies für das Sauerstoffhomologe Dibenzoylmethan gefunden wurde. Ursache dafür ist der bei annähernd gleichen Verteilungskoeffizienten beider Liganden beträchtliche Unterschied ihrer pK-Werte:

Dibenzoylmethan p$K \sim 9.35$[8]
Thiodibenzoylmethan p$K \sim 6.30$

Die Abhängigkeit der Extraktionsausbeute von der Konzentration zeigt, dass bereits ein geringer Überschuss an Thiodibenzoylmethan zur quantitativen Extraktion des Kupfers bzw. Nickels genügt (Fig. 4).

Die günstigen Extraktionsbedingungen erlauben es, Thiodibenzoylmethan für die extraktionsphotometrische Bestimmung von Kupfer, Nickel und Kobalt einzusetzen, sofern letztere Metalle nicht nebeneinander vorliegen. Während Kupfer dabei bereits aus schwach saurer Lösung extrahiert werden kann, muss bei Kobalt und Nikkel auf pH 9 bzw. 10 eingestellt werden (NH_3–NH_4Cl-Puffer); zur Extraktion dient eine 10^{-4} M Lösung von Thiodibenzoylmethan in n-Heptan oder CCl_4 (Bestimmung von Kobalt). Der Ligandüberschuss in der organischen Phase wird durch kurzes (2 min) Schütteln mit 0.1 N Natronlauge entfernt und dann die zurückbleibenden Metallchelate direkt photometrisch bestimmt. Störungen können durch eine Reihe thiophiler Elemente hervorgerufen werden. Durch Zusatz von Methanol als Lösungsvermittler kann die bei Extraktion aus sauren Lösungen nötige lange Schüttelzeit auf 2 Minuten reduziert werden.

Für die Extraktion von Kobalt ist n-Heptan wegen der geringen Löslichkeit des Tris-Chelates nicht geeignet. Andere Lösungsmittel besitzen aber den Nachteil, dass überschüssiger Ligand nur schwer wieder entfernt werden kann. Zur photometrischen Kobaltbestimmung muss man deshalb in einem Bereich messen, wo sich die Absorptionskoeffizienten von Ligand und Kobaltchelat genügend unterscheiden und trotzdem eine möglichst hohe Empfindlichkeit für die Kobaltbestimmung erhalten bleibt. Das Absorptionsmaximum erfüllt diese Bedingung nicht. Geeignet ist die

TABELLE IV

KENNGRÖSSEN FÜR DIE PHOTOMETRISCHE METALLBESTIMMUNG MIT THIODIBENZOYLMETHAN

Metall	*Absorptionsstelle (nm)*	*Extinktionskoeffizient*	*Empfindlichkeit nach Sandell*[9] *($\mu g/cm^2$)*	*Relative Standardabweichung (%)*	*Lambert–Beersches Gesetz*
Cu	410	24900	0.0026	±2.7	Gültig bis zur Löslichkeitsgrenze
Ni	430	11800	0.0049	±2	
	510	5160	0.0114	±1	
Co	490	7600	0.0078	±2.6	Gültig im untersuchten Bereich bis 60 µg Co/ml

Wellenlänge $\lambda = 490$ nm, für die der molare Extinktionskoeffizient des Liganden 280, der des Kobaltkomplexes aber 7600 beträgt. Als Lösungsmittel kam Tetrachlorkohlenstoff zum Einsatz. Nach der Extraktion muss die organische Phase zur Beendigung der Oxydation des Kobalts 10 Min stehen. Analytische Kenngrössen für die extraktionsphotometrische Bestimmung von Kupfer, Nickel und Kobalt mit Thiodibenzoylmethan sind in Tabelle IV zusammengestellt.

Die Schwerlöslichkeit des Kobalt-tris-Chelates, seine thermische Beständigkeit, sowie die solvatfreie, formelreine Zusammensetzung und das hohe Molekulargewicht ermöglichen die Verwendung von Monothiodibenzoylmethan als Fällungsreagenz zur gravimetrischen Kobaltbestimmung.

Herrn Prof. Dr. HOLZAPFEL danken wir herzlich für die Möglichkeit zur Durchführung dieser Arbeit und die dabei gewährte materielle Unterstützung.

ZUSAMMENFASSUNG

Für Thiodibenzoylmethan wurden die Löslichkeit, die Verteilungskoeffizienten zwischen Wasser und organischen Lösungsmitteln und die Enoldissoziationskonstante bestimmt. Die Extraktion von Kupfer, Nickel und Kobalt mit *n*-Heptan- bzw. Tetralösungen von Thiodibenzoylmethan in Abhängigkeit vom pH-Wert wurde untersucht und die nötige Reagenzmenge bestimmt. Die Extraktion dieser Metalle mit Thiodibenzoylmethan ist aus stärker sauren Lösungen möglich als mit Dibenzoylmethan. Für die quantitative Extraktion ist bereits ein geringer Überschuss des Reagenses über die stöchiometrische Menge ausreichend.

SUMMARY

The solubility of thiodibenzoylmethane, as well as its distribution coefficients between water and organic solvents, and the enol dissociation constant were studied. The extraction of copper, nickel, and cobalt by solutions of thiodibenzoylmethane in *n*-heptane or tetrachloromethane is described; these extractions are practicable at lower pH values than for dibenzoylmethane, and only a very small excess of reagent over the stoichiometric quantity is needed.

RÉSUMÉ

On a effectué une étude sur la solubilité du thiodibenzoylméthane, sur les coefficients de partage entre l'eau et les solvants organiques, ainsi que sur la constante de dissociation énolique. On décrit l'extraction du cuivre, du nickel et du cobalt à l'aide de solutions de thiodibenzoylméthane dans le *n*-heptane ou le tétrachlorure de carbon. Ces extractions s'effectuent à des pH inférieurs à ceux nécessaires avec le dibenzoylméthane. Un très léger excès de réactif seulement, par rapport à la quantité stoechiométrique est nécessaire pour une extraction quantitative.

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PRECIPITATION REACTIONS OF THIOBENZOYLPHENYLHYDROXYLAMINE AND ITS USE AS A REAGENT FOR COPPER*

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The analytical potential of thiobenzoylphenylhydroxylamine (TBPHA) was discussed in a previous paper[1]. TBPHA reacts with a wider range of metal ions than its oxygen counterpart, benzoylphenylhydroxylamine (BPHA). Formation constants for nickel, copper and zinc TBPHA chelates are higher than those of BPHA and precipitates are formed in more acid solutions. This paper records the results of further investigations of the analytical potential of TBPHA and describes its use for the gravimetric determination of copper.

EXPERIMENTAL

Preparation of thiobenzoylphenylhydroxylamine

TBPHA was prepared as previously described[1] but minor changes in procedure gave a significant increase in yield. Stirring of the solution for 3–5 h after the slow addition of Grignard reagent to carbon disulphide resulted in a higher yield of dithiobenzoic acid and hence of thiobenzoyl chloride. In addition, the TBPHA formed from the reaction of thiobenzoyl chloride with phenylhydroxylamine was extracted from the ether layer with concentrated ammonia and precipitated by slow neutralization, in an ice–salt bath, with cold 3 N hydrochloric acid. The yield of

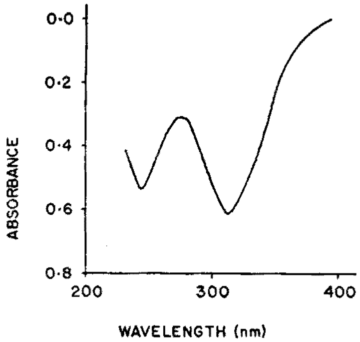

Fig. 1. Absorption spectrum for $4.15 \cdot 10^{-5}$ M TBPHA in $CHCl_3$.

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* Abstracted from the M.Sc. thesis of R. M. CASSIDY.

purified product (m.p. 101–102°), after recrystallisation from ethanol, was 24 g. (Found (%): C 68.0, H 5.0, S 13.9; calculated: C 68.1, H 4.8, S 14.0.)

Figure 1 shows the absorption spectrum obtained for a chloroform solution of TBPHA; there are two absorption bands in the ultraviolet region. The NMR spectrum shows a strong peak at 2.8 τ (phenyl hydrogens) and a small absorption at -1.5 τ (oxime hydrogen); integration is in the expected ratio of 10:1. TBPHA is insoluble in water but is soluble in strongly acidic or weakly basic solutions; the basic solutions, however, are not stable for more than a few days.

REACTIONS WITH METAL IONS

Precipitation reactions between TBPHA and metal ions were studied by adding 3–4 ml of a 0.5% solution of the reagent in 0.15 *N* ammonia to 5 ml of an acid solution containing 1 mg of metal; acid was added to compensate for the ammonia in the reagent solution. Solutions containing precipitates were allowed to stand for 10 min before filtration; the filtrates were spot-tested to determine if precipitation was quantitative. Reagent and metal ion blanks were run concurrently.

The hydrogen ion concentration was generally adjusted with hydrochloric acid. For silver(I), lead(II), and mercury(I), nitric acid was used until the acid concentration exceeded 3 *M*; higher nitric acid concentrations slowly decomposed TBPHA and sulphuric acid was used for acidities greater than 3 *M*. For tests in the presence of EDTA, 1 ml of a 0.25 *M* solution of the disodium salt was added. The results are summarized in Tables I and II. "Yes" and "no" in Table I indicate quanti-

TABLE I

PRECIPITATION REACTIONS OF METALS WITH TBPHA

Metal	*Detection limit (p.p.m.)*	H^+ (*M*)			
		0.1	*1.0*	*3.0*	*6.0*
Ag(I)	1	Yes	Yes	Yes	Yes
Bi(III)	0.2	Yes	Incomplete	No	—
Co(II)	1	Incomplete	No	—	—
Cu(II)	1	Yes	Yes	Yes	Yes
Fe(III)	5	Yes	Yes	Yes	Yes
Hg(I)	1	Yes	Yes	Yes	Yes
Hg(II)	1	Yes	Incomplete	No	—
Mo(VI)	2	Yes	Yes	Yes	Yes
Mn(II)	0.1	Incomplete	No	—	—
Nb(V)		Yes	Yes	Yes	—
Ni(II)	3	Yes	Incomplete	No	—
Pb(II)	0.8	Yes	No	—	—
Pd(II)	1.5	Yes	Yes	Yes	Yes
Pt(IV)	10	Yes	Incomplete	No	—
Sn(II)	1	Yes	Yes	Incomplete	No
Sn(IV)	1	Yes	Yes	—	No
Sb(III)	10	Yes	Incomplete	No	—
Ti(IV)	30	Yes	No	No	Yes
V(V)	10	Yes	Yes	Yes	Yes
Zr(IV)	10	Yes	Yes	Incomplete	No

tative precipitation and no reaction respectively; the data of Table II are visual only. Aluminium(III), cadmium(II), cerium(IV), thorium(IV), uranium(VI) and zinc(II) give precipitates in neutral solutions, but not at pH 1.

These results show that, although TBPHA reacts with a large number of metal ions, only a few metals are quantitatively precipitated in highly acidic solutions and some useful separations and determinations are suggested. An obvious possibility is the separation of copper from iron and other commonly associated metals.

TABLE II

PRECIPITATION REACTIONS OF METALS WITH TBPHA

Metal	*12 M HCl*	*24 N H_2SO_4*	*pH 2–3 plus EDTA*	*Stability of precipitate in strong ammonia*
Ag(I)	No	Yes	Yes	No
Bi(III)	No	—	No	Yes
Co(II)	—	No	No	Yes
Cu(II)	No	No	Yes	Yes
Fe(III)	No	No	No	Yes
Hg(I)	—	No	Yes	Yes
Hg(II)	No	No	Yes	Yes
Mn(II)	—	—	No	No
Mo(VI)	Yes	Yes	Yes	No
Nb(V)	Yes	No	No	No
Ni(II)	No	—	No	Yes
Pb(II)	No	—	No	Yes
Pd(II)	Yes	Yes	Yes	Yes
Pt(IV)	No	—	No	No
Sn(II)	—	—	No	No
Sn(IV)	No	—	No	No
Sb(III)	No	—	No	No
Ti(IV)	Yes	No	No	No
V(V)	Yes	No	No	No
Zr(IV)	No	—	No	No

The organic reagents reported to date for copper analysis have not been completely satisfactory, particularly in the presence of iron. α-Benzoinoxime, a member of the so-called "copper-specific group", is perhaps the most attractive copper reagent. Iron(III) does not react but the precipitate obtained is not pure and ignition to the oxide is recommended[2]; ignition to a pure copper oxide is difficult and the favorable gravimetric factor is lost.

GRAVIMETRIC DETERMINATION OF COPPER

Copper is quantitatively precipitated by TBPHA as a red-brown 1:2 (copper: reagent) species. A pure product is precipitated from water–ethanol solutions for which the stoichiometric factor for copper is 0.12217 .The following procedure permits the gravimetric determination of 10–30 mg of copper in the presence of iron and commonly associated metals.

Procedure

Adjust the pH of the copper-containing solution to 2.0–2.5 and dilute to 100 ml. Add sufficient 0.25 *M* EDTA solution (disodium salt) to complex possible interfering metals but avoid a large excess*. Make solutions approximately 45% by volume in ethanol and heat to 70° on a steam bath. Precipitate the copper by dropwise addition of a 1% TBPHA solution in ethanol until the supernatant liquid acquires a yellow color due to excess reagent. Filter through porous-based porcelain crucibles, wash well with hot 20% ethanol–water and dry at 100° to constant weight. Weigh as $Cu(C_{13}H_{10}NSO)_2$. Typical results are shown in Table III.

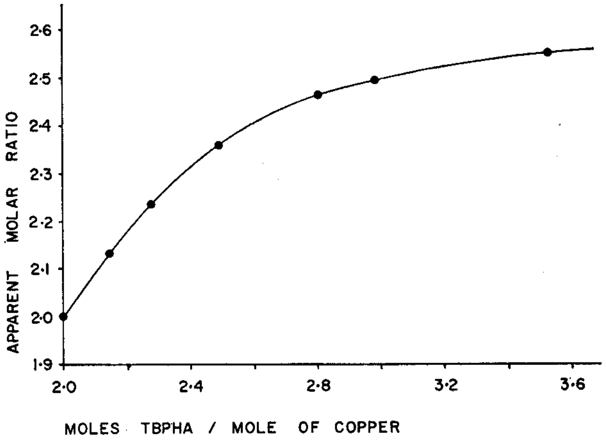

Fig. 2. Variation of composition of precipitate with reagent concentration.

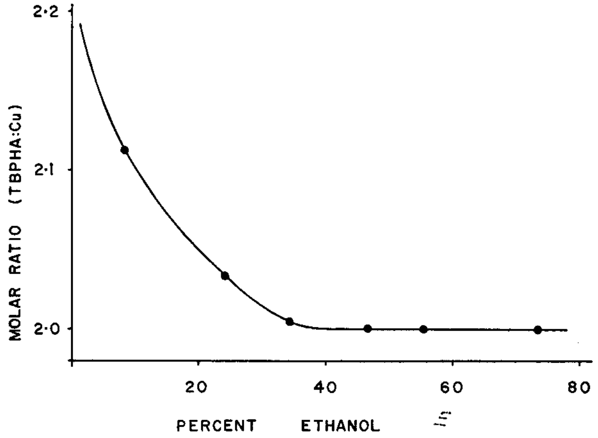

Fig. 3. Effect of ethanol content on composition of precipitate.

Factors affecting precipitation

Figure 2 shows the effect of excess of reagent if precipitation is done in aqueous solution. The molar ratios were determined from the weight of copper added and the weight of precipitate obtained; the precipitates were washed before weighing with

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* A large excess of EDTA will slowly precipitate as the free acid upon standing. This can be removed from the copper precipitate, if it becomes necessary, by washing with dilute ammonia.

0.15 *N* ammonia to dissolve excess of reagent. It is evident that the precipitate is badly contaminated by reagent which is not removed by the washing process. The ligand-to-metal ratio in compounds precipitated from solutions containing excess copper was 2.001 to 1.000. The infrared spectrum of this copper chelate was similar to that of TBPHA except for a strong absorption peak at 1380 cm^{-1} which is characteristic of reagent only; this peak is present, however, in the compound precipitated by addition of 2.1 moles of TBPHA to 1 mole of copper and shows the presence of unreacted TBPHA in the precipitate.

This reagent contamination is eliminated by precipitation from water–ethanol solutions. Figure 3 shows that excellent results are obtained if solutions are made 35–75% by volume in ethanol before reagent addition. All precipitates, except 75% ethanol samples, were filtered hot; precipitation from 75% ethanol is quantitative if samples are allowed to cool to room temperature before filtration, but results are 3% low if the solutions are filtered whilst hot.

TABLE III

ANALYSIS OF STANDARD COPPER SAMPLES

	Copper taken (mg)	*Copper found (mg)*	*Conditions*
1	14.07	14.15	Precipitated at room temperature
2	14.07	14.09	Precipitated from hot solution and filtered immediately
3	14.07	14.09	Allowed to cool before filtration
4	7.04	7.07	As 2
5	28.14	28.18	As 2
6	14.07	14.07	As 2 but volume 200 ml
7	14.07	14.07	As 2 but volume 300 ml
8	14.07	14.07	As 2 but volume 400 ml
9	14.07	14.08	As 2 but 2 ml of 0.25 *M* EDTA added
10	14.07	14.08	As 9 but 16 mg Fe present
11	14.09	14.10	As 9 but 32 mg Fe present
12	14.09	14.11	As 9 but 96 mg Fe present
13	14.09	14.10	As 9 but 160 mg Fe present
14	14.07	14.09	As 9 but 18 mg Ni present
15	14.07	14.08	As 9 but 18 mg Co present
16	14.07	14.08	As 9 but 19 mg Zn present
17	14.09	14.10	As 9 but 36 mg Sb present
18	14.09	14.07	As 9 but 62 mg Bi present
19	14.09	14.10	As 9 but 10 mg Al present
20	14.09	14.08	As 9 but 62 mg Pb present
21	14.09	14.05	As 9 but 35 mg Sn present

Slightly high results are obtained if precipitation is done at room temperature (1, Table III). The first 5 results of Table III were obtained in the presence of a phosphate buffer and are slightly high, owing to trace impurities in the buffer solution; no EDTA was present for the first 8 results recorded. An increase in solution volume has no effect on the results (6–8, Table III) and the low solubility of the precipitate would undoubtedly permit quantitative precipitation from much greater volumes (particularly if solutions were cooled to room temperature before filtration).

Copper was readily determined in a number of analyzed copper ores and alloys

(Smith and Underwood, Royal Oak, Mich., U.S.A.). An appropriate weight of sample was dissolved in concentrated nitric acid and heated below boiling to a volume of 5 ml. Concentrated sulphuric acid was added, and the solutions were evaporated to sulphur trioxide fumes and diluted to 50 ml. The pH was adjusted to 1.5 with 4 *N* sodium hydroxide, and the solutions were filtered through fine filter paper, and analyzed for copper by the above procedure; for the silver alloy, the silver was precipitated as the chloride before filtration. Results are shown in Table IV.

TABLE IV

ANALYSIS OF COPPER ORES AND ALLOYS

Sample	*Analyzed value (% Cu)*	*% Cu found*
Copper ore	6.31	6.34
Silver alloy	84.82	84.79
Monel metal	29.06	29.15
Brass	82.03	82.38

The analyzed values were unknown to the analyst before results were obtained by the TBPHA procedure. The high value (0.35% absolute) for the brass analysis is probably due to contamination by colloidal SnO_2 that was not removed in the filtration process before precipitation of copper.

TBPHA AS A COLORIMETRIC REAGENT

Although preliminary experiments suggested that TBPHA complexes extracted into chloroform might be useful for colorimetric determinations, the reagent cannot be recommended. Studies of the possible use of TBPHA for the colorimetric determination of titanium, vanadium, and iron showed that it is neither as selective nor as sensitive as BPHA. The use of BPHA for the selective determination of vanadium and of titanium has been discussed recently[3,4].

CONCLUSIONS

TBPHA is an excellent reagent for the gravimetric determination of copper and the data of Tables I and II suggest that quantitative precipitation and separation of several metals is possible from highly acidic solutions. In particular, TBPHA shows the potential as a copper and iron reagent that was initially expected for cupferron. Its wide range of reaction with metals in neutral and slightly acid solutions, combined with the ready extractability of reaction products into chloroform, suggests that TBPHA may be valuable for extractive separation or concentration of metals for determination by other techniques (*e.g.* atomic absorption). The potentialities of TBPHA are far from exhausted and further studies of this chelating agent will be rewarding.

This work was supported by grants from the National Research Council and Defence Research Board.

SUMMARY

Thiobenzoylphenylhydroxylamine (TBPHA) quantitatively precipitates copper as $Cu(C_{13}H_{10}NSO)_2$ which can be used as a weighing form for copper; the gravimetric factor is 0.12217. Iron, aluminium, chromium and commonly accompanying elements do not interfere. Quantitative precipitation and separation of several metals from highly acidic solutions is possible. The precipitation reactions of metals with TBPHA, over a wide range of acidity and in the presence of EDTA, are tabulated. TBPHA is of little value as a colorimetric reagent.

RÉSUMÉ

La thiobenzoylphénylhydroxylamine (TBPHA) précipite quantitativement le cuivre comme $Cu(C_{13}H_{10}NSO)_2$ pouvant être pesé directement; le facteur gravimétrique est de 0.12217. Le fer, l'aluminium, le chrome et les éléments accompagnant généralement Cu ne gênent pas. Une précipitation quantitative et une séparation de plusieurs métaux en solution fortement acide sont possibles. Les réactions de précipitation de métaux avec TBPHA, couvrant une large zone d'acidité et en présence d'EDTA sont données. En colorimétrie TBPHA ne présente pas beaucoup d'intérêt.

ZUSAMMENFASSUNG

Thiobenzoylphenylhydroxylamin (TBPHA) eignet sich als gravimetrisches Reagenz für Kupfer. Eisen, Aluminium, Chrom und andere Elemente, die das Kupfer im allgemeinen begleiten, stören nicht. Quantitative Fällung und Trennung zahlreicher Metalle aus stark salzsauren Lösungen ist möglich. Die Fällungsreaktionen der Metalle mit TBPHA in einem weiten pH-Bereich und in Gegenwart von AeDTE werden angegeben. TBPHA besitzt nur einen geringen Wert als colorimetrisches Reagenz.

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GRAVIMETRIC DETERMINATION OF GOLD WITH DI-2-THIENYLKETOXIME

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Standard procedures for the gravimetric determination of gold usually involve reduction to the metallic state and weighing in this form. One difficulty encountered with such procedures is the separation of the gold in a very finely divided state with the subsequent possibility of some loss on filtration. A wide variety of organic and inorganic reducing agents has been used[1-3]. BEAMISH *et al.*[4] report the quantitative precipitation of gold in cold solution.

A number of organic precipitants quantitatively precipitate gold which can be easily transferred and filtered without loss[5]. Most of these compounds, however, do not have a constant composition and cannot easily be washed free of impurities. This necessitates ignition and weighing as metal which sacrifices the advantages of a favourable gravimetric factor.

HARVEY AND YOE[6] used the sodium salt of N-(N-bromo-C-tetradecylbetanyl)-C-tetradecylbetaine as a reagent for the weighing form. MAHR AND DENCK[7] have used Reinecke salt for the precipitation. MUKHERJI[8] showed that thioglycollic acid can be utilized for the gravimetric estimation of gold.

In the present work, di-2-thienylketoxime was used for the gravimetric determination of gold. This reagent has been used for the gravimetric and nephelometric determination of palladium[9,10].

EXPERIMENTAL

Reagents and solutions

Di-2-thienylketoxime. This reagent was synthesized and purified by the method described previously[11]. A 2% solution was prepared by dissolving the reagent in Fisher Certified Reagent dioxane.

Standard gold solutions were prepared from gold chloride and the gold content was determined by the hydroquinone method[4].

Solutions of diverse ions. Reagent-grade chlorides, nitrates, sulfates or perchlorates were employed in the preparation of solutions of diverse cations. Sodium, potassium, ammonium, aluminum or calcium salts were used for diverse anions tested.

Recommended gravimetric procedure

An aliquot containing up to 22 mg of gold as the chloride was transferred to a 400-ml beaker and diluted to 250 ml with distilled water. The pH was adjusted to 2.4–3.0 with hydrochloric acid or potassium hydroxide. To a 50-ml beaker between

6.5 and 14.5 mg of reagent plus 2.125 mg for each mg of gold was added. No more than 53 mg of the oxime should be added to the system. Dioxane was then added to bring the volume to 20 ml. This was added dropwise to the gold solution with stirring. The resulting solution was diluted to *ca.* 300 ml with distilled water and allowed to stand for 12 h. The precipitate was filtered through a medium-porosity sintered glass filter, washed with a total of 500 ml of 4% dioxane–water solution and dried at 70° to constant weight. The weight of gold present was calculated by multiplying the weight of the precipitate by 0.3123.

RESULTS AND DISCUSSION

Composition of the gold complex

The precipitate was isolated as outlined above and analyzed for carbon, hydrogen and gold content. Elemental analysis showed the compound to be a 2:1 complex containing one hydroxide group. (Calculated for $Au(C_9H_6NOS_2)_2OH$: C 34.29%, H 2.08%, Au 31.23%; found C 34.12%, H 2.08%, Au 31.14%.)

Factors affecting precipitation

Temperature. The procedure gives satisfactory results when the precipitation is carried out below 30°.

Drying temperature. The organic complex may be dried to constant weight in 1–2 h at 65–70°. Decomposition occurs above a temperature of 80°.

pH. The pH can be adjusted to the required range with a few drops of 0.1 *N* hydrochloric acid or 0.1 *N* potassium hydroxide. The best pH range for precipitation was found to be 2.4–3.0. Below pH 2.4 the precipitation is incomplete and above pH 3.0 the composition of the precipitate is uncertain.

Dioxane concentration. The best results were obtained when the dioxane concentration was 5.5–6.8%. It is necessary to maintain this concentration to dissolve excess of reagent. Above a concentration of 7.0% there is a slight loss in weight.

Reagent concentration. Between 6.5 and 14.5 mg of reagent plus 2.125 mg for each mg of gold was added to the system. Below this amount precipitation is incomplete while above this amount the precipitate composition is uncertain.

Time of standing. When the reagent is added to the gold solution, the finely divided precipitate formed coagulates slowly. The orange suspension formed settles completely in 12 h. The precipitate is readily and rapidly filterable.

Precision and accuracy. The standard deviation from 12 determinations using a calculated amount of gold equal to 14.77 mg per sample was found to be 0.05. Results showing the accuracy of the method are given in Table I. Each value is an average of 6 determinations. The hydroquinone method of BEAMISH was used to standardize the gold solutions.

Effect of foreign ions

In each case 50 mg of foreign ion was added to a known gold solution unless specified. The results are given in Table II. The gold recovered is an average of at least 2 determinations.

Bromide, iodide, mercury(II), ruthenium(III), iron(III), palladium(II), bismuth(III), tin(IV) and silver(I) interfere. Interferences due to bromide and iodide

TABLE I

DETERMINATION OF GOLD BY DIRECT WEIGHING OF THE DI-2-THIENYLKETOXIME COMPLEX

Gold added (mg)	*Weight of complex (mg)*	*Gold found (mg)*	*Deviation (mg)*
5.0	16.0	5.0	0.0
10.0	32.1	10.0	0.0
15.0	48.1	15.0	0.0
20.0	64.3	20.1	+0.1
22.0	70.7	22.1	+0.1

TABLE II

EFFECT OF DIVERSE IONS (50 mg of diverse ion added in each case)

Diverse ion	*Gold added (mg)*	*Gold found (mg)*	*Deviation (mg)*
$Mg^{2+}[Mg(NO_3)_2 \cdot 6H_2O]$	15.0	15.0	0.0
$Ca^{2+}[Ca(NO_3)_2 \cdot 4H_2O]$	15.0	15.0	0.0
$Rh^{3+}[Rh(NO_3)_3]$	15.0	15.0	0.0
$Na^{+}[Na_2SO_4]$	15.0	15.0	0.0
$Al^{3+}[Al_2(SO_4)_3 \cdot 16H_2O]$	15.0	15.0	0.0
$K^{+}[KNO_3]$	15.0	15.1	+0.1
$Co^{2+}[(CoClO_4)_2 \cdot 6H_2O]$	15.0	15.0	0.0
$Ni^{2+}[Ni(NO_3)_2 \cdot 6H_2O]$	15.0	15.0	0.0
$Cu^{2+}[Cu(NO_3)_2 \cdot H_2O]$	15.0	15.0	0.0
$Os^{8+}[OsO_4]$	15.0	15.0	0.0
$Pt^{4+}[PtCl_4 \cdot 2HCl \cdot 6H_2O]$	15.0	15.0	0.0
$Ba^{2+}[Ba(NO_3)_2]$	15.0	15.0	0.0
$UO_2^{2+}[UO_2(NO_3)_2 \cdot 6H_2O]$	15.0	15.2	+0.2
$Re^{7+}[Re_2O_7]$	15.0	14.9	−0.1
$NO_3^{-}[Ca(NO_3)_2 \cdot 4H_2O]$ (150 mg)	15.0	15.0	0.0
$SO_4^{2-}[Al_2(SO_4)_3 \cdot 16H_2O]$ (100 mg)	15.0	15.0	0.0
$ClO_4^{-}[Co(ClO_4)_2 \cdot 6H_2O]$ (166 mg)	15.0	15.0	0.0
$Sr^{2+}[Sr(NO_3)_2]$	15.0	15.0	0.0
$Pb^{2+}[Pb(NO_3)_2]$	15.0	14.9	−0.1
$Mn^{2+}[MnSO_4 \cdot 4H_2O]$	15.0	15.0	0.0
$V^{5+}[NH_4VO_3]$	15.0	14.9	−0.1
$Tl^{4+}(TlNO_3)$	15.0	15.0	0.0
$Zn^{2+}[Zn(NO_3)_2 \cdot 6H_2O]$	15.0	14.8	−0.2
$Cd^{2+}[Cd(NO_3)_2 \cdot 4H_2O]$	15.0	14.9	−0.1
$NH_4^{+}[NH_4NO_3]$	15.0	15.0	0.0
$PO_4^{3-}[KH_2PO_4]$	15.0	14.9	−0.1
$Be^{2+}[Be(NO_3)_2 \cdot 3H_2O]$ (5 mg)	15.0	15.0	0.0
$Ir^{3+}[K_3Ir(NO_3)_6]$ (5 mg)	15.0	15.0	0.0
$F^{-}[NaF]$ (15 mg)	15.0	15.0	0.0
$Cl^{-}[KCl]$ (10 mg)	15.0	15.0	0.0
$Cr^{3+}[CrK(SO_4)_2 \cdot 12H_2O]$ (5 mg)	15.0	14.9	−0.1
$Mo^{6+}[(NH_4)_6Mo_7O_{24} \cdot 14H_2O]$ (15 mg)	15.0	14.9	−0.1
$Cr_2O_7^{2-}[K_2Cr_2O_7]$ (15 mg)	15.0	15.0	0.0
$CO_3^{2-}[Na_2CO_3]$ (5 mg)	15.0	15.0	0.0

were eliminated by passing chlorine gas through the solution and evaporating almost to dryness. Interference due to iron was eliminated by adding sodium fluoride. Interferences due to mercury(II), ruthenium(III), palladium(II), bismuth(III), and tin(IV) were eliminated by precipitating the gold with hydroquinone, igniting the filter paper, dissolving the gold residue in aqua regia, evaporating to dryness, adding hydrochloric acid and evaporating to near dryness 3 times. The residual solution was diluted with

TABLE III. RESULTS OF ELIMINATION OF INTERFERENCES

Diverse ion	*Gold added (mg)*	*Gold found (mg)*	*Deviation (mg)*
Br^-[KBr] (10 mg)	15.0	14.9	−0.1
I^-[KI] (15 mg)	15.0	15.0	0.0
Cl^-[NaCl] (240 mg)	15.0	15.0	0.0
Fe^{3+}[$Fe(NO_3)_3 \cdot 9H_2O$] (10 mg)	15.0	14.9	−0.1
Pd^{2+}[$PdCl_2$] (50 mg)	15.0	15.0	0.0
Ru^{3+}[$RuCl_3$] (50 mg)	15.0	15.0	0.0
Bi^{3+}[$BiCl_3 \cdot H_2O$] (50 mg)	15.0	15.1	+0.1
Sn^{4+}[$SnCl_4 \cdot 5H_2O$] (100 mg)	15.0	15.0	0.0
Hg^{2+}[$Hg(NO_3)_2 \cdot H_2O$] (50 mg)	15.0	14.9	−0.1

water and the recommended procedure followed. Interference due to silver could not be readily eliminated. The results of the above eliminations of interference are given in Table III.

If a large amount of chloride ion is present, any interference can be eliminated by a prior hydroquinone separation of the gold.

This work was supported by The National Research Council of Canada.

SUMMARY

Di-2-thienylketoxime may be used as a gravimetric reagent to determine gold. The error is of the order of ± 0.3%. There are few interfering ions and simple methods may be used to eliminate these.

RÉSUMÉ

La di-2-thiénylcétoxime est proposée comme réactif gravimétrique pour le dosage de l'or. L'erreur est de l'ordre de ± 0.3%. Peu d'ions gênent ce dosage; des méthodes simples peuvent être utilisées pour les éliminer.

ZUSAMMENFASSUNG

Di-2-thinylketoxim eignet sich als gravimetrisches Reagenz zur Bestimmung von Gold. Der Fehler beträgt etwa ± 0.3%. Wenige Ionen, die stören, können durch einfache Methoden eliminiert werden.

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THE USE OF QUINOXALINE-2-CARBOXYLIC ACID AND ITS DERIVATIVES AS ANALYTICAL REAGENTS

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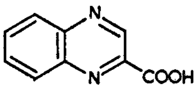
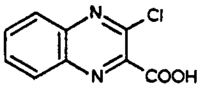
Quinaldinic acid was first used as an analytical reagent by Ray and Bose[1], and many papers[2] have been published on the determination of metals and their separations by this reagent. A new reagent, quinoxaline-2-carboxylic acid (I) has now been synthesised with a structure similar to quinaldinic acid. The 3-chloro (II) and 3-hydroxy (III) derivatives of this reagent have also been prepared and have been found to have some analytical applications. The present paper describes the preparation of the reagents, the preparation of their metallic salts, the optimum pH of precipitation of metals from their solutions, the determination of their solubility products, and the analytical applications of these reagents. The thermal behaviours of the metallic salts of the parent reagent were also investigated.



I



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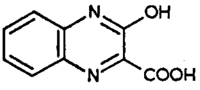

III

The present studies were made with 6 bivalent metals, *viz.* copper, cadmium, zinc, cobalt, nickel and palladium. Iron(II) forms red colours with reagents I and II, the detailed study of which will be reported at a later date.

EXPERIMENTAL

Preparation of quinoxaline-2-carboxylic acid (HR_1, I)

The preparation of this reagent involves 3 steps, *viz.*, preparation of *p*-toluyl-D-iso-glucosamine from D-glucose and *p*-toluidine, and the preparation of 2-D-arabotetrahydroxybutylquinoxaline from this and hydrazine hydrate and *o*-phenylenediamine; the 2-D-arabo compound on oxidation with hydrogen peroxide yields quinoxaline-2-carboxylic acid[3].

(i) Preparation of p*-toluyl-D-isoglucosamine.*
A mixture of 100 g of D-glucose, 80 g of *p*-toluidine, 25 ml of water and 5 ml of 2 *N* acetic acid was heated on a steam bath for 30 min. After addition of 100 ml of ethanol, the mass was left overnight and then filtered, and the crystalline residue after washing with alcohol–ether mixture (2:3, v/v) was air-dried (yield 90 g, m.p. 153°).

(ii) Preparation of 2-D-arabotetrahydroxybutylquinoxaline.
A mixture containing 9 g of *p*-toluyl-D-isoglucosamine, 3 g of hydrazine hydrate (100%),

7 g of *o*-phenylenediamine and 50 ml of 2 *N* acetic acid was heated on a steam bath for 30 min. The crystalline reaction product obtained after cooling was filtered and washed first with water, then with ether (yield 8 g, m.p. 152° (decomp.)).

(iii) Oxidation of 2-D-arabotetrahydroxybutylquinoxaline.
To a suspension of 10 g of the above compound in 600 ml of 6% hydrogen peroxide, 24 g of solid caustic soda was added in such a way that the temperature of the solution was never above 80° .When all solids had gone into solution and the initial vigorous reaction had subsided, the solution was kept on a water bath at 80° for about 30 min. At the end of this period some more hydrogen peroxide was added to turn the dark brown colour of the solution to yellow. To the hot solution some bone charcoal was added, and after some time, the mixture was filtered. Quinoxaline-2-carboxylic acid was obtained on acidification of the filtrate with concentrated hydrochloric acid. The compound was purified by dissolving it in caustic soda solution and reprecipitating it with hydrochloric acid (yield 4 g, m.p. 210°).

Preparation of 3-chloroquinoxaline-2-carboxylic acid[4] (HR_2, *II*)

o-Phenylenediamine (10.8 g) and 17.4 g of ethyl ketomalonate in 200 ml of ethanol was refluxed for 1 h. After filtration, the filtrate was diluted with 400 ml of water and boiled for 15 min with charcoal. On cooling, 3-hydroxyquinoxaline-2-carboxylate was obtained (yield 18 g, m.p. 176°). 11 g of this ester mixed with 50 ml of phosphorous oxychloride was heated at 110–120° for 15 min; excess phosphorous oxychloride was then removed at reduced pressure. The dark green coloured viscous residue was then poured into 600 g of crushed ice and the crude product of 3-chloroquinoxaline-2-carboxylate was directly recrystallised from aqueous methanol (charcoal); 4 g of this chloro ester mixed with 1 g of anhydrous sodium carbonate in 100 ml of 80% methanol was refluxed for 4 h, and then evaporated to dryness at reduced pressure. The residue was taken up with 30 ml of water, and acidified with hydrochloric acid. The 3.6 g of the chloro derivative (II) obtained, was recrystallised from water (m.p. 146° (decomp.)).

Preparation of 3-hydroxyquinoxaline-2-carboxylic acid[4] (HR_3, *III*)

3-Hydroxyquinoxaline-2-carboxylate (11 g), as obtained in the previous process, was hydrolysed with 3 *N* sodium hydroxide solution (100 ml) for 30 min on steam bath. The solution was brought to pH 4 when the hydroxy acid (III) was precipitated as long yellow brown needles. The acid was recrystallised from water (yield 8.5 g, m.p. 264°).

Preparation of the metallic salts of the reagents and their properties

The metallic salts of the reagents were prepared by adding aqueous 2% solutions of the sodium salts of the reagents to 100 ml of boiling metal salt solutions (containing about 50 mg of the respective metals) adjusted to pH 3–4, with vigorous stirring. The precipitate was then digested on a water bath for 15–20 min, filtered, washed with hot water until free from reagent (tested with iron(II)), dried in vacuum at room temperature and analysed. The results are given in Table I.

Reagents (II) and (III) gave either incomplete precipitations or soluble complexes with the metals tested except for palladium. Reagent (III) was found to produce with nickel and cobalt at higher pH values (*e.g.* pH 8) complexes of the type

$M(R_3)(OH)$, *i.e.* 1:1 complexes. Studies of the soluble complexes and 1:1 complexes of cobalt and nickel with reagent (III) are in progress. The compounds mentioned in Table I are highly crystalline in nature except for the palladium complexes. All of them are insoluble in common organic solvents, *e.g.* methanol, ethanol, acetone, chloroform, carbon tetrachloride, benzene, dioxane, ether, etc.

TABLE I

Composition of the metal salts	*Colour*	*% Metal*		*% Nitrogen*	
		Found	*Calcd.*	*Found*	*Calcd.*
$Cu(R_1)_2 \cdot 2H_2O$	Light green	14.18	14.25	12.61	12.57
$Cd(R_1)_2 \cdot 1.5H_2O$	White	23.35	23.30	11.66	11.61
$Zn(R_1)_2 \cdot H_2O$	White	15.30	15.23	12.97	13.04
$Co(R_1)_2 \cdot 2H_2O$	Bronze	13.33	13.39	12.75	12.70
$Ni(R_1)_2 \cdot 2H_2O$	Pale green	13.39	13.31	12.64	12.71
$Pd(R_1)_2$	Yellow	23.51	23.57	12.45	12.37
$Pd(R_2)_2 \cdot H_2O$	Yellow	19.78	19.68	10.39	10.35
$Pd(R_3)_2 \cdot H_2O$	Deep red	21.21	21.13	11.15	11.10

Optimum pH for precipitation and solubility products of metal salts

Slightly acidic metal salt solutions were mixed with a solution of the sodium salt of the reagent added and the volume was maintained at 100 ml. In these experiments, the effective metal ion concentration and reagent concentration usually lay in the range $(1.5–2) \cdot 10^{-3}$ M and $(3.5–8) \cdot 10^{-3}$ M respectively and the reagent : metal ratio was maintained between 2 and 4. Dilute sodium hydroxide solutions were then added from a burette with continuous stirring until a faint opalescence was observed. The pH of the solution at this stage was measured with a Cambridge pH meter (bench type). This is the approximate point of incipient precipitation. To obtain the actual value, a similar such solution was prepared in the same way but the pH value was adjusted to about 0.1 unit less than the previous one; dilute sodium hydroxide solution was then added dropwise and after each addition, the solution was stirred for 15 min until the first precipitation occurs. Other solutions were then prepared by adjusting the pH values at increasing values upto the point where hydrolytic equilibria began to occur. The solutions containing precipitate were kept at about 60° for 1–2 h to attain equilibria, and then cooled to room temperature and filtered; the pH of the filtrate was measured with a pH meter. The precipitate was collected on a G4 sintered glass crucible, washed thoroughly with water until free from reagent and dried at about 140° (see below). From the amount of metal ion taken, the fraction precipitated α was calculated. The solubility products were calculated by means of FLAGG's method[5], the values of α, pH, C_M, C_A and K_a being known; C_M and C_A are the initial metal ion and reagent concentration respectively. K_a represents the acid dissociation constant of the reagent, which in the cases of reagents I, II and III respectively are 2.80, 1.83, 2.58 [6]. The values of the solubility products are presented in Table II.

The observed pH values at the points of incipient precipitation of the metal salts of reagent I are shown in Table III along with the calculated values ($C_R/C_M = 3$ and $C_M \approx 2 \cdot 10^{-3}$ M) obtained by computing the solubility product values.

TABLE II

THE SOLUBILITY PRODUCT VALUES OF THE METAL CHELATES

Reagent	*Metal ion*	C_M *(M · 10³)*	C_A *(M · 10³)*	*pH*	*Fraction α of metal ion pptd.*	*pS*	*Av.pS*
I	Cu^{2+}	1.825	5.640	0.84	0.904	12.94	
		1.825	5.640	1.09	0.978	13.18	
		1.825	5.640	1.35	0.998	—	12.90
		1.825	8.076	1.02	0.970	12.58	
		1.825	8.076	1.22	1.004	—	
		1.825	8.076	7.26	1.000	—	
		1.825	8.076	7.40	0.976	—	
I	Cd^{2+}	1.411	2.868	2.52	0.5606	9.55	
		1.411	2.868	3.32	0.7591	8.71	
		1.411	2.868	3.61	0.8015	8.37	9.12
		1.411	4.143	2.15	0.3971	9.88	
		1.411	6.077	2.31	0.6861	9.10	
		1.411	6.077	3.07	1.003	—	
		1.411	6.077	7.28	1.002	—	
		1.411	6.077	7.76	0.9561	—	
I	Zn^{2+}	1.707	3.506	2.56	0.7695	9.99	
		1.707	5.099	2.18	0.7776	9.88	9.84
		1.707	7.425	2.26	0.9168	9.66	
		1.707	7.425	3.12	1.001	—	
		1.707	7.425	7.10	0.9969	—	
		1.707	7.425	7.24	0.9917	—	
		1.707	7.425	7.66	0.6916	—	
I	Pd^{2+}	1.346	4.099	0.98	0.9358	13.31	
		1.346	4.099	2.24	0.998	—	
		1.346	4.099	6.34	1.000	—	
		1.346	4.099	7.08	0.964	—	
I	Co^{2+}	2.004	4.130	2.09	0.881	11.49	
		2.004	4.130	2.30	0.9399	11.80	11.73
		2.004	4.130	2.67	0.9761	11.89	
		2.004	6.354	2.10	1.002	—	
		2.004	6.354	7.22	0.999	—	
		2.004	6.354	7.60	0.9561	—	
I	Ni^{2+}	2.305	4.652	2.05	0.9272	12.12	
		2.305	4.652	2.33	0.9548	12.21	12.25
		2.305	4.652	2.88	0.9813	12.43	
		2.305	6.831	2.07	0.9988	—	
		2.305	6.831	7.00	1.002	—	
		2.305	6.831	7.52	0.955	—	
II	Pd^{2+}	1.346	5.914	0.89	0.998	—	
		1.346	5.914	2.58	1.001	—	
		1.346	5.914	6.20	1.002	—	
		1.346	5.914	7.50	0.932		
III	Pd^{2+}	1.346	5.360	1.72	0.998	—	
		1.346	5.360	4.94	0.999	—	
		1.346	5.360	5.12	0.976		

TABLE III

OBSERVED AND CALCULATED pH VALUES FOR INCIPIENT PRECIPITATION

Metal ion	*Observed pH*	*Calculated pH*	*Metal ion*	*Observed pH*	*Calculated pH*
Cu^{2+}	—	~ 0	Co^{2+}	0.64	0.52
Cd^{2+}	1.85	1.81	Ni^{2+}	—	0.34
Zn^{2+}	1.47	1.45	Pd^{2+}	—	< 0

THERMAL STUDIES OF THE METAL SALTS OF QUINOXALINE-2-CARBOXYLIC ACID

The thermograms were run in a Chevenard thermobalance; DTA measurements were made with an apparatus essentially similar to that constructed by GRUVER[7] with slight modification, the details of which may be found elsewhere[8].

The samples taken for TG were usually 80–100 mg but in the case of the palladium complex, lower amounts were taken; the heating rate was 6°/min and the compounds were heated up to 700°. For DTA 200-mg samples were taken, the rate of heating was 6°/min and the compounds were heated until the oxide level is reached (about 700°). The results are summarized in Table IV. The TGA curves are shown in Fig. 1.

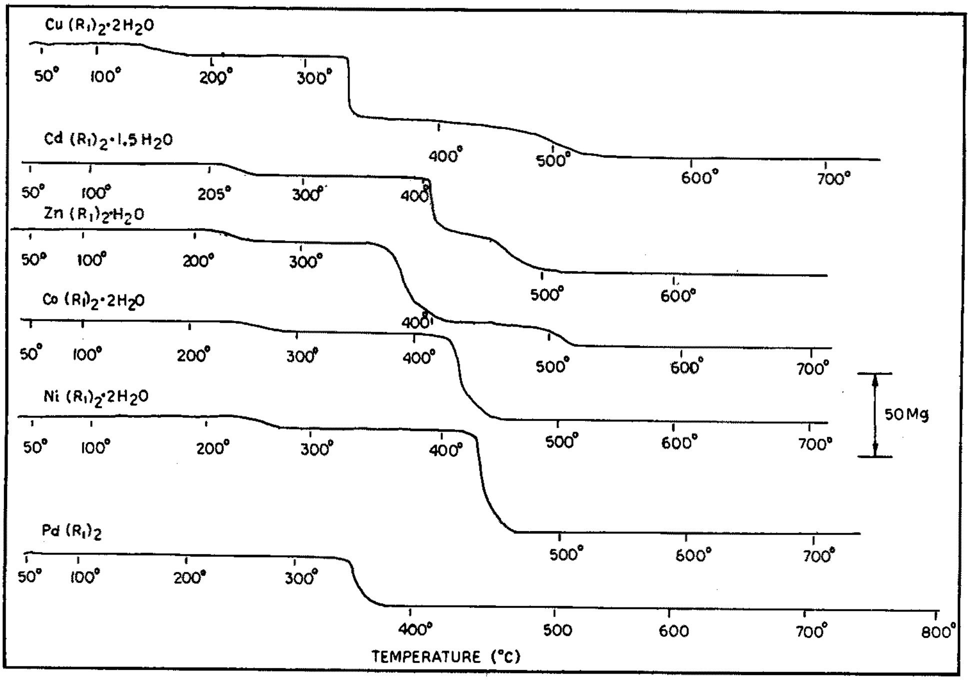

Fig. 1. TGA curves.

DISCUSSION

All the DTA curves except that of the palladium complex contained one exothermic peak indicating dehydration, and two endotherms, corresponding to melting and decomposition respectively. No attempts were made to assign processes to the other endotherms present in some cases. The thermogravimetric studies indicated the presence of some intermediate products in the cases of the copper, cadmium and zinc chelates during the decomposition of the anhydrous species before the oxide level was reached. The isolation and characterisation of these intermediate products are now being investigated.

From the thermal analyses it is clear that, for analytical purposes, the copper

TABLE IV

RESULTS OF THERMAL ANALYSIS

Metal	*Thermogravimetric analysis*								*Differential thermal analysis*			
	Composition of the compd. at the indicated temp.				*Wt. loss to dehydration (%)*		*Yield of oxide (%)*		*Dehydration (°)*	*Melting (°)*	*Decomposition (°)*	*Complete conversion to oxide (°)*
					Found	*Calcd.*	*Found*	*Calcd.*				
Cu	$Cu(R_1)_2 \cdot 2H_2O$ 130°	$Cu(R_1)_2$ 160°–330°	340°–370°[a]	CuO 540°	8.1	8.2	17.7	17.8	120	290	370	530
Cd	$Cd(R_1)_2 \cdot 1.5H_2O$ 210°	$Cd(R_1)_2$ 240°–390°	420°–460°[a]	CdO 520°	5.6	6	26.2	25.8	200	380	400	550
Zn	$Zn(R_1)_2 \cdot H_2O$ 210°	$Zn(R_1)_2$ 250°–350°	420°–460°[a]	ZnO 525°	4.2	4.5	19	18.8	200	350	400	500
Co	$Co(R_1)_2 \cdot 2H_2O$ 250°	$Co(R_1)_2$ 280°–420°	—	Co_3O_4 460°	8.2	8.4	18.2	18.1	250	370	400	540
Ni	$Ni(R_1)_2 \cdot 2H_2O$ 240°	$Ni(R_1)_2$ 270°–420°	—	NiO 460°	8.2	8.0	17.1	17.5	240	380	410	550
Pd	—	$Pd(R_1)_2$ 320°	—	PdO 370°	—	—	27.1	27.5	—	300	320	570

[a] Intermediate product formed.

complex must be heated above 140° to be weighable in its anhydrous form; in the other cases the hydrated forms are stable even up to about 200°. The palladium compound is anhydrous and stable up to 320°.

ANALYTICAL APPLICATIONS OF THE REAGENTS

Use of quinoxaline-2-carboxylic acid (I)

After the conditions for the quantitative precipitation of metal ions had been established, the parent reagent (I) was applied for the determination of these ions. The pH ranges for the determinations are as follows: Cu(1.5–7.2), Cd(4.0–7.3), Zn (3.0–7), Pd(2.0–6.3), Co(2.8–7.3), Ni (2.5–7.2). The actual procedures for the precipitation are similar in all cases, so that only a generalised procedure is given below.

Procedure. Dilute the metal salt solution containing 10–50 mg of the metal to 100–200 ml depending on the metal ion concentration. Adjust the pH of the solution as indicated above, heat to boiling and add a solution of the sodium salt of the reagent slowly with vigorous stirring. Finally, adjust the pH by addition of dilute alkali or acid if necessary. Except in the case of cadmium, the amount of reagent to be added is 50% excess of the theoretical amount required for complete precipitation of the metal ions; for cadmium, a 100% excess is necessary. After addition of the reagent, place the mixture on a steam bath for 15–20 min. In the cases of copper, palladium, cobalt and nickel, filter the precipitates hot, wash thoroughly with hot water (80°) and test the washings for freedom from reagent. Filter the zinc and cadmium precipitates after cooling to room temperature and wash with cold water. As established by the thermal studies, dry the copper compound at 140° to constant weight in its

TABLE V

THE DETERMINATION OF METALS WITH REAGENT I

Metal	*Wt. of ppt. (mg)*	*Metal taken (mg)*	*Metal found (mg)*	*Difference (mg)*
Cu	149.2	23.17	23.16	—0.01
	123.3	19.18	19.14	−0.04
	74.8	11.68	11.61	−0.07
	251.5	39.03	39.05	+0.02
	295.1	45.84	45.81	−0.03
Cd	85.5	19.92	19.80	−0.12
	169.0	39.13	39.15	+0.02
	252.3	58.52	58.41	−0.11
	338.2	78.30	78.31	+0.01
Zn	73.2	11.24	11.15	−0.09
	148.0	22.48	22.54	+0.06
	229.0	33.72	33.93	+0.21
Pd	60.7	14.37	14.32	−0.05
	92.0	21.45	21.69	+0.14
	152.7	35.93	36.00	+0.07
Ni	99.4	13.36	13.23	−0.13
	150.0	20.04	20.02	−0.02
	200.0	26.72	26.65	−0.07
Co	133.5	17.82	17.83	−0.01
	177.8	23.78	23.82	+0.04

anhydrous form; dry the cadmium (1.5 H_2O), zinc (1 H_2O), cobalt (2 H_2O), nickel (2 H_2O) and palladium (anhydrous) precipitates between 120° and 130°.

The results of typical analyses are shown in Table V. The determination of cobalt is particularly useful since the precipitate can be weighed directly as its dihydrate, after precipitation of cobalt(II).

Use of 3-chloro- and 3-hydroxy-quinoxaline-2-carboxylic acids

Only palladium could be determined with these two reagents. The pH range for quantitative precipitation was 0.9–7.2 for the 3-chloro derivative, and 1.6–5.0 for the 3-hydroxy derivative. The method of precipitation of palladium was similar to that described for reagent (I). Both the precipitates were weighed as the monohydrates after drying at 100°. Typical results are shown in Table VI.

TABLE VI

THE DETERMINATION OF PALLADIUM WITH REAGENTS II AND III

	Wt. of ppt. (mg)	*Pd taken (mg)*	*Pd found (mg)*	*Difference (mg)*
Reagent II	73.0	14.37	14.40	−0.03
	109.0	21.55	21.51	−0.04
Reagent III	67.5	14.37	14.30	−0.07
	101.4	21.55	21.49	−0.06

We gratefully acknowledge the kind help received from Prof. A. K. MAJUMDAR, Principal, Jadavpur University, Jadavpur, India, in obtaining the thermograms, and from the authorities of the Atomic Energy Establishment, Trombay, India, for the differential thermal analyses curves.

SUMMARY

Quinoxaline-2-carboxylic acid and 3-chloro and 3-hydroxy derivatives have been studied as analytical reagents. The solubility products of the metal salts, the optimum pH range for complete precipitation and the thermal behaviours of the metal complexes have been established. Quinoxaline-2-carboxylic acid allows the gravimetric determination of Cu(II), Cd(II), Zn(II), Co(II), Ni(II) and Pd(II); with the 3-chloro and 3-hydroxy derivatives, only palladium(II) could be precipitated quantitatively.

RÉSUMÉ

On a examiné l'acide quinoxaline-2-carboxylique et ses dérivés 3-chloro et 3-hydroxy en tant que réactifs analytiques. On a pu établir les produits de solubilité des sels métalliques, le domaine de pH optimum pour une précipitation quantitative et le comportement thermique des complexes métalliques. L'acide quinoxaline-2-carboxylique permet le dosage gravimétrique du Cu(II), Cd(II), Zn(II), Co(II), Ni(II) et Pd(II); avec les dérivés 3-chloro et 3-hydroxy, seul le palladium(II) peut être précipité quantitativement.

ZUSAMMENFASSUNG

Chinoxalin-2-carboxylsäure und 3-Chloro- und 3-Hydroxy-Derivate wurden auf ihre Eignung als analytisches Reagenz untersucht. Die Löslichkeitsprodukte der Metallsalze, die optimalen pH-Bereiche zur vollständigen Fällung und das thermische Verhalten wurden aufgesucht. Chinoxalin-2-carboxylsäure gestattet die gravimetrische Bestimmung von Cu(II), Cd(II), Zn(II), Co(II), Ni(II) und Pd(II); mit den 3-Chloro- und 3-Hydroxy-Derivaten konnte nur Pd(II) quantitativ gefällt werden.

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COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN 1,1′-DIANTHRIMIDE AND GERMANIUM(IV) OR TELLURIUM(IV)

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1,1′-Dianthrimide is chiefly known as an organic reagent for the photometric determination of boron, although it also forms complexes with selenium(IV), germanium(IV) and tellurium(IV). A series of contributions from this Institute had described the analytical application, the complex formation and the effect of some critical factors upon the reactions in concentrated sulfuric acid of 1,1′-dianthrimide with boron[1-4], selenium(IV)[5,6], germanium(IV)[7] and tellurium(IV)[8]. The present, final paper in this series describes the complex formation with germanium(IV) or tellurium(IV).

EXPERIMENTAL

Equipment

For the extinction measurements a Zeiss spectrophotometer PMQ II, a Beckman DB recording spectrophotometer and 1-, 2- and 5-cm glass cells were used.

All solutions were prepared in 50-ml bottles (Jena Geräteglas) with ground-glass stoppers. The solutions were heated in a thermostatically controlled drying oven.

Reagents

The 1,1′-dianthrimide (Fluka AG, Switzerland), the germanium and tellurium dioxides (Johnson, Matthey & Co., Ltd., Great Britain) and the other chemicals were of reagent-grade quality.

Standard solutions

Because of the low solubility of the germanium and tellurium dioxides in concentrated sulfuric acid, the standard solutions were prepared as follows. Primary 0.05 *M* standard solutions were prepared by dissolving the proper amounts of the oxides in 1% sodium hydroxide solution and diluting to a known volume with the same solution. These solutions were stored in plastic bottles. Secondary 0.005 *M* solutions were prepared by pipetting the proper volumes of the 0.05 *M* solutions into volumetric flasks and diluting to volume with 98.3% sulfuric acid. The final acid concentration was 93.2%. In the secondary standard solutions of tellurium a white precipitate appeared after about 2 weeks of standing, but the solutions of germanium remained clear for months.

A standard solution of 1,1′-dianthrimide was prepared by dissolving the proper amount in 93.2% sulfuric acid and diluting to a known volume with acid of the same concentration.

Effect of temperature

On the basis of previous[7,8] and new studies, a heating temperature of 70° was used in the investigations of both systems. At higher temperatures, the absorption curve of 1,1′-dianthrimide changed markedly.

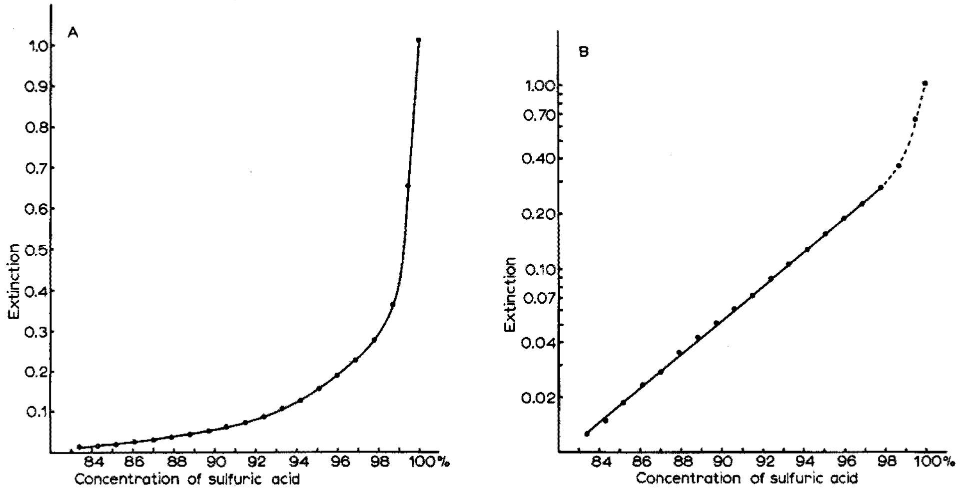
Effect of heating time

In previous investigations[7,8] a heating time of 16 h was used. For the tellurium–1,1′-dianthrimide system, however, new studies showed that a heating time of 40 h increased the extinction of the complex by about 100%. Prolonged heating to 64 h gave but little extra effect, consequently a heating time of 40 h was used in the present studies.

For the germanium–1,1′-dianthrimide system and in the sulfuric acid concentration range 83–100% the complex exhibited maximum extinction after 15 h of heating. A heating time of 16 h was used in the present investigations of this system.

Effect of concentration of sulfuric acid

For the germanium–1,1′-dianthrimide system and the concentration range 85–94% sulfuric acid, it was shown[7] that the extinction of the complex increased rapidly when the concentration of acid was increased. In a new investigation this effect was studied in the range 83–100% sulfuric acid. In a series of solutions the concentrations of germanium and 1,1′-dianthrimide were $6.25 \cdot 10^{-5}$ and $6.25 \cdot 10^{-4}$ *M*, respectively, while the concentration of acid was varied. The solutions were measured against blank solutions $6.25 \cdot 10^{-4}$ *M* with regard to 1,1′-dianthrimide and having the



Figs. 1a and 1b. Extinctions of solutions, $6.25 \cdot 10^{-5}$ *M* and $6.25 \cdot 10^{-4}$ *M* in germanium and 1,1′-dianthrimide, respectively, as a function of the concentration of sulfuric acid. The extinctions were measured at the absorption maximum (as apparent from Table I the maximum varies with the concentration of acid) of the complex against $6.25 \cdot 10^{-4}$ *M* 1,1′-dianthrimide blank solutions prepared in an acid of the proper concentration. In Fig. 1a the extinction scale is linear; in Fig. 1b it is on a logarithmic scale.

proper concentration of acid. The extinctions were then measured at the absorption maximum of the complex (as is apparent from Table I, the position of the maximum varies with the concentration of the acid). Figures 1a and 1b show the resulting curves.

It is interesting to note that when the extinction is plotted on a logarithmic scale, the curve is straight in the range 83–98% sulfuric acid. On the basis of Fig. 1a, a concentration of 93.2% sulfuric acid was chosen for the studies of the germanium–1,1'-dianthrimide system.

For the system tellurium–1,1'-dianthrimide, the effect of the concentration of acid upon the extinction of the complex was found to be the same as given previously[8]. In the present studies of this system the final acid concentration was also maintained at 93.2%.

Absorption curves

In 93.2% sulfuric acid the germanium complex was found to have a predominant absorption maximum at 660 nm, and in the present study the measurements were made at this wavelength. The absorption maximum, however, varies with the concentration of sulfuric acid. In Table I the absorption maximum of the germanium–1,1'-dianthrimide complex is given for different concentrations of acid.

TABLE I

THE EFFECT OF THE CONCENTRATION OF SULFURIC ACID ON THE POSITION OF THE ABSORPTION MAXIMUM OF THE GERMANIUM–1,1'-DIANTHRIMIDE COMPLEX

% H_2SO_4	82	90	94	98	100
Abs. max. (nm)	640	650	665	675	685

The tellurium complex has been shown[8] to exhibit absorption maxima at 550 nm and 600 nm. A new study of the effect of the heating time upon the development of the complex showed that when the time was increased from 16 h to 40 h, the absorption of the blank solution increased around 550 nm, while it remained constant at about 600 nm. For this reason the present absorption measurements of the tellurium complex were made at 600 nm; this maximum did not change when the concentration of sulfuric acid was varied.

COMPOSITION OF THE COMPLEXES

For the system germanium–1,1'-dianthrimide, a curve of continuous variation was recorded at 660 nm for a series of solutions with the total concentration 10^{-3} *M*. The curve exhibited a maximum at the mole fraction 0.5, the curve branches had no inversion and the gradient at the end-points was different from zero, these features pointing to the presence of a complex with the composition GeDi.

For the system tellurium–1,1'-dianthrimide, a curve of continuous variation was recorded at 600 nm for a series of solutions with a total concentration of $7.5 \cdot 10^{-4}$ *M*. The curve showed a rounded maximum at the mole fraction of tellurium of 0.4, the curve branches had no inversion and the gradient at the end-points was different from zero. Although the maximum did not appear at the mole fraction 0.5, it was concluded from the gradients at the end-points and the use of other methods that the actual composition of the complex was TeDi.

If the presence of a complex of the form Ge_mDi_n is assumed, the straight-line method of ASMUS[11], with the modification introduced by KLAUSEN AND LANGMYHR[12], gave the coefficients $m = 1$ and $n = 1$.

The method was then applied to the system tellurium–1,1′-dianthrimide, and the coefficients were again found to be $m = 1$ and $n = 1$.

The new straight-line method, recently introduced by HOLME AND LANGMYHR[13], was used to determine the quotient n/m of the complexes Ge_mDi_n and Te_mDi_n. For both systems the method gave the value $n/m = 1$.

For the two systems the above methods showed the presence of the species GeDi and TeDi.

With regard to the reaction mechanism and the structure of the complexes, very little can be said. The behaviour of the tellurium or germanium dioxides in the sulfuric acid solvent system is not known. However, it is highly probable that the carbonyl and/or imino groups of the 1,1′-dianthrimide are engaged in complex formation.

The stability constants

For the two complexes, the stability constants were calculated by two different methods, *viz.* the method of LANG[14] and the method of SILLÉN[15,16]. In the LANG method[14] eqn. (1) gives a straight line when ab/E and $(a+b-E/\varepsilon)$ are used as co-ordinates

$$\frac{ab}{E} = (a+b-E/\varepsilon)\frac{1}{\varepsilon} + \frac{1}{\varepsilon K} \qquad (1)$$

Here a and b are the concentrations of the reactants, E is the measured extinction, ε is the molar extinction coefficient and K the stability constant. A computer method based on linear least squares analysis was used to calculate K, ε and their standard deviation.

The SILLÉN "pit-mapping" method, based on non-linear least squares analysis, was also used to calculate the stability constant K, the molar extinction coefficient ε and the standard deviations. In these calculations the computer program recently used by GRUNDNES AND CHRISTIAN[17] was employed.

Special solutions were prepared for the calculations of the stability constants. The extinction measurements were made on solutions containing an excess of either germanium or tellurium, and the concentrations were chosen to insure the conditions of measurement recommended in the literature[18]. The stability constants were calculated from eqns. (2) and (3).

$$\mathrm{Ge} + \mathrm{Di} \rightleftharpoons \mathrm{GeDi} \qquad (2)$$

$$K_1 = \frac{[\mathrm{GeDi}]}{[\mathrm{Ge}]\cdot[\mathrm{Di}]} \qquad (2a)$$

$$\mathrm{Te} + \mathrm{Di} \rightleftharpoons \mathrm{TeDi} \qquad (3)$$

$$K_2 = \frac{[\mathrm{TeBi}]}{[\mathrm{Te}]\cdot[\mathrm{Bi}]} \qquad (3a)$$

TABLE II

STABILITY CONSTANTS FOR THE COMPLEXES OF GERMANIUM OR TELLURIUM WITH 1,1'-DIANTHRIMIDE

Complex	*Lang's method*				*Sillén's method*			
	K	σ_K	ε	σ_ε	K	σ_K	ε	σ_ε
GeDi	221	2	14480	120	221	4	14460	150
TeDi	222	10	26300	550	234	10	25400	740

The calculated values for K and ε, and their standard deviation, σ_K and σ_ε, respectively, are given in Table II.

The stability constants calculated for the GeDi and TeDi complexes are low compared with those of other 1,1'-dianthrimide complexes formed in concentrated sulfuric acid[6,9,10]. From Table II it can be seen that the data from the two methods are in good agreement, and that the two complexes have about the same stability.

SUMMARY

The complex formation in concentrated sulfuric acid between 1,1'-dianthrimide (Di) and germanium or tellurium(IV) was studied by spectrophotometry. The systems contained only one species, GeDi or TeDi; the stability constants in 93.2% sulfuric acid were calculated to be 221 and 228, respectively.

RÉSUMÉ

Une étude est effectuée par spectrophotométrie sur la formation du complexe en milieu acide sulfurique concentré, entre dianthrimide-1,1' (Di) et germanium, ainsi que tellure(IV). On ne peut déceler que GeDi ou TeDi; les constantes de stabilité calculées sont respectivement 221 et 228, dans l'acide sulfurique à 93.2%.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen 1,1'-Dianthrimid (Di) und Germanium(IV) oder Tellur(IV) in schwefelsaurer Lösung wurde spektralphotometrisch untersucht. Es wurden nur die Spezies GeDi oder TeDi gebildet. Die Stabilitätskonstanten in 93.2%iger Schwefelsäure betrugen 221 bzw. 228.

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THE DETERMINATION OF NICOTINE IN TOBACCO AND IN PARTICULATE MATTER OF SMOKE BY GAS CHROMATOGRAPHY

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The presently used methods for the determination of total alkaloids in tobacco are based on the procedure described by WILLITS *et al.*[1] and modified by GRIFFITH[2]. HARVEY *et al.*[3] replaced the steam distillation step of the WILLITS procedure by an acid–methanol extraction. CUNDIFF AND MARKUNAS[4] have developed a method for determining nicotine, nornicotine and total alkaloids in tobacco which involves an extraction and subsequent titration of extract aliquots with perchloric acid.

The total alkaloids in particulate matter of smoke may be determined by several methods[5–7], all of which involve a steam distillation step. The method of HARVEY *et al.*[3] (an extraction procedure) is also suitable for determining alkaloids in smoke particulate matter. In addition a gas chromatographic method for determining alkaloids in tobacco smoke has been presented by QUIN[8], while nicotine in cigarette smoke can also be determined by a method described by LYERLY[9].

Among the above-mentioned procedures, the wet chemical methods[1–7] are rather time-consuming while the gas chromatographic procedures[8,9] are applicable to tobacco smoke only. A rapid, reliable method for determining nicotine in tobacco and tobacco smoke would be most useful, especially where a series of samples has to be analyzed in a relatively short time. Such a method is herein described. The procedure involves an extraction and subsequent nicotine determination by gas chromatography. The retention time for nicotine is 5.5 min while the retention times for other alkaloids, such as nornicotine and anabasine, are considerably longer. The procedure is rapid and yields accurate and reproducible results.

EXPERIMENTAL

Extraction method

The extraction step is a modification of the CUNDIFF AND MARKUNAS[4] procedure. The method is as follows: A tobacco sample (0.3–0.5 g) was blended with 0.5 g of reagent-grade barium hydroxide octahydrate in a glass-stoppered 125-ml Erlenmyer flask. Saturated barium hydroxide solution (10 ml) was then added to the blend and the contents were mixed manually. A benzene–chloroform (9:1) mixture (50 ml) was quantitatively added from a burette to the Erlenmyer. The contents were shaken for 20 min on a wrist-action shaker. The flask was then removed from the shaker and aliquots of the benzene–chloroform layer were injected into the gas chromatograph for nicotine determination.

Determination of nicotine in the particulate matter of smoke.

Weight-matched commercial cigarettes (70 mm length) were smoked on a smoking machine, to a 23-mm butt length through a Cambridge filter. A 35-ml puff of 2-sec duration was taken once every minute. Five cigarettes were smoked through each Cambridge filter. The weights of the cigarettes, before smoking, and the weights of the butts were determined, thus allowing one to calculate the per cent nicotine on the basis of tobacco consumed. After smoking was completed, the Cambridge filter was removed, and placed in a screw-capped vial. A 10-ml volume of benzene–chloroform (9:1) was added and the mixture was shaken on the wrist-action type shaker for 20 min. An aliquot of the supernatant liquid was subsequently injected into the gas chromatograph for nicotine determination.

Gas chromatographic conditions

A Perkin-Elmer gas chromatograph (P-E 800), with a flame ionization detector was used.

The column dimensions were 6 ft. by $^1/_8$ inch. The support was Gas Chrom Q, 80–100 mesh, coated with 10% neopentyl glycol adipate. An injection temperature of 235° and a column temperature of 168° (isothermal) were used. The nitrogen flow was 33 ml per min and the chart speed one inch per min.

RESULTS AND DISCUSSION

In order to establish the stability of the column used for this separation, known quantities of nicotine were injected over an 8-h period and the obtained peak heights compared. The deviations in peak heights were within the range of experimental error, indicating that the column is stable and suitable for nicotine determinations.

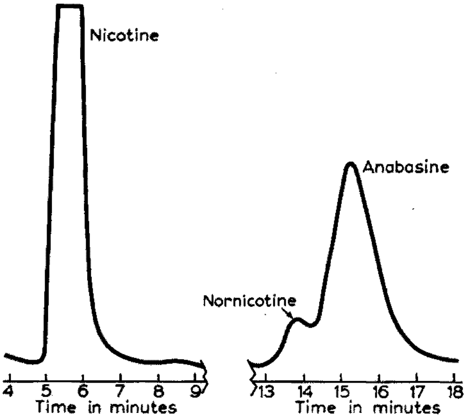

Fig. 1. Separation of tobacco alkaloids on a gas chromatography column.

Synthetic mixtures of nicotine, nornicotine and anabasine were separated on the above-mentioned gas chromatographic column. The individual peaks may be seen in Fig. 1. The nicotine was held for 5.5 min, the nornicotine for 14 min and the anabasine for 15.5 min. The graph also showed some unidentified peaks.

Known quantities of nicotine were injected and the peak heights determined.

The injection volume for all samples was kept at 3 μl. The peak shapes were highly reproducible from run to run. In a series of 9 nicotine samples of the same concentration and volume the over-all deviation in peak height was ±0.7%. The peak heights obtained for various nicotine quantities are listed in Table I. The values presented in the Table are an average of at least 3 determinations.

The calibration curve of peak height *versus* nicotine concentration constructed from the values shown in Table I was linear over the range *ca.* 0.3–0.6 mg nicotine/μl and showed slight curvature in the 0.1–0.3 mg range. This calibration curve was subsequently used in the analysis of tobaccos and condensates.

TABLE I

PEAK HEIGHTS OBTAINED FOR VARIOUS NICOTINE SOLUTIONS ON A GAS CHROMATOGRAPHY COLUMN

Nicotine concentration (mg/μl)	*Injection volume (μl)*	*Peak height (chart units)*
0.074	3·0	4·9
0.168	3·0	14·3
0.282	3·0	26.7
0.446	3·0	47·1
0.608	3·0	66.7

TABLE II

REPRODUCIBILITY OF NICOTINE DETERMINATIONS BY THE GAS CHROMATOGRAPHY METHOD

Tobacco	*Dry weight (g)*	*Nicotine found (%)*	*Mean*	*Deviation from mean (%)*
Maryland stems	2.91	1·35		−1·5
	1.88	1·37		0.0
	3·97	1·33		−3·0
	2.91	1.40		+2.0
	1.88	1·38		+1.0
	3·97	1·37	1·37	0.0
Burley stems	1.11	1.02		−2.5
	1.11	1.04		−1.0
	1.12	1.04		−1.0
	1.10	1.06		+1.0
	1.11	1.04	1.05	−1.0
Bright lamella	0.189	1.66		+3.0
	0.453	1.60		−1.0
	0.392	1.61	1.62	−0.5

The gas chromatographic method was applied to the determination of nicotine in lamella, stems, reconstituted tobacco sheet and in commercially available non-filter cigarettes. The reproducibility among samples of the same material was *ca.* ±3.0%. Examples of these determinations are shown in Table II. Repeat chromatograms of a nicotine determination carried out on tobacco shreds from commercial non-filter cigarettes showed identical retention times and similar peak heights.

In order to determine the accuracy of the method, known amounts of nicotine were added to tobacco samples and the mixtures were carried through the analytical procedure. The amount of nicotine recovered indicated the accuracy. The results for various samples are shown in Table III.

These data show a recovery of added nicotine within the range of ±3%, indicating good accuracy.

TABLE III

THE RECOVERY OF NICOTINE ADDED TO VARIOUS TOBACCO SAMPLES

Tobacco	*Dry wt. (g)*	*Nicotine added (mg)*	*Total nicotine found (mg)*	*Nicotine from tobacco (mg)*	*Nicotine recovered (mg)*	*% Recovery*
Maryland stem	2.84	26.3	65.6	38.9	26.7	101
	2.84	26.3	66.8	38.9	27.9	106
	2.79	26.3	63.8	38.2	25.6	97
	2.79	26.3	65.2	38.2	27.0	103
Bright stem	2.85	34.2	52.7	16.8	35.9	105
	2.85	34.2	52.2	16.8	35.4	103
Bright lamella	0.184	3.42	6.3	3.0	3.3	97
	0.169	6.84	9.6	2.7	6.9	101
	0.243	3.42	7.2	3.9	3.3	97
Reconstituted tobacco sheet	0.140	0.68	2.4	1.7	0.7	103
	0.123	1.37	2.9	1.5	1.4	103
	0.172	2.05	4.2	2.1	2.1	102

TABLE IV

A COMPARISON OF TOBACCO NICOTINE VALUES OBTAINED BY A GAS CHROMATOGRAPHY AND SPECTROPHOTOMETRIC METHOD

Tobacco	*Spectro-photometric*	*Gas chromatography*	*G.C. values as % of spectro-photometric*
Maryland stems	1.41	1.37	97.2
Burley stems	1.11	1.05	95.5
Bright stems	0.59	0.59	100
Bright lamella	1.74	1.62	93.5
Penn. stems	1.85	1.74	94.3
Turkish stems	0.47	0.41	87.5
Sweated Penn. stems	0.90	0.79	88.0
Penn. lamella	1.50	1.39	93
Reconstituted tobacco	1.23	1.21	98.5
Reconstituted tobacco	1.08	1.09	101
Commercial cigarettes	1.80	1.62	90

The above gas chromatographic procedure was compared with an Association of Official Agricultural Chemists' method[10] used in determining total alkaloids in tobacco as nicotine. The results are shown in Table IV. Each figure in the Table is an average of at least 3 determinations. Clearly, the nicotine values obtained by the chromatographic method are lower than those obtained by the spectrophotometric method. This is to be expected since the gas chromatographic method determines nicotine only, whereas the spectrophotometric determination includes other alkaloids. Figure 2 is a chromatogram exemplifying the composition of the steam distillate

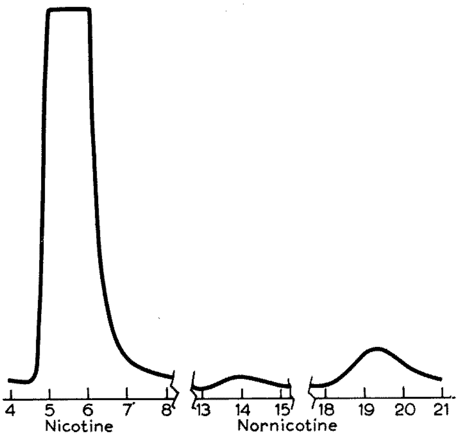

Fig. 2. Steam distillate produced for spectrophotometric determination of tobacco alkaloids. The gas chromatogram shows the presence of nicotine, nornicotine and unidentified alkaloid peak.

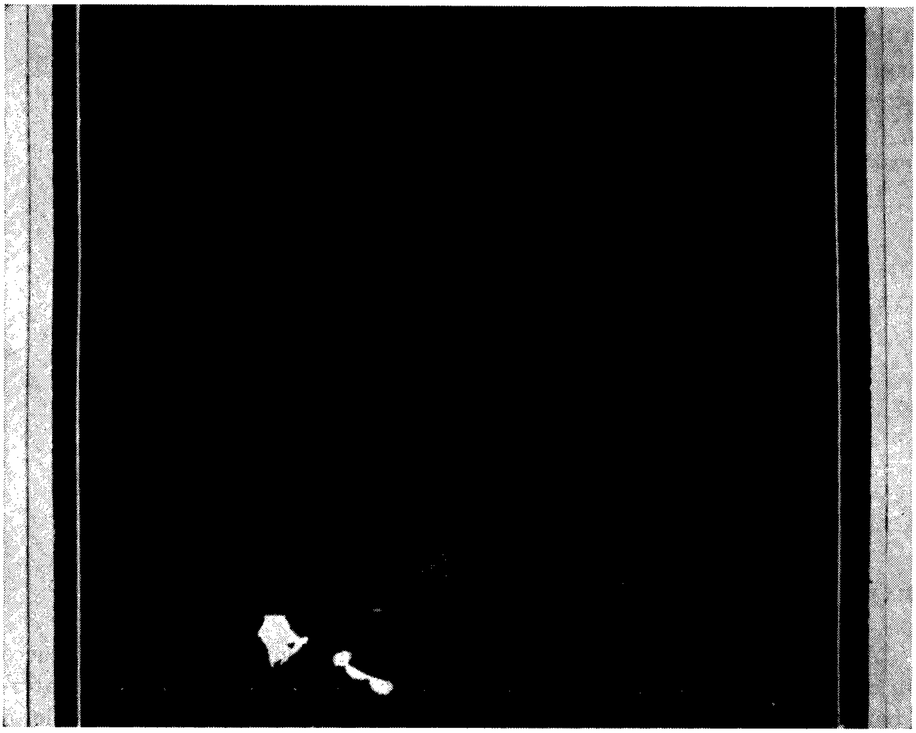

Fig. 3. Thin-layer chromatography of tobacco alkaloids. (Spots 1, 2, 3) anabasine. (Spots 4, 5) nicotine. (Spots 6, 7) nornicotine. (Spots 10, 11, 12) steam-distilled tobacco extract showing in ascending order nornicotine, anabasine, nicotine. (Spots 14, 15, 16) benzene–chloroform (9:1) extract of tobacco shows the same alkaloids as the steam distillate. (Spot 17) a mixture of nornicotine, anabasine, nicotine.

produced for the spectrophotometric determination from Bright lamella. It is apparent from the graph that alkaloids other than nicotine are present in the solution.

The presence of other alkaloids was confirmed by thin-layer chromatography. The support medium was silica gel-G in borate buffer pH 8.0 (0.02 *M*) and the plates were heated for 60 min at 100° before sample application. The developing solvent was benzene–methanol–ammonia (60:10:1), the plates being removed when the solvent front reached the 10-cm mark. The plates were air-dried for 45 min, sprayed as described by HODGSON *et al.*[11], dried for 15 min at 100° and placed in a sealed vessel that contained a few crystals of cyanogen bromide. The alkaloids appeared as yellow to brown spots on a white background. A photograph of the plate is shown in Fig. 3.

The thin-layer chromatography results show that the steam distillate contains anabasine, nornicotine and nicotine. The 3 materials have different R_F values and separate very well in this system, as evidenced by the separation effected in the case of spot 17 where a mixture of the 3 materials was used.

Commercial non-filter cigarettes were used for the determination of nicotine in particulate matter of smoke. A comparison was again made between the gas chromatographic and spectrophotometric results. The findings are shown in Table V. The deviation of about 3% for the gas chromatographic method is within the limit of reproducibility.

TABLE V

DETERMINATION OF NICOTINE IN PARTICULATE MATTER OF SMOKE

Dry weight of tobacco consumed (g)	*% Nicotine*	
	Spectrophotometric	*Gas chromatography*
2.74	0.177	—
2.97	—	0.226
3.05	0.245	—
2.98	—	0.241
2.84	—	0.248
2.86	0.270	—
3.08	—	0.231
2.94	0.248	—
2.91	—	0.215
2.86	0.276	—
3.01	0.233	—
2.97	—	0.243
	Average 0.242	Average 0.234

SUMMARY

A gas chromatographic method for the determination of nicotine in tobacco and in smoke particulate matter is described. Tobacco samples are extracted with saturated barium hydroxide solution, and nicotine is then extracted with benzene–chloroform (9:1), and determined by gas chromatography. The column separates tobacco alkaloids into several fractions, giving different retention times for nicotine, nornicotine and anabasine. The results obtained by this procedure are at least as good as those obtained by other methods presently available; the method is very simple and rapid.

RÉSUMÉ

Une méthode par chromatographie gazeuse est décrite pour le dosage de la nicotine dans le tabac et dans la fumée. Les échantillons de tabac sont extraits avec une solution saturée d'hydroxyde de baryum; la nicotine est ensuite extraite à l'aide de benzène–chloroforme (9:1) et dosée par chromatographie gazeuse. La colonne sépare les alcaloïdes du tabac en plusieurs fractions donnant différents temps de rétention pour nicotine, nornicotine et anabasine. Les résultats obtenus par ce procédé sont en tout cas aussi bons que ceux obtenus par d'autres méthodes. Ce procédé est très simple et rapide.

ZUSAMMENFASSUNG

Eine gaschromatografische Methode zur Bestimmung von Nikotin in Tabak und im Rauch wird beschrieben. Der Tabak wird mit einer gesättigten Bariumhydroxid-Lösung extrahiert, das Nikotin mit Benzol–Chloroform (9:1) ausgeschüttelt und in der organischen Lösung gaschromatographisch quantitativ bestimmt. Es konnten die Tabakalkaloide Nikotin, Nornikotin und Anabasin getrennt werden. Ein Vergleich der chromatographischen Methode mit einer klassischen spektralphotometrischen Methode zeigte, dass die hier beschriebene Methode ebenso gut ist.

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THE GAS DENSITY BALANCE IN THE QUANTITATIVE ANALYSIS OF GAS MIXTURES, WITHOUT PRIOR SEPARATION OF COMPONENTS

THE DETERMINATION OF SILICA

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The gas density balance[1,2] has frequently been used as a detector in gas chromatography[3]. Under special conditions, it can also be used in the quantitative analysis of gas mixtures without prior separation of the components. This is possible when one of the major components A has a molecular weight appreciably different from those of all the other components X, Y etc., the molecular weights of which are close together about an average value of m. When a sample of this gas is introduced into the gas density balance with a carrier gas of molecular weight m, the integral response of the balance is, as a good approximation, proportional to the amount of A in the sample, and is only slightly influenced by the concentration ratio X: Y, etc. For example, when a gas mixture of ammonia, water and carbon dioxide (molecular weights 17, 18 and 44 respectively) is analyzed in this way, and a carrier gas with a molecular weight of about 17.5 (*e.g.* a mixture of nitrogen with hydrogen or methane) is used, the integral response of the balance is proportional to the amount of carbon dioxide and is but little influenced by the ratio of ammonia to water in the sample.

A more detailed consideration of this principle is given below for the case of gas mixtures of hydrogen fluoride, water and silicon tetrafluoride (molecular weights 20.0, 18.0 and 104.1).

THEORY

The response δ of the gas density balance is proportional to the difference in the density of the reference gas (d) and that of the carrier gas loaded with the gas sample to be analyzed (d')[2,4]:

$$\delta = \alpha(d' - d) = \alpha \left[\frac{XM + (1-X)m}{Vo} - \frac{m}{Vo}\right] = \alpha X \frac{(M-m)}{Vo} \tag{1}$$

where M = (mean) molecular weight of the gas sample,
m = molecular weight of carrier and reference gas (as carrier and reference gas, the same gas is used),
X = mole fraction of the sample in the carrier gas,
Vo = molar gas volume at the temperature and pressure of the balance, and
α = instrumental constant.

Upon introduction of the flow rate of the carrier gas:

$$\Phi = \frac{dV}{dt}$$

eqn. (1) becomes:

$$\Phi \delta dt = \alpha (M - m) X \frac{dV}{Vo} \quad (2)$$

which upon integration yields:

$$\Phi R = \alpha q (M - m) \quad (3)$$

where R is the integral response $\int \delta dt$ (proportional to the recorded peak area) and q is the amount of sample (in moles) having passed through the balance.

If x is the mole fraction of silicon tetrafluoride in the sample and $(1-y)/y$ is the mole ratio of H_2O/HF in the sample, then

$$M = 104.1x + 20(1-x)y + 18(1-x)(1-y)$$

or $$M = (86.1 - 2y)x + 2y + 18$$

and $$R\Phi = \alpha q x (86.1 - 2y) + \alpha q (2y + 18 - m) \quad (4)$$

If silicon tetrafluoride is a major component in the sample (so that x is not a small number), the proportionality between $R\Phi$ and x would be expected to be nearly independent of y, the variations in $2y$ being small compared with 86.1. If eqn. (4) is used for the determination of x, an independent determination of q is necessary; this quantity is in general quite difficult to measure accurately. In many practical situations, however, the absolute amount qx of the component rather than its mole fraction x is of interest. If the second term in eqn. (4) is of negligible magnitude:

$$2y + 18 - m \simeq 0 \quad (5)$$

then $R\Phi$ is a linear function of this amount qx

$$R\Phi = \alpha (86.1 - 2y) qx \quad (6)$$

and the delicate determination of q can be avoided. Condition (5) can be fulfilled by choosing a carrier gas with a molecular weight m of about 18–20, that is between those of water and hydrogen fluoride. Now the product of the experimental quantities R and Φ is directly proportional to the amount of silicon tetrafluoride in the sample, the proportionality constant $\alpha(86.1 - 2y)$ being only little influenced (about 2% at maximum) by variations in the ratio of hydrogen fluoride to water in the sample.

The above method has been tested for the determination of silica. A silica-containing sample is reacted with ammonium hydrogen fluoride and sulphuric acid, the gaseous products silicon tetrafluoride, hydrogen fluoride and water being introduced into the gas density balance with an appropriate carrier gas. Neon could be used but we preferred a less expensive mixture of nitrogen and hydrogen with 69.3 vol% N_2 and 30.7 vol % H_2 (mean molecular weight 20.0). Provided that a quantitative conversion of silica to silicon tetrafluoride can be achieved, the integral response of the balance times the flow rate of the carrier gas is proportional to the silica content of the sample.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The Gow-Mac gas density balance[2] model 091 with filaments (hot wire) type W is kept at 90°, in a hot air thermostat (type 1452 SH, Becker, Delft). The bridge current used was 150 mA. A Becker unit type 1433 VT with a Philips recorder (recorder sensitivity 0.1 mV/cm) at a chart speed of 2 cm/min was used. With an integrator (low inertia motor with counter unit, Electro Methods Ltd, Stevenage, Herts, type 913 L) built into this unit, the peak area can be determined; one integrator unit = 0.0219 cm².

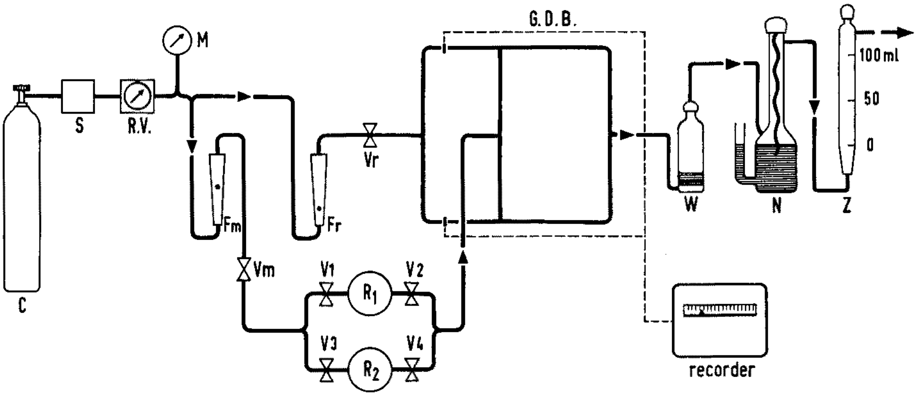

Fig. 1. Schematic diagram. (C) Cylinder with gas mixture. (S) Filter with molecular sieve. (R.V.) Reducing valve. (M) Manometer. (Fm, Fr) Flow meters, Fisher and Porter F.P. 1/16-10-G-4/81. (Vr, Vm) Low flow controller, Brooks no. 8943 ELF. (V1, V2, V3, V4) Stainless steel stopcock with a teflon plug. (R1, R2) Reaction cell (Fig. 2). (G.D.B.) Gas density balance. (W) Wash bottles, filter G3, filled with conc. sodium hydroxide. (N) Humidifier. (Z) Soap flow meter.

The reaction vessel was a silver or platinum crucible which could be inserted into a stainless steel reaction cell, kept at 55° with a hot water coil (Fig. 2, coil not shown). These reaction cells were provided with inlet and outlet tubes and with an injection system of the type most widely used in gas chromatography[5].

Reagents were injected into the reaction mixture with a V2A-steel injection needle through a self-sealing silicone rubber disc. By means of a polyethylene tube, the injection needle was connected to a 10-ml piston buret (Metrohm E 274), containing concentrated sulphuric acid. Reaction cells were provided with a magnetic stirrer. Preferably, two parallel cells were used, so that it was possible to keep the gas flow constant during several experiments.

Chemicals

Silica (B.D.H., pure precipitated). The water content was determined by drying at 1000° to constant weight. Values of 16.04, 15.92 and 15.93% (average: 15.96%) of water were found.

Ammonium hydrogen fluoride, NH_4HF_2 (B.D.H., not less than 94%). The silica content was found to be 0.04, 0.00 and 0.00% by colorimetric determination[6].

The sulfuric acid used was the commercially available 95–98% reagent.

The carrier and reference gas mixture (30.7% H_2 and 69.3% N_2) was commercially available from Loos Co, Amsterdam.

Procedure

With an inlet pressure of 1.7 atm., a reference gas flow of about 90 ml/min[7] is regulated with a needle valve Vr, and measured with a soap bubble meter Z. Then Vm, V1 and V2 are opened, V3 and V4 closed and the sum of the gas flows is measured.

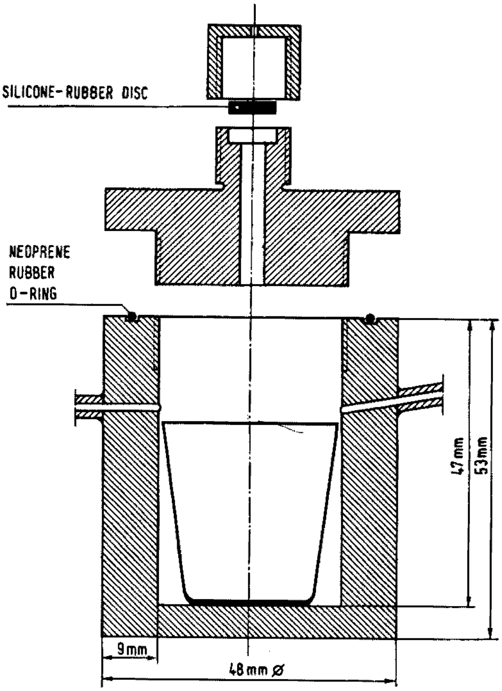

Fig. 2. Reaction cell.

The carrier gas flow is about 30 ml/min[7]. The atmospheric pressure (B) and room temperature (t) are registered so that the flow rates at the pressure and the temperature in the balance can be calculated by:

$$\Phi = \Phi_{\text{measured}} \cdot \frac{B-p}{B+\Delta} \cdot \frac{363}{(273+t)}$$

where Δ = pressure drop due to the wash bottles (about 2 mm mercury) and p = saturated vapour pressure of water at temperature t°. In a crucible 10–50 mg of silica are weighed, and 0.2–0.3 ml of water and 0.80 g of NH_4HF_2 are added; the crucible is placed in the reaction cell R2, the stirrer is started, and the reaction cell closed. The injection needle is put through the silicone rubber disc and filled with concentrated sulfuric acid. V1 and V2 are closed, and V3 and V4 opened. After the air has been flushed out of the reaction cell by the carrier gas and a constant base line on the recorder has been obtained, 5–6 ml of sulfuric acid is added. During or immediately after the injection, a peak is obtained on the recorder.

RESULTS AND DISCUSSION

Table I lists the measured values of $R\Phi$ (in mV·ml) obtained in a series of experiments with varying amounts of silica. By means of the method of least squares, the coefficients in the linear equation were calculated with the result:

$$R\Phi = 89.2w - 211.4$$

The standard deviation increases somewhat with w. In the interval 10–40 mg of silica, the relative standard deviation is approximately 2.5%. Although this precision is in the range expected from theoretical considerations, some improvements might be possible. Colorimetric analyses have shown that some silica is retained in the crucible; a better conversion to silicon tetrafluoride could probably be obtained by increasing the temperature of the reaction cell, which in this study was arbitrarily chosen at 55°. Care must be taken to work within the linear range of the balance. With the set-up described, the linearity of the balance was effective up to 40 mg of silica.

TABLE I

WEIGHT OF DRY SILICA (w) AND MEASURED SIGNAL ($R\Phi$)

Weight of dry silica w (mg)	*Measured signal RΦ (mV·ml)*	*Weight of dry silica w (mg)*	*Measured signal RΦ (mV·ml)*
4.3	189	25.2	2039
9.3	588	26.2	2069
11.5	780	27.5	2296
12.6	900	28.1	2294
13.1	967	30.8	2449
13 8	999	32.5	2568
15.4	1137	32.5	2759
17.6	1374	33.2	2765
19.5	1590	36.1	3097
21.9	1808	37.9	3111
23.7	1923		

We thank Mr. J. P. M. LANGHOUT for his help in the experimental work.

SUMMARY

When a gas mixture with a major component A which has a molecular weight considerably different from those of all other components (these being close together about a molecular weight of m) is introduced into the gas density balance with a carrier gas also of molecular weight m, the integral response of the gas density balance is essentially proportional to the amount of A in the sample and independent of the concentration ratios between all other components. The applicability of this principle is demonstrated in the determination of silicon tetrafluoride in mixtures with hydrogen fluoride and water, which were formed by reactions between silica, ammonium hydrogen fluoride and sulfuric acid. A direct determination of silica in solid samples containing 10–40 mg SiO_2 is possible with a relative standard deviation of 2.5%.

RÉSUMÉ

Quand un mélange de gaz avec un constituant principal A, ayant une masse moléculaire très différente de celle des autres composants gazeux, est introduit dans une balance à densité de gaz la réponse de la balance est proportionnelle à la concentration de A dans l'échantillon. La réponse est indépendante des rapports entre les concentrations de tous les autres composants, quand les masses moléculaires de ces composants et du gaz vecteur possèdent environ la même valeur. Une démonstration de ce principe est faite pour le dosage du tétrafluorure de silicium dans des mélanges d'acide fluorhydrique et d'eau; obtenus par les réactions entre la silice, le fluorure d'hydrogène et d'ammonium et l'acide sulfurique. Un dosage direct de la silice dans des échantillons renfermant 10–40 mg SiO_2 est possible avec une déviation standard relative de 2.5%.

ZUSAMMENFASSUNG

Wenn eine Gasmischung mit der Hauptkomponenten A, die ein Molekulargewicht besitzt, das sich von denen der anderen Komponenten stark unterscheidet, mit einem Trägergas in eine Gasdichtewaage eingeführt wird, so ist die Anzeige im wesentlichen proportional zum Gehalt von A und unabhängig von den Konzentrationsverhältnissen zwischen allen anderen Komponenten (vorausgesetzt dass diese und das Trägergas ein ähnliches Molekulargewicht besitzen). Die Anwendbarkeit dieses Prinzips wird an der Bestimmung von Siliciumtetrafluorid in Mischungen mit Fluorwasserstoff und Wasser gezeigt, die durch Reaktionen zwischen Kieselsäure, Ammoniumhydrogenfluorid und Schwefelsäure gebildet wurden. Eine direkte Bestimmung von Siliciumdioxid in festen Proben, die 10–40 mg enthalten, ist mit einer relativen Standardabweichung von 2.5% möglich.

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ANALYSIS OF MONOMERIC ALKYL- AND ARYLCHLOROSILANES

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Several workers[1,2] have reported the presence of silicon carbide in the silica residue from the acid decomposition of organosilicon compounds in wet methods of analysis for silicon, but give no experimental confirmation of its formation. KRESHKOV *et al.*[3] consider low values for silicon content to be due not only to losses by volatilisation, but also to the formation of a dark deposit which is difficult to oxidise and which weighs less than a molar equivalent of silica. SIR AND KOMERS[4] report on asphaltic or carbidic residue on decomposing organosilicon compounds containing aromatic groups.

MCHARD *et al.*[2] investigated the conditions for ignition and found that the formation of silicon carbide was prevented by providing an oxidising atmosphere and an ignition temperature below 800°. They considered that higher ignition temperatures favoured the formation of silicon carbide from free carbon.

Several authors report that if the sample contains a high percentage of carbon (*e.g.* aryl-silicon compounds), treatment with an oxidising agent in addition to sulphuric acid is necessary to oxidise the carbon, otherwise the silica obtained may contain silicon carbide. ANDREEV[5] recommended concentrated nitric acid, BOYE AND POST[6] fuming nitric acid, and KOHAMA[7] ammonium nitrate, as oxidising agents.

When volatile chlorosilanes are oxidised, losses due to volatilisation when the oxidants are added cause low silicon values. SIR AND KOMERS[4] converted these compounds into pyridine derivatives, and KRESHKOV *et al.*[3] converted them into acetoxy or sulpho derivatives before oxidation. ANDREEV[5] recommended preliminary hydrolysis to a non-volatile cross-linked polysiloxane with aqueous 20–25% ammonia, or 0.880 s.g. ammonia when hydrolysis is otherwise not rapid enough.

In the work described below the radioisotope carbon-14 was utilized to determine the percentage of active carbon retained when various labelled chlorosilanes are oxidised, in an attempt to evaluate the various methods for converting organosilicon compounds quantitatively to silica. The work also made possible an assessment of the importance of the position of a carbon atom relative to the silicon atom in relation to its retention in the oxidised residue.

When arylchlorosilanes were hydrolysed before oxidation, the weight of residue was found to be consistently higher than the theoretical weight of silica, whereas the conversion of some of the silicon to carbide would make the weight lower. The black residues from the oxidation of arylchlorosilanes were therefore examined for the presence of silicon carbide by X-ray powder photography and by photomicrography.

EXPERIMENTAL

Preparation of the labelled compounds

(a) [1-^{14}C] Ethyltrichlorosilane, [1-^{14}C]diethyldichlorosilane and [1-^{14}C] triethylchlorosilane. Ethyl bromide (87.5 ml), containing 50 μC of labelled [1-^{14}C] ethyl iodide in 250 ml of absolute ether was added to magnesium turnings (25 g). The ethereal solution of labelled ethylmagnesium bromide was added to silicon tetrachloride (57.3 ml) in 250 ml of ether[8]. The reaction mixture was filtered under nitrogen through glass wool and the solid was extracted with four 100-ml portions of ether. The ether extracts were combined with the filtrate and the whole subjected to fractional distillation at atmospheric pressure. The product consisted of 18 g of a fraction of b.p. 97–103°, 35 g of a fraction of b.p. 110–130° and 6 g of a fraction of b.p. 137–144°. Further fractionation gave 15 g of [1-^{14}C] ethyltrichlorosilane (b.p. 98–100°; found: Cl 65.0%; $C_2H_5SiCl_3$ requires Cl 65.17%), 25 g of diethyldichlorosilane (b.p. 129–131°; found: Cl 45.0%; $C_4H_{10}SiCl_2$ requires Cl 45.2%) and 4 g of triethylchlorosilane (b.p. 143–144°; found: Cl 23.3%; $C_6H_{15}SiCl$ requires Cl 23.57%). The compounds were further characterised from their I.R. spectra.

(b) [2-^{14}C] Ethyltrichlorosilane, [2-^{14}C] diethyldichlorosilane and [2-^{14}C] triethylchlorosilane. The labelled compounds were prepared as above using 50 μC of [2-^{14}C] ethyl iodide and characterised from their b.p., chlorine analysis and I.R. spectra.

(c) [^{14}C] Phenyltrichlorosilane and [^{14}C] diphenyldichlorosilane. The labelled compounds were prepared by the method described by SMITH[9]. A mixture of bromobenzene (78.5 g), containing 50 μC of labelled [^{14}C] bromobenzene, with 200 ml of absolute ether was added to magnesium turnings (12.1 g) and heated at 40–45° for 6.5 h. The ethereal solution of phenylmagnesium bromide was added dropwise over 9 h to silicon tetrachloride (42.2 g) in 150 ml of ether. The product was filtered under nitrogen through glass wool and then extracted 4 times with ether. The ethereal solution of the products and the ethereal washings from the magnesium salt were fractionated under vacuum. [^{14}C] Phenyltrichlorosilane (16 g; b.p. 90–91° at 20 mm; found: Cl 48.9%; $C_6H_5SiCl_3$ requires Cl 50.29%) and [^{14}C] diphenyldichlorosilane (25 g; b.p. 170–171° at 18 mm; found: Cl 26.9%; $C_{12}H_{10}SiCl_2$ requires Cl 28.0%) were collected. The compounds were further characterised from their I.R. spectra.

Infrared analyses were carried out on a Perkin-Elmer 21 Instrument. Chlorine was determined as described by HYDE AND DELONG[10].

(d) Ethylphenyldichlorosilane. Bromobenzene (35.2 ml) in 200 ml of absolute ether was added to magnesium turnings (10 g) and cooled in ice as soon as the reaction started. The ethereal solution of phenylmagnesium bromide was filtered under nitrogen through glass wool and added slowly with vigorous stirring to ethyltrichlorosilane (50 g, prepared from silicon tetrachloride and ethylmagnesium bromide in ether[8]), cooled in ice. The reaction mixture was left at ordinary temperature for 12 h and then refluxed for 2 h to complete the reaction. The products were filtered under nitrogen through glass wool and the residual magnesium salt was washed with 4 100-ml portions of ether. The ethereal solution and the washings were combined and the ether distilled. The yellow oily residue was repeatedly fractionated under vacuum to give ethylphenyldichlorosilane (20 g; b.p. 99–100° at 11 mm; found: C 47.05%, H 4.9%, Cl 34.4%; $C_8H_{10}SiCl_2$ requires C 46.8%, H 4.9%, Cl 34.4%). The compound was characterised from its I.R. spectrum.

(e) Ethyl[^{14}C]phenyldichlorosilane. The labelled compound was prepared as above using bromobenzene containing 60 µC of [^{14}C] bromobenzene and characterised from its I.R. spectrum. The radiochemical purity of the compound was determined by reverse isotope dilution analysis. Inactive ethylphenyldichlorosilane (2 g) was added to the labelled ethyl[^{14}C]phenyldichlorosilane (1 g) and mixed well. The specific activity of the mixture was measured and the diluted material then purified by 3 distillations under vacuum. The specific activity of the purified product was measured. The ratio of the two specific activities indicated a radiochemical purity of 99.6%.

(f) [1-^{14}C] Ethylphenyldichlorosilane. Ethyl bromide (21.3 ml), containing 50 µC of [1-^{14}C] ethyl iodide was mixed with 250 ml of absolute ether and added to 9 g of magnesium turnings. The ethereal solution of ethylmagnesium bromide was filtered under nitrogen through glass wool and added to phenyltrichlorosilane (50 g, prepared from silicon tetrachloride and phenylmagnesium bromide in ether[9]). The reaction mixture was left for 12 hours and then the preparation was completed as described above for ethylphenyldichlorosilane. The oily residue was repeatedly fractionated under vacuum to give [1-^{14}C] ethylphenyldichlorosilane (25 g; b.p. 99–100° at 11 mm). The labelled compound (radiochemical purity 99.8%) was characterised from its I.R. spectrum.

(g) [2-^{14}C] Ethylphenyldichlorosilane. The labelled compound (radiochemical purity 99.8%) was prepared as above from ethyl bromide containing 50 µC of [2-^{14}C] ethyl iodide and characterised from its I.R. spectrum.

General oxidation procedures

Alkylchlorosilanes. Samples (0.2–0.5 g) were weighed in small thin-walled glass ampoules provided with a narrow-bore capillary. The ampoule was introduced into a 25-ml quartz Kjeldahl flask and broken under the acid layer. Digestion was accomplished by gentle heating on a micro-Kjeldahl rack for 30 min. The temperature was then raised slowly over 2 h until the sample formed a gel. The flask was cooled, and distilled water (10 ml) was added followed by 1.0–1.5 ml of 2% gelatin solution to coagulate the precipitate. The precipitate was filtered, washed 4 times with distilled water and ignited to constant weight.

Arylchlorosilanes. About 0.2–0.5 g of the sample in a thin-walled glass ampoule with a narrow-bore capillary was added to the oxidising acid in a previously weighed platinum crucible. The ampoule was broken under the acid. The mixture was carefully warmed to dissolve the sample, and then heated gently to remove the acid fumes. The platinum crucible was finally ignited to constant weight.

The temperature of the ignitions was controlled in a Wild Barfield muffle furnace. The selected temperature was maintained to within ±10°. The temperature attained in a platinum crucible when heated with a Meker burner was in the range 1040–1050° as determined by means of a platinum–platinum/rhodium thermocouple.

Counting procedure

The residues from the analytical procedure, mainly silica, but containing some carbon in most cases, were counted as infinitely thick samples (>35 mg/cm^2) to ensure that specific activities were measured. To provide standards, solid radioactive sources of a polysiloxane (from ethyltrichlorosilane)[11], diethylsilanediol[12], sodium triethylsilanolate[13], phenylsilanetriol[14], diphenylsilanediol[15] and ethylphenylsilanediol[16] were prepared by hydrolysing the corresponding labelled chlorosilanes. Infinitely thick samples were spread uniformly on a plastic planchette, compressed and counted in the same equipment as the residues from the analysis.

Separate experiments were carried out to ensure that the method of standardisation was satisfactory. Amorphous carbon containing carbon-14 was intimately mixed with (a) the various hydrolysis products above and (b) silica, the principal constituent of the residue in the analysis. Counting of these samples showed the silica and the hydrolysis products to have closely similar absorption coefficients for the β-radiation.

The β-emission from the carbon-14 was counted using a Labgear D.4126 4π gas flow counter (converted to a 2π arrangement), and a Labgear D.4109 Automatic Scaler. The flow counter was operated as a windowless Geiger counter using a Q gas of 98.7% helium and 1.3% butane. A two-stage regulator was coupled to the supply cylinder and connection then made through a fine-bore capillary direct to the counter manifold. A bubbler containing silica gel was included before the input and a bubbler containing *n*-butyl phthalate was connected to the outlet. The operational gas flow rate was 6–10 bubbles per min.

RESULTS

Oxidation of labelled alkylchlorosilanes

The labelled compounds were decomposed with concentrated sulphuric acid (5 ml) and the residues were ignited at 450° for 1 h. From a radioassay the percentage

TABLE I

OXIDATION OF LABELLED ALKYLCHLOROSILANES WITH VARIOUS OXIDANTS

(Ignition at 450°)

	% deficiency in wt. of SiO_2	*% active C retained*	*% deficiency in wt. of SiO_2*	*%active C retained*
	Concentrated sulphuric acid		*Perchloric acid (60%)*	
[1-^{14}C] Ethyltrichlorosilane	7.2–10.3	2.4–2.6	9.1–10.7	0.1–0.2
	2.6– 2.8^{a}	3.1–3.3^{a}	2.1– 2.3^{a}	1.5–1.5^{a}
	1.7– 2.2^{b}	2.8–3.2^{b}	2.0– 2.5^{b}	1.3–1.5^{b}
[2-^{14}C] Ethyltrichlorosilane	9.9–15.1	0	9.9–12.8	0
[1-^{14}C] Diethyldichlorosilane	1.7– 1.8	1.8–1.9	1.1– 1.4	0.1–0.2
[2-^{14}C] Diethyldichlorosilane	2.3– 4.8	0	1.1– 1.8	0
[1-^{14}C] Triethylchlorosilane	2.1– 2.2	2.2–2.3	0.8– 0.9	0.1
[2-^{14}C] Triethylchlorosilane	3.3– 5.7	0	0.9– 1.6	0
	Fuming nitric acid		*Fuming HNO_3–fuming H_2SO_4*	
[1-^{14}C] Ethyltrichlorosilane	3.6– 5.0	0.1–0.2	6.3– 6.9	0.1
[2-^{14}C] Ethyltrichlorosilane	3.1– 4.3	0	6.7– 9.8	0
[1-^{14}C] Diethyldichlorosilane	26.9–28.7	0.5–0.6	14.9–15.0	0.1–0.2
	0.5– 0.7^{c}	0.8–0.9	0.3– 0.4^{c}	0.2–02.^{c}
[2-^{14}C] Diethyldichlorosilane	29.5–31.1	0	16.9–18.4	0
[1-^{14}C] Triethylchlorosilane	18.4–19.2	0.6–0.7	12.9–13.9	0.2–0.3
	0.7– 0.9^{c}	0.5–0.5^{c}	0.3– 0.5^{c}	0.5^{c}
[2-^{14}C] Triethylchlorosilane	15.5–20.9	0	13.3–16.4	0

[a] With dry ice surrounding the neck of the flask.
[b] With dry ice surrounding the neck of the flask and with preliminary hydrolysis.
[c] With dry ice surrounding the flask during sample addition.

of the active carbon retained was calculated. The percentage discrepancy from the theoretical weights of the residues together with the percentage of active carbon retained in them are shown in Table I. The experiments were repeated with (i) 60% perchloric acid (5 ml), (ii) fuming nitric acid (s.g. 1.5, 5 ml), and (iii) a 15% fuming sulphuric acid (2.5 ml)–fuming nitric acid (2.5 ml) mixture (Table I).

The residues obtained from ethyltrichlorosilane when oxidised with concentrated sulphuric acid or perchloric acid were much lighter than the theoretical weight. In an attempt to reduce losses due to volatility of the compound, oxidations of [1-^{14}C] ethyltrichlorosilane with concentrated sulphuric acid and with perchloric acid were also carried out in a Kjeldahl flask, the neck of which was cooled with dry ice during initial digestion of the sample. As the weights of residue were still low, further oxidations were done after preliminary hydrolysis with 10% aqueous ammonia (0.5 ml). The results (see Table I) indicate the improvement in retention during oxidation.

When fuming nitric acid was a constituent of the oxidant, the reactions with diethyldichlorosilane and triethylchlorosilane were strongly exothermic. In an attempt to reduce losses, the oxidations done with fuming nitric acid and with a fuming nitric acid–fuming sulphuric acid mixture were repeated with the Kjeldahl flask surrounded by dry ice during addition of the sample to the acids. The results (Table I) show a very large improvement compared with the earlier ones.

Experiments were also carried out in which potassium persulphate[17], hydrogen peroxide[17], potassium permanganate[18] and mercury[19] respectively were added to the sulphuric acid. The weights of silica were rather better than those using sulphuric acid alone and there was considerably less active carbon retained.

TABLE II

OXIDATION OF ALKYLCHLOROSILANES WITH CONCENTRATED SULPHURIC ACID (Ignition at 850°C)

Compound	*% deficiency in wt. of SiO_2*	*% active C retained*
[1-^{14}C] Ethyltrichlorosilane	8.5–11.6	2.1–2.6
[1-^{14}C] Ethyltrichlorosilane, acetoxy derivative[a]	0.5– 0.7	0.1–0.2
[1-^{14}C] Diethyldichlorosilane	2.1– 3.3	2.0–2.4
[1-^{14}C] Diethyldichlorosilane, sulpho derivative[a]	0.5– 0.6	0.1–0.2
[1-^{14}C] Triethylchlorosilane	1.8– 2.6	1.5–2.0
[1-^{14}C] Triethylchlorosilane, sulpho derivative[a]	0.5– 0.8	0.1

[a] Oxidation was done with fuming nitric acid–concentrated sulphuric acid mixture.

To assess the effect of the ignition temperature some of the labelled compounds were decomposed with concentrated sulphuric acid (5 ml) and the residues ignited at 850°. The percentage of active carbon retained was calculated from radioassay (Table II). Comparison with Table I indicates that ignition at the higher temperature caused essentially no improvement.

A further method was used in an attempt to improve the weights of silica obtained. The labelled alkylchlorosilanes were converted into acetoxy derivatives (ethyltrichlorosilane) and sulpho derivatives[20] (diethyldichlorosilane and triethylchlorosilane) by keeping a sample for 2 h with glacial acetic acid (1 ml) and 25% oleum (1 ml) respectively, before oxidation with a concentrated sulphuric acid–

fuming nitric acid mixture. The results (Table II) show this method to be effective in reducing losses.

Oxidation of labelled arylchlorosilanes

The effect of different oxidants. [^{14}C] Phenyltrichlorosilane was decomposed in a platinum crucible, as described under *General oxidation procedure,* with 15% fuming sulphuric acid (2 ml) and the residue was ignited over a Meker burner for 1 h. The experiment was repeated after a preliminary hydrolysis with 50% aqueous ammonia (1 ml) followed by evaporation to a low volume under an I.R. lamp. Further experiments were made with [^{14}C] diphenyldichlorosilane with and without preliminary hydrolysis with 0.880 ammonia followed by careful heating to an oily residue under an I.R. lamp. The results are listed in Table III.

TABLE III

OXIDATION OF LABELLED [^{14}C] ARYLCHLOROSILANES WITH VARIOUS ACIDS (Ignition at 1040–1045°)

Compound	*% discrepancy in wt. of SiO_2*		*% active C retained*	
	A[a]	*B*[b]	*A*[a]	*B*[b]
Fuming sulphuric acid				
[^{14}C] Phenyltrichlorosilane	− 3.0–9.1	+2.0–3.5	1.1–1.4	1.4–1.6
[^{14}C] Diphenyldichlorosilane	− 1.7–2.4	+1.8–4.0	1.0–1.4	0.9–1.3
Fuming nitric acid				
[^{14}C] Phenyltrichlorosilane	−38.7–42.5	−18.0–21.2	3.3–3.6	5.6–6.7
[^{14}C] Diphenyldichlorosilane	− 4.6– 5.3	− 3.2– 3.7	4.9–5.4	4.0–4.4
Perchloric acid (60%)				
[^{14}C] Phenyltrichlorosilane	−10.5–11.4	− 7.6–8.8	0.1	0.1–0.2
[^{14}C] Diphenyldichlorosilane	− 7.0–8.3	− 4.9–5.5	0.1	0.1
Fuming sulphuric acid–fuming nitric acid				
[^{14}C] Phenyltrichlorosilane	−12.3–13.7	− 7.8–9.6	0.8–0.9	0.7–0.9
[^{14}C] Diphenyldichlorosilane	− 4.8– 5.2	− 4.8–5.4	0.7–0.8	0.6–0.8

[a] Without preliminary hydrolysis.
[b] With preliminary hydrolysis.

The experiments above were repeated with (i) fuming nitric acid (s.g. 1.5, 2 ml), (ii) 60% perchloric acid (2 ml) and (iii) a mixture of 15% fuming sulphuric acid (1 ml), and fuming nitric acid (1 ml). The results (Table III) indicate that the preliminary hydrolysis improved somewhat the figures for silica, but affected carbon retention very little.

The effect of ignition temperatures. [^{14}C] Phenyltrichlorosilane was decomposed with 15% fuming sulphuric acid at different ignition temperatures (Table IV). The experiments were repeated after preliminary hydrolysis of phenyltrichlorosilane with 50% aqueous ammonia (1 ml) followed by evaporation to low volume under an I.R. lamp. Other experiments were made with diphenyldichlorosilane, without preliminary hydrolysis, and after hydrolysis with 0.880 ammonia, followed by careful heating to an oily residue under an I.R. lamp (Table IV).

The effect of additional oxidising agents. [^{14}C] Diphenyldichlorosilane was digested with 15% fuming sulphuric acid after preliminary hydrolysis with 0.880 ammonia.

TABLE IV

EFFECT OF IGNITION TEMPERATURE

Ignition temperature (°C)	% discrepancy in wt. of SiO_2				% active C retained			
	PTCS[a]		DDCS[b]		PTCS[a]		DDCS[b]	
	A[c]	B[d]	A	B	A	B	A	B
800	− 1.9–4.3	+ 0.2–0.5	− 0.7–3.8	+ 0.2–0.3	0.3–0.4	0.2–0.3	0.2–0.3	0.2–0.3
850	− 1.3–13.4	+ 0.2–0.5	− 1.8–4.0	+ 0.1–0.4	0.2–0.3	0.2–0.3	0.2–0.4	0.2–0.3
900	− 1.5–5.5	+ 0.2–0.5	− 1.8–6.6	+ 0.3–0.5	0.2–0.3	0.2–0.3	0.2–0.3	0.2–0.3
950	− 2.9–4.8	+ 0.8–1.4	− 1.6–4.6	+ 0.2–0.8	0.2–0.3	0.2–0.3	0.2–0.3	0.2–0.4
1000	− 3.4–5.9	+ 0.5–1.6	− 1.6–2.5	+ 0.8–1.1	0.4–0.5	0.4–0.6	0.4–0.5	0.4–0.5
1040–1050 (Meker)	− 3.0–4.1	+ 2.0–3.5	− 1.7–2.4	+ 1.8–4.0	1.0–1.4	1.4–1.6	1.0–1.4	0.9–1.3

[a] Phenyltrichlorosilane.
[b] Diphenyldichlorosilane.
[c] Without preliminary hydrolysis.
[d] With preliminary hydrolysis.

Successive 2-ml amounts of fuming nitric acid (s.g. 1.5) were added and the platinum crucible was heated gently after each addition, until no more nitric acid fumes were evolved. Finally the acids were evaporated and the crucible was then ignited over a Meker burner for 1 h (Table V).

Oxidation of labelled ethylphenyldichlorosilane

The labelled compounds ethyl [^{14}C] phenyldichlorosilane, [1-^{14}C] ethylphenyldichlorosilane, and [2-^{14}C] ethylphenyldichlorosilane were oxidised with 2 ml of fuming nitric acid (s.g. 1.5) and the residues ignited at 1000° for 1 h. The results are shown in Table VI. The experiment was repeated after preliminary hydrolysis of the labelled compounds with 10% aqueous ammonia (1 ml) followed by evaporation to an oily residue under an I.R. lamp. Oxidations were also done with 15% fuming sulphuric acid (2 ml) and 60% perchloric acid (2 ml) (Table VI).

As it was found that fuming sulphuric acid gave low silica weights but zero carbon retention and that fuming nitric acid gave high silica weights but high retention of carbon, ethyl [^{14}C] phenyldichlorosilane was then decomposed with various mixtures

TABLE V

EFFECT OF ADDITIONAL OXIDISING AGENTS FOR DIPHENYLDICHLOROSILANE WITH FUMING SULPHURIC ACID

(Ignition at 1040–1050°)

Amount added	*% discrepancy in wt. of SiO_2*	*% C retained*	*Amount added*	*% discrepancy in wt. of SiO_2*	*% C retained*
Fuming nitric acid (s.g. 1.5)			*Ammonium nitrate*		
2 ml (1 ×)	+ 1.0–2.8	0.8–0.9	0.5 g	+ 2.0–2.8	0.7–1.2
2 ml (2 ×)	+ 1.4–1.5	0.3–0.4	1.0 g	+ 1.2–1.5	0.3–0.4
2 ml (3 ×)	+ 0.1–0.5	0.1–0.2	1.5 g	+ 0.4–0.8	0.1–0.2
2 ml (4 ×)	− 0.1–0.7	0	2.0 g	− 0.3–0.6	0

TABLE VI

OXIDATION OF LABELLED ETHYLPHENYLDICHLOROSILANES WITH VARIOUS OXIDANTS

(Ignition 1000°)

Compound	*% discrepancy in wt. of SiO_2*		*% C retained*	
	A[a]	*B*[b]	*A*	*B*
Fuming sulphuric acid				
Ethyl [^{14}C] phenyldichlorosilane	− 3.2±1.3	−6.2±0.7	0	0
[1-^{14}C] Ethylphenyldichlorosilane			0	0
[2-^{14}C] Ethylphenyldichlorosilane			0	0
Perchloric acid				
Ethyl [^{14}C] phenyldichlorosilane			0	0
[1-^{14}C] Ethylphenyldichlorosilane	−26.1±7.5	−0.9±0.7	7.7–10.6	20.2–22.2
[2-^{14}C] Ethylphenyldichlorosilane			4.4– 8.0	10.3–13.9
Fuming nitric acid				
Ethyl [^{14}C] phenyldichlorosilane			4.5– 7.2	2.4– 1.6
[1-^{14}C] Ethylphenyldichlorosilane	+16.3±9.7	+4.9±4.1	22.9–24.8	21.8
[2-^{14}C] Ethylphenyldichlorosilane			13.5–13.7	12.1–15.8

[a] Without hydrolysis.
[b] With preliminary hydrolysis.

of fuming nitric acid and fuming sulphuric acid and the residues were ignited over a Meker burner for 1 h. The results are shown in Table VII. In other tests, [1-^{14}C] ethylphenyldichlorosilane and [2-^{14}C] ethylphenyldichlorosilane were decomposed with 2 ml of fuming nitric acid (s.g. 1.5) mixed with 0.5 ml of 15% fuming sulphuric acid (see Table VII).

[1-^{14}C] Ethylphenyldichlorosilane was oxidised in other experiments with 2 ml of fuming nitric acid mixed with increasing amounts of 60% aqueous perchloric acid, as well as with 15% fuming sulphuric acid mixed with 1 ml of 60% perchloric

TABLE VII

OXIDATION OF ETHYLPHENYLDICHLOROSILANES WITH FUMING SULPHURIC ACID–FUMING NITRIC ACID MIXTURES (Ignition 1040–1050°)

Acid mixture *H_2SO_4: HNO_3 (ml) (ml)*	*% discrepancy in wt. of SiO_2*	*% active C retained*
Ethyl [^{14}C] phenyldichlorosilane		
2.0 : 0	−3.5–7.1	0
2.0 : 0.5	−3.8–5.1	0
2.0 : 1.0	−2.7–3.6	0
2.0 : 1.5	−1.6–2.8	0
2.0 : 2.0	−0.1–0.2	0
1.5 : 2.0	−2.7–3.2	0
1.0 : 2.0	−9.0–10.5	0
0.5 : 2.0	−1.5–1.7	1.7–1.9
0 : 2.0	+13.9–15.6	5.9–6.2
[1-^{14}C] Ethylphenyldichlorosilane		
0 : 2.0	+15.6–26.0	22.9–24.8
0.5 : 2.0	+0.2–0.3	1.5–1.6
[2-^{14}C] Ethylphenyldichlorosilane		
0 : 2.0	+13.7–14.5	16.1–19.8
0.5 : 2.0	+0.4–0.9	2.3–3.8

TABLE VIII

OXIDATION OF [1-^{14}C] ETHYLPHENYLDICHLOROSILANE WITH ACID MIXTURES

(Ignition at 1000°)

Acid mixture	*% discrepancy in wt. of SiO_2*	*% active C retained*
Fuming HNO_3 : $HClO_4$ (ml) (ml)		
2.0 : 0	+15.6–26.0	22.9–24.8
2.0 : 1.0	+6.7–7.3	17.5–17.9
2.0 : 2.0	−2.2–2.6	6.6–6.8
Fuming H_2SO_4 : $HClO_4$ (ml) (ml)		
2.0 : 0	−2.0–3.9[a]	0
2.0 : 1.0	−22.9–25.0[b]	0.1

[a] After preliminary hydrolysis, the % error for SiO_2 was −2.0–3.9 and the % C retained was 0.

[b] After preliminary hydrolysis, the % error for SiO_2 was −2.9–3.4 and the % C retained was 1.4–1.6.

acid; in all cases, the residue was ignited at 1000° for 1 h (Table VIII). The latter experiment was repeated after preliminary hydrolysis of ethylphenyldichlorosilane with 10% aqueous ammonia (1 ml) followed by evaporation to an oily residue under an I.R. lamp (Footnote, Table VIII).

The composition of the black residue

In the belief that the colour of the black residue from the decomposition of diphenyldichlorosilane after ignition over a Meker burner was due to carbon, an attempt was made to oxidise it by supplying oxygen (100 ml/min) to the crucible by means of a suitable cover and inlet tube and igniting the contents in that atmosphere. The residue was unaltered in appearance but radiochemical assay showed a 15–25% decrease in the amount of carbon retained.

After the residue had been treated with hydrofluoric acid (39–43% w/w) for 12 h, the black powder obtained was filtered, washed with distilled water and dried. The experiment was repeated with hydrofluoric acid treatment for 5 d. Samples of these powders, previously evacuated with gently heating in a cracker (sealed under vacuum), were analysed for carbon by ignition in oxygen at 800–1000° (Table IX).

TABLE IX

COMPOSITION OF THE RESIDUE AFTER TREATMENT WITH HYDROFLUORIC ACID

Time of digestion with HF	*Weight of sample (mg)*	*% C (oxidisable)*	*% Ash*	*% H*
	13·57	38.1	58.2	0.8
12 h	9·15	12.1	58.2	1.9
	26.90	37·8	58.0	1.7
5 d	10.10	21.0	75·0	2·7

TABLE X

X-RAY POWDER PHOTOGRAPH ANALYSIS OF THE RESIDUES

Sample	*Spacing*[a] *(Å)*	*Intensity*	*Identification*
Residue from decompn. of diphenyldichlorosilane	4·33	s	Amorphous silica
Residue after treatment with hydrofluoric acid	4·33	s	Amorphous silica
	2.08	m	Amorphous carbon
Ash retained after analysis	4·33	s	Amorphous silica
	2.08	m	Amorphous carbon

[a] Spacings obtained from silicon carbide (600 mesh) in the same apparatus were not found in these residues.

Fusion of the unoxidisable ash with a 2:1 potassium carbonate–sodium carbonate mixture followed by addition of 2 *M* hydrochloric acid and distilled water, gave a colourless solution and no insoluble residue. A control experiment showed that the fusion mixture had no effect on silicon carbide.

The above observations suggested that carbon was retained either as some compound of silicon such as silicon carbide or as the element protected from oxidation by being fused into silica. X-Ray powder photographs of the amorphous residues (mounted by the Van Arkel method in a Müller Mikro-60 Crystallographic X-ray set, using Cu Kα radiation and a 9-cm powder camera) were compared with those of amorphous silica, amorphous carbon and silicon carbide (600 mesh). The positions of maximum intensity are shown in Table X. The carbon line at 2.08 Å was the only one clear enough to be used for identification. The residues were examined under a microscope (Carl Zeiss) with reflected and transmitted light from a tungsten lamp.

DISCUSSION

When volatile alkylchlorosilanes are decomposed in Kjeldahl flasks with concentrated sulphuric acid, perchloric acid, fuming nitric acid or a mixture of fuming sulphuric acid and fuming nitric acid, the most serious difficulty encountered is from losses through volatilisation. Losses on oxidising ethyltrichlorosilane with concentrated sulphuric acid and perchloric acid were reduced somewhat by cooling the neck of the Kjeldahl flask with dry ice; preliminary hydrolysis of the chlorosilane gave no apparent improvement. The oxidation of diethyldichlorosilane and triethylchlorosilane with fuming nitric acid or a fuming nitric acid–fuming sulphuric acid mixture resulted in excessive losses from volatilisation owing to a strongly exothermic reaction when the oxidants were added. Losses were reduced by cooling the Kjeldahl flasks in dry ice during addition of the oxidants. This procedure considerably increased the accuracy of the analysis, particularly when the fuming nitric acid–fuming sulphuric acid mixture was used. However, the most accurate silica values for these compounds were obtained when the alkylchlorosilanes were converted into acetoxy derivatives (in the case of ethyltrichlorosilane) or sulpho derivatives (diethyldichlorosilane, triethylchlorosilane) and then oxidised with a mixture of concentrated sulphuric acid and fuming nitric acid.

The active carbon retained in the silica residues was predominantly carbon adjacent to silicon but the amount was too small to be of analytical significance.

For arylchlorosilanes, the best existing methods for determination of silicon are those in which previous alkaline hydrolysis enables fuming nitric acid or ammonium nitrate to be added to the sulphuric acid without causing excessive loss through volatilisation. Oxidation of arylchlorosilanes with a fuming sulphuric acid–fuming nitric acid mixture resulted in low silica values, while the use of fuming sulphuric acid with subsequent addition of nitric acid or ammonium nitrate prevented losses and reduced the amount of carbon retained in the residues.

The effect of ignition temperature on the retention of carbon showed no marked trend below 950°, but above that temperature there was an increase in the amount of carbon retained. But high carbon retention was associated with high weight of residue, which was particularly evident when loss by volatilisation was prevented by alkaline hydrolysis of the arylchlorosilanes before oxidation with acid. This increase in weight over the theoretical weight of silica was not consistent with the conversion of some of the organosilicon compound to silicon carbide (molar mass 40.09) rather than silica (molar mass 60.09).

When the black residues from the diphenyldichlorosilane, after high-temperature ignition, were treated with hydrofluoric acid, much of the silica dissolved and a black powder was obtained. Analysis of the black powder for carbon, by ignition at 800–1000° in a stream of oxygen, showed that rather less than 39% of the powder was oxidisable. The residual black ash was shown, by comparison of X-ray powder photographs with those obtained from amorphous carbon and amorphous silica in the same apparatus, to consist of a mixture of these two materials. There were no groups of lines comparable with those obtained from silicon carbide.

Photomicrographs of the residue from the decomposition of diphenyldichlorosilane showed the occurrence of a predominant amount of a translucent substance, presumably silica, intermingled with an opaque material, presumably carbon. Photomicrographs of the residue after treatment with hydrofluoric acid showed that much of the silica dissolved in the acid but some was retained together with carbon. The black ash which resisted oxidation in a stream of oxygen at 800–1000° showed translucent grains permeated by black veins.

Experiments on alkylarylchlorosilanes enabled comparisons to be made of the effects of various wet methods of oxidation on the retention of aryl and alkyl carbon respectively.

When ethylphenyldichlorosilane was oxidised with fuming nitric acid a high proportion of carbon was retained, particularly the alkyl carbon attached directly to the silicon. The residues were significantly too heavy, though preliminary hydrolysis was effective in improving the weights.

Perchloric acid differed from fuming nitric acid in two important respects: (a) the weights of residue were low instead of high, although preliminary hydrolysis improved the weights to very nearly the theoretical values, (b) there was no retention of aryl carbon. However, in neither case did preliminary hydrolysis enable the retention of carbon to be reduced; in fact, in the case of perchloric acid more carbon was left in the residue.

Of the single acids, fuming sulphuric acid was much the best oxidant of those tested. Retention of carbon was reduced to zero and the residues had close to the theoretical weights if the ethylphenyldichlorosilane was treated with the acid without preliminary hydrolysis.

Of the mixtures which were used, that containing equal volumes of fuming nitric acid and fuming sulphuric acid was particularly good for oxidation of ethylphenyldichlorosilane. There was no retention of carbon and the weights of residue were very close to the theoretical quantitative yields of silica.

The addition of perchloric acid to sulphuric acid slightly increased the retention of carbon. Furthermore, the perchloric acid had an effect predominating over that of the sulphuric acid in that the loss of silica was as high as that with perchloric acid alone. This predominant role of the perchloric acid was also noticed in perchloric acid–nitric acid mixtures.

SUMMARY

The radioisotope carbon-14 was used to study the retention of carbon in the decomposition of alkyl- and arylchlorosilanes by wet methods. Losses by sample volatilisation were overcome by preliminary cooling in dry ice. Fuming sulphuric acid alone or in mixtures with fuming nitric acid was found to be the most effective oxidant of the acids tested. Examination of the carbon-containing silica residues by X-ray

powder photography indicated that amorphous carbon was present but there was no evidence of silicon carbide.

RÉSUMÉ

Le radioisotope carbone-14 est utilisé pour l'étude de la rétention du carbone dans la décomposition des alkyl- et arylchlorosilanes par voie humide. Des pertes par volatilisation de l'échantillon sont évitées par refroidissement préliminaire dans la glace sèche. L'acide sulfurique fumant, seul ou dans des mélanges avec acide nitrique fumant, s'est montré l'oxydant le plus efficace des acides testés.

ZUSAMMENFASSUNG

Radioaktives ^{14}C wurde benutzt, um das Zurückbleiben von Kohlenstoff bei der Nassveraschung von Alkyl- und Arylchlorosilanen zu untersuchen. Verluste durch Verdampfung wurden durch vorhergehendes Kühlen mit Trockeneis vermieden. Rauchende Schwefelsäure allein oder in Mischungen mit rauchender Salpetersäure waren die wirksamsten Oxydationsmittel von allein geprüften Säuren. Die Untersuchung der kohlenstoffhaltigen Siliciumdioxid-Rückstände durch Röntgen-Pulverphotographie zeigte, dass amorpher Kohlenstoff anwesend war jedoch kein Siliciumcarbid.

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SHORT COMMUNICATIONS

Fluorimetric determination of tungsten in almost pure tungsten, thoriated tungsten, and Co–Ni–Cr refractory alloys*

The fluorimetric determination of tungsten with flavonol and the application to nickel–tungsten alloys and steels have been described[1,2]. This communication concerns the application of the method to almost pure tungsten, thoriated tungsten, and cobalt–nickel–chromium refractory alloys.

Apparatus and reagents

The fluorimeter and the preparation of standard tungstate solution, flavonol solution, stock buffer solution (without cyanide), diluting solution, and test solutions have been previously described[1,2].

Analysis of almost pure tungsten and thoriated tungsten

Break or cut the specimens of rod or wire into pieces sufficiently small so that samples of 20–60 mg can be weighed out. Clean the pieces by washing in acetone, boiling in 20% potassium hydroxide for about 5 min, and finally washing with water and drying. Place the weighed sample in a 150-ml, 3-inch diameter platinum dish. Cover the sample with a mixture of 1.0 ml of 40% hydrofluoric acid and 0.75 ml of concentrated nitric acid. Set the platinum dish on an asbestos pad which has about a 2-inch hole in the center. Using a low flame, heat gently, as needed, to effect a sufficiently rapid but non-spattering rate of dissolution. When the sample has completely dissolved, add 2 ml of 70% perchloric acid and stir by swirling. Fume very gently until a white or tan precipitate begins to form around the edges of the solution.

Add about 7 ml of 4 *N* sodium hydroxide and then 2 drops of phenolphthalein. Continue to add 4 *N* sodium hydroxide until the solution is definitely alkaline. Add 50 ml of hot 1 *N* sodium hydroxide (pre-heated in a Vycor or stainless steel container). Pour the contents of the platinum dish into a 1-l volumetric flask which contains about 6 ml of hydrochloric acid and 100 ml of water. Wash the dish with water about 6 times. Add sodium hydroxide or hydrochloric acid as needed to neutralize the solution to the point where one drop of 1 *N* hydrochloric acid just discolors the indicator. When the solution has come to room temperature bring to volume with water.

The tungstate concentration of these solutions will be too high for immediate use. Dilute an aliquot to some suitable volume to obtain a solution containing 1–1.5 mg W/l. For samples up to 35 mg, a 25-ml aliquot is diluted to 500 ml, while for samples of 35–60 mg, a 25-ml aliquot is diluted to 1 l.

The test solutions for the fluorimetric readings are then prepared. Into 100-ml volumetric flasks place either exactly 10 ml of water (the blank), 10 ml of a standard tungstate solution (about 1.5 μg W/ml) or 10 ml of the unknown. Bring to volume with the flavonol–buffer mixture. The pH of these solutions will be 4.08. Measure as described previously.

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* Taken from the Ph.D. thesis of Br. A. TRUSK, University of Notre Dame, June, 1966. Part of this work was done at St. Mary's College, Winona, Minn.

This procedure was applied to 3 samples. The results are shown in Table I.

Analysis of Co–Ni–Cr refractory alloys

Into a 250-ml Vycor Erlenmeyer flask weigh out enough sample to supply about 1.5 mg of tungsten. If the tungsten concentration of the sample is completely unknown, use about 100 mg. Cover the sample with 25 ml of perchloric acid and 10 ml of sulfuric acid. Place the flask on a hot plate set at medium heat and take to dryness. (In practice the heat was turned on at the end of the working day and the samples allowed to heat overnight.) After about 12 h, raise the hot plate setting to high and fume off any remaining sulfuric acid. To the dried samples add 10 ml of hydrochloric acid and heat and swirl to dissolve or loosen the precipitate. Evaporate the hydrochloric acid to almost half volume. Wash down the flask with about 20 ml of water, add 2 drops of formaldehyde and return the flask to the hot plate. Add 4 *N* sodium hydroxide until precipitation of the metal hydroxides is complete. Then add about 10 ml in excess. Heat the alkaline solution to boiling, wash down the flask with water and boil again. Add hot water until the total volume of mixture in the flask is about 200 ml. Keep the flasks hot until ready for filtration.

TABLE I

ANALYSES OF ALMOST PURE TUNGSTEN AND THORIATED TUNGSTEN

Specimen	*Reported* % *W*	*Found* % *W*	*No. of samples*
A[a]	99.9	99.9±0.08[d]	9
B[b]	99.5	99.5±0.07	10
C[c]	98.0	98.0±0.08	12

[a] General Electric Type 218 99.9% tungsten rod.
[b] General Electric Thoriated tungsten wire, Lot. No. M-56-2-27 1/2% ThO_2.
[c] Pitman-Dunn Laboratories.
[d] Precision expressed as standard deviation.

TABLE II

ANALYSES OF Co–Ni–Cr REFRACTORY ALLOYS

N.B.S. no.	*Reported* % *W*	*Found* % *W*	*No. of samples*
167	4.50	4.50±0.16[a]	10
168	3.95	3.95±0.09	7

[a] Precision expressed as standard deviation.

A bulk quantity of 0.5 *N* sodium hydroxide is prepared. About 400 ml will be needed per sample. In a 1-l (or larger) stainless steel vessel, heat the sodium hydroxide wash solution. Prepare plastic funnels (top diameter 10 cm) with coarse filter paper (Whatman No. 4, 15 cm) set with the hot alkali. Prepare 1-l volumetric flasks to receive the filtrate by placing in each about 30 ml of hydrochloric acid and 70 ml of water. If necessary, allow the precipitate in the sample flasks to settle. Using a plastic stirring rod decant the supernatant solution into the filter funnel. Add the hot alkali wash to the precipitate until the total volume is again about 200 ml. Decant again, and finally pour the precipitate slurry into the funnel. Wash down the Vycor flask with about 20 ml of the hot alkali and pour 3 successive washings over the precipitate. Finally, generously wash the precipitate twice with the same wash solution. To the filtrate add 2 drops of phenolphthalein and neutralize with sodium hydroxide or hydrochloric acid to the point where one drop of 1 *N* hydrochloric acid will just discolor the indicator. Allow the solutions to come to room temperature before bringing to volume with water. These solutions are then used to prepare test solutions in the same manner which was used for the almost pure tungsten and thoriated tungsten samples.

The above procedure was applied to the only two samples of a Co–Ni–Cr refractory alloy available from the National Bureau of Standards. The results are given in Table II.

Discussion

Analysis of almost pure tungsten and thoriated tungsten. A large platinum dish is used to reduce loss by spattering. When a 30-ml crucible was used the results were less satisfactory. The asbestos pad was first introduced into the procedure when attempts were made to use a plastic cover on the dish. Such a lid proved to be unsatisfactory, probably because the condensate contained some hydrofluoric acid which was a source of interference. However the pad was retained to effect a more gentle heating. When the same procedure was tried with the dish on a clay triangle the results were erratic and low, probably because the rate of heating was too fast.

A hydrofluoric–nitric acid mixture is a standard solvent for tungsten. However, the fluoride tolerance is rather low (F/W weight ratio is 30). It is necessary to fume off most of the hydrofluoric acid. When the sample is a relatively three-dimensional piece (as opposed to a thin wire), the rate of dissolution is slow and much of the solvent is lost during this heating. With such a sample, the fuming time, after perchloric acid is added, is from 15 sec to a minute. Wire samples dissolve much faster with less loss of solvent. In these cases the fuming time will be between 3 and 6 min. It was found that, at the gentle rate of fuming, it takes about 7 min. It is critical that the rate of fuming be very gentle. At higher temperatures there is no apparent spattering, but some W–F combinations are volatile[3] and may be lost at higher temperatures. In practice it was found that consistent and satisfactory results could be obtained only with the slower fuming process.

Admittedly sulfuric acid is a better fuming agent than perchloric acid. There is an obvious break in the fuming when the more volatile compounds have been removed, but, again, the sulfate tolerance is not high, and it would be necessary to take the sample to dryness or near-dryness. There is much danger of spattering loss during such an evaporation. However, this method was tried. Even using a platinum lid, a successful evaporation and analysis could be obtained in only about 15% of over one hundred attempts.

In the treatment with sodium hydroxide, if phenolphthalein is added directly to the hot perchloric acid the indicator undergoes some change. The reaction is not violent but the indicator will be yellow rather than colorless in acid media. It is necessary that the perchloric acid be largely or totally neutralized before the phenolphthalein is added.

The sodium hydroxide was heated in Vycor or stainless steel because when alkali is heated and allowed to stand in a pyrex vessel the hot alkali dissolves something from the glass, possibly aluminum, which enhances the fluorescence of the tungstate flavonol complex. This reaction of hot alkali with glass is also the reason why acid and water are placed in the receiving volumetric flask. The recommended amount of acid is slightly in excess of the volume needed to neutralize the base completely.

Analysis of Co–Ni–Cr refractory alloys. Other solvents, such as nitric, nitric–hydrochloric, and nitric–sulfuric, were completely ineffective on these alloys. The possible danger of perchloric fumes made use of this acid a last resort. However, with suitable care in regard to the cleanliness and composition of the hood this method seems to be perfectly safe. The samples are taken to complete dryness, or to the end of heavy sulfuric acid fumes, to eliminate any fluorescence interference from sulfate ion.

The hydrochloric acid added to the dried precipitates will dissolve the salts of Cr(III), Ni(II), Co(II), and some other metals, as well as much or all of the tungstic acid. However, the oxides of Nb and Ta will remain as a white powder. If the sample has been baked too long there will also be some black oxides of other metals which will not readily dissolve in the hydrochloric acid. These will be caught on the filter paper and will not interfere with the fluorescence method.

Formaldehyde is used to reduce any possible chromium(VI) to chromium(III), since chromate interferes seriously with the fluorescence even at a chromate–tungsten weight ratio of 0.0001.

The dissolution of the tungstic acid in boiling alkali is similar to the procedure used on the Ni–W alloys. However, in this case the precipitate must be removed by filtration. The double decantation and washings with the hot dilute alkali effectively minimize any loss of tungsten by coprecipitation. Hydrochloric acid is first placed in the receiving volumetric flask to prevent the action of hot alkali on Pyrex glass. The total filtration time is about 1.5 h, but if one is treating 9 or more samples the time per sample is not prohibitively long.

In practice, if one works with 9 samples, about 4 l of 0.5 *N* sodium hydroxide will be needed. It was not necessary that this be heated all at once. An ordinary kitchen-type stainless steel pitcher was used. If this was kept on the hot plate and the solution replenished from time to time an adequate supply of hot wash was always available. The wash must be hot to provide faster filtration and more effective tungstate dissolution.

The samples used in the application of this method both contained about 4% tungsten. There seems to be no reason why the procedure could not be applied also to alloys of higher or lower tungsten concentrations.

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Determination of lanthanum in titania by activation analysis

During the determination of the cross-section of the (n,p) reactions on titanium resulting in radioactive scandium isotopes[1], a lanthanum impurity was discovered in the irradiated sample. The content of lanthanum was determined by activation analysis.

Standards, samples and irradiations

The analysed titania sample was "analytical grade"; 100–300 mg was weighed in a small silica vessel. The lanthanum standard was a solution containing 50 μg of lanthanum in 200 μl of 0.1 *N* bidistilled nitric acid. The irradiations were performed in the BR-1 reactor for 2 h at $4 \cdot 10^{11}$ n cm^{-2} sec^{-1}.

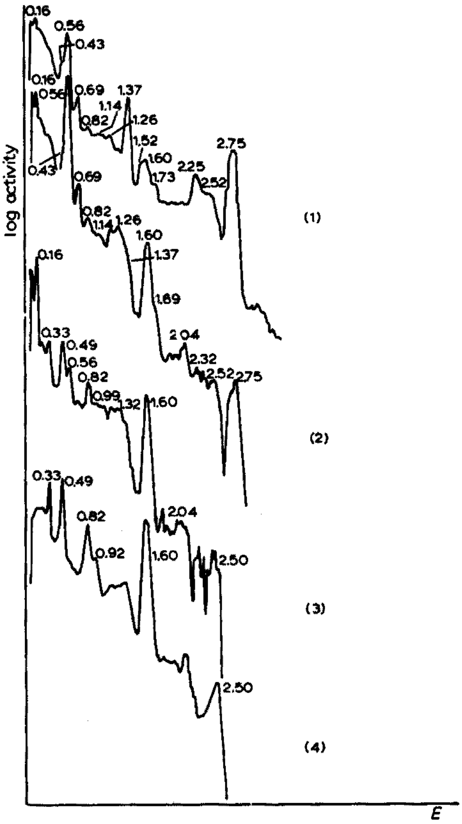

Fig. 1. Radiochemical separation of lanthanum from TiO_2. (4) ^{140}La; (3) 4 + ^{48}Sc (0.99–1.32–2.04) + ^{47}Sc (0.16) + ^{122}Sb (0.56); (2) 3 + ^{24}Na (1.37–2.75) + ^{122}Sb (0.69–1.14–1.26) + ^{124}Sb (1.69); (1) 2 + ^{24}Na (1.73–2.25) + ^{42}K (1.52).

Dissolution of the sample and separation

Titania was heated with a mixture of 15 ml of concentrated sulfuric acid and 10 g of ammonium sulfate. After cooling, this solution was diluted with 100 ml of water. γ-Spectrometry (Fig. 1, spectrum 1) showed the presence of ^{24}Na, ^{42}K, ^{122}Sb, ^{124}Sb, ^{76}As, ^{48}Sc, ^{47}Sc, ^{140}La.

Lanthanum was coprecipitated with titanium by addition of 14 *M* ammonia solution. The precipitate was separated by centrifugation, washed with water to which a drop of ammonia solution had been added (pH >10) and redissolved in 3 *N* hydrochloric acid (+ a few drops of hydrogen peroxide). In this step ^{24}Na, ^{42}K and partly ^{122}Sb and ^{76}As are eliminated as can be seen from Fig. 1, spectrum 2.

The titanium matrix can be separated from the rare earths by cation exchange. It is desorbed by 3 *M* hydrochloric acid while the rare earths remain on the column, but tailing occurs. The separation can be speeded up considerably by means of the titanium–peroxide complex. In 0.5 *N* hydrochloric acid + 2% hydrogen peroxide this complex is strongly adsorbed but in 3 *N* hydrochloric acid + 2% hydrogen peroxide it has a distribution coefficient of less than 1 and leaves the column without tailing.

The separation from the matrix was achieved by diluting the solution to 0.5 *M* hydrochloric acid and adding hydrogen peroxide till the colour intensity stayed constant. The titanium complex was first sorbed in a narrow band on a Dowex 50W-X8 100–200 mesh column (20 cm × 2 cm^2) and then eluted with 3 *N* hydrochloric acid +2% hydrogen peroxide. The rare earth group was eluted with 6 *N* hydrochloric acid. The eluate was evaporated and taken up again in 0.1 *N* hydrochloric acid. In this step, besides the titanium matrix, the following isotopes were eliminated: ^{51}Cr, ^{182}Ir, the rest of the ^{76}As, ^{24}Na and ^{42}K activities and part of the ^{122}Sb (Fig. 1, spectrum 3).

Separation of lanthanum and scandium

The 0.1 *N* hydrochloric acid solution was adsorbed on the top of a Dowex 50W-X8 200–400 mesh column (15 cm × 0.4 cm^2) and subsequently eluted with ammonium α-hydroxyisobutyrate solution. In a first experiment, an elution was performed with a linear ligand concentration gradient, under conditions where the rare earth activities should be separated well enough to allow identification of the individual elements. Four elution peaks were obtained: the first left the column during the 0.1 *M* hydrochloric acid adsorption stage and was due to ^{122}Sb, and another left immediately after starting the gradient (^{182}Ta); the two other peaks were ^{46}Sc + ^{47}Sc + ^{48}Sc formed by (n,p) reactions on titanium, and ^{140}La. Since no other rare earths were detected, Sb, Ta and Sc were separated from lanthanum as a group by elution with a ligand concentration of 0.1 *M*, lanthanum being eluted with 0.4 *M* ligand concentration. Some experiments were performed with added ^{153}Gd as a chemical yield monitor for the whole separation procedure. In this case, Sb, Ta and Sc were eluted with 0.06 *M* ligand concentration, Gd with 0.12 *M* and La with 0.4 *M*. A pure ^{140}La-spectrum was obtained (Fig. 1, 4). In each case the different fractions were collected in standard flasks (50 ml) and measured with a NaI(Tl) crystal coupled to a 400-channel analyser. The lanthanum standard was measured in the same geometry.

Results and discussion

Two series of determinations were performed, one with ^{153}Gd yield monitor and one without. The results are summarised in Table I.

It appears that yield monitoring is not necessary, a reproducible yield of 98–100% being obtained. From these data one concludes that the sample contained 12.5 p.p.m. $\pm 0.1^{5}$ La.

TABLE I

CONTENTS OF LANTHANUM IN TiO_2 (p.p.m.)

With yield monitor	*Without yield monitor*
13.0	12.3
12.2	12.7
12.6	12.4

The cross-section for (n,γ) capture of titanium is 8 barn. From this value it can be calculated that no appreciable self-shielding will occur in the sample. This was verified by irradiating a few mg of cobalt–aluminum foil in a 1.5-g titania sample and comparing the activity obtained with the activity of a similar foil irradiated without titania. A mean flux depression of 4.5% was found. Since in the analyses only 300 mg were irradiated, it may be concluded that flux depressions do not generate appreciable errors.

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Some preliminary studies of the analytical potentialities of the atomic-hydrogen plasma torch

A major problem in atomic absorption spectroscopy is the conversion of the sample solution or the solid material into atoms. For many easily oxidised elements this is often difficult, even with the hottest reducing flames normally available, because of the presence of some atomic oxygen. More recently, the use of the nitrous oxide–acetylene[1] flame has overcome some of these problems, although its application is as yet confined to solutions rather than solid samples and even then many elements are beyond its reach, *e.g.* cerium, thorium, etc.; moreover, such flames usually exhibit a very high background radiation, and whilst this may be partly overcome by modulating the source and detector, the radiation from the flame can still cause serious photomultiplier fatigue.

Plasmas appear to offer several advantages, hence their use as atom-reservoirs in analytical spectroscopy is of considerable interest. They can be divided into two distinct classes; the d.c. arc plasma jet and high-frequency coupled plasmas. The former have been used in emission spectroscopic studies with some success *inter alia* by GREENFIELD, JONES AND BERRY[2] who found that they were somewhat unstable and produced high background radiation. More recently WEBB AND WILDY[3] managed to overcome some of these problems by using an integrating spectrophotometer employing an additional photomultiplier and screening the stabiliser electrode.

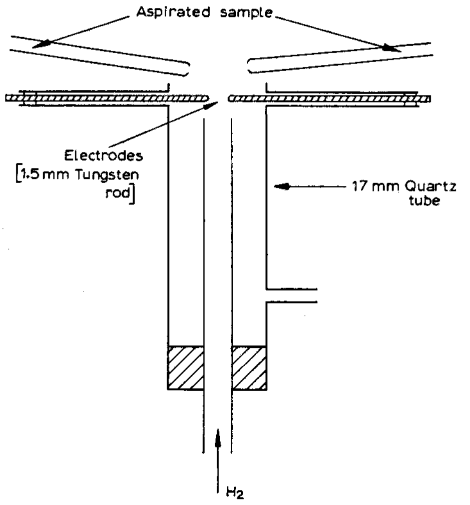
It appeared that the atomic-hydrogen plasma torch would be worth investigating. This device was first described by LANGMUIR[4] and has apparently been considered by many workers since, although only VAN DEN BOLD AND SMIT[5] seem to have realised its full potential. Their original apparatus was unsuitable as an atom-reservoir for analytical spectroscopy and they were only concerned with the "flame" temperatures, but they concluded that it was worthy of further study as a spectroscopic source. Essentially, this device involves passing hydrogen gas at atmospheric pressure through an arc formed between two tungsten electrodes. The gas receives sufficient energy to produce dissociation of molecular hydrogen and hence appreciable quantities of free atoms. These atoms recombine a few centimetres above the arc giving an energy of 4.75 eV per molecule. Metal surfaces will catalyse this recombination process and so receive additional heat. The highly reducing atmosphere involved, with the absence of oxygen, makes such a device particularly attractive in spectroscopy. In addition, because of the catalytic recombination process, the possibility exists for handling metallic samples directly.

The plasma temperature is dependent on the arc current, voltage and the gap between the electrodes and has been estimated to be $>3500°K$ as much as 4 cm above a 14-A arc with a 2-mm electrode gap[5]. LANGMUIR[4] has calculated the maximum temperature to be in excess of 4000°K.

The purpose of the following study was to develop a simple, easily controlled device which would be of use as an atom-reservoir in analytical spectroscopy and would be capable of handling both solutions and solid samples.

Torch design

The torch design is shown in Fig. 1. It is constructed entirely of fused quartz. The sleeves over the tungsten electrodes perform the dual role of preventing aerial oxidation of the electrodes and of allowing alignment of the electrodes within the quartz shield. The electrical power for the arc was taken directly from an a.c. mains



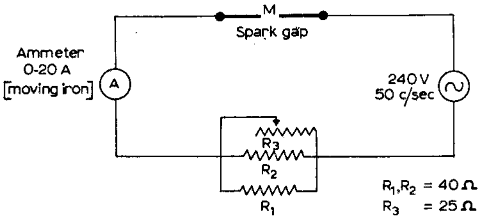


Fig. 1. Torch design.

Fig. 2. Electrical circuit.

supply through a number of resistances placed in parallel, such that the arc current was limited to 20 A (Fig. 2). R_1 and R_2 were 1-kW electric heater elements and R_3 was a variable resistance rated at a 10-A working current. All the resistances were air-cooled to reduce the running temperature. The circuit shown has no provision for initiating the arc, but this was achieved by lightly stroking an insulated carbon rod across the electrodes. This causes a current to flow and an arc is produced instantly.

Operating conditions

Electrodes. The tungsten electrode diameter, which was found to be quite critical, was optimal at *ca.* 1.5 mm. Larger diameters (*i.e.* 3 mm) caused large currents (>20 A) to flow owing to the reduced resistance of the arc gap. Reducing the open circuit voltage across the gap merely made initiation very difficult and produced a visibly unsteady and oscillating arc. The optimum arc gap appeared to be *ca.* 2 mm. A larger gap (*i.e.* 4 mm) again produced an oscillating arc and electrode burn off.

The hydrogen flow rate was not very critical; but a very low flow caused electrode consumption because of excessive air entrainment whilst too fast a flow appeared to cool the arc.

Under these conditions the arc could be maintained for periods of up to 1 h without adjustment of the arc gap. At a current of *ca.* 12 A, a plume of plasma was clearly visible extending 2–3 cm above the arc and this was in turn surrounded by an outer mantle of burning hydrogen, the appearance of the "flame" being as described by VAN DEN BOLD AND SMIT[5]. The hottest part of the plasma appeared to be about 2 cm above the arc and even pieces of tungsten metal held in this position melted without difficulty (m.p. 3600°K). Tantalum foil melted immediately and stainless steel and other lower-boiling metals (*e.g.* Al, Cd, Zn) were vaporised almost instantaneously. However, materials which did not aid the recombination of atomic hydrogen, such as quartz, were in comparison almost unaffected and only melted slowly.

Effect of foreign gases. If the system as described is to be of any practical use, it must be possible to introduce liquid samples into the plasma by conversion to an aerosol.

The normal method of nebulisation is also capable of being used with the atomic-hydrogen plasma provided that the carrier gas has no influence on the plasma properties.

The effects of air, nitrogen, argon and hydrogen were studied using a conventional EEL flame photometer nebuliser, the gas stream being introduced through a side arm in the quartz tube (Fig. 1). The effect of spraying water, alcohols, ketones, ethers and hydrocarbons was also investigated. Air, even in small quantities, produced a spluttering arc and appreciable electrode "burn off". With nitrogen a slight visible brightening of the arc occurred. When the hydrogen flow rate was decreased relative to the nitrogen, severe spluttering was again observed. The visible increase in intensity was probably due to the decrease in the resistance of the arc on adding nitrogen. In the hydrogen arc, thermal energy is carried away from the electrodes by the dissociation of hydrogen molecules plus the rapid diffusion of the hydrogen atoms formed. These processes will not occur so readily with nitrogen (dissociation energy 10.0 eV). In addition, nitrogen reacts with tungsten at high temperatures forming nitrides. Argon gave similar results, but in this instance no spluttering was observed. A satisfactory nebulisation with hydrogen can only be obtained with a pneumatic nebuliser by using a large hydrogen pressure, because it has a low density. Most conventional nebulisers will not function efficiently because of this and the volume of hydrogen which flows overcools the arc.

Nebulising water on nitrogen into the plasma produced no noticeable effect, although the arc could not be maintained for such long periods without electrode adjustment. Organic solvents produced a similar effect and at the same time imparted a green-violet colouration to the plasma due to the production of carbonaceous radicals.

Nebulisation. In view of the above observations, nitrogen was selected as the nebulising gas and the sample spray was introduced through 2 quartz tubes (5-mm internal diameter), each running above the 2 tungsten electrodes and inclined slightly towards the arc (Fig. 1). An EEL nebuliser unit was used with a T-piece in the output tube connected to the 2 quartz tubes. This arrangement directs a spray cloud into the hottest part of the plasma about 2 cm above the arc. The upward hydrogen flow minimises contact of the spray and nebulising gas with the electrodes. The distance between the ends of the quartz tubes was *ca.* 3 cm, *i.e.* sufficient to prevent fusion of the quartz. No noticeable electrode "burn off" was observed and the arc could be maintained for long periods (up to 1 h) without gap adjustment.

Background measurements

Measurements were made using a Unicam SP 900 A atomic absorption/flame emission spectrophotometer both in the arc region and 2–3 cm above it. In the latter instance, the monochromator slit was shielded from the arc glare by a pair of parallel slits. Under these conditions a continuum was observed over the region 4500–6500 Å corresponding to the NO+O reaction with a maximum intensity at *ca.* 5500 Å. The only emission observed in the ultraviolet region was very weak and was due to OH bands. No tungsten lines were observed in this region of the plasma. The arc, on the other hand, showed considerable background both in the visible and ultraviolet regions and was abundant in tungsten lines. The Balmer lines were also strongly visible. These spectra were almost identical to those obtained by VAN DEN BOLD AND SMIT[5].

Some preliminary studies were made on nebulising metal ion solutions into the plasma. Considerable resonance line emission was observed for many elements, *e.g.* aluminium, lead, cadmium, zinc, magnesium, titanium, etc., but mains fluctuations have so far led to fluctuations in quantitative measurements. It is hoped that this

TABLE I

SOME LINES IDENTIFIED IN THE ATOMIC-HYDROGEN PLASMA TORCH FROM ASPIRATED METAL ION SOLUTIONS

Element	*Resonance lines (Å)*
Aluminium	3962, 3944
Cadmium	2288
Lead	2833
Magnesium	2852
Mercury	2537
Titanium	3636, 3643, 3654
Zinc	2139

may be overcome by stabilising the a.c. mains output, or by using a d.c. supply. Results obtained using a more refined system will be described at a later date. (Some of the observed lines are shown in Table I.)

The availability of a greater power output than that used above would no doubt give more control of the arc conditions and it has been shown to increase the rate of surface heating[4]. However, the measurements of VAN DEN BOLD AND SMIT[5] show that there is little gain in plasma temperature and the generator unit required becomes appreciably more complex and bulky.

Conclusions

The plasma as described is simple and is remarkably easy to operate and maintain. Once the problem of mains fluctuations has been overcome, it should also be sufficiently stable for analytical purposes. Its mode of operation produces, above the arc, an intensely hot reducing atmosphere with a rapid rate of surface heating, but with negligible background radiation in the ultraviolet region.

The inability of atomic hydrogen to recombine on quartz enables solutions to be nebulised into the hottest plasma regions without introduction through the electrodes. This avoids electrode contamination, etc. Another important consideration, which also arises from the catalytic recombination process, is its ability to volatilize solid samples directly. Variation of the arc current and voltage or adjustment of the hydrogen flow rate gives a very broad control of the plasma conditions.

The atomic-hydrogen plasma torch serves as a useful adjunct to work recently done in this laboratory with cool nitrogen/hydrogen diffusion flames which, upon aspiration of a solution of metal ions, have been shown to contain an anomalously high concentration of metal atoms[6].

The same favourable characteristics appear to be associated with this high-temperature (atomic) analogue of the cool (molecular), diffusion flame[7], but additionally the latter should be free from some of the matrix effects inescapably associated with the cool flame. It is envisaged that the atomic-hydrogen plasma should be particularly effective for the atomic spectroscopy (absorption, emission or fluorescence) of those elements which, at the present time, can only be dealt with in flame spectroscopy by the nitrous oxide–acetylene flame.

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Atomic absorption with an electrodeless high-frequency plasma torch

The use of the electrodeless high-frequency plasma torch as a source for emission spectroscopy has been described previously[1,2]. It has now been found that the length of the outer coolant tube of the plasma cell, made of silica as described previously[1], can be increased to 21 inches with a considerable increase in stability of the plasma. The length of the "tail flame" is now *ca.* 2 feet, and it has also been found that it is possible to bend the "tail-flame" of the plasma through a right angle. In the preferred form of apparatus for carrying this discovery into effect, the plasma torch is in the form of a T, the stem of which is constituted by a plasma torch substantially of the form described previously[1]. The exit end of this torch opens into the side wall of a tube, perpendicular to the body portion of the torch, this tube constituting the cross member of the T. The tube may be open at both ends, in which case the "tail-flame" splits on passing through the side wall of the tube, and extends in opposite directions along the tube; alternatively, the tube may be closed at one end by an optical flat, in which case the "tail-flame" on entering the tube will turn through 90° away from the end closed by the optical flat.

It was possible to control the power, and hence the temperature, of the plasma with reasonable accuracy, by varying the tuning capacitor of the H.F. generator, so that the technique appeared to have applications in the field of atomic absorption spectroscopy. The temperature range is in the region of 3000–8000°K, depending on the position in the plasma tail-flame which is focussed on the slits. The position can be controlled to 0.1 mm and the power can be controlled to ±5% of the total power, hence the temperature reproducibility is good. The high temperature of the "tail-flame" minimises the depressant effects of "chemical interference" due to the formation of stable refractory compounds of the element under investigation. This advantage, together with the lower background radiation emitted by the "tail-flame" of an argon or argon/nitrogen plasma, indicated that it would be superior to combustion flames in atomic absorption spectroscopy. It has been shown that elements which are difficult to obtain in an atomic-absorbing state, require higher temperatures than can be obtained with combustion flames; these temperatures can be obtained with the plasma torch. The temperature, however, must be controlled to a level where the majority of the atoms of the element are in the ground state, hence the need for a reasonably high degree of control of the plasma temperature.

One other possible advantage of the H.F. plasma torch in atomic absorption is that the atmosphere can be made oxidising, neutral or reducing; *e.g.*, oxygen, nitrogen, argon, chlorine and hydrogen gases have been used by the authors and doubtless many more can be used.

Atomic absorption using an electrodeless plasma torch has been described by WENDT AND FASSEL[3] using a multi-pass optical system, perpendicular to the axis of the torch, to increase the length of the absorption path in the "tail-flame". With the technique described here, it is possible to dispense with the multi-pass optical system with its disadvantages of light losses and relatively short path length.

The plasma torch as the absorption source

Atomic absorption was measured using a hollow-cathode lamp, focussed onto the slits of a spectrophotometer through the plasma "tail-flame" contained in the horizontal tube of the T-shaped plasma cell. Water was nebulised into the plasma and the output signal due to the hollow-cathode lamp noted. An aqueous solution of the test material was then nebulised into the plasma and the new output signal noted. The difference between these two signals is the atomic absorption. If the spectrophotometer includes an A.C. amplifier, the light from the hollow-cathode lamp is chopped or otherwise interrupted to provide an alternating component in the output signal; any chopper motor or other interruption system used internally in the spectrophotometer must be removed. If the spectrophotometer has an A.C. amplifier tuned to 100 c.p.s., then the signal due to emission from the plasma itself must be considered. This output signal is due to the small ripple of 100 c.p.s. on the plasma, despite considerable smoothing of the power supply. This signal can be found by switching off the hollow-cathode lamp. Table I shows some results obtained for the atomic absorption of copper.

TABLE I

ATOMIC ABSORPTION OF COPPER

(Measurements at the Cu 3248 Å line)

One end of horizontal tube of T-shaped cell closed by optical flat		*Horizontal tube of T-shaped cell open both ends*	
Cu present (p.p.m.)	*Absorption*[a]	*Cu present (p.p.m.)*	*Absorption*[a]
1.0	1.7	10	7.1
2.5	3.6	25	10.1
4.0	6.6	50	12.9
6.0	9.1	100	21.0

[a] Divisions on recorder

The plasma torch as the emission source

The high "tail-flame" temperature offers the possibility of exciting atoms of an element to emit radiation suitable for absorption by other atoms of the element which are in the ground state. These ground-state atoms can be the result of nebulising an aqueous solution of the element into a combustion burner or further H.F. plasma acting as the atomic-absorption media.

With proper control of the plasma temperature, this scheme proved feasible. There was no significant line broadening due to the high temperature, and the half-line widths of 0.05 Å obtained were comparable with those of the hollow-cathode lamp.

The emission of the electrodeless H.F. plasma torch was focussed onto the slits of a spectrometer through an air/acetylene combustion burner which was acting as the atomic-absorption medium. The minimum emission was set by passing water through the nebuliser of both the emission source and the absorption unit, and then the maximum emission was obtained by injecting a suitable standard aqueous solution of the element under test into the plasma emission source. The test solution was then nebulised into the absorption burner; the change in output emission signal corresponds to the atomic absorption. If a spectrophotometer with an A.C. amplifier is used, the emission from the plasma torch must be chopped or otherwise interrupted at the required frequency unless this frequency is 100 c.p.s. when the 100 c.p.s. ripple on the plasma will be sufficient to achieve this end. Some results obtained by this technique are shown in Table II.

TABLE II

ATOMIC ABSORPTION OF CALCIUM, MAGNESIUM AND COPPER

(Calcium 4227 Å; magnesium 2852 Å; copper 3248 Å)

Ca present[a]	4	10	20	30	40	50
Absorption[b]	8	16.5	28	36.5	44	48.5
Mg present[a]	0.5	1.0	3.0	7.0	10.0	
Absorption[b]	13.7	27.0	56.4	76.9	80.2	
Cu present[a]	6	10	25	50		
Absorption[b]	15.4	24.0	49.3	74.7		

[a] p.p.m.
[b] Divisions on recorder.

The advantages of this method of atomic absorption are:

(a) The emission can be varied by atomising different concentrations of aqueous solutions of the element under test into the plasma, such that the concentration giving the maximum sensitivity can be found.

(b) The emission can be far higher than for the corresponding hollow-cathode lamp.

(c) Elements for which hollow-cathode lamps are difficult or impossible to construct can be excited using a plasma torch as the emission source.

(d) Only one plasma torch is required for all the elements, whereas a separate hollow-cathode lamp is normally required for each element.

It must be emphasised that these results in no way represent the ultimate sensitivity for an element, as no optimisation procedure was carried out. Work on detection limits and on elements for which it is difficult to construct hollow-cathode lamps, is proceeding.

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A study of the reactions of some metal ions and mixtures of metal ions with cupferron by high-frequency titrations

High-frequency titrations involving complex formation were first studied by BLAEDEL AND KNIGHT[1] and by HARA AND WEST[2], who examined the reactions of EDTA and similar complexing agents with some metallic ions. Further work in this field has been done by RYABCHIKOV AND ZARINSKY[3], who studied the complexes formed by thorium, indium, plutonium and boron with a variety of polyaminopolycarboxylic acids, the results being confirmed by other physicochemical methods.

In previous work from this Institute[4], the high-frequency method was utilized in studies of the reactions of cupferron with Fe(III), Sn(II), Sn(IV), Ti(IV), V(V), V(IV) and Zr(IV). In the present paper, it is shown that, in a suitable pH range, the formation of the 1:1 and 1:2 complexes of molybdenum(VI) with cupferron, the 1:2 uranium(VI)–cupferron complex and the 1:4 thorium(IV)–cupferron complex, can be followed by means of high-frequency titrations. The formation of the uranium(IV)–cupferron complex was confirmed colorimetrically, and the molybdenum complexes were also studied potentiometrically. It proved possible to analyze mixtures of iron(III) with various other ions by high-frequency titrations when hydrogen peroxide was used as masking agent. Appropriate pH adjustment allowed the analysis of U(VI)/V(V), U(VI)/Mo(VI) and V(V)/V(IV) mixtures. The concentrations of the various solutions ranged from $2 \cdot 10^{-3}$ to $5 \cdot 10^{-5}$ *M*.

Apparatus and reagents

A Sargent oscillometer Model V with a 100-ml glass titration vessel, a Metrohm E 388 direct-reading pH meter and a Hilger Uvispek spectrophotometer with 4-ml glass cuvettes were used.

Thorium–cupferron complex

When thorium solutions in the concentration range $6 \cdot 10^{-5}$ to $2.4 \cdot 10^{-4}$ *M* at pH values from 3.1 to 3.6 were titrated with 0.1 *M* cupferron, a stable 1:4 Th(IV): cupferron complex was found (Fig. 1, curve a).

Molybdenum–cupferron complexes

It is known that molybdenum(VI) forms both 1:1 and 1:2 complexes with cupferron[5]. This was confirmed by the high-frequency titrations with 0.1 *M* cupferron solution; the two breaks obtained on the titration curve corresponded to the formation of the 1:1 and 1:2 molybdenum(VI)–cupferron complexes (Fig. 1, curve b). When the pH was higher than 2.6, the inflection at a molar ratio of 1:1 remained clearly defined, but the break at the 1:2 molar ratio tended to disappear (Fig. 1, curve c). When the reaction was followed potentiometrically in buffered solution at pH 4.6, only the 1:1 complex was found.

Uranium–cupferron complex

At pH 4.6–4.8 the reaction between uranium(VI) and cupferron could readily be utilized for high-frequency titrations. A 1:2 uranyl–cupferron complex was formed (Fig. 1, curve d). This was confirmed by a spectrophotometric study, in which the absorption of the solutions prepared according to the method of Yoe and Jones, at 470 nm, the wavelength of maximum absorption, was plotted. It was also shown that the uranyl cupferronate obeyed Beer's Law up to ca. $6 \cdot 10^{-4}$ M concentrations when measurements were made at pH 4.6 and at a wavelength of 470 nm. The useful concentration range for photometric measurements is, of course, fairly small, for an aqueous saturated solution of the complex at room temperature is only $7 \cdot 10^{-4}$ M in the complex.

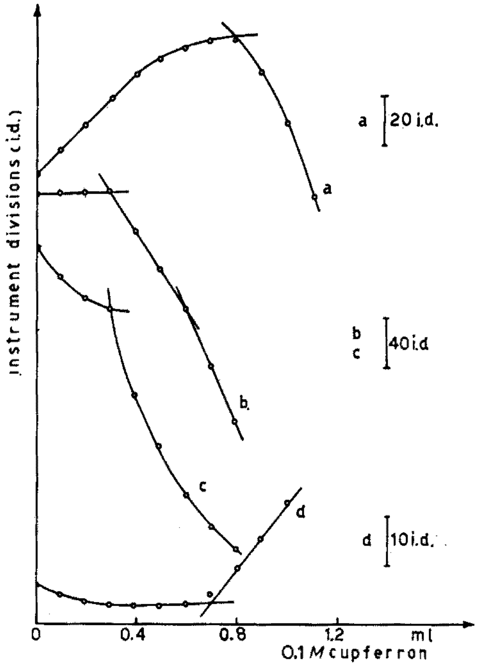

Fig. 1. Representative high-frequency titration curves with 0.1 M cupferron.
Curve a, Titration of $2 \cdot 10^{-2}$ mM of thorium(IV); instrumental reading at the end-point = 3834 i.d. Curve b, Titration of $3 \cdot 10^{-2}$ mM of molybdenum(VI) at pH 2.4; instrumental reading at the end-point 3760 i.d. for the 1:1 complex, and 3665 i.d. for the 1:2 complex. Curve c, Titration of $3 \cdot 10^{-2}$ mM of molybdenum(VI) at pH 3.3; instrumental reading at the end-point 3665 i.d. Curve d, Titration of $4 \cdot 10^{-2}$ mM of uranium(VI); instrumental reading at the end-point 2900 i.d.

Determination of iron(III) in solutions containing Ti(IV), V(IV), V(V), Mo(VI), Th(IV) or Zr(IV)

For the determination of mixtures of iron(III) with the above-mentioned ions, it was necessary first to determine the total concentration of the two ions by titration with cupferron, using the high-frequency technique, and then to determine iron(III) in another sample, after masking the other element by the addition of a small amount of hydrogen peroxide (1 ml of 30%). Checks were made to ensure the absence of breaks on the titration curves of Ti(IV), Mo(VI), V(V), V(IV), Zr(IV) and Th(IV) in the presence of an excess of hydrogen peroxide, and the insensitivity of cupferron to the peroxide. The results obtained for these determinations are shown in Table I. The pH of the solutions was maintained in the range 2.5–2.7 both for the titration of iron alone and for that of the mixture. Iron forms a 1:3 iron(III)–cupferron complex.

Analysis of U(VI)/V(V), U(VI)/Mo(VI) and V(V)/V(IV) mixtures

As already mentioned, uranium forms the 1:2 uranyl–cupferron complex with cupferron at pH 4.5–4.6, while vanadium and molybdenum form the 1:1 complexes at pH 2.4–2.6. When the determination is done in the correct pH range, one of the two elements in the sample does not interfere. The possibilities of this procedure are shown in Table II.

TABLE I

DETERMINATION OF IRON(III) IN BINARY MIXTURES WITH Ti(IV), V(IV), V(V), Mo(VI), Th(IV) OR Zr(IV) IN PRESENCE OF HYDROGEN PEROXIDE

Mixtures	*Formed complexes*	*Overall concentration: maximum limit* ($M \cdot 10^4$)	*Molar ratio Fe/Me maximum limit*
Fe(III), Ti(IV)	Ti(cup)$_4$	3·5	Fe/Ti = 1
Fe(III), V(V)	V cup	5	Fe/V(V) = 1/4
Fe(III), V(IV)	VO^{2+}(cup)$_2$	5	Fe/V(IV) = 1/4
Fe(III), Mo(VI)	Mo cup	5	Fe/Mo = 1/5
Fe(III), Th(IV)	Th(cup)$_4$	7	Fe/Th = 1/1
Fe(III), Zr(IV)	Zr(cup)$_4$	4·5	Fe/Zr = 1/1

TABLE II

ANALYSIS OF U(VI)/V(V), U(VI)/Mo(VI) AND V(V)/V(IV) MIXTURES

Mixtures	*Ion to be determined*	*pH range*	*Concentration: maximum limit* ($M \cdot 10^4$)	*Molar ratio limit*
U(VI)/V(V)	U(VI)	4.5–4.6	5	U/V = 1/3
	V(V)	2.4–2.6	3	V/U = 1
U(VI)/Mo(VI)	U(VI)	4.5–4.6	1.5	U/Mo = 2
	Mo(VI)	2.4–2.6	3	Mo/U = 6
V(V)/V(IV)	V(V) + V(IV)	2.5–2.7	10	
	V(IV)	3.9–4.1	5	V(IV)/V(V) = 1/5

Conclusions

High-frequency titrations can give valuable information about the processes of complex formation in solution; the breaks on the titration curves indicate the composition of the complexes formed. The satisfactory use of these titrations with cupferron for the analysis of binary mixtures is particularly to be noted. The experimental error does not exceed 0.5% and the minimum concentration that can be determined is $5 \cdot 10^{-5}$ *M*.

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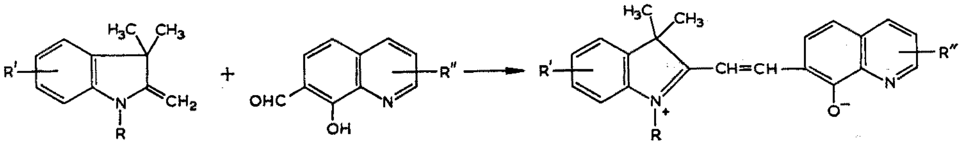
Photochromic 8-quinolinols

In order to obtain a variety of substituted photochromic chelating agents[1], several 8-quinolinol aldehydes were prepared[2] and reacted with 1,3,3-trimethyl-2-methyleneindoline or its derivatives according to the following equation:



By virtue of the ability of the highly colored merocyanine form shown in the equation to cyclize to a less colored spiropyran form, all products of this reaction are photochromic at low temperatures in appropriate solvents. The compounds (see Table I) in the solid state are usually white or off-white after crystallization from non-polar solvents such as ligroin but green or purple from polar solvents such as alcohols.

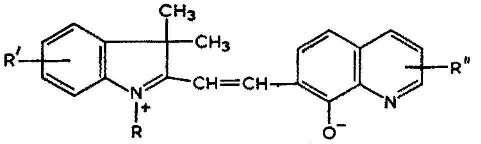
An example of reversible photochromism in solution is shown in Fig. 1: an initially red-violet solution is almost completely decolorized by about a minute of exposure to a strong tungsten light source and then colored again by a few seconds under ultraviolet light. As long as the temperature is kept low, the color produced by irradiation remains fixed in the absence of further illumination. Although the cycle of color changes illustrated in the figure can be repeated many times, deterioration of the solution to a permanently colored condition overnight can be expected.

In general, the compounds in Table I are red, violet or blue in 95% ethanol (with blue generally associated with the presence of a substituent in the 8-quinolinol part of the molecule), and at −78° can be rendered colorless or nearly so by ultraviolet light and colored again by a tungsten light source. Similar behavior in 2-propanol as solvent is generally observed if a trace of acid is present, but in 2-propanol without acid both ultraviolet and visible radiation intensify the color and only warming to room temperature can reverse the effect.

Other solvents tended to produce highly varied behavior. Thus, compound 11 in benzyl alcohol at −10° suffered a decrease in color with either ultraviolet or visible light, with restoration of color achieved by warming to room temperature. The same compound in dimethyl sulfoxide at 17° could be decolorized by either ultraviolet or visible light, but the color returned almost instantly when the light source was turned off.

TABLE I

PHOTOCHROMIC 8-QUINOLINOL DERIVATIVES



No.	R	R′	R″	M.p. (°)	Formula	% Carbon		% Hydrogen		% Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
2	CH_3	H	2-CH_3	191	$C_{23}H_{22}N_2O$	80.67	80.86	6.47	6.70	8.17	8.28
3	CH_3	H	5-Br	195	$C_{22}H_{19}BrN_2O$	64.87	65.07	4.70	4.98	6.87	6.58
4	C_2H_5	H	H	168	$C_{23}H_{22}N_2O$	80.67	80.44	6.47	6.55	8.17	8.05
5	C_2H_5	H	5-CH_3	173	$C_{24}H_{24}N_2O$	80.87	80.60	6.78	6.76	7.85	7.90
6	*n*-Pr	H	H	128	$C_{24}H_{24}N_2O$	80.87	80.78	6.78	6.75	7.85	7.65
7	*n*-Pr	H	5-CH_3	133	$C_{25}H_{26}N_2O$	81.05	81.27	7.07	7.22	7.55	7.39
8	CH_3	5-Cl	2-CH_3	185	$C_{23}H_{21}ClN_2O$	73.29	72.85	5.62	5.72	7.43	7.17
9	CH_3	5-F	H	212	$C_{22}H_{19}FN_2O$	76.27	76.09	5.53	5.53	8.08	7.93
10	CH_3	5-F	5-CH_3	195	$C_{23}H_{21}FN_2O$	76.64	76.83	5.87	6.00	7.74	7.62
11	CH_3	7-CH_3	H	195	$C_{23}H_{22}N_2O$	80.67	80.40	6.47	6.61	8.17	7.96
12	CH_3	7-CH_3	5-CH_3	203	$C_{24}H_{24}N_2O$	80.87	80.54	6.78	6.77	7.85	7.86
13	CH_3	7-CH_3	2-CH_3	197	$C_{24}H_{24}N_2O$	80.87	80.61	6.78	6.66	7.85	7.84
14	CH_3	5-Cl	H	195	$C_{22}H_{19}ClN_2O$	72.81	73.17	5.28	5.30	7.72	7.51
15	CH_3	5-Cl	5-CH_3	164	$C_{23}H_{21}ClN_2O$	73.29	73.05	5.62	5.49	7.43	7.47

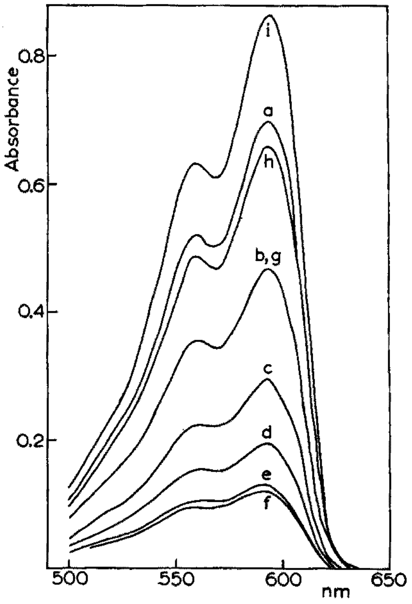


Fig. 1. Changes in the visible spectrum of 2-[2-(8-hydroxy-7-quinolyl)-vinyl]-1,3,3,7-tetramethyl-3H-indolium hydroxide inner salt (compound 11 in Table I) in 95% EtOH at −79°. Curve a is the initial solution; curves b–f are spectra after successive 10-sec increments of irradiation with a tungsten floodlight; curves g–i are subsequent 10-sec increments of irradiation with a short wavelength mercury lamp. Concentration is 0.000107 *M*.

The merocyanine form of these reagents would be expected by analogy with other merocyanines to exhibit a fairly pronounced negative solvatochromism[3], and while the equilibrium between merocyanine and spiropyran forms of these compounds is a complicating factor, differences in color as a function of solvent at room temperature did follow expectations. Thus, compound 11 diminished in its wavelength of maximum absorption near 590 nm by about 30 nm in passing from 10% 2-propanol as solvent (high dielectric constant) to pure 2-propanol (low dielectric constant). Interestingly, the molar absorbancy also dropped quite sharply, an indication of a shift to a higher proportion of the relatively colorless spiropyran form, which would be favored by non-polar solvents.

Temperature effects in the absorbancies of short and long wavelength bands are consistent with thermal shifting of the position of equilibrium of the two forms. Thus, for compound 11 in slightly acidic 95% ethanol, the 595 nm band more than triples in rising from −78° to 70° with a concomitant decrease in a somewhat weaker band at 460 nm. An increase of temperature would be expected to favor the charge separation of the more intensely colored merocyanine form, and a low temperature might favor the neutral spiropyran form.

Because the ability of these reagents to chelate with metal ions should be confined to the merocyanine form which alone contains the 8-quinolinol type chelating center, the chelates should resemble those of solvatochromic compounds that we have previously studied[3], being soluble because cationic, and differing only a little in color and absorption spectra from each other and from the reagent itself. However, since it is possible to prepare nearly colorless solutions of the photochromic reagents in some solvents (presumably because they are mainly in the spiropyran form), addition of any chelating ion yields a change of color to an intense red. With the exception of copper, the actual shift in the absorption spectrum of the metal complex relative to the merocyanine form of the reagent is slight or even negligible, as shown in Table II for one example.

The NMR spectrum of compound 11 in deuterated chloroform showed 4 methyl peaks at 3.1, 2.4, 1.2 and 1.1 δ. The first two correspond respectively to the $N{-}CH_3$ and $7{-}CH_3$ groups, and the last two are the $3{-}CH_3$ groups, which are not equivalent in the spiropyran form that is expected in this relatively non-polar solvent. Three much

TABLE II

VISIBLE ABSORPTION MAXIMA OF COMPOUND 14 AND ITS METAL COMPLEXES[a]

	λ_{max} at apparent pH of		
	2.5	*5.2*	*8.7*
Reagent	382(4.29)	364(3.94)	350(3.77)
	460(4.09)	410s(3.68)	410(3.42)
	575(4.49)	558(4.26)	560(4.10)
Cu complex[b]	545(4.59)	545(4.61)	550(4.46)
Ni complex	571(4.52)	581(4.65)	591(4.57)
Co complex	572(4.49)	571(4.57)	555(4.45)
Zn complex	572(4.49)	561(4.60)	584(4.25)
Cd complex	575(4.49)	575(4.40)	586(4.28)
			560s(4.22)

[a] In 50% ethanol buffers.

[b] Metal complex bands are recorded only for the 500–600 nm region.

smaller peaks in the methyl region (3.5, 2.5 and 1.7 p.p.m.) may be attributed to the presence of some of the open merocyanine form in which the 3-CH_3 protons are all equivalent and give only one peak rather than two. Confirmation of this interpretation is provided by the increase of these 3 peaks upon acidification and the collapse of the 4 larger peaks.

Experimental

Preparation of compounds. To the appropriate 7-formyl-8-quinolinol (0.03 mole) dissolved in 60 ml of isopropyl alcohol was added with stirring an equivalent amount of the appropriate Fischer methylene base and the solution was refluxed for 4 h. Upon cooling the product crystallized, or the solution was concentrated until it crystallized. The highly colored products were separated by filtration, washed with isopropyl alcohol and dried to give the compounds of Table I in yields that ranged from 35 to 75%. Recrystallizations from ligroin gave very lightly colored or white products, while recrystallizations from alcohols generally gave green, blue or purple solids. At the melting point of the white forms there was a change of color to purple.

Spectra. A specially designed spectrophotometer cell with provision for cooling to dry ice–acetone temperatures was used for measurements at low temperatures in a Cary Model 14 Spectrophotometer. Irradiation of the cell contents was performed at approximately two inches distance from a 250-W tungsten bulb or a Hanovia short wavelength mercury arc, as appropriate. Spectra were recorded immediately after irradiations, though as long as the temperature was kept low, no changes in the absence of irradiation were observed.

Chelate tests. Tests of each reagent with a few metal ions were performed in solutions at several pH values, and spectra of some of the resulting solutions were also recorded (Table II).

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The consecutive titration of iodate and periodate

Several titrimetric methods have been described for the determination of periodate in the presence of iodate or for the determination of both ions when present together[1,2]. Periodate is usually determined by reduction to iodate in a buffered, alkaline solution. This reaction appears to have been studied first by MÜLLER *et al.*[3] at the turn of this century. The various reductants that have been used are iodide[3], arsenic(III)[3,4], manganese(II) sulphate[4,5], bromide[6], mannitol[7] and hydrogen peroxide[8]. The sum of iodate and periodate is determined on another aliquot by reaction of both ions with iodide in an acidic medium to produce iodine, which is titrated with thiosulphate. Only one titrimetric method is known in which both ions can be determined in one aliquot[9]. It involves the selective precipitation of periodate as $Zn_5(IO_6)_2$, which is filtered off, dissolved in dilute acid and titrated iodimetrically. Iodate in the filtrate is also determined by an iodimetric titration. Although this is probably an accurate method, it is lengthy, for the precipitate has to stand for 30 min even before filtration and subsequent manipulation.

A new method for the determination of iodate in the presence of periodate has been described recently[10,11]. Periodate is masked by molybdate (6-molybdoperiodate, $[I(MoO_4)_6]^{5-}$, is formed) at pH 3 and iodate can be titrated iodimetrically in the presence of periodate when an excess of molybdate is present. This masking effect has also been utilised for the detection of iodate formed during the reaction of periodate with *vic*-dihydroxy compounds[11]. If periodate could be demasked after the titration of iodate, the periodate could then be titrated in the same solution. Although numerous reagents are available that readily form complexes with molybdenum[12], it was not possible to predict which would be most suitable for demasking because the stability of 6-molybdoperiodate is not known.

Molybdate–oxalate complexes of various stoichiometries have been reported[12]. FEIGL[13] noted that when oxalate is complexed with molybdate, it is no longer oxidised by permanganate. The only analytical application of this complexing reaction, however, appears to be the masking of molybdenum by oxalate to prevent interference in the diphenylcarbazide test for chromium[14].

This paper describes the development of a titrimetric method for iodate and periodate on one aliquot of solution by masking of periodate with molybdate and the subsequent demasking and titration of periodate.

Results

Preliminary experiments confirmed the previous observation[10] that a large excess of molybdate completely prevents the reaction of periodate with iodide at pH 3. Masking was instantaneous, and 10 ml of 2 M molybdate completely masked up to $5 \cdot 10^{-4}$ moles of periodate. Likewise, masking occurred at pH 4.9, and even at pH 6.9 the periodate–iodide reaction was markedly retarded by molybdate. It was also confirmed that molybdate did not interfere with the iodate–iodide titration at pH 3, so that 10 ml of 0.002–0.006 M iodate could be titrated accurately with thiosulphate, after adding iodide, in the presence of similar amounts of periodate, when molybdate was present. Tungstate also masked periodate at pH 3, but did not appear to be as effective as molybdate.

The following reagents were added (as solids) to an iodide–6-molybdoperiodate solution at pH 3 to ascertain how effective they were as demasking agents: oxalic acid, sodium dihydrogen phosphate, sodium fluoride, boric acid, EDTA. Only oxalic acid gave any demasking under the conditions used; the addition of 1.5 g of oxalic acid rapidly demasked the periodate at room temperature. Masking and demasking of periodate in this way did not affect the titre of 10^{-3}–10^{-2} M periodate solutions. The consecutive titration of iodate and periodate was carried out as follows. Iodate was determined while the periodate was masked with molybdate, by reaction with iodide, and titration with thiosulphate of the iodine formed. The periodate was then demasked with oxalic acid, and the iodine liberated again titrated with thiosulphate. Results obtained by this procedure are given in Table I, and show that accurate results for mixtures of iodate and periodate can be obtained. The end-point of both titrations was sharp, and there was no "after-blueing" in either instance. The pH of the solution after both titrations was 1.7.

TABLE I

CONSECUTIVE DETERMINATION OF IODATE AND PERIODATE

Iodate (mole·10⁵)		*Periodate (mole·10⁵)*	
Taken	*Found*	*Taken*	*Found*
2.58	2.60	3.99	4.00
5.14	5.16	4.99	4.97
5.14	5.13	4.99	5.01
7.69	7.63	4.99	4.96
2.62	2.63	9.98	9.95

An alternative method of titrating iodate and periodate in the same solution was briefly considered. Periodate could be titrated iodimetrically in a bicarbonate buffer[1], followed by acidification, and titration of the iodine liberated by reaction of iodide with iodate (including that formed in the first titration). However, it would be necessary to titrate with arsenic(III) in the first titration, because of side reactions that could occur in an iodine–thiosulphate titration at this pH[1]. On acidification, some iodide would be oxidized by arsenic(V), so that high results would be obtained in the second titration. Theoretically, if the solution is made alkaline after reduction of iodate, the iodine liberated by arsenic(V) should recombine with the arsenic(III) formed and so should not affect the results. Nevertheless, the oxidation of iodide by arsenic(V) is subject to various side reactions and atmospheric oxidation of iodide is promoted. This was confirmed experimentally; when the iodine liberated from iodate was titrated in either acidic or bicarbonate media after the titration of periodate in a bicarbonate solution, abnormally high results were obtained. Even if this procedure could be made to work it would be inferior to that using the masking–demasking reactions, for it takes more time, it is not so direct and only one-quarter of the amount of iodine is liberated from periodate, so that the accuracy is much less.

Buffer solution (pH 2.9).

Chloroacetic acid (25 g) dissolved in water (70 ml) and adjusted to pH 2.9 with strong sodium hydroxide solution.

Procedure for the consecutive titration of iodate and periodate

To the sample solution add 5 ml of buffer solution and 10 ml of aqueous 2 *M* sodium molybdate solution followed by 0.2 g of A.R. potassium iodide. Titrate with $4.0 \cdot 10^{-2}$ *M* thiosulphate solution, adding a little Thyodene when the solution becomes straw-coloured, to the disappearance of the blue colour. This titre gives the amount of iodate. Add 1.5 g of A.R. oxalic acid, swirl for 1 min, and titrate as above. The second titre gives the amount of periodate. Standardize the thiosulphate solution against a $5 \cdot 10^{-3}$ *M* solution of dried A.R. potassium iodate.

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Indium, gallium and germanium concentration levels in high-purity silica

Silica of very high purity can be used quite effectively to check the level of contamination introduced in grinding and other sample preparation steps during the analysis of silicate materials. During the development of a procedure for the neutron-activation determination of In, Ga and Ge in chondritic meteorites, it became clear that the indium sample-preparation blank was comparable to the low concentrations (*ca.* 0.1 p.p.b.) found in some of these objects. Accordingly, the indium as well as the gallium and germanium sample-preparation blanks were determined by subjecting high-purity silica to our normal handling operations.

Very few studies of the trace-element content of commercially available high-purity silica have been reported. For the 3 elements of interest, no previous work on germanium was found. KERN[1] reported an upper limit of gallium in Spectrosil of 4 p.p.b., and GLEIT *et al.*[2] found 0.11 p.p.b. of indium in Suprasil. We have obtained data on these 3 elements in 3 leading types of high-purity silica.

Experimental

Sample descriptions. (*1*) A solid rod segment of Engelhard "Suprasil" silica was obtained from Engelhard Industries, Inc. The lot No. was not listed, but the analytical data for this grade of silica show the following results: Fe$<$0.2 p.p.m.; Al, Mg and B$<$0.1 p.p.m.; other elements not detected. (*2*) Johnson-Matthey "Specpure" silica powder (catalog No. J.M. 425, lot No. S. 3819) was obtained from the Jarrell-Ash Company. The lot analysis showed: Na$<$2 p.p.m.; Cu, Mg$<$1 p.p.m.; and other elements not detected. (*3*) Spex "6-9's" silica powder (catalog No. 1250, lot No. 08661) was obtained from Spex Industries, Inc. The lot analysis showed: Cu, 0.5–1.0 p.p.m.; Al, Ti and Mg, 0.1–0.5 p.p.m.; other elements not detected.

Procedure. The neutron-activation analytical procedures were very similar to those described previously for gallium and germanium[1] and for indium[2]. Samples of Suprasil were irradiated as single fragments and the surface cleaned by etching following the irradiation. The other samples were irradiated in the powdered form in which they were received. The samples were dissolved in hydrofluoric acid, evaporated to dryness, and taken up in water. The remainder of the procedure was very similar to those given in refs. 3 and 4.

γ-Counting was used exclusively. All processed samples were of good radiochemical purity except for occasional contamination of indium by ^{31}Si. In such cases the indium sample was repurified or the 1.10-MeV peak was summed for the determination.

Results and discussion

The results of our study are shown in Table I. The lowest concentrations of In, Ga and Ge were found in the Engelhard "Suprasil" silica. In this material no definite γ-ray peaks could be distinguished for germanium or indium in any of the 3 replicate samples. Upper limits have been assigned on the basis of the observed amount of decay observed in the γ-ray energy range normally counted, plus 2 standard deviations based on counting statistics. The median value was somewhat arbitrarily chosen as the mean upper limit for these elements. The actual concentration may be considerably lower than these upper limits.

A surprising degree of variation was observed in the gallium content of the Engelhard silica and in the gallium and germanium contents of the Spex silica. The mean values listed for these samples are geometric means. We interpret these variations as sampling inhomogeneities, but such variations are surprising since the host material consists of a single phase. We have not observed such large variations in our stony meteorite analyses[4,5]. The variations in the Spex samples may result from small bits of foreign matter introduced in the grinding. We are unable to explain the variations in the Engelhard sample. The Johnson-Matthey sample was the more uniform. However, it showed the highest indium and gallium contents of the 3 samples. The Suprasil indium upper limits reported are considerably lower than the value of 0.11 p.p.b. reported by GLEIT *et al.*[2].

Engelhard "Suprasil" is clearly well suited to the determination of sample-

TABLE I

In, Ga AND Ge CONCENTRATIONS IN HIGH-PURITY SILICA

Sample	*In* *(p.p.b.)*	*Ga* *(p.p.b.)*	*Ge* *(p.p.b.)*
Engelhard "Suprasil"	≤ 0.004	6.7	≤ 15
	≤ 0.02	15.6	≤ 47
	≤ 0.015	1.5	≤ 7
	Mean ≤ 0.02	Mean[a] 5.4	Mean ≤ 15
Johnson-Matthey "Specpure"	16	39	$2.3 \cdot 10^2$
	10	24	$2.5 \cdot 10^2$
	15	24	$2.3 \cdot 10^2$
	Mean 14	Mean 29	Mean $2.4 \cdot 10^2$
Spex "6-9's"	0.35	—	—
	0.32	49	$8.1 \cdot 10^2$
	0.30	5.5	$2.0 \cdot 10^2$
	0.55	4.3	$1.1 \cdot 10^2$
	Mean 0.38	Mean[a] 10.5	Mean[a] $2.6 \cdot 10^2$

[a] The listed mean is the geometric mean.

preparation blanks. The results of 5 replicate runs on this material ground in a "Diamond" steel mortar gave In, Ga and Ge concentration levels of *ca.* 0.1 p.p.b., *ca.* 15 p.p.b. and <50 p.p.b., respectively[5]. Thus, our blanks were found to be appreciable for indium; they were negligible for the other elements (as compared to chondritic concentration levels) and perhaps as low as the Suprasil concentration levels. These values may all be somewhat higher than true silicate analysis blanks because of a larger amount of erosion of the mortar resulting from the greater hardness of the silica.

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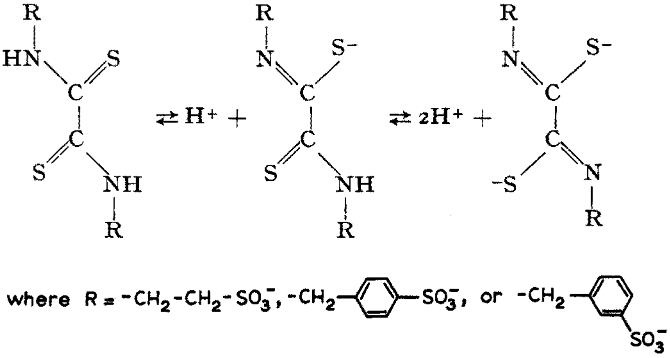
Spectrophotometric determination of the dissociation constants of N,N'-bis(2-sulphoethyl)dithiooxamide, N,N'-bis(*p*-sulphobenzyl)dithiooxamide and N,N'-bis(*m*-sulphobenzyl)dithiooxamide

This paper deals with the results of the spectrophotometric determination of the dissociation constants of N,N'-bis(2-sulphoethyl)dithiooxamide (SEDTO), N,N'-bis(*p*-sulphobenzyl)dithiooxamide (*p*-SBDTO) and N,N'-bis(*m*-sulphobenzyl)-dithiooxamide (*m*-SBDTO). As reported earlier[1-4], dithiooxamide (DTO) derivatives behave as weak dibasic acids. The dissociation can be described in the following manner[5].



$$H_2X^{2-} \rightleftarrows H^+ + HX^{3-} \rightleftarrows 2\,H^+ + X^{4-}$$

For the estimation of the dissociation constants of weak dibasic acids, spectrophotometric methods have been preferred by several workers[6,7].

As discussed in a previous report[3], the following transformation of the equation, giving a general relationship between the optical absorbance and the hydrogen ion concentration, was used in this investigation:

$$(\varepsilon_1 - \varepsilon_n)\,[H^+]^2/K_1 + \varepsilon_2[H^+] + \varepsilon_3 K_2 - \varepsilon_n K_2 = \varepsilon_n[H^+] \qquad (1)$$

where $K_1 = (HX^{3-})[H^+]/(H_2X^{2-})$ and $K_2 = (X^{4-})[H^+]/(HX^{3-})$; and ε_1, ε_2 and ε_3 are the molar extinction coefficients of the species H_2X^{2-}, HX^{3-} and X^{4-} respectively. ε_n is the apparent extinction coefficient and is obtained from the measurement of the optical absorbance.

$$E = \varepsilon_n \cdot L \cdot C_{H_2X^{2-}}$$

where L = optical path length (cm) and $C_{H_2X^{2-}} = (H_2X^{2-}) + (HX^{3-}) + (X^{4-})$.

The value of ε_1 is directly obtained from absorbance measurements at low pH values where $C_{H_2X^{2-}} = (H_2X^{2-})$ and hence $E = \varepsilon_1 \cdot L \cdot C_{H_2X^{2-}}$. Considering this, eqn. (1) is linear in 4 unknown parameters: $1/K_1$, ε_2, $\varepsilon_3 K_2$ and K_2.

Absorbance measurements at different pH values give a set of equations from which the best estimates for these unknowns are obtained by means of the weighted least squares method[3].

TABLE I

DISSOCIATION CONSTANTS OF N,N′-BIS(2-SULPHOETHYL)DITHIOOXAMIDE AT DIFFERENT IONIC STRENGTHS

Wavelength (nm)	$\mu = 0.01$		$\mu = 0.025$		$\mu = 0.05$		$\mu = 0.1$		$\mu = 0.2$		$\mu = 0.3$		$\mu = 1.0$			
	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_2 $(\cdot 10^{-13})$	pK_2
270	3.13	11.51	3.93	11.41	4.81	11.32	6.17	11.21	7.89	11.10	9.21	11.04	2.24	10.65	4.94	13.31
271	3.20	11.50	3.98	11.40	4.84	11.32	6.14	11.21	7.88	11.10	9.27	11.03	2.21	10.65	4.50	13.35
272	3.19	11.50	3.94	11.41	4.80	11.32	6.07	11.22	7.58	11.12	9.27	11.03	2.26	10.65	4.68	13.33
273	3.17	11.50	4.00	11.40	4.78	11.32	6.11	11.21	7.86	11.10	9.35	11.03	2.32	10.64	4.68	13.33
274	3.24	11.49	4.00	11.40	4.82	11.32	6.08	11.22	7.77	11.11	9.31	11.03	2.28	10.64	4.66	13.33
275	3.17	11.50	3.94	11.41	4.71	11.33	6.01	11.22	7.98	11.10	9.41	11.03	2.36	10.64	4.98	13.30
Mean	3.18	11.50	3.97	11.40	4.79	11.32	6.10	11.21	7.38	11.11	9.48	11.03	2.28	10.64	4.74	13.33
Std. dev.		±0.01		±0.01		±0.01		±0.01		±0.01		±0.01		±0.01		±0.03

TABLE II

DISSOCIATION CONSTANTS OF N,N′-BIS(SULPHOBENZYL)DITHIOOXAMIDES AT DIFFERENT IONIC STRENGTHS

Wave length (nm)	$\mu = 0.01$		$\mu = 0.05$		$\mu = 0.1$		$\mu = 0.26$		$\mu = 0.5$		$\mu = 1.0$			
	K_1 $(\cdot 10^{-12})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_1 $(\cdot 10^{-11})$	pK_1	K_2 $(\cdot 10^{-14})$	pK_2
N,N′-bis(p-sulphobenzyl)dithiooxamide														
265	9.56	11.02	1.47	10.83	1.62	10.79	2.10	10.68	2.90	10.54	3.25	10.49		
266	9.41	11.03	1.49	10.83	1.69	10.77	2.11	10.68	2.91	10.54	3.40	10.47		
267	9.38	11.03	1.51	10.82	1.64	10.79	2.11	10.68	2.95	10.53	3.31	10.48		
268	9.53	11.02	1.49	10.83	1.64	10.79	2.12	10.67	2.89	10.54	3.43	10.45		
269	9.67	11.01	1.51	10.82	1.64	10.79	2.11	10.68	2.89	10.54	3.30	10.48		
270	9.48	11.02	1.48	10.83	1.63	10.79	2.14	10.67	2.87	10.54				
280											3.38	10.47	3.24	13.49
281											3.22	10.49	3.04	13.52
282											3.80	10.42	2.93	13.53
Mean	9.51	11.02	1.49	10.83	1.64	10.79	2.11	10.68	2.90	10.54	3.39	10.47	3.07	13.51
Std. dev.		±0.01		±0.01		±0.02		±0.01		±0.01		±0.02		±0.02
N,N′-bis(m-sulphobenzyl)dithiooxamide														
265	8.52	11.07	1.30	10.89	1.62	10.79	1.97	10.71	2.31	10.64	2.63	10.58		
266	8.93	11.05	1.30	10.89	1.60	10.80	1.97	10.71	2.31	10.64				
267	8.65	11.06	1.30	10.89	1.66	10.78	1.96	10.71	2.24	10.65	2.35	10.63		
268	8.59	11.07	1.35	10.87	1.67	10.78	2.05	10.69	2.32	10.63				
269	8.87	11.05	1.35	10.87	1.68	10.78	1.98	10.70	2.33	10.63				
270	8.81	11.06	1.36	10.87	1.69	10.79	1.98	10.70	2.35	10.63	2.64	10.58		
280											2.55	10.59	2.50	13.60
281											2.46	10.61	2.51	13.60
282											2.50	10.60	1.98	13.70
Mean	8.73	11.06	1.32	10.88	1.65	10.78	1.98	10.70	2.31	10.64	2.52	10.60	2.32	13.63
Std. dev.		±0.02		±0.01		±0.02		±0.02		±0.01		±0.02		±0.07

At low pH values, only the first step dissociation occurs. Since $K_1 \gg K_2$, the term $K_2(\varepsilon_3 - \varepsilon_n)$ may be neglected in the general eqn. (1).

Equation (1) becomes:

$$(\varepsilon_1 - \varepsilon_n)[\mathrm{H}^+]/K_1 + \varepsilon_2 = \varepsilon_n \qquad (2)$$

with only 2 unknowns: $1/K_1$ and ε_2.

Apparatus

Absorbance measurements were made with a Hilger Uvispek spectrophotometer. Matched silica cells of 1 cm light path were used. The pH values were determined by means of a lithium glass electrode and a Pye Dynacap pH millivolt meter. All measurements were made at 25°.

Reagents and solutions

The dithiooxamide derivatives were prepared as reported in a previous study[8]. The total concentration $C_{\mathrm{H_2X^{2-}}}$ in all measurements was $5 \cdot 10^{-5}$ *M* for N,N'-bis(2-sulphoethyl)dithiooxamide, and $1 \cdot 10^{-4}$ *M* for N,N'-bis(*p*-sulphobenzyl)dithiooxamide and N,N'-bis(*m*-sulphobenzyl)dithiooxamide.

Buffer solutions were obtained by mixing adequate amounts of 0.2 *M* glycine solution with 0.2 *N* potassium hydroxide solution as described by KRATZ[9].

To control the ionic strength, potassium chloride was used as an indifferent electrolyte. The measured optical absorbance was corrected for absorption of the solvent, buffer and indifferent electrolyte.

Results

The results obtained by the described method are summarized in Tables I and II. For the calculation of K_1, eqn. (2) was used for ionic strengths up to $\mu = 0.5$. Equation (1) giving K_1 and K_2, could only be used at ionic strength $\mu = 1$. Indeed, the second dissociation, even at the highest pH values obtainable with lower ionic strengths, was too weak to obtain reliable measurements.

When the Debye–Hückel[10] equation was applied for the activity coefficient f_1 for ionic strengths up to $\mu = 0.1$, a mean value of the thermodynamic $\mathrm{p}K_1{}^{\mathrm{T}}$ was obtained from the formula $\mathrm{p}K_1{}^{\mathrm{T}} = \mathrm{p}K_1 + \log f_1$.

TABLE III

CALCULATED VALUES FOR $\log f_1$ AND THERMODYNAMIC VALUES OF THE FIRST DISSOCIATION CONSTANT $K_1{}^{\mathrm{T}}$ OF SEDTO, *m*-SBDTO AND *p*-SBDTO OBTAINED FROM EQN. (3) FOR IONIC STRENGTHS UP TO $\mu = 0.1$

μ	$\log f_1$	SEDTO			*p*-SBDTO			*m*-SBDTO		
		pK_1	pK_1^T	K_1^T $(\cdot 10^{-12})$	pK_1	pK_1^T	K_1^T $(\cdot 10^{-12})$	pK_1	pK_1^T	K_1^T $(\cdot 10^{-12})$
0.01	0.22	11.50	11.72	1.91	11.02	11.24	5.75	11.06	11.28	5.25
0.025	0.32	11.40	11.72	1.91						
0.05	0.41	11.32	11.73	1.86	10.83	11.24	5.75	10.88	11.29	5.13
0.10	0.53	11.21	11.74	1.82	10.79	11.32	4.79	10.78	11.31	4.90
		Mean	11.73	1.87	Mean	11.27	5.43	Mean	11.29	5.09

Since H_2X^{2-} and HX^{3-} behave as 2–1 and 3–1 electrolytes

$$\log f_1 = 5 \cdot 0.506 \cdot \sqrt{\mu}/(1 + 1.6\sqrt{\mu}) \qquad (3)$$

The results obtained by eqn. (3) are summarized in Table III.

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Spectrofluorimetric determination of trace amounts of cerium in yttrium oxide

The determination of trace amounts of cerium has been accomplished by various spectrophotometric methods which are based on the oxidation of different dyes by cerium(IV)[1–3]. A serious shortcoming of these methods is the interference by other oxidizing agents, notably Fe^{3+} ion. Traces of cerium have also been determined by complex formation[4,5] and extraction[6,7]; and by direct spectrophotometric determination of the cerium(III) ion[8]. These methods, however, present difficulties when analyses are made in the region below 10 p.p.m. cerium.

ARMSTRONG *et al.*[9] suggested the possibility of determining the cerium(III) ion by a fluorimetric technique; later, KIRKBRIGHT *et al.*[10] applied the fluorescence of the cerium(III) ion to the indirect determination of arsenic(V), iron(III) and iodide.

The determination of trace amounts of cerium in yttrium oxide is not feasible in a sulfuric acid medium because of the low solubility of yttrium sulfate. KIRKBRIGHT *et al.*[11] reported interferences from copper(I), lead(II) and tin(II) in hydrochloric acid solution. The fluorescence of cerium(III) does not materialize in a nitric acid media. Perchloric acid was found to be a favorable solvent owing to the high solubility of yttrium perchlorate and to the absence of interferences in yttrium oxide.

The following procedure is a rapid, direct method for the determination of cerium in yttria. It is based on the dissolution in perchloric acid, reduction of cerium(IV) to cerium(III), and the measurement of the fluorescence of cerium(III) with 260 nm as the excitation wavelength and 355 nm as the emission wavelength. With this method, the detection of 0.1 μg of cerium per gram of yttrium oxide was possible.

Apparatus

A Beckman DU Spectrophotometer was used with a Beckman No. 73500 fluorescence attachment. To provide the necessary excitation at 260 nm, a short-wave (germicidal) mercury lamp was used as the source instead of the "black lamp" supplied by the manufacturer. A narrow bandpass filter (Baird Atomic Interference filter, type A-2, wavelength 2540 Å), which passed 253 nm but filtered out 350-nm radiation, was applied. In this manner the cerium 355-nm emission wavelength was measured without any interference from the radiation of the mercury germicidal lamp. In order to achieve a high degree of reproducibility of measurements, it was necessary to shield the detector from stray radiation from fluorescent room lights.

Reagents

Cerium(IV) sulfate stock solution. 1.006 mg of cerium per milliliter in 3% sulfuric acid media. This solution was standardized by the classical oxalate method, and further dilutions of the stock solution were prepared as necessary.

Titanium(III) sulfate stock solution. 100 mg of titanium sponge metal (LECO 501-94) was dissolved in 100 ml 25% sulfuric acid. This solution must be prepared fresh daily.

Procedure

Weigh a 0.5-g sample of yttrium oxide into a 50-ml beaker, and add 1 ml of distilled water followed by 1.5 ml of 70–72.5% perchloric acid. Place on a hot plate and heat gently until the sample has dissolved, swirling the beaker to prevent bumping. Add 5 ml of distilled water, cool and transfer to a 10-ml volumetric flask; add 1 ml of titanium(III) solution, mix, dilute to mark with distilled water and mix. Transfer the solution to a 15-ml Beckman Vycor cuvette supplied with the Beckman instrument, use the following instrument settings and read.

Instrument settings

Sensitivity switch: FULL position
Sensitivity control knob: Extreme counter clockwise position
Slit: 1.8 mm
Wavelength: 355 nm
Range setting: 0.1 for concentrations below 7 p.p.m. Ce, and 1.0 for concentrations above 7 p.p.m. Ce.

Calibration curve. Into a series of volumetric flasks each containing about 3 ml of water, transfer 0, 0.1, 0.3, 0.5, 0.7 and 1.0 ml of cerium(III) stock solution (10 μg/ml). To each flask add 1.5 ml of 70–72% perchloric acid followed by 1 ml of titanium(III) solution, mix, dilute with distilled water to the mark and mix. Transfer the solutions to the 15-ml cuvette and continue as described above.

Results and discussion

The analytical curve for the above procedure was found to be linear over the range 0.1 to at least 150 μg of cerium per g of Y_2O_3. The standards were stable for a period of 24 h. A typical calibration curve intersected the relative fluorescence axis at a value of *ca.* 18, the relative fluorescence reading for 10 p.p.m. Ce being *ca* 110.

Synthetic samples containing 0.5 g of Y_2O_3 and different amounts of cerium(IV) sulfate were prepared and analyzed; the results are presented in Table I. The analytical data presented in Table II compare the results obtained on samples previously analyzed by solid-state mass spectroscopy or by extraction and spectrophotometric techniques employing thenoyltrifluoracetone[7], with those obtained by the proposed technique.

TABLE I

ANALYSIS OF SYNTHETIC SAMPLES

(Matrix: 0.5 g of Ce-free yttrium oxide)

Ce added (µg)	*Ce recovered (µg)*
1.0	1.0, 0.7, 1.0. Av. 0.9
3.0	3.05, 3.05, 3.10. Av. 3.05
5.0	5.0, 4.8, 4.8. Av. 4.9

TABLE II

COMPARATIVE ANALYTICAL RESULTS

A. Comparison with solid state mass-spectroscopic results		*B. Comparison with TAA-spectrophotometric results*	
Spectrofluorimetric results Ce (p.p.m.)	*Mass. spec. results Ce (p.p.m.)*	*Spectrofluorimetric results Ce (p.p.m.)*	*TTA results Ce (p.p.m.)*
0.1	<1	3	2
0.1	<1	5	9
0.5	<1	7	10
1	2	25	23
5	3	43	34
11	8		
27	23		

The fluorescence of cerium(III) was not affected by varying the amount of perchloric acid in the range 0.5 to 2.5 ml per 10 ml.

Interference studies

Solid-state mass spectroscopy indicated that the Y_2O_3 employed in this study contained impurities of the 4f-type rare earths, and Th, Fe, Pb, Ni, Cr, Ca, F and Cl. The effect of these impurities on the proposed method was examined (Table III). Iron(III) interfered seriously since $Fe(ClO_4)_3$ absorbs strongly in the UV region at 260 nm which is the excitation wavelength for cerium(III). Similarly, trace amounts of nitrates caused an interference. Thus, the analytical fluorescence of cerium(III) cannot materialize in the presence of iron(III) and nitrate ions since these ions absorb most of the excitation energy. The interference of iron(III) present in Y_2O_3 (*ca.* 50 p.p.m. Fe), can be eliminated by reducing iron(III) to iron(II).

TABLE III

INTERFERENCE STUDY

(5.0 μg of Ce taken)

Foreign ion	*Ce recovered (μg)*	*Foreign ion*	*Ce recovered (μg)*
—	5.0	1 mg Lu^{3+}	5.0
1 g Y^{3+}	5.0	1 mg Th^{4+}	5.4
1 mg La^{3+}	5.2	1 mg Ca^{2+}	5.5
1 mg Pr^{3+}	4.5	1 mg Pb^{2+}	5.1
1 mg Nd^{3+}	4.5	1 mg Cu^{2+}	4.5
1 mg Sm^{3+}	5.1	1 mg Ni^{2+}	5.4
1 mg Eu^{3+}	5.0	50 μg Fe^{3+}	0
		200 μg Fe^{2+}	4.8
1 mg Gd^{3+}	5.3	1 mg Fe^{2+}	1.5
1 mg Tb^{3+}	5.0		
1 mg Dy^{3+}	4.8	1 mg Cl^-	4.5
1 mg Ho^{3+}	4.8	1 mg F^-	5.2
1 mg Tm^{3+}	5.0	50 μg NO_3^-	0
1 mg Yb^{3+}	5.0		

Hydrazine, hydroxylamine, hydrogen peroxide, *o*-phenylenediamine, hypophosphite, sulfurous acid, tartaric acid, tin(II) sulfate, thioglycolic acid, zinc metal or zinc amalgam will not reduce iron(III) quantitatively at the given perchloric acid concentration. Ascorbic acid, iodide or thiosulfate will accomplish this reduction in the given media, but quench the fluorescence of cerium(III). It was found, however, that titanium(III) sulfate employed as a reductant not only reduced iron(III) quantitatively, but did not affect the fluorescence of cerium(III).

Accuracy and precision

The accuracy and precision of the proposed method was found to be ±10% and the standard deviation for the 5 μg level was 6%.

The authors gratefully acknowledge the cooperation of DANIEL OBLAS, SOL WEISBERGER and EDWARD LANNING in providing data from mass spectroscopy, emission spectroscopy and absorption spectroscopy.

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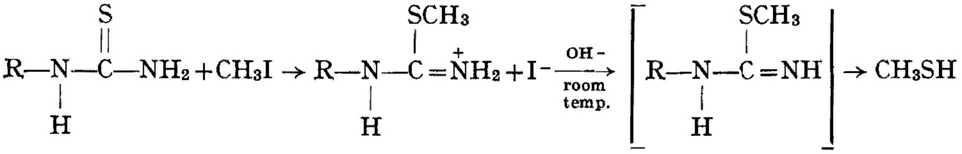
Categorization of N-substituted thioureas via their S-methyl derivatives

In the course of our work, a difference was noticed in the rate of alkaline hydrolysis of S-alkyl derivatives of thioureas which was dependent on the extent of N-substitution rather than on the nature of the substituents themselves. On the basis of this observation, it was established that thioureas, when grouped according to the degree of N-substitution, give S-alkyl derivatives which behave toward alkali in a characteristic manner. A procedure was developed to categorize thioureas which was based on the differences in the rate of methyl mercaptan formation from their easily prepared S-methyl derivatives.

S-Methylisothiuronium salts were obtained by refluxing an ethanol solution of the thiourea with 1.1 equivalents of methyl iodide. Evaporation of the solvent under reduced pressure gave the corresponding S-methylisothiuronium compounds which were generally purified by recrystallization from ethanol–ether. An alternative preparation of these salts was reported by Jensen and Nielsen[1] in which they used cold benzene or ether as a solvent. Many of the thioureas investigated by us were insoluble in these 2 solvents, hence, ethanol was preferred as the reaction medium.

The sensitive nitroprusside test was used as a means of detecting the liberated mercaptan. About 1 mg of the S-methyl derivative of the thiourea was dissolved in 0.2 ml of methanol and about 1 mg of sodium nitroprusside was added to the solution at room temperature. The mixture was agitated for a moment, and 1 drop of aqueous 10% sodium hydroxide was added. The immediate appearance of an intense red or reddish-purple color indicated the presence of the mercaptan. If a yellow (negative) or a very transient red color was produced, the test was repeated in the following manner. The S-methyl derivative (about 1 mg) was dissolved in 0.2 ml of methanol to which was added 1 drop of 10% sodium hydroxide. The mixture was heated on a steam bath for about 30 sec, cooled to room temperature, and about 1 mg of sodium nitroprusside was added. An intense red color indicated the liberation of methyl mercaptan. If the red color which developed was transient, regeneration of the red color by more nitroprusside was required for the test to be considered positive. The sodium nitroprusside was found to be best added to a solution at room temperature.

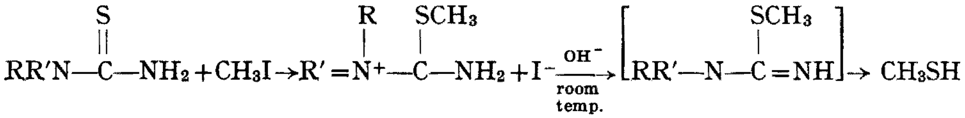
Thiourea and monosubstituted thioureas reacted with methyl iodide to give S-methyl derivatives that were unstable to alkaline treatment. Treatment of these isothiuronium salts with aqueous sodium hydroxide at room temperature as described above gave methyl mercaptan whose presence was readily detected with nitroprusside. Representative monosubstituted thioureas which were investigated included (thiourea, m.p. of S-methylisothiuronium iodide): 1-phenyl, 146°[2]; 1-(1-naphthyl), 183°[3]; 1-allyl, 69°[2]; 1-ethyl, 87°. When S-methyl-1-acetylisothiuronium iodide was prepared in ethanol, it underwent immediate hydrolysis with the



$$R{-}\underset{\substack{|\\ H}}{N}{-}\overset{\substack{S\\ \|}}{C}{-}NH_2 + CH_3I \rightarrow R{-}\underset{\substack{|\\ H}}{N}{-}\overset{\substack{SCH_3\\ |}}{C}{=}\overset{+}{N}H_2 + I^- \xrightarrow[\text{room temp.}]{OH^-} \left[R{-}\underset{\substack{|\\ H}}{N}{-}\overset{\substack{SCH_3\\ |}}{C}{=}NH \right] \rightarrow CH_3SH$$

evolution of methyl mercaptan. Because of the extreme sensitivity of S-methyl-1-acetylisothiuronium iodide (m.p. 162°) to hydrolysis, it was prepared using dry acetonitrile as a solvent. S-Methylisothiuronium sulfate, m.p. 235°[4], also liberated methyl mercaptan when treated with alkali.

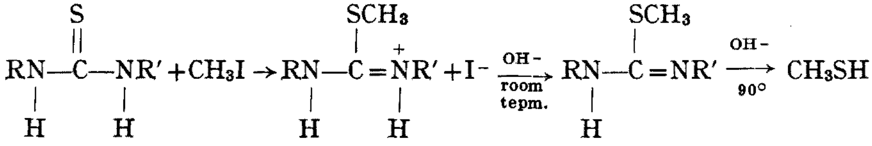
S-Methyl salts of 1,1-disubstituted thioureas gave free bases that were unstable to alkali. Therefore, treatment of these isothiuronium salts with aqueous sodium hydroxide at room temperature liberated methyl mercaptan.



$$RR'N-\overset{\overset{S}{\|}}{C}-NH_2+CH_3I\rightarrow R'=\overset{\overset{R}{|}}{N^+}-\overset{\overset{SCH_3}{|}}{C}-NH_2+I^-\xrightarrow[\text{room temp.}]{OH^-}\left[RR'-N-\overset{\overset{SCH_3}{|}}{C}=NH\right]\rightarrow CH_3SH$$

1,1-Disubstituted thioureas which were investigated included (thiourea, m.p. of S-methylisothiuronium iodide): 1,1-diphenyl, 160°[5]; 1-ethyl-1-phenyl, 170°; 1-ethyl-1-naphthyl, 181°.

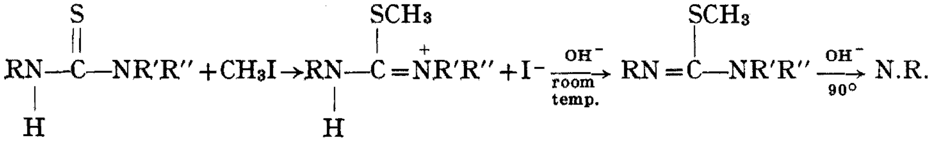
S-Methyl salts of 1,3-disubstituted thioureas gave free bases which were stable and isolable. Since treatment of these isothiuronium salts with sodium hydroxide at room temperature gave the S-methylisothiourea, a negative nitroprusside test was obtained. Heating the isothiourea with alkali for about 30 sec caused hydrolysis to



$$\underset{\underset{H}{|}}{RN}-\overset{\overset{S}{\|}}{\underset{\underset{H}{|}}{C}}-NR'+CH_3I\rightarrow \underset{\underset{H}{|}}{RN}-\overset{\overset{SCH_3}{|}}{C}=\underset{\underset{H}{|}}{\overset{+}{N}}R'+I^-\xrightarrow[\text{room tepm.}]{OH^-}\underset{\underset{H}{|}}{RN}-\overset{\overset{SCH_3}{|}}{C}=NR'\xrightarrow[90^\circ]{OH^-}CH_3SH$$

occur and liberated methyl mercaptan. 1,3-Disubstituted thioureas which were investigated included (thiourea, m.p. of S-methylisothiuronium iodide): 1,3-diethyl, 76°[2]; 1,3-di-*tert.*-butyl, 147°; 1,3-dibenzyl, 108°; 1,3-diphenyl, 165°[3]; 1-ethyl-3-phenyl, 113°; 1,3-di-*p*-tolyl, 171°; 1-thiazoyl-3-phenyl, 181°.

Trisubstituted thioureas gave S-methyl derivatives whose free bases were stable to alkali treatment, even for several hours. Therefore, heating the test mixture on a steam bath for 30 sec with alkali did not cause the formation of methyl mercaptan. This contrasts with the results obtained with the S-methyl derivatives of 1,3-disubstituted thioureas, described above. The stability of S-methyl-1,1,3-trimethylisothiourea was observed by LECHER AND HENCH in 1924[6]. Trisubstituted thioureas which were investigated included (thiourea, m.p. of S-methylisothiuronium

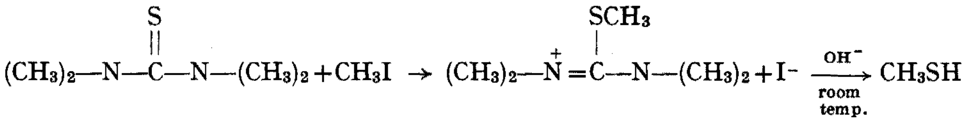


$$\underset{\underset{H}{|}}{RN}-\overset{\overset{S}{\|}}{C}-NR'R''+CH_3I\rightarrow \underset{\underset{H}{|}}{RN}-\overset{\overset{SCH_3}{|}}{C}=\overset{+}{N}R'R''+I^-\xrightarrow[\text{room temp.}]{OH^-}RN=\overset{\overset{SCH_3}{|}}{C}-NR'R''\xrightarrow[90^\circ]{OH^-}\text{N.R.}$$

iodide): 1-phenyl-3,3-pentamethylene, 140°; 1,1,3-trimethyl, oil; 1,1-dimethyl-3-phenyl, 133°[2]; 1,1-dimethyl-3-(1-naphthyl), 139°; 1,1-dimethyl-3-octadecyl, 85°.

1,1,3,3-Tetramethyl-2-thiourea gave an S-methyl derivative that behaved like

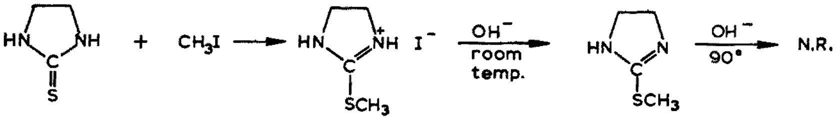
S-methyl monosubstituted thioureas in that it was unstable to base at room temperature resulting in the rapid formation of methyl mercaptan.



$$(CH_3)_2\text{—N—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—N—}(CH_3)_2 + CH_3I \rightarrow (CH_3)_2\text{—}\overset{+}{N}=\overset{\overset{\displaystyle SCH_3}{|}}{C}\text{—N—}(CH_3)_2 + I^- \xrightarrow[\text{room temp.}]{OH^-} CH_3SH$$

S-(2-Aminoethyl)-1,1,3,3-tetramethylisothiuronium bromide hydrobromide was also unstable to alkaline treatment and gave a positive nitroprusside test after treating with aqueous sodium hydroxide. Presumably, other tetraalkyl-substituted thioureas would behave in a like manner.

The two disubstituted cyclic thioureas that were studied were stable to alkali treatment and thus behaved like trisubstituted thioureas. Methyl mercaptan was not liberated by heating with alkali on a steam bath for 30 sec; therefore, the nitroprusside test was negative. The two cyclic thioureas that were studied are (thiourea, m.p. of S-methylisothiuronium iodide): 2-imidazolidinthione, 143°; hexahydropyrimidine-2-thione, 148°.



Further qualitative information can be obtained by using the silver nitrate test[7] for thiourea. This test consisted of dissolving 2 mg of the thiourea in a minimum of methanol, adding 1 drop of 28% ammonium hydroxide, followed by 2 drops of ethanolic 2% silver nitrate. With thiourea and mono- and disubstituted thioureas, a black precipitate of silver sulfide was rapidly formed. However, trisubstituted thioureas did not give a black precipitate with this reagent nor did 1,1,3,3-tetramethyl-2-thiourea.

In summary, it was observed that the S-methyl derivatives of mono-, 1,1-disubstituted thioureas and 1,1,3,3-tetramethyl-2-thiourea liberated methyl mercaptan when treated with aqueous sodium hydroxide at room temperature. S-Methyl derivatives of 1,3-disubstituted thioureas did not liberate methyl mercaptan when treated with sodium hydroxide at room temperature, but did so when heated with alkali on a steam bath. S-Methyl derivatives of trisubstituted and cyclic thioureas did not liberate methyl mercaptan when treated with sodium hydroxide either at room temperature or when heated for a short time on a steam bath.

Satisfactory analyses were obtained for all new compounds synthesized in this work. The test results were based on work with pure samples; impure samples usually gave ambiguous results.

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BOOK REVIEWS

P. DELAHAY (Editor), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, Interscience Publishers–John Wiley and Sons, New York–London–Sydney, 1966, 389 pp., 120 s.

Ce 4ème volume de la série est, comme les précédents, consacré à des revues sur des sujets d'électrochimie particulièrement actuels.

C. WAGNER traite de la force électromotrice des cellules galvaniques comportant des variations locales de composition (46 pages). Le calcul de la force électromotrice à partir des équations de la thermodynamique irréversible est appliqué à des exemples variés comportant des solvants, des solvants mixtes, des sels fondus et des solides.

Une revue de A. C. RIDDIFORD porte sur l'électrode tournante à disque de platine (70 pages). Après la théorie fondamentale, puis la description des divers types d'électrode, le principe des applications, aujourd'hui très nombreuses, est abordé.

Les processus à l'électrode dans les sels fondus sont traités par A. D. GRAVES, G. J. HILL ET D. IMMAN (68 pages). Après un rappel des propriétés des sels fondus et la description de la technique des opérations, les phénomènes rapides et lents aux électrodes sont abordés sur de nombreux exemples dans des sels fondus variés.

G. J. HILLS ET P. J. OVENDEN traitent des propriétés électrochimiques sous des pressions élevées (64 pages). L'effet de la pression allant jusqu'à plusieurs milliers d'atmosphères a été étudié en ce qui concerne diverses propriétés; constante de dissociation des électrolytes, conductivité, nombres de transport, etc. Les techniques mises en oeuvre et les méthodes de mesure sont décrites.

La théorie des réactions d'oxydo–réduction en solution a été traitée par V. G. LEVICH (124 pages) dans un article particulièrement important. La cinétique, le mécanisme du transfert d'électrons, l'influence et la caractérisation du solvant ont été abordés.

La bibliographie est abondante. Le choix des auteurs et des sujets maintiennent l'intérêt du physicochimiste et aussi du chimiste pour cette collection.

G. CHARLOT (Paris)

A. E. MARTIN, *Infra-red Instrumentation and Techniques*, Elsevier Publishing Company, Amsterdam, 1966, x+180 pp., price Dfl. 32.50.

The wide availability and application of infrared measurements ensures considerable interest in any work describing the instrumentation and techniques of this branch of spectroscopy particularly when the author occupies a position of the eminence and authority of Dr. MARTIN. His book falls into two parts: the longer (120 pp.) providing an account of instrument design and theory; the shorter dealing with accessories and experimental methods.

The range of the subject matter is necessarily wide but space has been found to include useful descriptions of much equipment only recently made available. Less happily, the pressure on space elsewhere has reduced the treatment of many sections to a superficial level and this must seriously restrict the book's utility for reference purposes. It is particularly unfortunate that no room was found for any adequate discussion of intensity measurements. The author's aim of providing a satisfactory guide for prospective instrument users, research workers and instrument designers is laudable but it seems unlikely that the present book will satisfy the needs of any of these audiences.

K. J. MORGAN (Lancaster)

D. O. HUMMEL, *Infrared Spectra of Polymers*, Interscience Publishers–John Wiley & Sons, New York, 1966, viii + 207 pp., price 90 s.

One of the most valuable recent developments in the analytical application of infrared spectroscopy has been the interest devoted to the far infrared region (600–200 cm^{-1}). The utility of this spectral region in providing structural information for polymer samples is well recognised and the need for a catalogue of published spectra is increasingly apparent. Dr. HUMMEL's book seeks to provide such a survey of the spectral data.

The main part of the text (76 pp.) contains a survey of the literature of the far infrared spectra of polymers and monomers covering the period to 1963–1964. The survey is by no means comprehensive and is largely uncritical but the collection of references provides a useful guide to the older literature. It is however surprising to find so much of this short review section devoted to data for the near infrared spectral region, a region which has received extensive discussion elsewhere.

The second and largest part of the book contains the spectra of 192 specimens of polymers, monomers, plasticizers and solvents over the range 800–250 cm^{-1}. While an atlas of such spectra must be useful, the method chosen for presentation of the spectra minimises its effectiveness. In particular, the scale of the diagrams is small and the quality of the spectra is poor. Despite this, space is found to include the spectra of similar samples in the rock salt regions but in addition to the small scale and variable quality of these spectra the reproduction is in many cases indistinct. Further whereas the far infrared spectra are recorded linear in wavenumber, the near infrared spectra are shown linear in wavelength. In view of the potential market for this book both by virtue of the subject's growing interest and its listing as Volume 14 of Polymer Reviews the publishers cannot be complimented on the quality of this work.

K. J. MORGAN (Lancaster)

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562 E

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(continued on page 4 of cover)

(contents, continued from page 3 of cover)

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