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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 35, No. 3, July 1966

POLAROGRAPHIC REDUCTION OF PYRIDINIUM ION IN PYRIDINE

TETRAETHYLAMMONIUM PERCHLORATE AS BACKGROUND ELECTROLYTE

Tetraethylammonium perchlorate, compared to lithium perchlorate as background electrolyte for the reduction of pyridinium ion in pyridine, is effective over a wider potential range, but is more difficult to obtain in a pure state; slight amounts of impurities do not, however, affect the pyridinium wave. The pyridinium wave produced in 0.1 M $\mathrm{Et_4NClO_4}$ may occur at a more negative potential than the main pyridinium wave in 0.1 M $\mathrm{LiClO_4}$, depending on the source of the pyridinium ion, but still appears to be due to a diffusion-controlled reduction, whose limiting current is linearly proportional to concentration; the prewave observed in $\mathrm{LiClO_4}$ background generally does not appear in $\mathrm{Et_4NClO_4}$ background. Specific differences in the effect of Li(I), Na(I) and $\mathrm{Et_4N}$(I) background cation appear to be due to electrocapillary phenomena and perhaps to the extent of solvation of the ions. The constancy of current for solutions containing acetic acid with added acetate, pyridinium nitrate with added nitrate, and benzoic acid with added benzoate indicate that the pyridinium reduction is independent of anion concentration.

J. E. Hickey, M. S. Spritzer and P. J. Elving,
Anal. Chim. Acta, 35 (1966) 277–285

COMPLEX FORMATION OF COPPER(II) WITH CHROME AZUROL S

The complex formation of copper(II) with chrome azurol S (CAS) was studied by spectrophotometric and potentiometric methods. In the pH range 5–7, two complexes with the composition $\mathrm{Cu(H_2O)_2}$-$\mathrm{HCAS^-}$ and $\mathrm{(Cu(H_2O)_2)_2CAS}$ were detected; the stability constants were calculated to be $\log K = 4.02 \pm 0.05$ and $\log K = 13.7 \pm 0.1$, respectively (at 25° and ionic strength 0.1 (KCl)). A comparison is made between the copper(II)–CAS and iron(III)–CAS systems.

A. Semb and F. J. Langmyhr,
Anal. Chim. Acta, 35 (1966) 286–292

STABILIZATION OF GERMANIUM(II) BY COMPLEX FORMATION IN IODIMETRIC TITRATION OF GERMANIUM

Four factors are important in the reduction of germanium(IV) by hypophosphite, namely, proper acidity, temperature, proper concentration of complexing ligand, and time of heating. The complexing ligand is needed to stabilize the germanium(IV) ions. Halides, with the exception of fluoride, and phosphate are good complexing ligands for germanium. Tin is quantitatively reduced and titrated under the same conditions. Many foreign ions do not interfere, so that prior separation of germanium can often be avoided. Successful results are presented for titrating germanium in the presence of many metals and for direct determination of germanium in actual samples. Germanium after reduction may be titrated with an iodate solution potentiometrically. The formal oxidation potentials of some germanium half-reactions were estimated and used to interpret the stabilization of germanium(II) by complex formation. Phosphoric acid is recommended as the reduction medium.

K. L. Cheng,
Anal. Chim. Acta, 35 (1966) 293–302

SPECTROFLUORIMETRIC TRACE DETERMINATION OF TERBIUM(III) WITH POTASSIUM OXALATE

Potassium oxalate acts as a specific reagent in enhancing the fluorescence intensity of terbium in aqueous solutions. Maximum fluorescence intensity is obtained by irradiating (at 255 mμ) terbium(III) dissolved in 0.01 M potassium oxalate solution at pH 7.8. The enhancement and quenching phenomena caused by other lanthanides, errors in the determination, and various examples of spectrofluorimetric analysis of traces of terbium in mixtures with other lanthanides are described. The sensitivity of the method is $5 \cdot 10^{-2}$ μg/ml of terbium.

G. Alberti and M. A. Massucci,
Anal. Chim. Acta, 35 (1966) 303–308

DIRECT FLUORIMETRIC DETERMINATION OF SUBMICRO TRACES OF BORON IN HIGH PURITY SODIUM HYDROXIDE WITH 2-HYDROXY-4-METHOXY-4′-CHLOROBENZOPHENONE

(in French)

A method based on the highly sensitive fluorescent reaction of boric acid with 2-hydroxy-4-methoxy-4′-chlorobenzophenone (H.M.C.B.), is described for the direct determination of traces of boron in "analytical grade" sodium hydroxide. In the nanogram range, the reliability of the H.M.C.B. method is satisfactory; the fluorescent reaction is not affected by up to 8% (v/v) of water. The sample is dissolved directly in concentrated sulfuric acid and no preliminary separation is needed. Interferences from other impurities of sodium hydroxide are negligible. Results for five different "analytical grade" reagents were: $(0.9 \pm 0.2) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(4.0 \pm 0.4) \cdot 10^{-6}$ and $(2.0 \pm 0.16) \cdot 10^{-6}$% B.

M. Marcantonatos, D. Monnier and J. Daniel,
Anal. Chim. Acta, 35 (1966) 309–316

SPECTROPHOTOMETRIC DETERMINATION OF NITRATE USING CHROMOTROPIC ACID

A spectrophotometric method is described for the determination of nitrate in the 0.5 to 50 μg range using chromotropic acid as the reagent and masking agents for the elimination of possible critical interferences due to chloride, chlorine, iron(III) and oxidants. The method can be applied directly for the determination of 0.2–20 mg of nitrate/l in 2.5-ml samples of water. Over 4000 mg of chloride/l can be tolerated. The method is simple, rapid and reliable. At the 1 mg/l level for nitrate the coefficient of variation at the 95% confidence limit is 4%. There are no interferences.

P. W. WEST AND T. P. RAMACHANDRAN,
Anal. Chim. Acta, 35 (1966) 317–324

SPECTROPHOTOMETRIC DETERMINATION OF DIETHYLLEAD AND DIETHYLTIN IONS WITH 4-(2-PYRIDYLAZO)-RESORCINOL

A study was made of the reaction of diethyllead and diethyltin ions with 4-(2-pyridylazo)-resorcinol; the compositions and the molar extinction coefficients of the compounds formed were determined. Methods are outlined for the determination of these organometallic cations. A method is described for the determination of lead chloride in the presence of $(C_2H_5)_2PbCl_2$.

G. PILLONI AND G. PLAZZOGNA,
Anal. Chim. Acta, 35 (1966) 325–329

SPECTROPHOTOMETRIC DETERMINATION OF HYDRAZINE AND 1,1-DIMETHYLHYDRAZINE, SEPARATELY OR IN ADMIXTURE

A rapid, sensitive spectrophotometric method for the determination of hydrazine and 1,1-dimethylhydrazine, separately or in mixtures of varying proportions, is described. The analysis is based on the well-known reaction of these compounds with salicylaldehyde to form, in the case of hydrazine, a symmetrical azine, or with 1,1-dimethylhydrazine, a hydrazone. Absorbance measurements were made in the ultraviolet at wavelengths characteristic of the derivatives and of salicylaldehyde; the results were calculated by means of simultaneous equations. The procedure is sensitive to concentrations of hydrazine as low as 0.3 μg/ml and of 1,1-dimethylhydrazine as low as 0.25 μg/ml. This corresponds to initial sample solutions having a concentration of 3.0 mg of hydrazine and 1.25 mg of 1,1-dimethylhydrazine per ml.

L. C. BAILEY AND TH. MEDWICK,
Anal. Chim. Acta, 35 (1966) 330–336

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH 2-NAPHTHOHYDROXAMIC ACID

2-Naphthohydroxamic acid in methanol gives an intense and stable red-orange color with vanadium(V), sensitive to 0.009 μg V/cm^2, for log $I_0/I = 0.001$ abs. unit at wavelength 450 mμ. The value for σ is $\pm$ 0.006 a.u., equivalent to $\pm$ 0.08 p.p.m. V. The colored complex obeys Beer's law over the range 1–10 p.p.m. vanadium. The absorbance (in 1-cm cell) at 10 p.p.m. was so great that no data were obtained at higher concentrations. Under the conditions of the reaction, the combining ratio of vanadium and 2-naphthohydroxamic acid appears to be 1 to 2. Optimum conditions for the use of 2-naphthohydroxamic acid as a spectrophotometric reagent for vanadium(V) were established; the procedure was applied to the determination of vanadium in steels and non-ferrous alloys with good precision and accuracy.

V. C. Bass and J. H. Yoe,
Anal. Chim. Acta, 35 (1966) 337–344

GRAVIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF MERCURY WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

N-Benzoyl-N-phenylhydroxylamine (BPHA) is suggested for the gravimetric determination of mercury(II) at pH 3.0–6.0; the precipitate, $Hg(C_{13}H_{10}O_2N)_2$, is dried at 105° and weighed. Separation from NH_4^+, Pb, Bi, Sb, As, Cd, Sn, etc. is possible, but chloride, cyanide and EDTA interfere. Mercury(II) can also be extracted with a BPHA solution in chloroform; the extracted mercury complex is yellow and shows an absorbance maximum at 340 mμ. The optimum concentration range for determination is 15–52 μg Hg/ml, the molar extinction coefficient is 2693 $\pm$ 10 and the sensitivity is 0.075 μg/cm^2. Interferences are similar to those found in the gravimetric method.

B. Das and S. C. Shome,
Anal. Chim. Acta, 35 (1966) 345–350

CATALYTIC MICRODETERMINATION OF MERCURY

An automatic spectrophotometric reaction-rate method is described for the microdetermination of mercury. The method is based on the catalytic effect of mercury on the reaction of ferrocyanide with nitrosobenzene. The time required for production of a small fixed amount of the violet product as given by a preselected change in the output voltage of a photoconductive circuit, is measured automatically and related directly to the mercury concentration. The possibility of masking interfering ions with EDTA was examined. Amounts of mercury in the range 0.25–2.5 μg were determined with relative errors of 1–2% in measurement times of only 15–120 sec. Results obtained with mercurial compounds, treated with bromine water, were within 1–2% of the theoretical values and results obtained with pharmaceutical preparations were within the range assigned to those preparations.

T. P. Hadjiioannou,
Anal. Chim. Acta, 35 (1966) 351–359

MICRODETERMINATION OF MOLYBDENUM BY AN AUTOMATIC REACTION-RATE METHOD

An automatic reaction-rate method is described for the microdetermination of molybdenum; the method is based on the hydrogen peroxide–iodide reaction which is catalyzed by molybdenum. The effect of reagent concentrations was studied and the maximum tolerable amounts of interfering ions were determined. Procedures for the determination of 0.01–0.15 μg and 0.1–1.0 μg molybdenum per milliliter are given; 0.036–2.5 μg of molybdenum could be determined with relative errors of about 2%.

T. P. HADJIIOANNOU,
Anal. Chim. Acta, 35 (1966) 360–364

THE AUTOMATIC DETERMINATION OF FLUORIDE IN SEA WATER AND OTHER NATURAL WATERS

A Technicon AutoAnalyzer has been used for the determination of 0–1.5 μg fluoride/ml in sea water and other natural waters. Photometric measurement is made on the blue complex formed by reaction with the chelate formed between lanthanum and alizarin fluorine blue. The method has a coefficient of variation of *ca.* 0.9% at a fluoride level of 1.5 μg/ml.

K. M. CHAN AND J. P. RILEY,
Anal. Chim. Acta, 35 (1966) 365–369

THE DETERMINATION OF TRACE COPPER IN HIGH-PURITY ARSENIC BY NEUTRON ACTIVATION

(in French)

The determination of traces of copper (< p.p.m.) in arsenic is impossible by non-destructive γ-spectrometry because of the similarity in the half-lives and spectra of the two isotopes used. The proposed separation and decontamination of copper are based on the following operations: bromine attack, hydrolysis, precipitation of barium arsenate, anion exchange, separation of copper as sulfide and recovery by electrolysis. Amounts of copper in the range 20–100 ng can be determined.

G. NIZET, J. FOUARGE AND G. DUYCKAERTS,
Anal. Chim. Acta, 35 (1966) 370–375

THE ANALYSIS OF DINITROTOLUENE ISOMER MIXTURES BY NUCLEAR MAGNETIC RESONANCE

NMR data are given for all the dinitrotoluene isomers. It is shown that the components in mixtures of these isomers produced for example, by the direct nitration of toluene, can be recognised readily by NMR. Quantitative analyses can be performed using the heights of the methyl proton peaks of the various isomers. The accuracy of the method and the effects of any residual toluene or mononitrotoluenes are discussed.

A. MATHIAS AND D. TAYLOR,
Anal. Chim. Acta, 35 (1966) 376–382

TRACE ANALYSIS WITH AUTOMATIC PRINTOUT BASED ON REACTION RATE MEASUREMENTS: DETERMINATION OF OSMIUM

An instrument is described which measures reaction rates and converts the information to a voltage which is calibrated to read the concentration of the desired constituent. It is applied to the determination of trace amounts of osmium in solution, based upon catalysis of the Ce(IV)–As(III) reaction. The instrument is versatile, sensitive, and capable of high precision. After a short calibration procedure, it is necessary only to activate the instrument once between runs, and the concentration of sample is printed on tape automatically. Osmium is determined in the 1–60 p.p.b. range with relative standard deviations and accuracy of about 1%. At the lower end of the concentration range this corresponds to an error of about $2.5 \cdot 10^{-11}$ g of osmium. Measurement times range between 15 and 150 sec with average analysis time of 3–4 min per sample, including initial calibration and other manipulations.

H. L. Pardue and R. L. Habig,
Anal. Chim. Acta, 35 (1966) 383–390

A FAST AND PRECISE HETEROMETRIC DETERMINATION OF THALLIUM(I) WITH SODIUM TETRAPHENYLBORATE

The heterometric titration of thallium(I) with sodium tetraphenylborate, at various pH values and in the presence of salts and different complexing agents, was studied; 1.5–0.75 mg of thallium(I) could be determined within 3–4 min, and the error was negligible. Of the complexing agents studied, sodium pyro- and tripolyphosphate had a specific influence, raising the sensitivity about 4-fold, and no interference was caused by the presence of 30–130-fold molar excesses of the following metals: Ca, Mg, Zn, Mn, Co, Ni, Fe(III), Al, UO$_2$(II), Cd, Cu(II), Pb, Bi(III), Ag, V(V), Mo(VI), W(VI) and Th. Pd, Au(III) and Pt(IV) did not interfere.

(the late) M. Bobtelsky and I. Barzily,
Anal. Chim. Acta, 35 (1966) 391–394

A DEVICE FOR MEASURING SPECTRAL REFLECTANCE ON THIN-LAYER PLATES WITH A ZEISS SPECTROPHOTOMETER

(Short Communication)

L. de Galan, J. van Leeuwen and K. Camstra,
Anal. Chim. Acta, 35 (1966) 395–397

DETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS. TITRATION WITH LEAD NITRATE

(Short Communication)

T. L. Hunter,
Anal. Chim. Acta, 35 (1966) 398–399

COMPOSITION, STABILITY AND STRUCTURE OF THE VANADIUM(IV)–ALIZARIN RED S COMPLEX

(Short Communication)

P. Sanyal and S. P. Mushran,
Anal. Chim. Acta, 35 (1966) 400–403

OXIDIMETRY OF IRON(II) AND THE PEROXIDE EFFECT

(Short Communication)

R. A. Chalmers, D. A. Edmond and W. Moser,
Anal. Chim. Acta, 35 (1966) 404–406

A GRAN TITRATION TO DETERMINE THE CHLORINITY OF SEA WATER

(Short Communication)

D. Dyrssen and D. Jagner,
Anal. Chim. Acta, 35 (1966) 407–409

SILVER(II) OXIDE OXIDATION AND SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III)

(Short Communication)

J. Appelbaum and J. Mashall,
Anal. Chim. Acta, 35 (1966) 409–410

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by R. Belcher
Professor of Analytical Chemistry,
The University of Birmingham, Great Britain

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by J. H. Beynon, R. A. Saunders and A. E. Williams
Research Department, Imperial Chemical Industries Ltd.,
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These tables are intended to make it easy to determine the ionic reaction which gives rise to any meta-stable peak in a mass spectrometer, and will prove indispensable to any laboratory possessing this equipment. The introduction is given in English, German, French and Russian, to make the tables more generally useful.

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography
Group of the Czechoslovak Chemical Society, at Liblice
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POLAROGRAPHIC REDUCTION OF PYRIDINIUM ION IN PYRIDINE

TETRAETHYLAMMONIUM PERCHLORATE AS BACKGROUND ELECTROLYTE

JANICE E. HICKEY, MICHAEL S. SPRITZER AND PHILIP J. ELVING
The University of Michigan, Ann Arbor, Mich. (U.S.A.)
(Received December 15th, 1965)

As part of the current interest in the use of nonaqueous solvents for analytical techniques, the utility of pyridine as a polarographic and voltammetric solvent is being systematically investigated. Although the dielectric constant of pyridine is quite low (12.3 at 25°), it is a good solvent for a large number of inorganic and organic substances; this solubility compensates for the low dielectric constant, for it is possible to dissolve sufficient "inert" electrolyte to lower the solution resistance to a convenient level and to suppress the effect of migration of the electroactive ions. Lithium salts are among the most soluble and perchlorates are among the most completely dissociated of salts in nonaqueous solvents; these have been extensively used as backgound electrolytes for polarography in organic solvents.

Lithium perchlorate (0.1 *M*) was used in the investigation of the polarographic reduction of pyridinium ion produced by the Lewis acid–base reaction of solvent pyridine with Brønsted acids of aqueous pK_a less than 9, Lewis acids such as alkyl halides, and alkylpyridinium salts, which allowed the direct analytical determination of such acids[1].

The investigation of another background electrolyte, specifically 0.1 *M* tetraethylammonium perchlorate, for the reduction of pyridinium ion was undertaken in hope of obtaining more information on possible ion-pair formation between the acid anion and the pyridinium ion, as well as in further improving the analytical procedure. The perchlorate anion is commonly used in background electrolytes because of its lack of surface activity and low tendency to ion-pairing. The tetraethylammonium ion is considerably larger in ionic radius than lithium or other alkali metal ions and thus is less prone to ion-pair formation; it is also less surface-active than the larger tetra-*n*-butylammonium ion and, in general, would have less effect on polarograms than similar ions of larger *n*-alkyl groups[2].

EXPERIMENTAL

Reagents

Merck reagent-grade pyridine was dried with Linde molecular sieves type 4A[3]. $LiClO_4$ (G. F. Smith, anhydrous), Et_4NClO_4 (Eastman white label), C_6H_5COOH (National Bureau of Standards Standard Sample No. 39g), $LiNO_3$ (Baker's Analyzed), C_6H_5COOEt (Matheson), C_6H_5COONa (Merck U.S.P.), CH_3COOH (DuPont reagent grade), LiOAc (Fisher Purified), and $C_6H_5COONEt_4$ (Southwestern Analytical Chem-

TABLE I

POLAROGRAPHIC REDUCTION OF PYRIDINIUM ION IN PYRIDINE SOLUTION AT 25° IN THE PRESENCE OF VARIOUS ADDED SUBSTANCES

Pyridinium ion precursor & (Concn., mM)	*Background electrolyte (0.1 M)*	*Compound added & (Concn., mM)*	*No. of runs*	$-E_{1/2}$ *(V)*		*Notes*[b]
				Prewave	*Main wave*	
C_6H_5COOH (0.1–10)	Et_4NClO_4		40	None	1.62 ±0.01	$i_d/C = 3.25\ \mu A/mM$
C_6H_5COOH (1)	Et_4NClO_4	$LiClO_4$ (1–10)	13	None	1.62–1.41	$E_{1/2}/\log C = 106$
C_6H_5COOH (1)	$LiClO_4$	Et_4NClO_4 (0–8)	6	1.20–1.16	1.31–1.38	Waves merge: $E_{1/2}/\log C = -17$
C_6H_5COOH (1)	$LiClO_4$	Et_4NClO_4 (0–10)	22	1.09–1.12	1.30–1.33	No merging: $E_{1/2}/\log C = -13$
C_6H_5COOH (3)	Et_4NClO_4	ØCOONEt$_4$ (0–8)	18	None	1.67 ± 0.02	
C_6H_5COOH (2)	$LiClO_4$	ØCOONEt$_4$ (0–7)	21	1.09 ± 0.02	1.35 ± 0.01	
—	Et_4NClO_4	ØCOONEt$_4$ (0–8)	15	None	1.67 ± 0.02	$i_d/C = 0.73\ \mu A/mM$; see text
HOAc (32)	Et_4NClO_4	ØCOONEt$_4$ (0–6)	21	None	1.72 ± 0.02	
—	Et_4NClO_4	ØCOONa (0–5)	18	None	None	No waves; $E_{\text{discharge}} = -1.9$ V
C_6H_5COOH (3)	Et_4NClO_4	ØCOONa (0–5)	21	None	1.62 ± 0.01	i_d is constant
C_6H_5COOH (3)	Et_4NClO_4	ØCOOEt (0–4)	12	None	1.60 ± 0.08	i_d is constant
—	Et_4NClO_4	ØCOOEt (0–10)	6	None	None	No waves: $E_{\text{discharge}}$ does not shift
HOAc (3.2)	Et_4NClO_4	LiOAc (0–6.7)	21	None	1.72–1.58	i_d is constant; $E_{1/2}/\log C = 110$
$HpyrNO_3$ (2)	Et_4NClO_4	$LiNO_3$ (0–7.1)	18	1.07 ± 0.01	1.31 ± 0.01	i_d and $E_{1/2}$ are constant
C_6H_5COOH (4)[a]	Et_4NClO_4	ØCOONEt$_4$ (0–6.25)	13	None	1.65 ± 0.08	

[a] Temperature for this set of runs: 40°.

[b] C refers to the concentration in millimoles per liter of the compound added (Column 3); number is in mV per log millimolar concentration.

icals) were used without further purification. Pyridinium nitrate was prepared as described previously[1]. Argon (99.99% pure), used for deoxygenation of solutions, was first dried over Drierite and then equilibrated with pyridine at the temperature of use before being bubbled through the solution. The mercury used in the D.M.E. was triple-distilled.

Apparatus

Polarograms, obtained with a three-electrode configuration, were recorded with a Sargent Model XV Polarograph, equipped with a Sargent Model A IR Compensator. The D.M.E. was made from marine barometer tubing; $m^{\frac{2}{3}}t^{\frac{1}{6}}$ in 0.1 M Et_4NClO_4 at 0.00 V, 25° and h=68.6 cm was 1.462 (m=1.212 mg/sec, t=4.51 sec). The 1 M $AgNO_3$–Ag reference electrode, NAgE[3], and the counter electrode (platinum wire, 26 gauge by 8 in.) were inserted in separate compartments (containing background electrolyte) of a jacketed three-compartment cell, which permitted bubbling argon through the solution before the run and passing argon over the solution during the run; the third compartment, in which the D.M.E. was inserted, was filled with the test solution. Gels of methyl cellulose containing 0.1 M Et_4NClO_4 in pyridine and glass frits separated the compartments. The temperature was regulated to $25 \pm 0.2°$, except where otherwise indicated.

Procedures

Stock solutions of the background electrolytes were prepared by dissolving weighed quantities and diluting to known volume. Stock solutions of other reagents were prepared by dissolving weighed quantities and diluting to known volume with stock background solution. Test solutions were prepared by pipetting appropriate amounts of reagent stock solutions into 10-ml volumetric flasks and diluting to volume with background solution. Argon was bubbled through each test solution for 15 min; the D.M.E. was then inserted, and the polarogram taken with argon passing over the solution. The starting potential and current sensitivity were adjusted in each case on the basis of the portion of the polarogram of particular interest.

Potentials reported are *vs.* the NAgE and are presumably corrected for potential drop due to solution resistance.

Potentiometric titration of the acidity of the tetraethylammonium benzoate was carried out in aqueous solution with a Leeds & Northrup Model 7401 pH meter with a glass indicating electrode and a saturated calomel reference electrode, using standard 0.1 N sodium hydroxide and magnetic stirring.

RESULTS AND DISCUSSION

Data for various solution compositions and experiments subsequently described are summarized in Table I. Representative polarograms are shown in Fig. 1.

Comparison of Et_4NClO_4 and $LiClO_4$ as background electrolytes

The properties of Et_4NClO_4 and of $LiClO_4$ as background electrolytes for reduction in pyridine are compared in Table II. Solutions of Et_4NClO_4 have an appreciably more negative decomposition potential, as well as a markedly lower resistance. A prewave, which is attributed to impurities in the pyridine, appeared at *ca.* −2.1 V in

Et_4NClO_4 solution; its height varied between 0.3 and 1.0 μA with an average of 0.7 μA. In addition, a wave of negligible magnitude (average, 0.13 μA) usually appeared at approximately −0.8 V; since this wave is at such a positive potential compared to that of the pyridinium ion reduction, it was not studied further. A similar wave appeared in 0.1 *M* $LiClO_4$ but at a slightly more positive potential. This minute wave is probably due to impurities in the solvent or a small amount of dissolved oxygen; the use of Et_4NClO_4, which had been recrystallized from acetonitrile and benzene, did not appreciably change the height.

Electrocapillary curves of 0.1 *M* Et_4NClO_4 solutions are rather flat on top, which may indicate some sort of adsorption phenomenon; the electrocapillary maximum is at about −0.55 V.

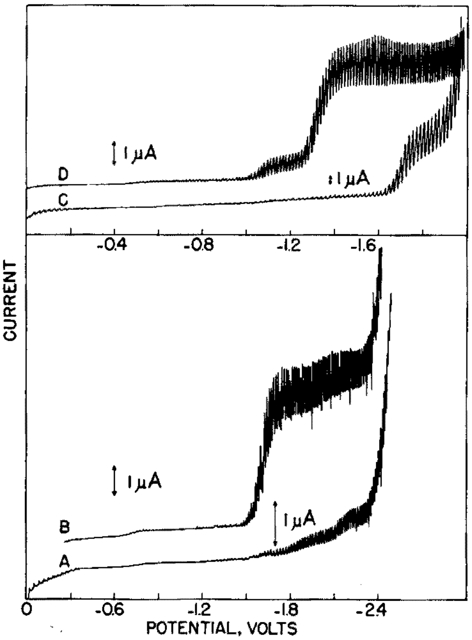

Fig. 1. Polarograms of background electrolytes and pyridinium reduction in pyridine. (A) 0.1 *M* Et_4NClO_4; (B) 2 m*M* benzoic acid in 0.1 *M* Et_4NClO_4; (C) 0.1 *M* $LiClO_4$; (D) 2 m*M* benzoic acid in 0.1 *M* $LiClO_4$.

TABLE II

COMPARISON OF $LiClO_4$ AND Et_4NClO_4 AS BACKGROUND ELECTROLYTES IN PYRIDINE SOLUTION AT 25°

Background	*No. of runs*	*Resistance (kohm)*	*Impurity wave*		*Prewave*		*Decomposition potential*[a] *(V)*
			$-E_{\frac{1}{2}}$ *(V)*	i_d *(μA)*	$-E_{\frac{1}{2}}$ *(V)*	i_d *(μA)*	
0.1 *M* $LiClO_4$	11	7	0.56±0.04	0.21±0.13	1.70±0.02	0.42±0.08	−1.98±0.03
0.1 *M* Et_4NClO_4	16	4.2	0.77±0.06	0.13±0.05	2.09±0.10	0.66±0.21	−2.41±0.10

[a] Potential corresponding to intersection of extrapolated residual current and decomposition current lines.

Pyridinium reduction wave

On addition of benzoic acid to a 0.1 *M* Et_4NClO_4 background solution, a wave ($E_{\frac{1}{2}} = -1.62 \pm 0.01$ V) was produced, whose height increased linearly with acid concentration and which presumably was due to reduction of pyridinium ion produced by reaction of pyridine with benzoic acid. Its $E_{\frac{1}{2}}$ differed appreciably from that reported for the reduction of the same species with 0.1 *M* $LiClO_4$ as background electrolyte ($E_{\frac{1}{2}} = -1.36 \pm 0.04$ V)[1]. In addition, no prewave appeared before the main reduction wave, as was observed when 0.1 *M* $LiClO_4$ was used. The diffusion current constant, I, in 0.1 *M* Et_4NClO_4 solution is 1.40 ± 0.22 compared to 2.23 ± 0.25 (sum of wave and prewave) in 0.1 *M* $LiClO_4$ solution.

A plot of log *h* *vs.* log i_d for the wave produced by benzoic acid in Et_4NClO_4 solution for 4 values of the height of the mercury column, *h*, between 55 and 70 cm was a straight line with a slope of 0.68. In spite of some erratic behavior at 40°, the temperature coefficient of the limiting current was about 2%/degree. Since a square-root dependence of *i* on *h* and a temperature coefficient between 1 and 2%/degree are usually indicative of diffusion control, the current-producing reaction would appear to be diffusion-controlled.

Because of the appreciable difference in $E_{\frac{1}{2}}$ for the reduction of pyridinium ion in the 2 background electrolytes and the presence of a prewave just preceding the main wave for this reduction only in 0.1 *M* $LiClO_4$, the effect of addition of one background electrolyte to the other was investigated. On addition of 1–10 m*M* $LiClO_4$ to 0.1 *M* Et_4NClO_4 solution containing 1 m*M* benzoic acid, the $E_{\frac{1}{2}}$ shifted toward that found in 0.1 *M* $LiClO_4$ alone. A plot of $E_{\frac{1}{2}}$ *vs.* log [$LiClO_4$] was a straight line with a slope of 0.106 V per ten-fold change in $LiClO_4$ concentration. No prewave to the pyridinium reduction wave appeared on addition of the $LiClO_4$.

On adding Et_4NClO_4 to a solution 1 m*M* in benzoic acid and 0.1 *M* in $LiClO_4$, the 2 waves corresponding to the pyridinium prewave and the main pyridinium reduction seemed to merge, *i.e.*, the prewave became less sharply defined; the total current did not change. $E_{\frac{1}{2}}$ for both main pyridinium wave and prewave shifted to slightly more negative potentials on the addition of Et_4NClO_4 (a plot of $E_{\frac{1}{2}}$ *vs.* log [Et_4NClO_4] was a straight line with a slope of -0.017 V).

When, however, a separate solution was prepared for each Et_4NClO_4 concentration (0–8 m*M*), prewave and main wave remained separate and well defined. Again, the $E_{\frac{1}{2}}$ values of both waves became more negative; a plot of $E_{\frac{1}{2}}$ *vs.* log [Et_4NClO_4] was a straight line whose slope was -0.013 V, which is quite close to the previous value of -0.017 V. Thus, although the merging of the waves is not consistent, the magnitude of the shift in $E_{\frac{1}{2}}$ is. This shift, however, is quite small and it may be concluded that Et_4NClO_4 in concentration up to 10 m*M* has very little effect on $E_{\frac{1}{2}}$ in 0.1 *M* $LiClO_4$.

Effect of anion addition

The effect of addition of an excess of the anion of the pyridinium salt present was investigated; if ion-pairing were an appreciable factor, the limiting current for the pyridinium wave would be expected to decrease with increasing anion concentration.

Addition of sodium benzoate (0–5 m*M*) in 0.1 *M* Et_4NClO_4 solution, which was 3 m*M* in benzoic acid, produced no change in diffusion current; the maximum change in i_d was about 0.5 μA in a current of 7.13 μA at 0.0 mM added benzoate; the average i_d for the 0–5 mM range was 7.18 μA. $E_{\frac{1}{2}}$ remained constant at −1.62 V, but maxima appeared on the pyridinium wave. No wave appeared at −1.6 V when the same salt was added in 1 mM concentration in the absence of benzoic acid, but both the impurity prewave and the discharge potential shifted by about 0.4 V to more positive potentials; this shift may be due to the presence of sodium. No shift in the electrocapillary maximum was observed from the current oscillations on the polarograms.

The results on addition of ethyl benzoate (0–4 mM), in both the absence and presence of benzoic acid, were similar to those for sodium benzoate with the exception that the discharge potential was not shifted, even at 10 mM ethyl benzoate.

Two other acid–salt systems were examined. On addition of lithium acetate (0–6.7 mM) to solutions of 3 mM acetic acid in 0.1 M Et_4NClO_4, i_d remained constant, but $E_{\frac{1}{2}}$ became more positive; a plot of $E_{\frac{1}{2}}$ *vs.* log [LiOAc] was a straight line of slope +0.110 V/ten-fold concentration change, which is quite comparable to the slope (+0.106) for the addition of $LiClO_4$ to a solution of benzoic acid in 0.1 M Et_4NClO_4. The change in $E_{\frac{1}{2}}$ is consequently due to the addition of lithium(I).

The waves in solutions of pyridinium nitrate in 0.1 M Et_4NClO_4 closely resemble those obtained when 0.1 M $LiClO_4$ is used as background electrolyte (Table III). When lithium nitrate (0–7.1 mM) was added to pyridinium nitrate in 0.1 M Et_4NClO_4, both $E_{\frac{1}{2}}$ and i_d remained essentially constant.

TABLE III

COMPARISON OF BEHAVIOR OF PYRIDINIUM ACETATE, PYRIDINIUM NITRATE AND PYRIDINIUM BENZOATE IN PYRIDINE

Pyridinium species	*Background*	$-E_{\frac{1}{2}}$ *(V) (prewave)*	$-E_{\frac{1}{2}}$ *(V) (main wave)*	I[a]
HOAc	0.1 M $LiClO_4$[b]	1.12 ± 0.04	1.36 ± 0.07	2.16 ± 0.10
	0.1 M Et_4NClO_4	(none)	1.72 ± 0.02	1.82 ± 0.39
$HpyrNO_3$	0.1 M $LiClO_4$[b]	1.13 ± 0.05	1.39 ± 0.03	2.01 ± 0.07
	0.1 M Et_4NClO_4	1.07 ± 0.010	1.31 ± 0.01	1.92 ± 0.07
Benzoic acid	0.1 M $LiClO_4$[c]	1.13 ± 0.05	1.39 ± 0.03	2.01 ± 0.07
	0.1 M Et_4NClO_4	(none)	1.62 ± 0.01	1.40 ± 0.22

[a] $I = i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$; I represents the sum of the main wave and prewave, where the latter appeared.
[b] Data taken from ref. 1.
[c] Corresponding values in ref. 1 are −1.10 ± 0.03 V, −1.36 ± 0.04 V and 2.23 ± 0.25 V.

Addition of tetraethylammonium benzoate (0–8 mM) to solutions containing 3 mM benzoic acid in 0.1 M Et_4NClO_4, resulted in a linear increase of i_d with concentration of the benzoate salt, equivalent to 0.93 μA/mmole; $E_{\frac{1}{2}}$ became slightly more negative, *i.e.*, from −1.65 V at 0 mM quaternary salt to −1.70 V at 8 mM. Potentiometric titration of the tetraethylammonium benzoate in aqueous solution with a standard sodium hydroxide solution produced a titration curve with a well-defined end-point, which indicated that the benzoate salt contained an acid impurity equivalent to 16.7% benzoic acid by weight. On a molar basis, 16.7% benzoic acid corresponds to 1 mole of acid impurity for each 2 moles of tetraethylammonium benzoate in the preparation. This is in agreement with the current–concentration ratios of 3.25 μA/mmole for benzoic acid and 0.93 μA/mmole for the benzoate.

CONCLUSIONS

Tetraethylammonium perchlorate is at least as good, if not better, than lithium perchlorate as a background electrolyte for the reduction of pyridinium ion in pyridine. Its decomposition potential in 0.1 *M* solution is much more negative than that of the corresponding lithium solution, which makes available a greater potential range. There is a slight problem in obtaining pure samples of Et_4NClO_4, but the reduction wave observed for the impurity in the sample used occurs at a potential far removed from that of pyridinium ion reduction. The fact that the prewave observed in $LiClO_4$ solutions does not always appear in Et_4NClO_4 solution adds to the ease of data interpretation, although the cause for the difference is not yet known.

The wave patterns produced by benzoic acid, pyridinium nitrate, and acetic acid in 0.1 *M* Et_4NClO_4 are not all similar; the variation in $E_{\frac{1}{2}}$ for reduction of the pyridinium ion produced by each of these acids (Table III) may have obvious analytical value if other electroactive species are present in the sample. A prewave appears only in solutions of pyridinium nitrate.

The addition of lithium(I) in the form of acetate or perchlorate to Et_4NClO_4 solutions shifts $E_{\frac{1}{2}}$ for the pyridinium wave to more positive potential at a rate of about 0.1 V per unit change in the log of the lithium(I) concentration. Lithium nitrate did not seem to have the same effect, which may indicate that $LiNO_3$ is more strongly ion-paired than the other 2 lithium(I) salts. Addition of sodium(I) as sodium benzoate shifts the prewave and discharge potentials of Et_4NClO_4 when this substance is used as the background electrolyte.

No change in i_d for the LiOAc–HOAc, pyridinium nitrate–$LiNO_3$, benzoic acid–sodium benzoate, and benzoic acid–ethyl benzoate systems was observed on adding the indicated salt containing the acid anion; furthermore, no shift in $E_{\frac{1}{2}}$ could be associated with the addition of the excess acid anion. The fact that excess anion has no noticeable effect on the polarographic reduction of the pyridinium ion, would indicate either a lack of ion association effects between anion and pyridinium ion, or formation of a stable ion-pair. In this regard, those species most difficult to reduce in 0.1 *M* Et_4NClO_4, as indicated by their more negative half-wave potentials (Table III), *i.e.*, those derived from acetic and benzoic acids, also have lower diffusion current-constant values. Such a phenomenon is compatible with a situation in which the ions involved are highly associated in solution and hence are both less easily reduced and less available for reduction.

The potential phenomena summarized in the previous paragraphs may be due to electrocapillary effects associated with the nature of the double layer in Et_4NClO_4 solution; in $LiClO_4$ solution, the presence of the large excess of lithium(I) would seem to "level" such potential phenomena. For example, the electrocapillary maximum (E.C.M.) occurs at -0.35 V in 0.1 *M* $LiClO_4$ and at -0.55 V in 0.1 *M* Et_4NClO_4. The shifts in $E_{\frac{1}{2}}$ for the main pyridinium reduction wave in going from $LiClO_4$ to Et_4NClO_4 solution (Table III) are -0.36 ± 0.08 V for pyridinium acetate, $+0.08 \pm 0.04$ V for pyridinium nitrate and -0.22 ± 0.04 V for pyridinium benzoate. These shifts parallel the E.C.M. shift in 2 of the 3 cases. The third case is that involving nitrate, whose solutions also show differences in other respects, as discussed.

In connection with the behavior encountered in the present study it is interesting to note that LARSON AND IWAMOTO[4] observed that $E_{\frac{1}{2}}$ for metal ion reductions in acetonitrile varied with $LiClO_4$ concentration, but not with Et_4NClO_4 concentration; this difference in behavior of the two background electrolytes was ascribed to a probable difference in nature of the "solvated" cations.

Conductance data for solutions of salts in pyridine, summarized by DRAGO AND PURCELL[5], indicate the extensive association of such electrolytes in pyridine, presumably because of its low dielectric constant. The equivalent conductances at infinite dilution, Λ_0, and association constants (in parentheses) of some salts of interest are pyridinium nitrate 102 (19,600), silver nitrate 87 (1070) and sodium nitrate 80. DRAGO AND PURCELL conclude that "anion solvation through specific interaction does not occur in pyridine but the cation Li^+ is co-ordinated and solvated more than Na^+ and K^+".

The data (polarographic and titrimetric) for tetraethylammonium benzoate indicate that the polarographic reduction of pyridinium ion can be used to determine the free acid in such ester preparations.

Because of the variation in $E_{\frac{1}{2}}$ for pyridinium ion reduction in Et_4NClO_4 solution with anion nature and in the presence of alkali metal ions, the use of $LiClO_4$ as background electrolyte would be advisable in determining total acid concentration of unknown samples[1].

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SUMMARY

Tetraethylammonium perchlorate, compared to lithium perchlorate as background electrolyte for the reduction of pyridinium ion in pyridine, is effective over a wider potential range, but is more difficult to obtain in a pure state; slight amounts of impurities do not, however, affect the pyridinium wave. The pyridinium wave produced in 0.1 *M* Et_4NClO_4 may occur at a more negative potential than the main pyridinium wave in 0.1 *M* $LiClO_4$, depending on the source of the pyridinium ion, but still appears to be due to a diffusion-controlled reduction, whose limiting current is linearly proportional to concentration; the prewave observed in $LiClO_4$ background generally does not appear in Et_4NClO_4 background. Specific differences in the effect of Li(I), Na(I) and Et_4N(I) background cation appear to be due to electrocapillary phenomena and perhaps to the extent of solvation of the ions. The constancy of current for solutions containing acetic acid with added acetate, pyridinium nitrate with added nitrate, and benzoic acid with added benzoate indicate that the pyridinium reduction is independent of anion concentration.

RÉSUMÉ

Les auteurs ont examiné la réduction de l'ion pyridinium dans la pyridine en comparant le perchlorate de tétraéthylammonium (Et_4NClO_4) au perchlorate de lithium. La vague du pyridinium obtenue avec Et_4NClO_4 0.1 *M* peut se produire à un potentiel plus négatif que celle obtenue avec $LiClO_4$ 0.1 *M*. La prévague observée avec $LiClO_4$ comme solution de base n'apparaît généralement pas avec Et_4NClO_4. Ces différences dans l'influence de Li, Na et Et_4N, comme cations de base, semblent être dues à des phénomènes d'électrocapillarité et probablement à la solvatation des ions. La réduction du pyridinium est indépendante de la concentration de l'anion.

ZUSAMMENFASSUNG

Es wird die polarographische Reduktion von Pyridinionen in Pyridin untersucht. Es zeigt sich, dass Tetraäthylammoniumperchlorat im Vergleich zu Lithiumperchlorat als Grundelektrolyt über einen grösseren Potentialbereich wirksam ist. Geringe Verunreinigungen beeinflussen die Pyridinstufe nicht. Die Pyridinstufe, welche in 0.1 *M* Et_4NClO_4 erzeugt wird, tritt bei negativeren Potentialen auf als die in 0.1 *M* $LiClO_4$. Die beim $LiClO_4$ allgemein beobachtete Vorstufe tritt beim Et_4NClO_4 nicht auf. Spezifische Unterschiede zwischen Li(I), Na(I) und Et_4N(I) können auf ein Elektrokapillarphänomen und vielleicht auf das Ausmass der Solvation der Ionen zurückzuführen sein. Die Reduktion des Pyridins ist unabhängig von der Anionenkonzentration.

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COMPLEX FORMATION OF COPPER(II) WITH CHROME AZUROL S

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In analytical chemistry chrome azurol S (CAS) (3''-sulpho-2'',6''-dichloro-3,3'-dimethyl-4'-hydroxyfuchson-5,5'-dicarboxylic acid, sodium salt) has found application as a metal indicator and a photometric reagent. A number of CAS–metal complexes have been studied previously, as apparent is from the survey given in Table I.

TABLE I

A SURVEY OF THE CAS–METAL COMPLEXES INVESTIGATED

Metal ion	*Composition (metal : ligand) of the species detected*	*Ref.*	*Metal ion*	*Composition (metal : ligand) of the species detected*	*Ref.*
Al^{3+}	1:2	1	Fe^{3+}	1:1, 1:2, 2:1, 2:2	10
Al^{3+}	1:1	2	Hf^{4+}	1:1	11
Be^{2+}	1:1	3	In^{3+}	1:1	12
Be^{2+}	1:1	4	Pd^{2+}	1:1	13
Be^{2+}	1:1	5	Th^{4+}	1:1	14
Cd^{2+}	1:2	6	Ti^{4+}	1:1	11
Cr^{3+}	1:2, 2:3	7	UO_2^{2+}	1:1	15
Cu^{2+}	1:1	8	Zr^{4+}	1:1	11
Fe^{3+}	1:1	9			

The comparatively long distance between the two bidentate groups of CAS makes it improbable that both participate in complex formation with the same metal ion. In accordance with this assumption, a characteristic tendency of CAS to form, in addition to other species, ring-formed 2:2 complexes has been established[10]. Steric considerations lead to the assumption that the ring structure is only formed with octahedrally coordinated metal ions, such as iron(III). It was considered of interest to study a system involving a metal ion of different coordination symmetry. For this purpose the copper(II) ion was selected, as it is known to participate in most chelating reactions as a square planar coordinated species.

EXPERIMENTAL

Apparatus

The extinction measurements were made with a Beckman DB recording spectrophotometer, a Zeiss PMQ II spectrophotometer and 1- and 4-cm cells.

For the potentiometric titrations and for the measurement and regulation of pH, a Beckman Zeromatic pH meter, with glass (pH range 0–11) and calomel electrodes, was used. The instrument was calibrated against a 0.05 M solution of potassium hydrogen phthalate, pH = 4.00 at 20°, and a 0.025 M solution of potassium dihydrogen phosphate, pH = 6.88 at 20°.

The temperature of the solutions measured potentiometrically was maintained constant with a thermostat.

For the potentiometric titrations a special double-walled titrating vessel of glass was constructed.

Reagents

From the commercially available trisodium salt of CAS (Geigy, Switzerland) the pure tetrabasic acid was prepared as described previously[10]. The acid was used in all experiments. Standard solutions of copper(II) were prepared either from copper foil (British Drug Houses) or from copper(II) sulphate pentahydrate (Merck, Germany). All other chemicals were of reagent-grade quality.

Standard solutions

Aqueous $5 \cdot 10^{-4}$ M solutions of CAS and of copper were prepared by weighing out the proper amounts of the tetrabasic acid, copper foil or copper(II) sulphate pentahydrate. The copper foil was dissolved in nitric acid, and after dissolution sulphuric acid was added and the solution evaporated to dryness; the residue was dissolved in water and diluted to a known volume.

Ionic strength

In all solutions the ionic strength was kept relatively constant by maintaining a concentration of 0.10 M potassium chloride and low concentrations of ligand and metal ion.

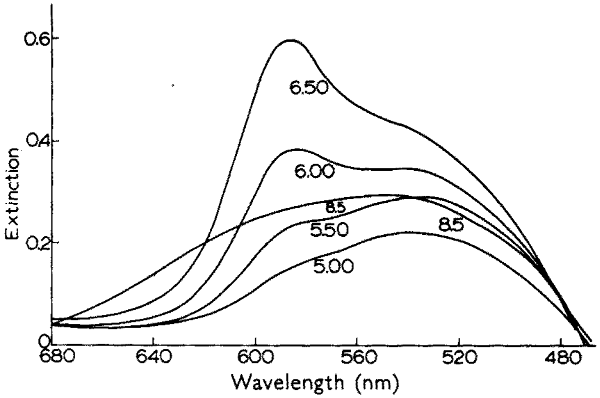

Fig. 1. Absorption curves at different pH values of solutions containing the reactants in equimolar amounts. $c_{Cu} = c_{CAS} = 2.00 \cdot 10^{-5}$ M.

Photometric investigations

Absorption curves of aqueous solutions of CAS have been recorded previously[10,15,16]. The complex formation was first studied by recording absorption curves at different pH values of mixtures of the reactants, all mixtures being measured against corresponding blank solutions.

In Fig. 1 the curves plotted at higher pH values show a predominant maximum at 586 nm, while at lower pH values the curves exhibit a maximum in the range 530–540 nm.

In solutions containing an excess of copper (see Fig. 2) a complex with absorption maximum at 586 nm predominates in all mixtures. In this series of solutions the extinction increases with pH up to pH 6.80; at higher pH values lower extinctions were obtained. In these mixtures copper(II) hydroxide precipitated at pH about 7. Figure 3 shows that similar maxima were obtained when the reactants were present in different mole ratios.

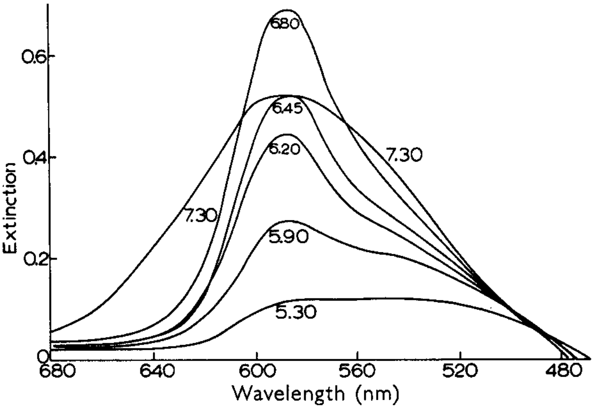

Fig. 2. Absorption curves at different pH values of solutions containing an excess of copper(II). $c_{Cu} = 5.00 \cdot 10^{-5}$ *M*. $c_{CAS} = 5.00 \cdot 10^{-6}$ *M*.

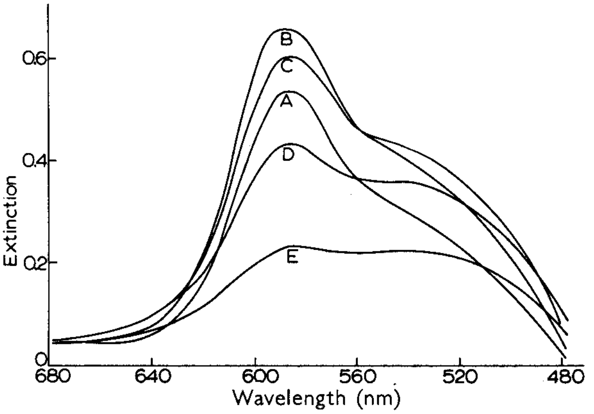

Fig. 3. Absorption curves plotted at pH 6.50 of mixtures containing the reactants in different mole ratios and having the constant mole sum $4.00 \cdot 10^{-5}$ *M*. Mole ratios (metal : ligand): curve A 3:1; curve B 2:1; curve C 1:1; curve D 1:2 and curve E 1:3.

The absorption curves indicated that two complexes were present, one with an absorption maximum at 586 nm, and the other with a maximum in the range 530–540 nm.

To elucidate the composition of the complexes, the molar ratio method was first employed. Four series of solutions were prepared, all at pH 6.50. In two series the concentration of CAS was constant, 10^{-5} *M* and $2 \cdot 10^{-5}$ *M*, while the concentration of copper was varied. In two other series the concentration of metal ion was constant, $2 \cdot 10^{-5}$ *M* and $3 \cdot 10^{-5}$ *M*, while the concentration of CAS was varied. All measurements were made at 586 nm. The form of the curves plotted for varying concentrations of copper indicated that, with an excess of CAS, the complex contained two or more copper atoms. Similarly, the form of the curves recorded for varying concentrations of CAS showed that, in mixtures containing an excess of metal ion, the complex contained one ligand molecule.

Curves of continuous variation were recorded at 540 and 586 nm for a series of solutions at pH 6.50 with a constant total concentration of $4 \cdot 10^{-5}$ *M*. The curve plotted for the wavelength 540 nm exhibited a rounded maximum at the mole fraction 0.5. The curve had no inversions and the gradients at the end-points were different from zero. This curve clearly pointed to the presence of a complex consisting of one copper atom and one ligand molecule.

The curve resulting from the measurements at 586 nm showed a maximum in the mole fraction range ($c_{Cu}/c_{Cu}+c_{CAS}$) 0.6–0.7. At low mole fractions of copper the curve had an inversion and approached the end-point parabolically. The curve branch on the other side of the maximum had no inversion and the gradient at the end-point was different from zero. These characteristic features, as well as the position of the maximum, demonstrated the predominance of a complex consisting of two copper atoms and one ligand molecule.

Potentiometric titrations

Solutions (50 ml) which were 10^{-3} *M* in CAS, 0.10 *M* in potassium chloride and 0.50, 1.00, 2.00 or $4.00 \cdot 10^{-3}$ *M* in copper(II) were titrated potentiometrically with a 0.0540 *N* sodium hydroxide solution. The base was added in small increments from a 5-ml burette and the pH was recorded as soon as constant values were obtained. Titration curves were also recorded of solutions of the ligand and of copper(II). The curves are reproduced in Fig. 4.

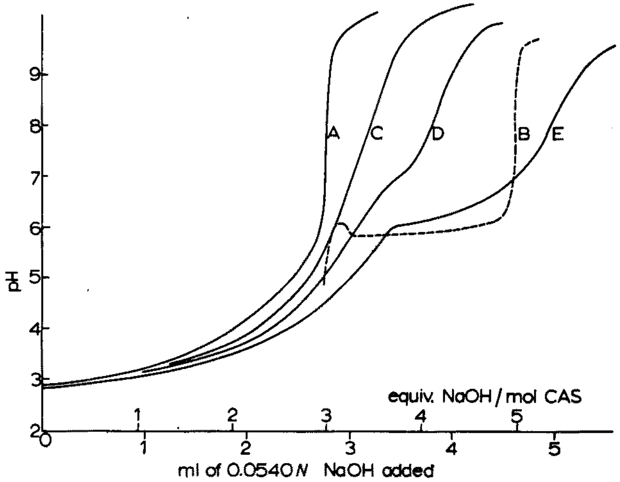

Fig. 4. Potentiometric titration curves. Curve A of a 10^{-3} *M* solution of the ligand as the tetrabasic acid. Curve B of a $2.00 \cdot 10^{-3}$ *M* solution of copper(II). Curves C, D and E of solutions containing 10^{-3} *M* CAS and $0.50 \cdot 10^{-3}$ *M*, 10^{-3} *M* and $2.00 \cdot 10^{-3}$ *M* copper(II), respectively.

The ligand curve exhibited a distinct end-point at three equivalents of base added. The titration curve of a $2.00 \cdot 10^{-3}$ *M* solution of copper(II) demonstrated that the precipitation of copper(II) hydroxide started at pH about 5.5. The titration curves of the different mixtures of metal ion and ligand showed one or more inversions, but no distinct end-points. No definite conclusions could be extracted from a visual study of the curves. The curves, however, indicated that, on average, more than 3, but less than 4 protons were liberated by the complex formation.

RESULTS AND DISCUSSION

Two complexes were detected, one consisting of one copper atom and one ligand molecule (absorption maximum 540 nm) and the other containing two copper atoms and one ligand molecule (absorption maximum 586 nm). The effect of pH on the absorption curves led to the assumption that the former complex contained one proton, as apparent from the following complex reaction:

$$Cu(H_2O)_4^{2+} + H_4CAS \rightleftharpoons Cu(H_2O)_2HCAS^- + 3\ H^+ + 2\ H_2O$$

The second complex was believed to be formed by the reaction:

$$2\ Cu(H_2O)_4^{2+} + H_4CAS \rightleftharpoons (Cu(H_2O)_2)_2CAS + 4\ H^+ + 4\ H_2O$$

Structural formulae for the two compounds are suggested in Figs. 5 and 6.

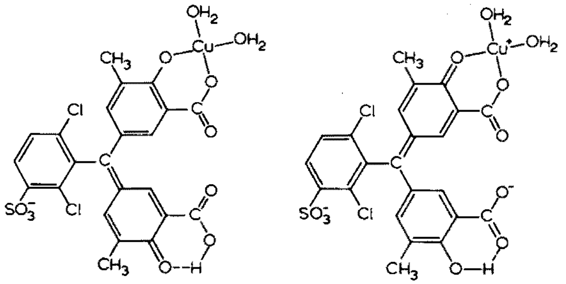

Fig. 5. Possible structural formula for $Cu(H_2O)_2HCAS^-$.

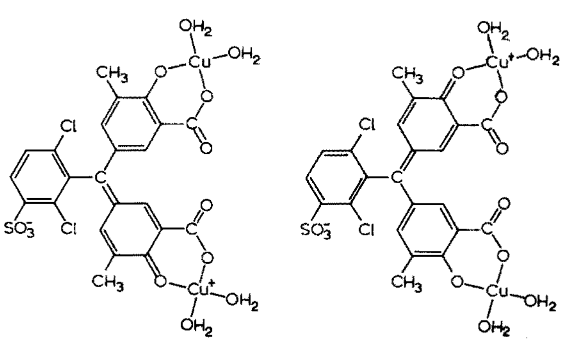

Fig. 6. Possible structural formula for $(Cu(H_2O)_2)_2CAS$.

The investigation demonstrated that the copper(II) ion, considered to participate in most chelating reactions as a square planar coordinated ion, did not react with CAS to produce ring-formed 2:2 compounds. A presupposition for the formation of such compounds was believed to be the presence of octahedrally coordinated metal ions.

It is interesting to note that, in contrast to the CAS–iron(III) system, the copper(II) ion did not engage in complex formation with 2 ligand molecules.

Stability constants

The stability constants for the two complexes were calculated using the data from the potentiometric titration by a method based on stepwise approximations[17]. In these calculations the values for the dissociation constants of CAS were taken from a previous investigation[10], the formation of copper(II) hydroxo complexes was corrected for by using data given in the literature[18]; the activity coefficient $f_{H^+}=0.82$ valid at 25° and the ionic strength $\mu=0.1$ were used.

The stability constants for the complexes $Cu(H_2O)_2HCAS^-$ and $(Cu(H_2O)_2)_2CAS$ were calculated to be $\log K=4.02\pm0.05$ and $\log K=13.7\pm0.1$, respectively.

SUMMARY

The complex formation of copper(II) with chrome azurol S (CAS) was studied by spectrophotometric and potentiometric methods. In the pH range 5–7, two complexes with the composition $Cu(H_2O)_2HCAS^-$ and $(Cu(H_2O)_2)_2CAS$ were detected; the stability constants were calculated to be $\log K=4.02\pm0.05$ and $\log K=13.7\pm0.1$, respectively (at 25° and ionic strength 0.1 (KCl)). A comparison is made between the copper(II)–CAS and iron(III)–CAS systems.

RÉSUMÉ

La formation du complexe de cuivre(II) avec le chrome azurol S (CAS) a été examinée par spectrophotométrie et potentiométrie. Entre les pH 5 et 7, on a décelé deux complexes $Cu(H_2O)_2HCAS^-$ et $(Cu(H_2O)_2)_2CAS$; les constantes de stabilité calculées sont respectivement $\log K=4.02\pm0.05$ et $\log K=13.7\pm0.1$ (à 25° et force ionique$=0.1$). On a effectué une comparaison entre les systèmes cuivre(II)–CAS et fer(III)–CAS.

ZUSAMMENFASSUNG

Es wurde die Komplexbildung von Kupfer(II) mit Chromazurol S (CAS) mit spektralphotometrischen und potentiometrischen Methode untersucht. Im pH-Bereich 5–7 wurden 2 Komplexe der Zusammensetzung $Cu(H_2O)_2HCAS^-$ und $(Cu(H_2O)_2)_2CAS$ nachgewiesen. Die berechneten Stabilitätskonstanten betrugen $\log K=4.02\pm0.05$ bzw. $\log K=13.7\pm0.1$ bei 25° und einer Ionenstärke von 0.1 (KCl). Die Systeme Kupfer(II)–CAS und Eisen(III)–CAS wurden miteinander verglichen.

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STABILIZATION OF GERMANIUM(II) BY COMPLEX FORMATION IN IODIMETRIC TITRATION OF GERMANIUM*

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Since germanium is a semiconductor, its oxides and sulfides have also shown photoconductive and ferromagnetic properties; it has achieved prominence in the electronic industry. The difficulty in determining germanium in these materials led to the development of a procedure which can be used to determine germanium accurately and rapidly as a major constituent.

Among several volumetric methods for determining germanium, the iodimetric method is probably most accurate and simplest, being based on the reduction of Ge(IV) to Ge(II) by hypophosphite on boiling followed by iodimetric titration of Ge(II) to Ge(IV) below 20°, at which the excess hypophosphite is not rapidly oxidized by iodine. The iodimetric procedures originally proposed by IVANOV–EMIN[1] and modified by ABEL[2] require separation of germanium as its chloride by distillation. The method of IVANOV–EMIN requires a preliminary reduction in 6 *N* hydrochloric acid for 40–50 min to remove the arsenic present, followed by a further 15–20-min reduction. ABEL's modification indicates the optimum hydrochloric acid concentration to be 3–5.5 *N*. No interference study was made by either author as their methods involved a preliminary separation of germanium. The previous investigators used no acid other than hydrochloric acid and little information is available about the importance of complexing ligand and acidity for quantitative reduction of germanium.

The present investigation indicates that the iodimetric method for germanium is quite selective; in most cases separation is unnecessary if the conditions for reduction are controlled. The interfering elements such as arsenic and tin cannot be simply separated from germanium by distillation with hydrochloric acid. The results of using all halogen acids and other strong acids as reduction media and the importance of complex-forming ligands for the stabilization of germanium(II) are reported below. A medium of 4.5–10 *M* phosphoric acid is recommended for the reduction as it gives better accuracy and requires less critical control. The redox reactions of germanium in various acid media have been studied potentiometrically.

EXPERIMENTAL

Reagents

Standard germanium solution, 0.05 M. Dissolve 5.2300 g of pure germanium

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dioxide by heating with *ca.* 200 ml of water and a minimum amount of 50% sodium hydroxide solution. Cool, dilute to 1 l, and mix. Store in a polyethylene bottle.

Standard iodate solution, 0.05 N. Transfer 0.05 g of sodium carbonate, 1.7834 g of potassium iodate, and 20 g of potassium iodide to a 1-l volumetric flask. Dissolve in water, dilute to the mark with water and mix.

Other reagents used were reagent grade.

A Beckman pH meter, Model M, or equivalent was used for E.M.F. measurement.

Procedures

Reduction in hydrochloric acid medium. Transfer 20.00 ml of standard germanium solution to a 500-ml Erlenmeyer flask, and add 80 ml of water, 85 ml of concentrated hydrochloric acid, *ca.* 7 g of $NaH_2PO_2 \cdot H_2O$, a few boiling chips, and *ca.* 15 ml of water. Close the flask with a 2-hole stopper, one hole being fitted with a 1/4-in. glass tube connected to a carbon dioxide source, and the other open as a gas outlet and for the subsequent insertion of a buret tip. Heat the solution to boiling, and boil gently for 5–10 min while passing CO_2 slowly. On completion of the boiling step, increase the CO_2 flow and cool the flask in water and ice to $< 20°$. Add 5 ml of 0.1% starch solution through the stopper hole, using a pipet. Disconnect the CO_2 source. Immediately titrate with the iodate solution to a purplish-blue end-point which lasts for a few seconds.

Reduction in phosphoric acid medium. The procedure is approximately the same as described above except that 70 ml of 85% phosphoric acid are added and the final solution is diluted to *ca.* 200 ml with water, and that the solution is gently boiled for 15 min.

Determination of germanium in sulfides of germanium and cadmium. Mix well 0.5 g of the fine powdered sample with 1 g of mannitol, 0.5 g of potassium perchlorate, and 15 g of sodium peroxide in a Parr bomb nickel fusion cup. Assemble the bomb and ignite. After cooling, dismantle the bomb, remove the head and dip it into a 600-ml beaker containing 50 ml of distilled water previously heated almost to boiling. Lay the fusion cup on its side in the same beaker of hot water, covering the beaker immediately with a watch glass. After the melt has dissolved, remove the head and cup and wash thoroughly with a fine jet of hot water. Carefully add concentrated sulfuric acid until the solution is slightly acidic, as indicated by disappearance of turbidity. Transfer the sample solution to a 500-ml Erlenmeyer flask, rinse the beaker with 70 ml of 85% phosphoric acid and dilute with water to about 200 ml. Add 10 g of $NaH_2PO_2 \cdot H_2O$, and proceed the reduction and titration as directed above.

Determination of germanium in oxides of zinc, nickel, germanium and iron. Decompose the sample from pyrosulfate fusion with gentle heating and dissolve the melt by heating with 50 ml of 1 *N* hydrochloric acid. Transfer the sample solution to a 500-ml Erlenmeyer flask and proceed with the reduction and titration as directed for phosphoric acid medium.

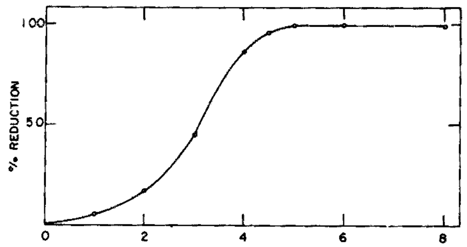
DISCUSSION AND RESULTS

Standardization of iodate solution

It has been common practice for the iodimetric titration of germanium[2] or tin[3] to standardize the iodate solution against pure germanium or tin because the reduction may not be 100% or a slight loss of germanium or tin may occur during reduction. Accurate results may be obtained by careful control of experimental conditions and application of an empirical correction factor from standardization; the amount of germanium or tin used for standardization should be close to that in the unknown. Everest[4] stressed that hydrochloric acid solutions of germanium(IV) must not be rapidly heated initially, otherwise germanium tetrachloride may be volatilized; further, the amount of hypophosphorous acid must be strictly controlled (not above 0.3–0.35 *N*). Germanium(IV) is only slowly reduced by hypophosphite below 90° (b.p. for $GeCl_4$ is 86°), hence slow heating will minimize the loss of germanium, rather than completely avoid it. The reduction in a phosphoric acid medium, however, was found to be complete and there was no evidence for germanium losses during reduction. The phosphate complexes of germanium(II) and germanium(IV) are much more stable and less volatile than the chloride complexes, and no special precaution is necessary in heating. Accordingly, there is no need for empirical standardization of the iodate solution when germanium (presumably also tin) is reduced in a phosphoric acid medium. For precise work, an indicator blank may be applied.

Effect of acidity on reduction

Ivanov–Emin recommended a 6 *N* hydrochloric acid medium and Abel found an optimum hydrochloric acid concentration of 3–5.5 *N* for reduction of germanium. As shown in Figs. 1 and 2, the acidity and the concentration of chloride are interrelated.



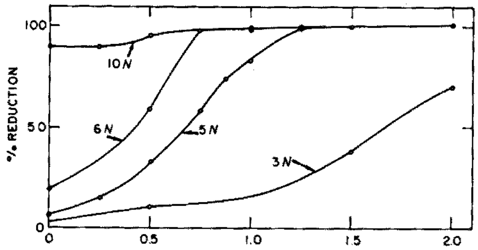
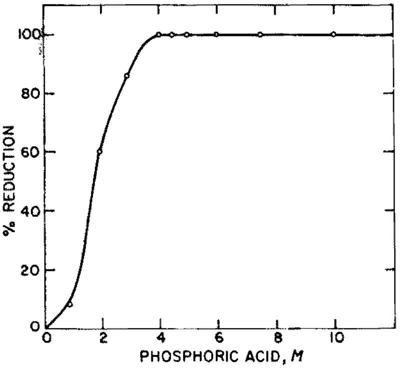


Fig. 1. Effect of acidity on reduction of germanium in presence of chloride. 1.0 mmole Ge, 0.3 mole NH_4Cl, 0.05 mole NaH_2PO_2; total volume 200 ml.

Fig. 2. Effect of chloride on reduction of germanium at various concentrations of sulfuric acid.

The previous authors used hydrochloric acid only and did not vary the acidity and chloride concentration separately. Actually these two different factors affect the reduction. The results in Fig. 1 were obtained at a fixed 1.5 *M* chloride concentration; germanium was reduced at various acidities by adding various amounts of sulfuric acid. Clearly, the reduction of germanium was not appreciably decreased at an acidity higher than 6 *N*. Abel reported decreased reduction at hydrochloric acid concentrations higher than 5.5 *N*. This may be explained by the fact that at high acidity and high chloride concentration, the decrease in reduction is due to loss of germanium by volatilization of its chloride. The results in Fig. 2 indicate that at low acidity, complete reduction required a higher chloride concentration; and at high acidity, complete reduction could be obtained at a lower chloride concentration.

The reduction of germanium and tin has only been studied in hydrochloric acid medium. It was found that phosphoric acid is an excellent medium for reduction of germanium or tin using hypophosphite as a reductant, the optimum phosphoric acid concentration being above 4.5 M (Fig. 3). A solution containing phosphoric acid higher than 7 M becomes viscous and inconvenient for titration unless it is diluted; a 5–6 M phosphoric acid concentration is recommended. It should be noted that higher phosphoric acid concentrations do not cause loss of germanium.



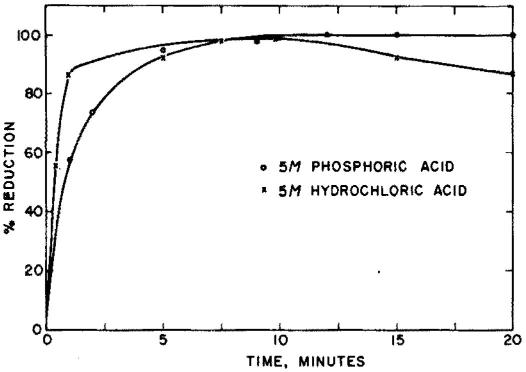


Fig. 3. Effect of phosphoric acid on reduction of germanium.

Fig. 4. Effect of time on reduction of germanium.

TABLE I

REDUCTION OF GERMANIUM WITH HYPOPHOSPHITE IN VARIOUS ACID MEDIA

(One mmole of germanium was taken)

Acid	*Normality*	*% Reduction*
Hydrofluoric acid	4.0	None
Hydrochloric acid	4.0	98.0
	5.0	98.5
Hydrobromic acid	2.5	95.5
	4.0	96.5
Hydriodic acid	4.0	97.0
Phosphoric acid	5.0 M	100.0
Perchloric acid	5.0	None
Sulfuric acid	5.0	7.5
	6.0	18.2
	10.0	90.0

Acid	*Normality*	*% Reduction*
Nitric acid	5.0	None
Tartaric acid	1.0 M	None
Citric acid	3.0 M	None
Fluoboric acid (in 5 N H_2SO_4)	5.0 M	None
Glycerol (in 5 N H_2SO_4)	5.0 M	53.0
Mannitol (in 5 N H_2SO_4)	0.5 M	None

Role of complex formation in reduction of germanium

A study was made of the reduction of germanium in various acidic media (Table I); only phosphoric or hydrochloric acid was suitable, various percentages of reduction being obtained in acidic media containing other complexing ligands. The complexing ligand obviously plays an important role in the reduction of germanium by hypophosphite; only when germanium is complexed, by formation of its chloride or phosphate, is reduction possible. Such complex formation is required for stabilization of germanium(II) in solution.

Germanium in an acidic medium is presumably in the form of $Ge(OH)_4$ which will be complexed in the presence of ligand (L).

$$Ge(OH)_4 \rightarrow [Ge(OH)_4L]^- \rightarrow [Ge(OH)_{6-x}L_x]^{2-}$$

EVEREST AND HARRISON[5] showed the existence of $[Ge(OH)_3Cl_3]^{2-}$ and $[Ge(OH)_4Cl_2]^{2-}$ in 6–9 *N* hydrochloric acid and $GeCl_4$ in 9 *N* hydrochloric acid. UDOVENKO AND FIALKOV[6] showed the existence of $[Ge(OH)Cl_4]^-$ and $[GeCl_6]^{2-}$ in 12 *N* hydrochloric acid. The complexing ligand may be bromide, iodide, or phosphate. In 5 *M* phosphoric or hydrochloric acid,

$$[Ge(OH)_4L_2]^{2-} \text{ or } [Ge(OH)_3L_3]^{2-} \underset{I_2}{\overset{H^+, e}{\rightleftharpoons}} GeL_2 \text{ or } [GeL_3]^-$$

Probably the replacement of OH by L depends on the concentration of L and on the acidity, which, in addition to temperature and time, are the important factors affecting percentage of reduction of germanium by hypophosphite.

Except for the iodides of germanium, the oxidation potentials of the germanium complexes are not given in the literature. During the course of this investigation, the oxidation potentials of some germanium complexes were estimated in a 5 *M* acid medium (Table II). The data show that when germanium reacts with a complexing ligand, its oxidation potential becomes more negative; the germanium(II) complex is relatively stable in solution in the absence of oxidizing agent, whereas the uncomplexed germanium(II) would probably disproportionate.

TABLE II

FORMAL OXIDATION POTENTIAL OF SOME GERMANIUM COMPLEX HALF CELLS AT 25°

Half-reaction	*Medium*	*Approximate potential (V)*	*Reference*
$GeO + H_2O = GeO_2 + 2\,H^+ + 2\,e$		0.12	8
$[GeCl_3]^- + 3\,H_2O = [Ge(OH)_3Cl_3]^{2-} + 3\,H^+ + 2\,e$	5 *M* HCl	−0.15	
$[GeBr_3]^- + 3\,H_2O = [Ge(OH)_3Br_3]^{2-} + 3\,H^+ + 2\,e$	5 *M* HBr	−0.15	
$[GeI_3]^- + 3\,H_2O = [Ge(OH)_3I_3]^{2-} + 3\,H^+ + 2\,e$	5 *M* HI	−0.08	
$GeI_2 + 2\,I^- = GeI_4 + 2\,e$		−0.2	8
$[GePO_4]^- + 3\,H_2O = [Ge(OH)_3PO_4]^{2-} + 3\,H^+ + 2\,e$	5 *M* H_3PO_4	−0.14	

Hydrochloric acid as reduction medium. Germanium(II) chloride is very much less volatile than germanium(IV) chloride. During the reduction process germanium may be lost if the solution is heated quickly or too much hypophosphorous acid is added[4]. The time of boiling is also important, the optimum being 7–10 min (Fig. 4). Accurate results are obtained when the reduction is carefully controlled and the iodate solution is standardized under the same conditions; without standardization, the results were found to be 1% low. In a 5 *N* sulfuric acid medium, a minimum of 1.5 *M* chloride is required for reduction of 1 mmole of germanium (Fig. 2).

Phosphoric acid as reduction medium. Phosphoric acid was found to be superior to hydrochloric acid as a reduction medium. From the quantitative results of reduction, the phosphate complexes of germanium appear to be quite stable. In a 5 *N* sulfuric acid medium, a minimum of 1.75 *M* phosphate is required for reduction of 1 mmole of germanium. The minimum time for boiling is 10 min, but longer boiling has no effect (Fig. 4).

Hydrobromic or hydroiodic acid as reduction medium. Both hydrobromic acid and hydroiodic acid gave approximately 97% reduction (Table I). Either may be used provided that the iodate solution is standardized accordingly, but these acids are not recommended because the reduction requires an acidity of at least 5 *N* and a large volume of either acid is needed to obtain a concentration above 4 *N*. Probably a solution containing 5 *N* sulfuric acid and 2 *M* bromide or iodide would allow quantitative reduction but there appears to be no advantage over hydrochloric or phosphoric acid. The results shown in Table I confirm the relationship between reduction of germanium and complex formation.

Sulfuric acid as reduction medium. The stability of germanium sulfate complexes is not very high[7]. Sulfuric acid cannot be used alone as a quantitative reduction medium but it may be used along with other ligands since it is a very efficient proton supplier.

Glycerol as reduction medium. Germanium was not reduced by hypophosphite in a 5 *N* sulfuric acid solution containing 1 *M* mannitol and it was impossible to prepare a 5 *M* mannitol solution. Only 53% reduction of germanium was obtained with a solution containing 5 *N* sulfuric acid and 5 *M* glycerol; it is not known if the reduction of germanium in such medium gives only one electron change instead of two. However, glycerol shows no advantages over hydrochloric or phosphoric acid, and has a disadvantage in that some glycerol may be charred by fast gas heating. Nevertheless, the result demonstrates the complex formation between germanium and glycerol in a strongly acidic medium. Under the same conditons, tin(IV) was practically unreduced by hypophosphite (for 0.5 mmole of tin, 0.5 ml of 0.1 *N* iodate solution was used); this may offer a possibility of determining germanium in the presence of tin. Complicated reactions occur between 5 *N* sulfuric acid and glycerol in hot solution; the color changes to light yellow and an unpleasant odor is obtained.

When hydrofluoric, tartaric, citric or fluoboric acid, all of which form complexes with germanium, were used, there was no significant reduction of germanium by hypophosphite.

Choice of acid as reduction medium

Phosphoric acid (above 4.5 *M*) is recommended for reduction of germanium by hypophosphite because it offers several advantages over hydrochloric acid. (*1*) Since the phosphate complexes of germanium(II) and (IV) are non-volatile, no strict control of conditions and empirical standardization are needed. (*2*) No decrease in reduction occurs at phosphoric acid concentrations above 6 *M*. (*3*) Heating a 5 *M* phosphoric acid gives no acid fumes. (*4*) The reduction is quantitative. (*5*) Longer boiling times do not cause loss of germanium in a phosphoric acid medium. (*6*) Antimony does not interfere in a phosphoric acid medium in the presence of more than 7 g of sodium hypophosphite.

Effect of amount of hypophosphite

For complete reduction of 1.0 mmole of germanium in 200 ml of 4.5 *N* hydrochloric acid 5 g of $NaH_2PO_2 \cdot H_2O$ are recommended (Fig. 5). If oxidants such as iron(III) or copper(II), are present, more hypophosphite may be needed. When antimony was present, it inhibited the reduction of germanium unless more hypophosphite was added (Fig. 5). The same amounts of hypophosphite should be used for the sample and for the standardization of the iodate solution with a standard germanium solution. From 7 to 10 g of sodium hypophosphite are suitable in a phosphoric acid medium.

Selectivity of iodimetric determination of germanium

Both germanium and tin can be quantitatively titrated under the conditions previously described. The selectivity of the iodimetric method for germanium is about the same as that for tin[3]. Both IVANOV–EMIN and ABEL recommended prior separation of germanium from interfering elements. Since the iodimetric method is relatively selective, in many cases the separation of germanium from other elements seems unnecessary. Many elements do not interfere as they are not titrated by iodine in a 5 M hydrochloric or phosphoric acid solution; interferences such as tin, antimony and arsenic cannot be separated from germanium by a simple distillation. In order to eliminate the tedious step of distillation and any possible incomplete separation by distillation, an attempt was made to titrate germanium directly in the presence of other foreign elements. As shown in Table III, many elements did not interfere. Tin was quantitatively reduced and titrated. Arsenic was reduced by hypophosphite to its elemental form, but caused no serious difficulty in detecting the end-point. When the amount of arsenic (also selenium or tellurium) was much larger than that of germanium, the bulk of precipitate interfered with the observation of the starch end-point, but the precipitate could be filtered off or a potentiometric end-point applied (Fig. 6). In a phosphoric acid medium, copper(II) was reduced to copper(I) and metallic copper. In a 200-ml solution containing 40 ml of 85% phosphoric acid and 50 ml of concentrated sulfuric acid, copper(II) was completely reduced to metallic copper by hypophosphite after 20 min of gentle boiling. The metallic copper was filtered off and the filtrate was reduced again with hypophosphite.

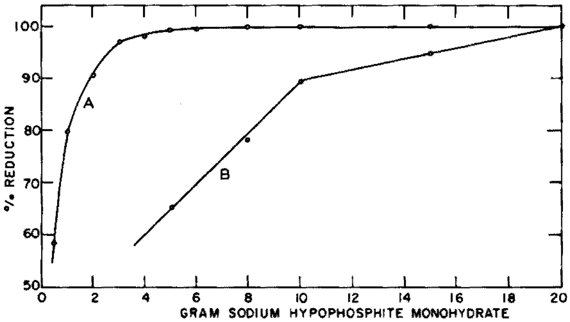


Fig. 5. Effect of hypophosphite on reduction of germanium in 5 N HCl medium. (A) 1 mmole Ge; (B) 1 mmole Ge + 1 mmole Sb.

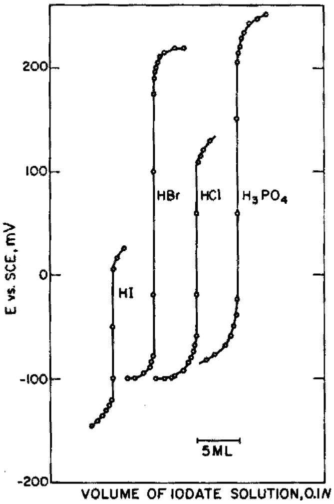


Fig. 6. Potentiometric titration of germanium with iodate.

When the acidity of a sample solution is not known, it suffices simply to neutralize with either sulfuric acid or sodium hydroxide, then add a suitable amount of phosphoric or hydrochloric acid and dilute with water so that the final acid concentration is 5 *M* with a volume of approximately 200 ml. Based on this principle, satisfactory results were obtained in the direct determination of germanium in actual samples (Table IV).

Potentiometric study of germanium complexes

Little information is available about the germanium complexes and their standard potentials. In order to interpret the stabilization of germanium(II) in a

TABLE III

DETERMINATION OF GERMANIUM IN PRESENCE OF FOREIGN IONS

(One mmole of germanium and one mmole of foreign ion were taken)

Foreign ion	*% Recovery*		*Remarks*
	HCl medium[a]	*H_3PO_4 medium*	
Arsenic	100.0	100.0	Reduced to elemental As
Cadmium	100.0	100.0	
Chromium(III)		99.8	
Copper	100.0	100.0	Cu^{2+} reduced to Cu^+ or Cu^0
Cobalt	100.0	100.0	
Iron(III)	99.9	100.0	Fe^{3+} reduced to Fe^{2+}
Lead	100.0	100.0	
Nickel	100.0	100.0	
Selenium	99.0	100.0	Reduced to elemental Se
Tellurium	100.0	100.0	Reduced to elemental Te
Thallium	99.0	99.5	TlI precipitate formed
Tin	199.6	200.0	Sn^{4+} reduced to Sn^{2+}
Titanium	99.5	100.0	
Vanadium(V)	96.0	100.0	Vanadium also reduced
Vanadium(IV)	95.0	100.0	
Zinc	100.0	100.0	

[a] For HCl medium, the iodate solution was standardized against a standard germanium solution

TABLE IV

DIRECT DETERMINATION OF GERMANIUM IN ITS OXIDE AND SULFIDE IN PRESENCE OF OTHER IONS

Sample	*Germanium (%)*	
	Calculated[a]	*Found*
Cd–Ge–S		
A	8.85	9.06
B	9.26	9.10
D	10.16	10.10
Zn–Ge–Ni–Fe–O		
1–733	16.94	17.06
1–574	14.66	14.66

[a] The germanium contents were calculated by difference after other elements had been determined.

complexing ligand medium, an attempt was made to estimate the formal oxidation potentials of some germanium complexes. The potentials were measured with a pH meter using platinum and saturated calomel electrodes. It was thought that the stabilization of germanium(II) must be due to a shift in oxidation potential to more negative values as a result of complex formation. This was found to be true as shown in Table II. In the case of phosphoric acid, the net change of potential was approximately 0.26 V.

When the solution is dark colored or contains large quantities of precipitate, the visual end-point may become impossible, then the potentiometric end-point may be applied as demonstrated in Fig. 6. For the potentiometric titration of germanium(II) with an iodate solution, a special flask is needed in which a platinum electrode, a saturated calomel electrode and a buret tip are inserted while the solution is protected from air oxidation by passing a stream of inert gas such as carbon dioxide; a magnetic stirrer should be provided.

SUMMARY

Four factors are important in the reduction of germanium(IV) by hypophosphite, namely, proper acidity, temperature, proper concentration of complexing ligand, and time of heating. The complexing ligand is needed to stabilize the germanium(II) ions. Halides, with the exception of fluoride, and phosphate are good complexing ligands for germanium. Tin is quantitatively reduced and titrated under the same conditions. Many foreign ions do not interfere, so that prior separation of germanium can often be avoided. Successful results are presented for titrating germanium in the presence of many metals and for direct determination of germanium in actual samples. Germanium after reduction may be titrated with an iodate solution potentiometrically. The formal oxidation potentials of some germanium half-reactions were estimated and used to interpret the stabilization of germanium(II) by complex formation. Phosphoric acid is recommended as the reduction medium.

RÉSUMÉ

Lors de la réduction du germanium(IV) par l'hypophosphite, 4 facteurs sont importants: Acidité, température, concentration du complexant, durée de chauffage. Le complexant est nécessaire pour stabiliser les ions germanium(II). Les halogénures, à l'exception du fluorure, sont de bons complexants, de même que le phosphate. Après réduction le germanium peut être titré potentiométriquement au moyen d'iodate. L'étain est également réduit quantitativement et titré dans les mêmes conditions; de nombreux métaux ne gênent pas.

ZUSAMMENFASSUNG

Vier Faktoren sind bei der Reduktion von Germanium(IV) mit Hypophosphit wichtig: Der Säuregrad, die Temperatur, die Konzentration des komplexbildenden Liganden und die Erhitzungszeit. Die Komplexbildung ist für die Stabilisation der Germanium(II)-Ionen notwendig. Mit Ausnahme des Fluorids sind dafür die Halogenide und Phosphate gut geeignet. Zinn wird unter denselben Bedingungen quantitativ reduziert und titriert. Zahlreiche Fremdionen stören nicht, so dass eine vorhergehende Abtrennung des Germaniums häufig vermieden werden kann. Es werden gute Ergebnisse für die Titration des Germaniums in Gegenwart zahlreicher Metalle angegeben. Das Germanium kann nach der Reduktion mit einer Jodatlösung potentiometrisch titriert werden. Die formalen Oxydationspotentiale einiger Reaktionen wurden abgeschätzt und zur Deutung der Stabilisierung des Germanium(II) durch Komplexbildung verwendet. Phosphorsäure wird als Reduktionsmedium vorgeschlagen.

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SPECTROFLUORIMETRIC TRACE DETERMINATION OF TERBIUM(III) WITH POTASSIUM OXALATE

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As reported in a previous paper[1], traces of samarium, europium, terbium and dysprosium can be determined fluorimetrically by means of the intense fluorescence that these lanthanides produce in aqueous sodium tungstate solutions. It is possible to determine europium and dysprosium in rather complex rare-earth mixtures, but some difficulties due to enhancement arise in the determination of traces of terbium in the presence of considerable quantities of dysprosium, and in the determination of samarium in the presence of europium and dysprosium.

For the determination of traces of terbium in presence of dysprosium, enhancements can be eliminated or considerably reduced by measuring the terbium fluorescence intensity in dilute potassium oxalate solutions. In such solutions dysprosium exhibits a markedly lower fluorescence intensity than in sodium tungstate solution[2]. Terbium, on the other hand, shows practically the same fluorescence intensity in both solutions. Therefore it seemed profitable to study the possibility of employing potassium oxalate as a specific reagent for the fluorimetric determination of traces of terbium.

As already discussed[2], the high fluorescence intensity of terbium in oxalate solution is connected with complex formation between terbium and oxalate ions, and with a transfer of the energy absorbed from the complex at 255 mμ to the terbium ion.

EXPERIMENTAL

Fluorescence measurements

All fluorescent measurements were made with an Aminco-Bowman spectrofluorimeter as described previously[3].

Since the spectrofluorimeter sensitivity may decrease over a period of time (due to aging of the Xenon light, and the photomultiplier tubes), all measurements were related to a quinine sulfate solution (concentration 0.1 μg/ml, $\lambda_e = 250$ mμ, $\lambda_f = 450$ mμ, initial relative fluorescence intensity = 3.0 for the 1P21 photomultiplier tube; with slit arrangement: 0; 3/16; 0; 0; 3/16; 0; 3/16).

Materials

Lanthanide chloride solutions were prepared by dissolving the respective oxides (Johnson–Matthey Co., London, 99.9% purity) in hydrochloric acid solution.

All other reagents were Erba RP products.

Potassium oxalate solution containing borax. In about 70 ml of distilled water, 0.333 g of potassium oxalate monohydrate and 2.38 g of borax were dissolved; 12.7 ml of 0.5 *M* hydrochloric acid were added, and the solution diluted to 100 ml with distilled water.

RESULTS AND DISCUSSION

The lanthanide fluorescence intensity in potassium oxalate solutions depends considerably on the excitation light wavelength, the potassium oxalate concentration, the pH of the solution and the temperature.

The optimum fluorescence conditions for terbium ($5 \cdot 10^{-2}$–10 μg/ml) are obtained by irradiating this lanthanide at 255 mμ in 0.01 *M* potassium oxalate solution, at pH 7.8 (λ_f=545 mμ; photomultiplier employed 1P21 RCA). In such solutions the calibration curve is linear for terbium concentrations below 10 μg/ml.

For terbium concentrations higher than 10 μg/ml, it is necessary to use solutions more concentrated with respect to oxalate to avoid precipitation of terbium oxalate[2]. However, increasing the oxalate concentration decreases the terbium fluorescence intensity, since the oxalate ions absorb ultraviolet light at the excitation wavelength and so act as internal filters.

TABLE I

RELATIVE FLUORESCENCE INTENSITY FOR TERBIUM(III) IN POTASSIUM OXALATE AND IN HYDROCHLORIC ACID SOLUTIONS

Instrumental parameters: λ_f = 545 mμ; photomultiplier = 1P21; sensitivity = 50; slit arrangement = 0; 3/16; 0; 0; 3/16; 0; 3/16.

Tb(III) (µg/ml)	*Potassium oxalate*			*HCl 0.1 M*[(d)]
	0.01 M pH = 7.8[(a)]	*0.27 M pH = 8.5*[(b)]	*0.55 M pH = 8.5*[(c)]	
10	3.8	0.125	0.10	0.08
25	*	0.330	0.26	0.22

[(a)] λ_e = 255 mμ; [(b)] λ_e = 275 mμ; [(c)] λ_e = 285 mμ; [(d)] λ_e = 220 mμ

* Precipitate formed.

In Table I the relative fluorescence intensity values (R.F.I.) for terbium in 0.01 *M*, 0.27 *M*, and 0.55 *M* potassium oxalate solutions are reported. These values have been corrected for the contribution due to the blank. FASSEL AND HEIDEL[4] estimated terbium directly in hydrochloric acid solution by irradiation at 220 mμ, employing a suitably modified Beckmann DU spectrophotometer (sensitivity limit 50 μg terbium in 10 ml of solution); accordingly, in Table I, for the purposes of comparison the relative fluorescence intensities of terbium in 0.1 *M* hydrochloric acid are also reported. It can be seen that the terbium fluorescence in 0.01 *M* potassium oxalate solutions is about 50 times more intense than that in 0.1 *M* hydrochloric acid. Potassium oxalate may thus be employed more suitably than hydrochloric acid solutions in the fluorimetric determination of terbium traces ($5 \cdot 10^{-2}$–10 μg/ml).

With gradual increase in terbium concentration (along with an increase in oxalate concentration), the advantages of the potassium oxalate method decrease compared with the fluorimetric method in hydrochloric acid. Therefore, the oxalate method is preferred only for terbium concentrations lower than 10 μg/ml. For higher concentrations, the hydrochloric acid method may be used.

Potassium oxalate solution is also preferable for concentrations of terbium greater than 10 μg/ml, when this lanthanide has to be determined in the presence of praseodymium. Since praseodymium exhibits a fluorescence peak at 535 mμ it can enhance the reading at 545 mμ in the terbium determination. However, in potassium oxalate solutions praseodymium is not fluorescent, and therefore produces no enhancement.

The standard deviation determined on 15 solutions of 0.01 *M* potassium oxalate each containing 1 μg/ml of terbium, was 1.4%. Quantities of the order of $5 \cdot 10^{-2}$ μg/ml terbium could be estimated to within 50%.

Determination of traces of terbium in rare-earth mixtures

In Table II the relative fluorescence intensity values of 1 μg/ml of terbium, dysprosium and europium in sodium tungstate solution (0.6 *M*, pH 9) and potassium oxalate solution (0.01 *M*, pH 7.8) are shown. It can be observed that enhancement by dysprosium for terbium is negligible in potassium oxalate solution, but as reported previously[1] is considerable in sodium tungstate solutions. However, as in the case of fluorescence in tungstate solutions, a negative interference or quenching, in some

TABLE II

RELATIVE FLUORESCENT INTENSITY AT 545 mμ FOR 1 μg/ml OF TERBIUM, DYSPROSIUM AND EUROPIUM IN 0.6 *M* SODIUM TUNGSTATE (pH 9) AND IN 0.01 *M* POTASSIUM OXALATE (pH 7.8) SOLUTIONS RESPECTIVELY

(Instrumental parameters: photomultiplier = 1P21; sensitivity = 50; slit arrangement = 0,3/16,0; 0,3/16,0; 3/16)

Ion	*R.F.I. in tungstate soln. (λ_e = 265 mμ)*	*R.F.I. in oxalate soln. (λ_e = 255 mμ)*
Tb^{3+}	0.540	0.343
Dy^{3+}	0.083	< 0.005
Eu^{3+}	0.012	< 0.005

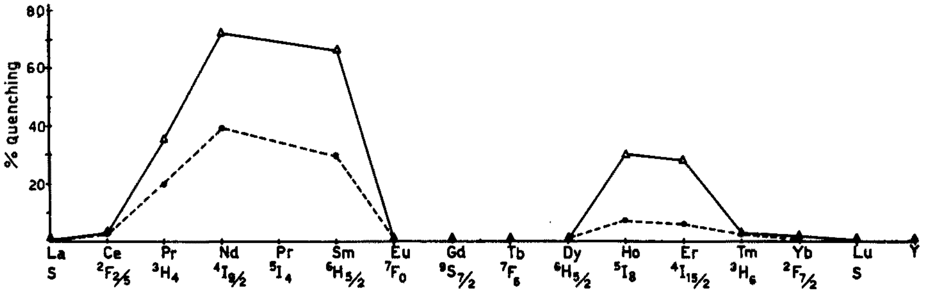

Fig. 1. Percentage quenching of the fluorescence of 1 μg/ml of Tb(III) in 0.01 *M* potassium oxalate solution caused by 1 μg/ml (curve dotted line) and 5 μg/ml (curve full-line) respectively of various rare earths. Instrumental parameters as for column (a) in Table I.

cases fairly high, may occur in potassium oxalate solutions. Figure 1 shows the percentage quenching caused by various concentrations of lanthanide ions.

It can be noted that the highest interferences are obtained with the trivalent lanthanides which have an I fundamental state (Nd, Ho, Er), whereas ions of the S and F fundamental states (Gd, Ce, Eu, Yb) do not interfere to a marked extent. This behaviour is similar to that observed by VAN UITERT AND SODEN[5] in the case of the terbium hexa-antipyrene triiodide. The percentage quenching depends only upon the concentration of the ion causing quenching, and in the concentration ranges studied is independent of the terbium concentration.

As an example, the procedure followed for the determination of terbium traces in a rare-earth oxide mixture is reported. A sample (5–10 mg) of the mixture was dissolved by warming in 10 ml of 2.5 M hydrochloric acid and the solution was diluted to 250 ml with distilled water. To 1 ml of this solution were successively added 3 ml of potassium oxalate solution containing borax (prepared as described above), and 1 ml of 0.01 M hydrochloric acid (final pH of solution $\simeq 7.8$). The terbium content was obtained from the calibration curve after fluorimetric measurement. To correct for the

TABLE III

SPECTROFLUORIMETRIC DETERMINATION OF TERBIUM(III) IN SYNTHETIC RARE-EARTH MIXTURES

(Instrumental parameters as in Table I, column (a))

Mixtures[a]	*μg/ml found*	*μg/ml of Tb calcd. from the addition method by eqn. (1)*	*μg/ml present*	*% Error*
M_1	0.303	—		
M_1 + 0.5 μg/ml Tb	0.620	0.477		
M_1 + 1 μg/ml Tb	0.945	0.472		
		Average 0.475	0.500	−5
M_2	0.460	—		
M_2 + 1 μg/ml Tb	0.927	0.985		
M_2 + 3 μg/ml Tb	1.750	1.070		
		Average 1.027	1.000	+2.7
M_3	0.520	—		
M_3 + 1 μg/ml Tb	1.025	1.030		
M_3 + 2 μg/ml Tb	1.530	1.030		
		Average 1.030	1.000	+3
M_4	0.855	—		
M_4 + 0.5 μg/ml Tb	1.153	1.430		
M_4 + 2.5 μg/ml Tb	2.180	1.600		
		Average 1.515	1.500	+1
M_5	0.625	—		
M_5 + 0.5 μg/ml Tb	0.920	1.030		
M_5 + 1 μg/ml Tb	1.300	0.930		
		Average 0.980	1.000	−2

[a] *Composition of mixtures*:
M_1 = 2.5 μg/ml Tb + 5 μg/ml Nd + 5 μg/ml Gd + 5 μg/ml Yb = 17.5 μg/ml of T.R.
M_2 = 5 μg/ml Tb + 10 μg/ml Nd + 2.5 μg/ml Dy + 3 μg/ml Lu = 20.5 μg/ml of T.R.
M_3 = 5 μg/ml Tb + 2.5 μg/ml Nd + 2.5 μg/ml Eu + 10 μg/ml Ho = 20 μg/ml of T.R.
M_4 = 7.5 μg/ml Tb + 5 μg/ml Nd = 12.5 μg/ml of T.R.
M_5 = 5 μg/ml Tb + 5 μg/ml Nd + 10 μg/ml Ho = 20 μg/ml of T.R.

error caused by the quenching effect of other rare earths present in the mixture, the following procedure was employed: 3 ml of potassium oxalate solution containing borax, and 1 ml of 0.01 M hydrochloric acid containing a known concentration of terbium (of the same order of magnitude as the amount of terbium found by the first measurement on the unknown solution) were added to 1 ml of the original sample solution.

The concentration of terbium(III) in the unknown solution was obtained by the following relationship:

$$A_x = \frac{A_{t_1} \cdot A_a}{A_{t_2} - A_{t_1}} \qquad (1)$$

where $A_x = \mu$g/ml of terbium(III) present in the solution,
$A_a = \mu$g/ml of terbium(III) added,
$A_{t_1} = \mu$g/ml of terbium(III) found without addition,
$A_{t_2} = \mu$g/ml of terbium(III) found after addition.

In Table III some fluorimetric determinations of terbium(III) in known rare-earth mixtures are reported as examples.

CONCLUSION

From the work described in the present paper, and in a previous paper[2], it can be concluded that potassium oxalate is a very suitable reagent for the determination of traces of terbium(III) in complex rare-earth mixtures.

From an analytical point of view the selectivity of chemical reagents in enhancing the fluorescence of some lanthanide ions is of particular importance, since owing to the close similarity in their chemical properties, it is difficult to find specific colour or precipitation reagents. Further research on lanthanide complexes which absorb in suitable regions of the spectrum, so as to enhance selectively the fluorescence of individual ions, would certainly be useful for further progress in the analytical chemistry of the lanthanides.

ACKNOWLEDGEMENT

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SUMMARY

Potassium oxalate acts as a specific reagent in enhancing the fluorescence intensity of terbium in aqueous solutions. Maximum fluorescence intensity is obtained by irradiating (at 255 mμ) terbium(III) dissolved in 0.01 M potassium oxalate solution at pH 7.8. The enhancement and quenching phenomena caused by other lanthanides, errors in the determination, and various examples of spectrofluorimetric analysis of traces of terbium in mixtures with other lanthanides are described. The sensitivity of the method is $5 \cdot 10^{-2}$ μg/ml of terbium.

RÉSUMÉ

L'oxalate de potassium agit comme un réactif spécifique en augmentant l'intensité de fluorescence du terbium, en solution aqueuse. L'intensité maximum de fluorescence est obtenue en irradiant (à 255 mμ) du terbium(III), dissous dans une solution d'oxalate de potassium 0.01 M au pH 7.8. L'influence des autres lanthanides est examinée et divers exemples d'analyse spectrofluorimétrique de traces de terbium dans des mélanges renfermant d'autres lanthanides sont décrits. Sensibilité de la méthode: $5 \cdot 10^{-2}$ μg/ml de terbium.

ZUSAMMENFASSUNG

Kaliumoxalat wirkt als spezifisches Reagenz zur Anregung der Fluoreszenzintensität von Terbium in wässrigen Lösungen. Die maximale Fluoreszenzintensität erhält man (bei 255 mμ) in 0.01 M Kaliumoxalatlösung beim pH 7.8. Anregungs- und Löscheffekte, die durch andere Lanthaniden verursacht werden, stören die Bestimmung. Verschiedene Beispiele einer spektralfluorimetrischen Analyse von Spuren Terbium in Mischungen mit anderen Lanthaniden werden beschrieben. Die Empfindlichkeit der Methode beträgt $5 \cdot 10^{-2}$ μg/ml Terbium.

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DOSAGE DIRECT DE SUBMICROTRACES DE BORE DANS LA SOUDE DE PURETE ANALYTIQUE PAR LA METHODE FLUORIMETRIQUE A L'HYDROXY-2-METHOXY-4-CHLORO-4'-BENZOPHENONE

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Lors de la recherche et du dosage de traces de bore dans un échantillon déterminé, on est le plus souvent contraint à concentrer ou même évaporer à sec les solutions aqueuses d'acide borique après la mise en solution et les séparations éventuelles. Ceci exige l'emploi de certains réactifs formant avec l'acide borique des complexes ou des composés non volatils, afin d'éviter les pertes par entraînement ou volatilisation. Parmi ces réactifs, la soude est la plus utilisée car elle permet non seulement de concentrer les solutions aqueuses d'acide borique, mais aussi d'évaporer à sec, sans aucune perte.

La soude intervient presque toujours, dans la séparation du bore par la méthode la plus sélective: celle qui a recours à la distillation du triméthylborate. En effet, le distillat est recueilli dans une solution de soude qui hydrolyse le triméthylborate, on évite ainsi les pertes durant l'élimination ultérieure du mélange eau–méthanol.

Enfin, la soude sert à la mise en solution de certains échantillons, lors du dosage du bore dans le silicium et le germanium ultra-purs par exemple.

La soude est donc un réactif très utilisé pour le microdosage du bore quelle que soit la méthode utilisée. Un moyen de détermination rapide et précis de la teneur en bore de ce réactif s'avère donc nécessaire et ce d'autant plus que les traces de bore, contenues dans les échantillons à doser, sont plus faibles.

A notre connaissance le problème de la détermination du bore dans la soude n'a pas encore été résolu, ce qui rend impossible un dosage de bore précis dans des échantillons où celui-ci est en micro ou submicrotraces.

Le présent travail nous a permis de mettre au point une méthode rapide ne présentant pas de difficulté particulière, de dosage direct de traces de bore dans la soude. Elle a été appliquée aux produits de pureté analytique et nous a permis une détermination précise de la teneur en bore de 5 soudes "pour analyse" de marque différente (soudes S-1 à S-5).

PARTIE EXPÉRIMENTALE

Réactifs et matériel

(*a*) Hydroxy-2-méthoxy-4-chloro-4'-benzophénone (H.M.C.B.). (*b*) Acide sulfurique (d=1.84), p.a. Merck. (*c*) Solutions d'acide borique (p.a. Merck) à 2 μg/ml et 0.2 μg/ml dans H_2SO_4 conc., conservées dans des flacons en quartz. (*d*) Eau bidistillée

TABLEAU I

ÉTUDE DE LA FIDÉLITÉ DE LA MÉTHODE À L'H.M.C.B. COURBES D'ÉTALONNAGE (l.b.f. = 0.032 μ^{-1} à 2.04 μ^{-1})
(l.b.f. = largeur de la bande de fluorescence; $T\%$ = transmission par rapport au témoin; $T_t\%$ = transmission du témoin (blanc); $\bar{X}$ = moyenne des $T\%$; s = écart-type; s_m = erreur-type ($s/\sqrt{N}$); $\pm t_{s_m}$ = limites de confiance)

ng B/3 ml		*2*	*4*	*6*	*8*	*10*	*12*	*14*	*16*	*18*	*20*	*22*	*24*	*26*	*28*	*30*
Courbe	$T_t\%$	$T\%$														
a	42.8	3.9	7.2	14.2	15.9	16.8	19.3	27.2	28.5	36.7	42.7	45.5	47.2	49.9	55.1	59.2
b	42.5	2.2	7.2	9.7	12.7	19.7	25.2	26.8	32.7	33.5	36.9	43.2	46.5	51.5	56.2	60.0
c	43.3	1.6	7.4	11.7	14.7	20.2	23.3	29.7	31.2	33.7	37.2	42.2	44.7	50.4	55.6	58.2
d	44.8	3.2	6.1	11.6	13.4	21.5	23.2	29.7	30.8	32.2	38.7	45.9	48.6	53.4	58.8	62.7
e	41.8	2.6	5.9	12.2	14.5	21.7	22.4	29.2	29.8	34.7	40.9	48.8	49.9	50.8	54.6	60.4
f	46.0	2.8	5.9	12.7	16.5	19.2	21.1	28.6	29.9	35.4	36.0	46.0	46.0	50.7	53.5	60.4
g	45.2		6.1	11.8	14.5	17.5	20.9	26.9	27.4	33.3	38.4	44.1	47.5	52.2	56.9	
$\bar{X}$		2.7	6.5	12.0	14.6	19.5	22.2	28.3	30.0	34.2	38.7	45.1	47.2	51.1	55.8	60.1
$\pm s$		0.79	0.69	1.34	1.32	1.97	1.94	1.31	1.75	1.50	2.37	2.17	1.71	1.21	1.71	1.51
$\pm s_m$		0.32	0.26	0.51	0.50	0.74	0.73	0.49	0.66	0.57	0.89	0.82	0.65	0.46	0.65	0.62
$\pm t_{s_m}$		0.83	0.63	1.24	1.22	1.82	1.79	1.21	1.62	1.39	2.19	2.01	1.58	1.12	1.58	1.58

dans du quartz. (*e*) Hydroxyde de sodium "pour analyse": S-1 à S-5. (*f*) Tubes à essai en quartz transparent, diamètre 14 mm, longueur 130 mm et ballons de Kjeldahl en quartz, capacité environ 250 ml (Société Electrothermique de la Tout-de-Trême), pipettes graduées 0.5, 1 et 2 ml.

Appareillage. Spectrofluorimètre Zeiss (modèle ZFM4C); lampe à mercure; étalon fluorescent Zeiss; cuves de quartz $l = 1$ cm.

Etude préliminaire

Pour doser le bore dans les différentes soudes, nous avons eu recours à la réaction fluorescente de l'acide borique avec l'H.M.C.B.[1]. Ce réactif est très sensible et sélectif du bore; il permet de doser des quantités de l'ordre du nanogramme. Une étude précédente montre que les 41 éléments étudiés ne donnent pas de fluorescence supérieure à une solution témoin[1] (réactif $+ H_2SO_4$ conc.). Toutefois nous avons crû indispensable, avant d'utiliser ce réactif, de contrôler la fidélité de la méthode et de rechercher les éventuelles interférences dues à la soude elle-même ou aux impuretés qu'elle renferme.

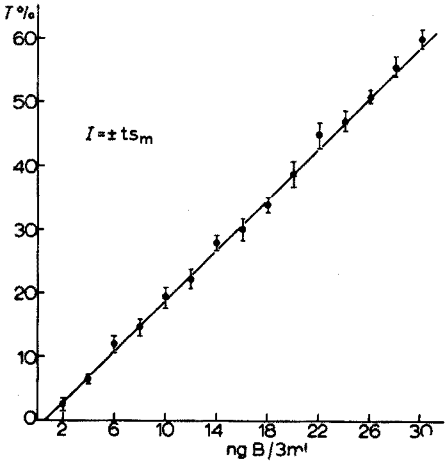
Contrôle de la fidélité de la méthode fluorimétrique à l'H.M.C.B. Pour déterminer la dispersion probable par rapport à une courbe moyenne, représentant la variation de l'intensité de fluorescence en fonction de la quantité d'acide borique, nous avons établi, au cours d'une période de 45 jours, 7 courbes d'étalonnage pour des quantités de bore comprises entre 2 et 30 ng/3 ml. Chaque courbe a été tracée au moyen de quinze points dont chacun est le résultat d'une mesure isolée. Afin que ce contrôle de la fidélité de la méthode à l'H.M.C.B. soit aussi rigoureux que possible et pour que l'on puisse en tirer des conclusions valables, nous n'avons pas pris aucunes précautions autres que celles qu'exige généralement un dosage de submicrotraces d'un élément quelconque.

Nous avons utilisé pour le nettoyage des tubes à essai et du matériel de verre et de quartz indifféremment, l'acide nitrique concentré, un mélange sulfonitrique et un liquide nettoyant alcalin. Les différentes solutions ont été préparées dans l'atmosphère du laboratoire dont le degré d'humidité variait d'un jour à l'autre et la fluorescence a été développée dans une étuve à $70 \pm 2°$. La durée de chauffage des solutions a été fixée à volonté de 35 à 45 min et leur refroidissement s'effectue à l'aide d'eau froide immédiatement après leur sortie de l'étuve. Enfin nous avons employé durant toute cette étude 4 lots différents d'acide sulfurique Merck p.a.

Dans le Tableau I nous donnons les résultats de nos mesures qui nous ont permis d'établir les calculs statistiques.

La Figure 1 représente d'autre part, la courbe d'étalonnage moyenne obtenue et les limites entre lesquelles elle peut varier pour une probabilité $P = 0.05$. On constate que le degré de reproductibilité est élevé et on en conclut, en tenant compte des concentrations de bore utilisées, que la fidélité de la méthode à l'H.M.C.B. est très satisfaisante.

Etude des interférences. La mise en solution directe des différentes soudes dans l'acide sulfurique concentré (voir p. 313) fournit des solutions qui présentent une légère fluorescence bleuâtre. La composition spectrale de cette fluorescence est différente de celle des solutions de complexe "BO_3H_3–H.M.C.B.". Elle a une certaine intensité à 490 nm (maximum du complexe) inférieure pourtant à celle d'une solution du réactif (voir Figs. 3A et 3C). D'autre part, le spectre de fluorescence d'une solution sulfurique de soude en présence de réactif est identique à celui d'une solution sulfurique du complexe "BO_3H_3–H.M.C.B." (voir Fig. 2). Ceci indique non seulement la présence de bore dans la soude mais montre aussi que la fluorescence observée sur les solutions acide sulfurique–soude a disparu. On peut donc supposer que cette fluorescence parasite est masquée par le réactif. En effet la fluorescence d'une solution sulfurique de soude disparait dès l'adjonction de l'H.M.C.B. Ceci se remarque en comparant les Figs. 3A, 3B et 3C.



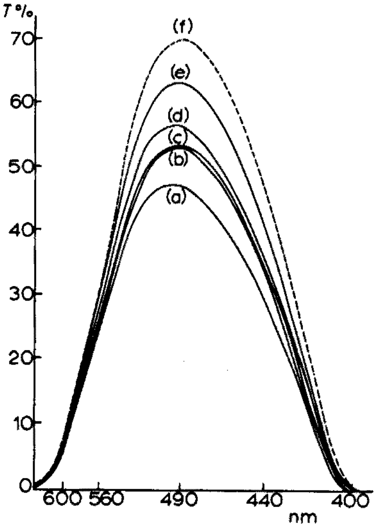


Fig. 1. Courbe d'étalonnage.

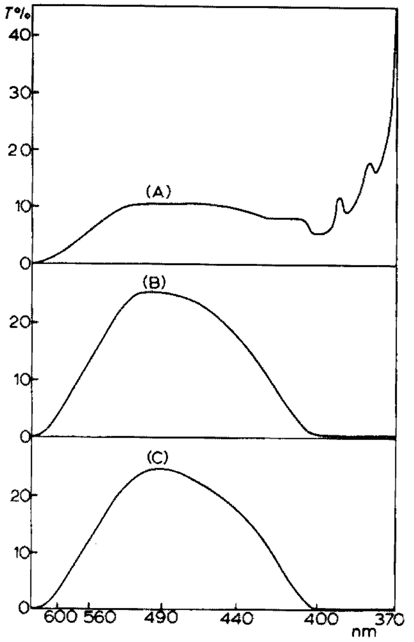
Fig. 2. Spectres de fluorescence des solutions sulfuriques de soude en présence de réactif. 21 μg H.M.C.B./3 ml H_2SO_4 conc. mg de soude contenus dans 3 ml: (*a*) S-1: 153.84; (*b*) S-5: 150.53; (*c*) S-2: 139.77; (*d*) S-3: 149.53; (*e*) S-4: 150.32; (*f*) acide borique: 12 ng B/3 ml.

Les mêmes constatations ont été faites avec toutes les soudes étudiées, de sorte que, lors du microdosage de bore dans une soude de haute pureté par l'H.M.C.B., une séparation préalable n'est pas nécessaire.

Influence de l'eau. Lors de la dissolution de la soude dans l'acide sulfurique concentré, il se forme de faibles quantités d'eau qui en modifient la concentration. Pour se placer dans les conditions optimums pour le développement de la fluorescence nous avons éliminé cette eau par chauffage des solutions sulfuriques de soude jusqu'à commencement de vapeurs blanches. Cependant cette opération augmente la fluorescence parasite qui devient importante et gênante de sorte qu'un dosage direct du bore n'est plus possible. Pour éviter le chauffage à vapeurs blanches, nous avons été amenés à étudier l'influence de l'eau sur la formation du complexe "BO_3H_3–H.M.C.B.".

La Fig. 4, représentant la variation de l'intensité de fluorescence en fonction de la teneur en eau des solutions sulfuriques d'acide borique en présence de H.M.C.B., montre que la fluorescence est constante pour des teneurs en eau comprises entre 0% et 6% et qu'elle ne diminue sensiblement qu'à partir de 10% (H_2O dans H_2SO_4 conc.).

Une augmentation de la concentration en acide sulfurique des solutions de soude par chauffage à vapeurs blanches n'est donc point nécessaire, d'autant moins



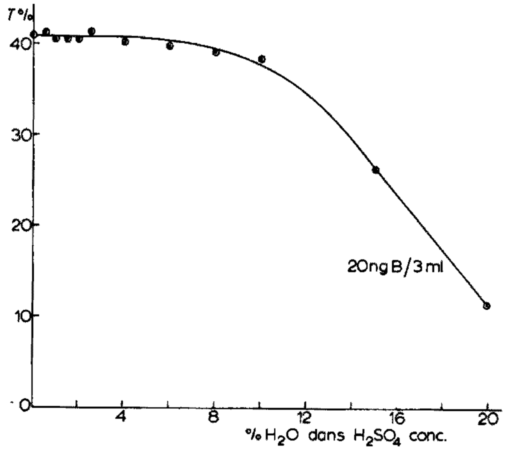


Fig. 3. Spectres de fluorescence. (A) 137.87 mg NaOH/3 ml H_2SO_4 conc.; (B) 137.87 mg NaOH + 21 μg H.M.C.B./3 ml H_2SO_4 conc.; (C) 21 μg H.M.C.B./3 ml H_2SO_4 conc.

Fig. 4. Variation de l'intensité de fluorescence en fonction de la teneur en eau des solutions sulfuriques de H_3BO_3 et de H.M.C.B.

que les quantités d'eau produites par une mise en solution directe de la soude dans l'acide sulfurique sont très inférieures à 10% (voir ci-dessous).

Dosage direct de traces de bore dans la soude

Mise en solution. Dans un Kjeldahl en quartz de 250 ml refroidi extérieurement à l'aide d'un bain de glace, on introduit 45 ml d'acide sulfurique concentré et 5 à 5.6 g de soude (de préférence en pastilles) par petites portions en agitant énergiquement et en prenant les précautions qui s'imposent. Après cette opération une partie seulement de la soude est dissoute et pour accélérer la dissolution on élève graduellement la température du bain jusqu'à 80°.

Lorsque la mise en solution est complète, on refroidit et transvase dans un ballon jaugé de 100 ml. On lave l'agitateur et le ballon de Kjeldahl, transvase et complète au trait de jauge par l'acide sulfurique concentré.

Développement de la fluorescence et mesures. Dans des tubes à essai en quartz, numérotés de 1 à 6, on introduit successivement:

Numéros des tubes	1	2	3	4	5	6
Acide sulfurique conc. (ml)	2.8	2.8	2.7	2.7	0.1	0
v ml de solution sulfurique de soude	0	0	0	0	2.7	2.7
Solution de H.M.C.B. à 0.0105% dans H_2SO_4 conc. (ml)	0.2	0.2	0.2	0.2	0.2	0.2
Solution d'acide borique à 100 ng B/ml dans H_2SO_4 conc. (ml)	0	0	0.1	0.1	0	0.1

Après homogénéisation des solutions, on chauffe 35 min dans une étuve à 70°, ferme les tubes avec des bouchons en polyéthylène, refroidit, introduit dans une cuve de quartz de 1 cm d'épaisseur et mesure la transmission (T) à 490 nm (2.04 μ^{-1}), en excitant la solution par le triplet de mercure (filtre 365 nm). Avant chaque mesure l'appareil doit être calibré au moyen d'un étalon fluorescent stable.

RÉSULTATS

Si T_1, T_2, ... T_6 sont les valeurs des transmissions des solutions 1, 2, ... 6 et si T_B = transmission moyenne du blanc, T_A = transmission moyenne de la solution étalon, t_A = transmission de 10 ng de bore dans les conditions de l'expérience, t_5 = transmission de x ng renfermé dans 2.7 ml de la solution de l'échantillon, t_6 = transmission de $x+10$ ng, on a:

$T_A=(T_3+T_4)/2 \qquad T_B=(T_1+T_2)/2 \qquad t_A=T_A-T_B \qquad t_5=T_5-T_B$ et $t_6=T_6-T_B$

on a alors:

par la méthode de l'étalon externe (b):

$$\% \text{ bore} = \frac{t_5}{t_A}\frac{10^{-4}}{v \cdot p}$$

par la méthode de l'étalon interne:

$$\% \text{ bore} = \frac{t_5 \cdot 10^{-4}}{(t_6-t_5) \cdot v \cdot p}$$

par la méthode mixte (a):

$$\% \text{ bore} = \frac{(t_6-t_A) \cdot 10^{-4}}{t_A \cdot p \cdot v}$$

p étant le poids en g de l'échantillon et v ml le volume prélevé pour l'analyse de la solution de 100 ml de l'échantillon (v.p. 313).

Si une courbe d'étalonnage a été préalablement établie, la teneur en bore peut

TABLEAU II

RÉSULTATS POUR SOUDE S-1

Méthode NaOH (g)	*% B · 10⁶*			*Moyenne*
	a	*b*	*c*	
0.09116	1.30	0.44	0.88	0.87
0.10256	0.46	0.89	1.17	0.84
0.11396	0.60	0.60	0.79	0.66
0.11965	0.30	0.52	0.75	0.52
0.12535	0.95	0.96	1.12	1.01
0.13105	1.23	0.92	1.07	1.07
0.13675	0.72	0.53	0.66	0.64
0.14244	1.28	1.13	1.33	1.25
0.14814	1.34	0.59	0.74	0.89
0.15384	1.25	0.98	1.17	1.13

$X = 0.89$, $s = \pm 0.23$, $s_m = \pm 0.072$, $t_{s_m} = \pm 0.16$, $B = (0.9 \pm 0.2) \cdot 10^{-6}\%$.

TABLEAU III

RÉSULTATS POUR SOUDE S-2

Méthode NaOH (g)	*% B · 10⁶*			*Moyenne*
	a	*b*	*c*	
0.08603	2.67	2.67	3.02	2.79
0.09678	2.52	2.69	3.05	2.76
0.10754	2.51	3.72	3.99	3.41
0.11291	2.28	2.97	3.28	2.84
0.11829	2.62	3.63	3.89	3.38
0.12367	2.76	3.07	3.31	3.05
0.12904	2.91	3.60	3.84	3.45
0.13442	2.71	3.20	3.42	3.11
0.13979	3.65	3.83	4.04	3.84
0.14517	3.59	3.99	4.18	3.92

$X = 3.25$, $s = \pm 0.416$, $s_m = \pm 0.131$, $t_{s_m} = \pm 0.296$, $B = (3.2 \pm 0.3) \cdot 10^{-6}\%$

Soude S-3	*Soude S-4*	*Soude S-5*
$B = (3.2 \pm 0.3) \cdot 10^{-6}\%$	$B = (4.0 \pm 0.4) \cdot 10^{-6}\%$	$B = (2.0 \pm 0.16) \cdot 10^{-6}\%$

aussi bien être directement déterminée sur cette courbe (méthode (c)) qui est très reproductible. Dans les Tableaux II et III nous donnons les résultats de nos déterminations pour deux soudes pro analyse. Les valeurs figurant dans la cinquième colonne de chaque Tableau sont les moyennes de résultats obtenus selon les trois méthodes (a), (b) et (c). X est la moyenne de ces valeurs (5e colonne), s l'écart-type, s_m l'erreur-type, $\pm t_{s_m}$ les limites de confiance et B est la teneur en bore.

Nous remercions le Fonds National Suisse grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

On décrit une méthode pour le dosage direct de traces de bore dans l'hydroxyde de sodium de pureté analytique; elle est basée sur la réaction de fluorescence très sensible de l'hydroxy-2-méthoxy-4-chloro-4'-benzophénone. On peut ainsi doser des quantités de bore de l'ordre du nanogramme. L'échantillon à analyser est dissous directement dans l'acide sulfurique concentré, sans séparation préalable; des teneurs en eau jusqu'à 8% (v/v) ne modifient pas la fluorescence. Les résultats obtenus pour 5 produits différents, de pureté analytique, sont les suivants: $(0.9 \pm 0.2) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(4.0 \pm 0.4) \cdot 10^{-6}$ et $(2.0 \pm 0.16) \cdot 10^{-6}\%$ B.

SUMMARY

A method based on the highly sensitive fluorescent reaction of boric acid with 2-hydroxy-4-methoxy-4'-chlorobenzophenone (H.M.C.B.), is described for the direct determination of traces of boron in "analytical grade" sodium hydroxide. In the nanogram range, the reliability of the H.M.C.B. method is satisfactory; the fluorescent reaction is not affected by up to 8% (v/v) of water. The sample is dissolved directly in concentrated sulfuric acid and no preliminary separation is needed. Interferences from other impurities of sodium hydroxide are negligible. Results for five different "analytical grade" reagents were: $(0.9 \pm 0.2) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(4.0 \pm 0.4) \cdot 10^{-6}$ and $(2.0 \pm 0.16) \cdot 10^{-6}$% B.

ZUSAMMENFASSUNG

Es wird eine Methode zur direkten Bestimmung von Spuren Bor in analytisch reinem Natriumhydroxid beschrieben, die auf der hochempfindlichen Fluoreszenzreaktion von Borsäure mit 2-Hydroxy-4-methoxy-4'-chlorobenzophenon (HMCB) beruht. Im Nanogrammbereich ist die Zuverlässigkeit der Methode befriedigend; bis hinauf zu 8% (v/v) Wasser wird die Fluoreszenzreaktion nicht beeinflusst. Die Probe wird direkt in konzentrierter Schwefelsäure gelöst, ohne dass eine vorhergehende Trennung erforderlich ist. Störungen durch andere Verunreinigungen des Natriumhydroxids sind vernachlässigbar. Die Ergebnisse von 5 verschiedenen analytisch reinen Reagenzien waren: $(0.9 \pm 0.2) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(3.2 \pm 0.3) \cdot 10^{-6}$, $(4.0 \pm 0.4) \cdot 10^{-6}$ und $(2.0 \pm 0.16) \cdot 10^{-6}$% B.

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Anal. Chim. Acta, 35 (1966) 309–316

SPECTROPHOTOMETRIC DETERMINATION OF NITRATE USING CHROMOTROPIC ACID

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Nitrate and the oxides of nitrogen are recognized as important pollutants in water and air respectively. There are many sources of pollution, including the manufacture and use of fertilizers, automobile exhausts and various industrial operations. Nitrates in water often indicate the final stages of biological oxidation. Infant methemoglobinemia has been traced to high nitrate content in well waters. In Minnesota alone, from 1947 to 1950, there were 139 cases with 14 deaths traced to the use of contaminated farm water supplies[1]. Oxides of nitrogen in air are especially significant in smog formation. Several spectrophotometric methods for the determination of nitrate have been reported in the literature which involve the use of common reactions such as reduction followed by diazotization[2,3], or Nessler's reaction[4], nitration reactions[5-10] or others[11]. Determinations of nitrates using redox reactions are not selective and are generally inferior to nitration methods[12]. The most widely used method at present is based on the nitration of phenoldisulfonic acid[13-15]. This method is time-consuming because a relatively large volume of sample must be evaporated carefully and the reaction is not sensitive enough to be applicable for low levels of nitrate. Even more critical, the method suffers from a large number of interferences, the most serious being chloride, and is generally quite unreliable. Other methods are reported utilizing 2,4-xylenol[4,5], 2,6-xylenol[7-9], or phenarsazenic acid[16] as reagents. The 2,6-xylenol method has been improved[17] to tolerate up to 700 mg/l of chloride using mercury(II) sulfate as a masking agent. It involves a solvent extraction separation procedure.

WEST AND SARMA[18] introduced a specific and sensitive spot test for nitrate based on its reaction with a solution of chromotropic acid (1,8-dihydroxy-3,6-naphthalene disulfonic acid) in concentrated sulfuric acid. WEST AND LYLES[19] have shown that this reaction is free of interferences from most common ions. Of special interest was the observation that chlorides do not form a color with the reagent alone, but in the presence of nitrate they do increase the intensity of the yellow color produced. Using a large excess of chloride in the form of hydrochloric acid (1 ml of concentrated hydrochloric acid added to 100 ml of a 0.01 % solution of the reagent in concentrated sulfuric acid), they found that the reaction complied with Beer's law in the range of 0.1 to 1 mg/l of nitrate and applied this to the determination of nitrate in samples of water or air. Above 1 mg/l the curve showed a discontinuity and a positive deviation from Beer's law. BATTEN[20] has used this method for the determination of nitrate in samples containing traces of formaldehyde but no chloride, the interference due to the former being removed by oxidation to formic acid.

A further investigation of the reaction between nitrate and chromotropic acid and the influence of chloride, nitrite and oxidants has been carried out. A procedure is now proposed in which the discontinuity previously noted has been eliminated and reliable results can be obtained directly on 2.5-ml samples of water over the range 0.2–20 mg/l of nitrate. The procedure is free of significant interferences.

EXPERIMENTAL

Reagents and apparatus

All aqueous solutions were made using double-distilled water.

Standard nitrate solution. A stock solution was prepared by dissolving 1.371 g of reagent-grade sodium nitrate and diluting to 1 l to give a 1.0 mg nitrate/ml solution. By suitable dilution, a series of standards was prepared for the concentration range 0.2–20 mg/l.

Sulfuric acid. Analytical reagent-grade (Mallinckrodt) concentrated acid was found to be free from nitrate and was used throughout the procedure.

Purified chromotropic acid. A saturated solution of disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid (technical grade, Eastman Organic Chemicals) was processed twice using decolorizing charcoal. The purified reagent was crystallized from the filtered solution by the addition of sulfuric acid. The product was filtered, washed several times with ethanol and dried below 80°. A 0.1% solution of the reagent in concentrated sulfuric acid was prepared and then stored in low actinic bottles. The reagent solution was colorless (a check on freedom from nitrate contamination of the sulfuric acid) and was found to be adequately stable for two weeks.

Sulfite–urea solution. 5 g of urea and 4 g of reagent-grade anhydrous sodium sulfite were dissolved and diluted to 100 ml with distilled water. The solution was used for the elimination of interfering substances such as nitrite or oxidizing agents.

Antimony solution. The solution was prepared by heating 0.5 g of antimony metal in 80 ml of concentrated sulfuric acid until all of the metal was dissolved. The solution was cooled and added to 20 ml of ice water. Any salt which crystallized when kept overnight was redissolved by heating. Two milliliters of this solution added to 2.5 ml of sample can mask up to 2000 mg/l of chloride.

Apparatus. A Beckman Model DK recording spectrophotometer was used in the study of absorption spectra. Absorbance measurements were made in a Beckman Model DU spectrophotometer equipped with matched 1-cm quartz cells.

Preliminary experiments

The absorption maximum of the yellow reaction product of nitrate with chromotropic acid was found to be at 410 mμ. Preliminary experiments were made by pipetting 2.5 ml of nitrate solution into 10-ml volumetric flasks and diluting to 3 ml by adding 0.5 ml of double-distilled water. Next, 1 ml of concentrated sulfuric acid was added, the solution was swirled and the flasks were allowed to stand for 4 min in a tray of cold water at 10–20°, in which the water level was slightly above that in the flask. One ml of chromotropic reagent was added to each flask which was swirled and then allowed to stand for an additional 3 min. The volume of solution in each flask was next made up to 10 ml by the addition of concentrated

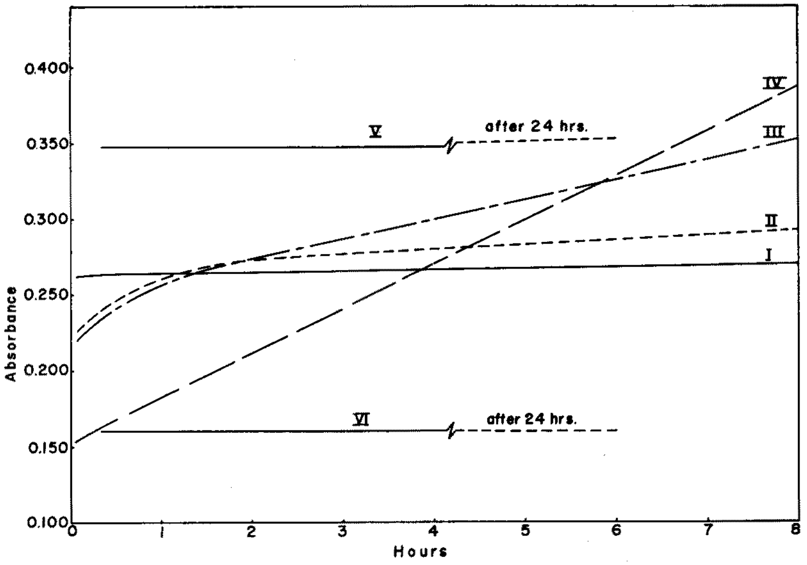

Fig. 1. Variation of absorbance with respect to time and the influence of chloride on color development.
(I) 15 mg of nitrate/l and no chloride;
(II) 15 mg of nitrate/l with 200 mg of chloride/l;
(III) 15 mg of nitrate/l with 400 mg of chloride/l;
(IV) 15 mg of nitrate/l with 1000 mg of chloride/l;
(V) 20 mg of nitrate/l with 2000 mg of chloride/l;
(VI) 9.15 mg of nitrate/l with 4000 mg of chloride/l and 20 mg of antimony(III).

sulfuric acid, the flasks were stoppered and the contents mixed thoroughly. Sufficient heat was developed to promote the reaction without the solutions boiling or spattering. After the flasks were cooled to room temperature the volume was again adjusted to 10 ml. Blank experiments were run substituting double-distilled water instead of nitrate solution.

Studies of the reaction revealed that the maximum color was developed within 10 min and was found to be stable for 24 h as shown in Fig. 1. The temperature of the cooling bath was found not to be critical and may vary anywhere from 10 to 20°. Heat developed during mixing has no harmful effect as was shown by reproducibility of the final absorbances. The cooling bath served simply to dissipate sufficient heat to avoid boiling of the solutions with resultant formation of bubbles. Maximum and constant absorbance was obtained when the total aqueous phase was between 2.7 and 3.1 ml and the final volume was made up to 10 ml using concentrated sulfuric acid. The mole ratio method showed that two moles of nitrate react with one mole of chromotropic acid.

Study of potential interferences. Substances which ordinarily interfere seriously in nitrate determinations such as nitrite, oxidizing agents, chloride and iron(III) were studied specially.

Chlorine and certain other oxidizing agents can react with chromotropic acid producing yellow products. The absorption spectrum appears similar to the nitrate–chromotropic acid system with the maximum shifted to 460 mμ. However, addition of excess sodium sulfite before the addition of the reagent completely eliminated

TABLE I

ELIMINATION OF INTERFERENCES

Interference (mg/l)	*Nitrate (mg/l)*	*Masking agent*	*Absorbance*	*Corrected absorbance*
Nitrite				
0.0	0.0	2.5 mg urea	0.015	Blank
30	0.0		1.2	1.2
30	0.0	2.5 mg urea	0.015	0.000
30	3.0	2.5 mg urea	0.069	0.054
30	5.5	2.5 mg urea	0.113	0.098
Oxidant (MnO_4^-)				
0.0	0.0	1.2 mg SO_3^{2-}	0.015	Blank
40	0.0		0.620	0.605
40	0.0	1.2 mg SO_3^{2-}	0.015	0.000
40	3.0	1.2 mg SO_3^{2-}	0.069	0.054
40	5.5	1.2 mg SO_3^{2-}	0.113	0.098
Iron(III) (+ chloride[a])				
0.0	0.0	10 mg Sb^{3+}	0.015	Blank
40	0.0		0.115	0.100
40	0.0	10 mg Sb^{3+}	0.015	0.000
40	0.8	10 mg Sb^{3+}	0.030	0.015

[a] Added with the iron in each case in the amount of 1000 mg/l.

the interference due to oxidizing agents, as shown in Table I, and was without influence on the nitrate–chromotropic acid reaction.

Nitrite produced an intense color similar to that produced by nitrate. The absorption maximum in this case occurred at 440 mμ. Addition of urea before the addition of the reagent eliminated all nitrite as nitrogen gas, yet did not affect the nitrate–chromotropic acid system. This provided an effective and simple means for avoiding interferences due to nitrite.

Chloride may react with nitrate in highly acidic solutions giving the following products

$$HNO_3 + 3\ HCl \rightarrow NOCl + Cl_2 + 2\ H_2O.$$

This is a potential disadvantage inherent in all methods employing high acid concentrations. In the present case the products react with chromotropic acid and might account for the increase in sensitivity as observed by WEST AND LYLES, in which chloride and chromotropic acid were introduced simultaneously into a nitrate solution. The color developed was similar to that produced with nitrate and reagent alone but was not stable. In Fig. 1, plots II, III, and IV show the chloride interference at the 15 mg/l nitrate level when the study was carried out according to the preliminary procedure. The rate of color development was suppressed by chloride initially, since nitrate and chloride reacted with each other in acidic solution before the reagent was added. It can be seen from Fig. 1, plot IV, that with 1000 mg/l of chloride, more than 50% of the nitrate reacted with chloride when such mixtures were kept for 4 min in a 1:2 (v/v) sulfuric acid–water medium.

Because of the unreliability of the reactions involving both nitrate and chloride with chromotropic acid, a procedure which would eliminate chloride or the effect of chloride was indicated. Precipitation of chloride would be effective but very tedious. The elegance of masking techniques was tempting but challenging. However, gratifying results were obtained using the sequestering action of antimony and it has been established as an effective and convenient means for conditioning the test reaction.

Among possible masking agents for chloride that were studied, mercury(II) and antimony(III) each showed promise. However, mercury could not be used in the present system because it was easily reduced by the reagent. Fortunately, antimony was found to mask chloride so completely that true test colors developed and remained stable even after 24 h (Fig. 1, plots V and VI). Antimony did not interfere with the nitrate–chromotropic acid system, yet it effectively masked up to 2000 mg of chloride/l when used in the recommended procedure (Table II).

Iron(III) causes serious interference in many colorimetric procedures due to the yellow color of its chloro-complex. In the present method this interference was overcome by the addition of antimony which completely discharged the color by demasking the chloroferrate(III) complex. Up to 40 mg of iron(III) per l showed no interference (Table I).

Recommended procedure

Pipet 2.5 ml of nitrate solution (standard or sample) having a nitrate content in the range 0.2–20 mg/l into dry 10-ml volumetric flasks. To each flask add 1 drop of sulfite–urea solution, place the flasks in a tray of cold water (10–20°) and add 2 ml of the antimony sulfate solution. The flasks should be swirled during the addition of each solution. After the mixtures have stood in the bath for about 4 min, add 1 ml of chromotropic acid reagent, swirl the flasks again and then allow to stand in the cooling bath for an additional 3 min. Next add concentrated sulfuric acid to

TABLE II

ABSORBANCE OF NITRATE–CHROMOTROPIC ACID SYSTEM

(At 410 $m\mu$ using 1-cm cell)

Nitrate (mg/l)	*Corrected absorbance series # 1*	*Corrected absorbance series # 2*	*Corrected absorbance series # 3*	*Corrected absorbance series # 4*
0.0	0.015	0.015	0.015	0.015
0.2	0.0035	0.0035	0.004	0.0035
0.3	0.005	0.005	0.005	0.005
0.4	0.007	0.007	0.008	0.007
0.8	0.015	0.014	0.015	0.016
1.6	0.028	0.028	0.029	0.028
4.0	0.071	0.073	0.072	0.071
6.0	0.107	0.107	0.107	0.107
8.0	0.142	0.141	0.144	0.142
12.0	0.211	0.212	0.211	0.211
16.0	0.277	0.280	0.278	0.278
20.0	0.347	0.347	0.350	0.351

Series # 1. With nitrate only.
Series # 2. Nitrate in presence of urea and sulfite.
Series # 3. Nitrate in presence of urea and sulfite and 10 mg of antimony(III).
Series # 4. Nitrate in presence of urea and sulfite and 10 mg of antimony(III) together with 2000 mg of chloride/l.

adjust the volume to the 10-ml mark, stopper the flasks and mix the contents by inverting them 4 times. Finally allow the solutions to stand for 45 min at room temperature and again adjust the volume to the 10-ml mark with concentrated sulfuric acid. Final mixing should be done very gently so as not to introduce gas bubbles. Double-distilled water was substituted for nitrate solution for running blank experiments.

The absorbance reading should be taken 15 min or more after the last adjustment of volume. The cell should be rinsed with the solution and then filled carefully so as to avoid trapping bubbles. For this operation it was found expedient to keep the cell in a slanting position (30° to horizontal) with a ground side facing up and pouring the solution very slowly down the side of the cell. The absorbance may be measured in a Beckman DU or other suitable spectrophotometer at 410 mμ using water in the reference cell.

RESULTS AND CONCLUSIONS

Table II gives the corrected absorbances of the nitrate–chromotropic acid system at various concentrations of nitrate, both in the absence and in the presence of chloride. Beer's law was obeyed up to 20 mg of nitrate/l. Table III presents results of a statistical evaluation of nitrate determinations at various levels containing different amounts of chloride (0–2000 mg/l). The standard deviation and relative standard deviation for a 95% confidence limit is given at various levels. It is also possible to get better results at low nitrate levels using a 5-cm cell and Beckman model B spectrophotometer for absorbance measurement. Color may be developed from 5 ml of standards or samples by adding a proportional amount of reagents and adjusting the final volume to 25 ml.

The method can be directly applied to the analysis of water without recourse to evaporation or precipitation steps. However, appreciable amounts of suspended impurities should be removed by centrifugation or filtration. Table IV presents the data from analyses of turbid samples. Tolerance to chloride can be extended from 2000 to 4000 mg/l by doubling the strength of the antimony solution. Interferences due to iron(III), nitrite, and oxidizing agents have also been eliminated. In addition, studies have been made of diverse ions in concentrations of 200 mg/l, both in the

TABLE III

STATISTICAL ANALYSIS OF ABSORBANCE AT VARIOUS LEVELS OF NITRATE

Number of experiments	*Nitrate taken (mg/l)*	*Average absorbance difference*	*± Standard deviation (mg/l)*	*± Coefficient of variation for 95% confidence limit (%)*
20	0.3	0.0049	0.030	20
10	0.6	0.0115	0.030	10
10	1.2	0.0227	0.024	4
10	3.1	0.0560	0.0042	2.7
10	6.5	0.115	0.093	3
10	10.0	0.178	0.100	2
10	16.6	0.290	0.160	2
10	19.5	0.340	0.180	2

TABLE IV

ANALYSIS OF WATER SAMPLES

Nature of sample	*Amount of NO_3^- added (mg/l)*	*Chloride present (mg/l)*	*Nitrate found (mg/l)*	*Number of experiments*
Baton Rouge tap water	0.00	50	Nil	5
Baton Rouge tap water	2.50	50	2.5 ± 0.02	10
Synthetic sample[a]	2.00	4000	2.0 ± 0.02	5
	4.00	4000	4.0 ± 0.05	5
	8.00	4000	8.0 ± 0.05	5
No. 37[b]	0.00	1120	4.30	3
No. 37	3.00	1120	7.30	3
No. 38[b]	0.00	1176	4.35	3
No. 38	3.00	1176	7.35	3
No. 39[b]	0.00	1006	4.70	3
No. 39	3.00	1006	7.70	3
No. 40[b]	0.00	1016	8.10	3
No. 40	3.00	1016	11.10	3
No. 41[b]	0.00	950	4.60	3
No. 41	3.00	950	7.60	3
No. 42[b]	0.00	1016	4.60	3
No. 42	3.00	1016	7.60	3

[a] The antimony(III) solution used was double strength because of the high chloride concentration.

[b] Water samples received from Kem-Tech Laboratories, Inc., Baton Rouge, were analyzed according to recommended procedure after removal of suspended matter by centrifugation.

absence and in the presence of 4 mg of nitrate/l. There were no significant interferences disclosed when the recommended test procedure was applied to the following:

Li^+, Na^+, K^+, Cu^{2+}

Be^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}

BO_2^-, $B_4O_7^{2-}$, Al^{3+}

CO_3^{2-}, Ti^{4+}, Zr^{4+}, Sn^{2+}, Sn^{4+}

NH_4^+, HPO_4^{2-}, $P_4O_7^{4-}$, VO^{2+}, As^{3+}, Bi^{3+}

S^{2-}, SO_3^{2-}, Cr^{3+}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}

F^-, Cl^-, ClO_3^-, ClO_4^-, Mn^{2+}, MnO_4^-, Br^-, BrO_3^-, OCl^-

Fe^{2+}, Co^{2+}, Ni^{2+}.

It should be noted, however, that Ba^{2+}, Sr^{2+}, Pb^{2+}, I^-, IO_3^-, SeO_3^{2-} and SeO_4^{2-} are incompatible with the system and form precipitates. They would not be expected to be present in significant amounts in ordinary waters and so do not offer any complications. If present in concentrations greater than 20 mg/l, Cr^{3+} interferes to the absorbance of its sulfato-complex.

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SUMMARY

A spectrophotometric method is described for the determination of nitrate in the 0.5 to 50 µg range using chromotropic acid as the reagent and masking agents for the elimination of possible critical interferences due to chloride, chlorine, iron(III) and oxidants. The method can be applied directly for the determination of 0.2–20 mg of nitrate/l in 2.5-ml samples of water. Over 4000 mg of chloride/l can be tolerated. The method is simple, rapid and reliable. At the 1 mg/l level for nitrate the coefficient of variation at the 95% confidence limit is 4%. There are no interferences.

RÉSUMÉ

Les auteurs décrivent une méthode pour le dosage spectrophotométrique des nitrates (0.5 à 50 µg) au moyen d'acide chromotropique, comme réactif, et d'agents masquants pour empêcher les interférences dues aux chlorures, au chlore, au fer(III) et aux oxydants. Ce procédé peut être appliqué directement au dosage des nitrates (0.2 à 20 mg/l) dans des échantillons de 2.5 ml d'eau. On peut tolérer jusqu'à 4000 mg/l de chlorures. La méthode est simple, rapide et sûre. Il n'y a pas d'interférences.

ZUSAMMENFASSUNG

Es wird eine einfache und schnelle spektralphotometrische Methode zur Bestimmung von 0.5–50 µg Nitrat beschrieben, bei der Chromotropsäure als Reagenz und maskierende Reagenzien zur Elimination möglicher Störungen durch Chlorid, Chlor, Eisen(III) und Oxidationsmittel verwendet werden. Die Methode kann direkt zur Bestimmung von 0.2–20 mg Nitrat/l in 2.5 ml einer Wasserprobe verwendet werden. Über 4000 mg Cl^-/l sind zulässig. Bei einem Gehalt von 1 mg Nitrat/l beträgt der Variationskoeffizient 4% bei einem Vertrauensbereich von 95%. Störungen treten nicht auf.

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SPECTROPHOTOMETRIC DETERMINATION OF DIETHYLLEAD AND DIETHYLTIN IONS WITH 4-(2-PYRIDYLAZO)-RESORCINOL

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The most widely used and most sensitive spectrophotometric methods for the determination of organolead and organotin cations are undoubtedly those based on reaction with dithizone[1,2], but these methods suffer from lack of selectivity, photodecomposition of dithizone, and insolubility of the complexes in aqueous media.

The use of 4-(2-pyridylazo)-resorcinol (PAR) for the photometric determination of many metals has been widely described[3-8]. In an analytical research program on organometallic compounds, we have found that PAR reacts with organometallic halides of the R_2MCl_2 type ($M = Sn$ or Pb; $R = CH_3$, C_2H_5, C_6H_5) to form coloured complexes. No detectable colour reaction takes place under the same conditions with compounds of the R_3MCl type. The present paper describes a study of PAR as an analytical reagent in the selective spectrophotometric determination of diethyllead and diethyltin dichlorides.

EXPERIMENTAL

Reagents

Diethyllead dichloride (m.p. 220°) was prepared by the method of HEAP *et al.*[9].

Diethyltin dichloride (m.p. 84°) was prepared by the method of KOZESCHKOW[10].

Aqueous solutions of these materials were used in the tests described.

$2.0 \cdot 10^{-3}$ M PAR solution. Dissolve 0.4744 g of PAR (monosodium salt, RP, C. Erba, Italy) in water and dilute to 1 l. The purity of the PAR sample was checked by potentiometric titration with sodium hydroxide.

Buffer pH 9. Adjust 0.1 *M* ammonium nitrate to pH 9 with ammonia solution.

Apparatus

Spectrophotometer. Unicam SP 800, with 1-cm cuvettes.

pH-meter. Knick, Berlin, model "pH 350".

RESULTS AND DISCUSSION

Figures 1a and 1b show respectively the differences in absorbance between $(C_2H_5)_2Pb$–PAR and $(C_2H_5)_2Sn$–PAR complexes and PAR blanks at various pH values. The pH values were adjusted by the addition of perchloric acid and sodium hydroxide and accurately measured with a pH meter. No buffer solutions were used,

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* Ricercatore aggiunto del C.N.R.

in order to exclude any possible interference. From the absorption spectra, it can be seen that the wavelengths of maximum absorption are unchanged at pH 5–10 for $(C_2H_5)_2PbCl_2$, and at pH 3–8 for $(C_2H_5)_2SnCl_2$ being 512 mμ and 514 mμ respectively. It was observed that the maximum colour intensity of the $(C_2H_5)_2M$–PAR complexes developed immediately and was stable for at least 24 h. The absorbance of the reagent alone was very small at the wavelength of maximum absorption of the complexes.

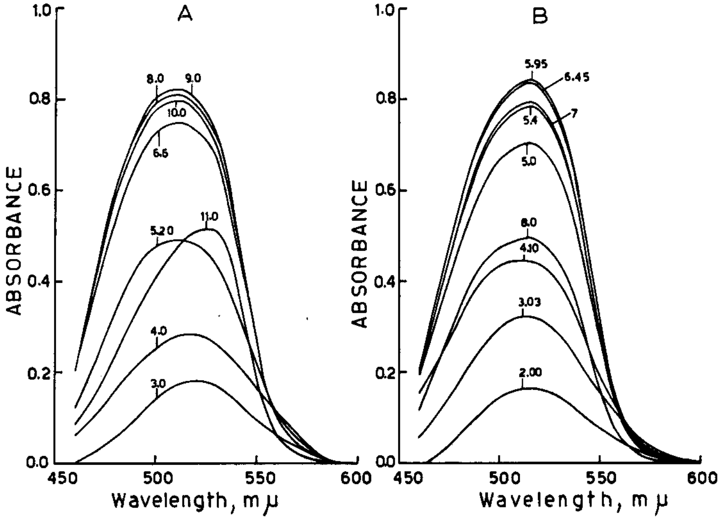


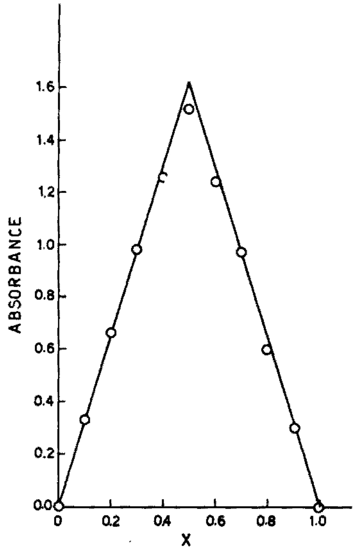
Fig. 1a. Difference in absorbance between $(C_2H_5)_2Pb$–PAR complex and PAR blank at various pH values. 1 ml of $2 \cdot 10^{-3}$ *M* $(C_2H_5)_2PbCl_2$ + 5 ml of $2 \cdot 10^{-3}$ *M* PAR diluted to 100 ml.
Fig. 1b. Difference in absorbance between $(C_2H_5)_2Sn$–PAR complex and PAR blank at various pH values. 1 ml of $2 \cdot 10^{-3}$ *M* $(C_2H_5)_2SnCl_2$ + 5 ml of $2 \cdot 10^{-3}$ *M* PAR diluted to 100 ml.

A plot of the absorbance at constant wavelength *vs.* pH indicated that the optimum pH values were 9 and 6 for $(C_2H_5)_2PbCl_2$ and $(C_2H_5)_2SnCl_2$ respectively. Subsequent determinations were therefore carried at these pH values. For diethyllead dichloride, similar results were obtained with an ammonia–ammonium nitrate buffer of pH 9 and with the pH adjustment indicated above, but for diethyltin dichloride all the buffer solutions employed interfered with the formation of the coloured complex.

The method of continuous variations[11,12] and the slope ratio method[13] are most frequently used to establish the empirical formulae of coloured complexes. Because of the impossibility of employing a buffer solution for the organotin dihalide, only the slope ratio method was used in the present work. Two series of solutions were prepared; in the first series, 0.2–1.0 ml of a $2.0 \cdot 10^{-3}$ *M* solution of diethyltin dichloride was added to 100 ml of a $4.0 \cdot 10^{-4}$ *M* PAR solution, and in the second series 0.2–1.0 ml of a $2.0 \cdot 10^{-3}$ *M* PAR solution was added to 100 ml of a $4.0 \cdot 10^{-4}$ *M* diethyltin dichloride solution. The pH of the solutions was adjusted to 6.0 and the optical density measured at 514 mμ against a reagent solution (first series) and water (second series) as reference. The same procedure was employed for the organolead compound in a buffered solution of pH 9.0. The slopes obtained for the two complexes were exactly the same and clearly indicated the formation of only 1:1 complexes of PAR with diethyltin or diethyllead.

The plot obtained for the organolead compound by the method of continuous variations is shown in Fig. 2. This confirms the formation of the 1:1 complex with diethyllead.

Under the optimum conditions as established above, Beer's law was obeyed between $2 \cdot 10^{-6}$ and 10^{-4} M of organometallic ion; molar extinction coefficients of 41,000 and 42,500 were obtained for the $(C_2H_5)_2Pb$–PAR and $(C_2H_5)_2Sn$–PAR complexes respectively.



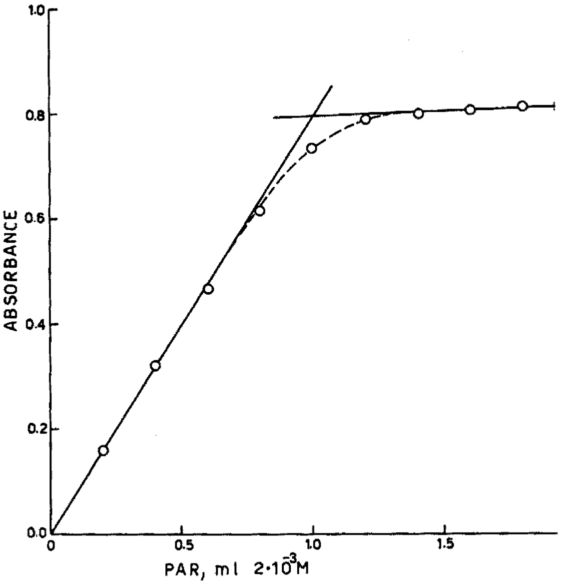


Fig. 2. Corrected continuous variation curve for $(C_2H_5)_2Pb$–PAR (pH 9, 512 mμ, [PAR] + $[(C_2H_5)_2Pb^{2+}] = 8.0 \cdot 10^{-5}$ M, $X = (C_2H_5)_2Pb^{2+}/PAR + (C_2H_5)_2Pb^{2+}$).

Fig. 3. Spectrophotometric titration curve of 100 ml of 2.10^{-5} M $(C_2H_5)_2PbCl_2$ with $2 \cdot 10^{-3}$ M PAR (pH 9, 1-cm cuvettes, 512 mμ).

For the diethyllead and tin cations, spectrophotometric determination was possible provided that the molar ratio of reagent to cation exceeded 4. The minimum detectable amount of cation was about 0.7 p.p.m. for 0.1 absorbance in a 10-mm cell. Because of the great solubility of PAR (monosodium salt) in water, the dilution factor may be as low as 2 and hence the sensitivity ($\varepsilon \cdot 10^{-3}$/dilution factor) may reach 20.

In the case of $(C_2H_5)_2PbCl_2$, the complex is so stable that spectrophotometric titrations with standard PAR solution can be carried out. An example of a titration of 0.6725 mg of diethyllead dichloride is shown in Fig. 3; the error is less than 0.5%.

Determination of $PbCl_2$ in the presence of $(C_2H_5)_2PbCl_2$

Compounds of the type R_2PbCl_2 readily decompose to lead chloride both in the solid state and in solution[14]. Moreover, these compounds are commonly prepared by treating tetraalkyllead with hydrogen chloride in organic solvents. Therefore samples of diethyllead dichloride often contain small amounts of lead chloride as an impurity and the possibility of determining the latter is of interest. In the present work, it was observed that the absorbance of the $(C_2H_5)_2Pb$–PAR complex did not change on addition of EDTA, whereas the Pb–PAR complex[8] was quantitatively destroyed by a stoichiometric amount of EDTA; this was proved by spectrophotometric titrations.

Accordingly, if an excess of PAR is added to a sample of diethyllead dichloride, any lead salt impurity can be determined by a spectrophotometric titration with EDTA at 512 mμ. Typical titration curves are shown in Fig. 4. Since it is necessary to work with transmittances above 10%, this method allows the determination of more than 5% of lead chloride in the mixture, with an error of 0.5–1%.

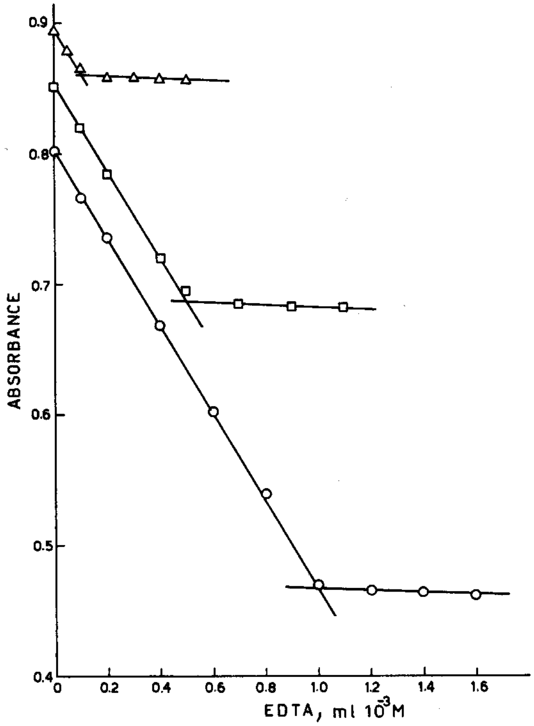


Fig. 4. Spectrophotometric titration curves of $PbCl_2$ in $(C_2H_5)_2PbCl_2$ with EDTA. (○) 1 ml of $1 \cdot 10^{-3}$ M $(C_2H_5)_2PbCl_2$ + 1 ml of $1 \cdot 10^{-3}$ M $Pb(NO_3)_2$ + 2 ml of $2 \cdot 10^{-3}$ M PAR; (□) 1.5 ml of $1 \cdot 10^{-3}$ M $(C_2H_5)_2PbCl_2$ + 0.5 ml of $1 \cdot 10^{-3}$ M $Pb(NO_3)_2$ + 2 ml of $2 \cdot 10^{-3}$ M PAR; (△) 1.9 ml of $1 \cdot 10^{-3}$ M $(C_2H_5)_2PbCl_2$ + 0.1 ml of $1 \cdot 10^{-3}$ M $Pb(NO_3)_2$ + 2 ml of $2 \cdot 10^{-3}$ M PAR (pH 9, 1-cm cuvettes, 512 mμ, V = 100 ml).

The determination of lower percentages of lead chloride is better done by a potentiometric technique, and this will be discussed in a forthcoming paper.

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SUMMARY

A study was made of the reaction of diethyllead and diethyltin ions with 4-(2-pyridylazo)-resorcinol; the compositions and the molar extinction coefficients of the compounds formed were determined. Methods are outlined for the determination of these organometallic cations. A method is described for the determination of lead chloride in the presence of $(C_2H_5)_2PbCl_2$.

RÉSUMÉ

On a étudié la réaction des ions diéthylplomb et diéthylétain avec le 4-(2-pyridylazo)-résorcinol-1, en déterminant la composition et le coefficient d'extinction moléculaire des produits. Une méthode est développée pour le dosage du chlorure de plomb en présence de $(C_2H_5)_2PbCl_2$.

ZUSAMMENFASSUNG

Es wurde die Reaktion zwischen Diäthylblei- und Diäthylzinn-Ionen mit 4-(2-Pyridylazo)-resorzin untersucht und die Zusammensetzungen und molaren Extinktionskoeffizienten der Verbindungen bestimmt. Es wird eine Methode zur Bestimmung von Bleichlorid in Gegenwart von $(C_2H_5)_2PbCl_2$ beschrieben.

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SPECTROPHOTOMETRIC DETERMINATION OF HYDRAZINE AND 1,1-DIMETHYLHYDRAZINE, SEPARATELY OR IN ADMIXTURE

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The increased commercial availability of hydrazine and its congeners and their extensive use as industrial chemicals and rocket fuels has led to the development of numerous methods for the determination of these compounds, separately and in mixtures. The majority of these have been based on titration of hydrazines either as bases[1] or as reducing agents[1,2]. The familiar reaction between a hydrazine and an aldehyde to form a hydrazone has also been widely utilized. Several authors[3–5] have determined hydrazine by measuring the absorbance of the product formed from its reaction with *p*-dimethylaminobenzaldehyde. After reaction of the sample with salicylaldehyde, nonaqueous titrimetry has been used in analyzing mixtures of hydrazine and 1,1-dimethylhydrazine (UDMH)[6,7] and mixtures of hydrazine and 1-methylhydrazine (MMH)[8]. A polarographic method has been reported for analyzing mixtures of the benzaldehyde derivatives of hydrazine and UDMH, but it was not applied to mixtures of the hydrazines themselves[9].

This paper reports a simple spectrophotometric analysis which is based on the well-known reaction of hydrazine and 1,1-dimethylhydrazine with salicylaldehyde to yield products with well-defined ultraviolet spectra and high molar absorptivities. The interference caused by spectral overlap and the presence of excess salicylaldehyde is corrected for by considering the contribution of all absorbing species to the absorbance measured at a specific wavelength[10–12]. The procedure and results are presented for the analysis of hydrazine and 1,1-dimethylhydrazine, separately and in mixtures.

EXPERIMENTAL

Apparatus

The ultraviolet spectra were recorded using a Beckman model DK-2 ratio recording spectrophotometer. Routine analysis and molar absorptivity determinations were accomplished using a Beckman model DU quartz spectrophotometer equipped with a Beckman model 73600 power supply.

Reagents

Salicylaldehyde (from Bisulfite Compound), Matheson, Coleman and Bell (MCB).

Hydrazine, anhydrous (95+%), MCB. Analysis by titration with standard potassium iodate solution[1] showed a hydrazine content of 96.2%, standard deviation 0.4%.

1,1-Dimethylhydrazine (UDMH), anhydrous (99+%), MCB. Analysis by the method of BURNS AND LAWLER[7] indicated a UDMH content of 98.8%, standard deviation 0.6%.

All other chemicals were reagent grade. Salicylaldazine, m.p. 216–218.0° (uncorrected), and salicylaldehyde 1,1-dimethylhydrazone, b.p. (4 mm Hg) 126–128° (uncorrected), were synthesized. Purity was confirmed by elemental analysis.

Sampling

Because of the tendency of both hydrazines to be oxidized by atmospheric oxygen, to absorb carbon dioxide and to fume in air, the special sampling technique described by CLARK AND SMITH[13] was used throughout.

General procedure

A sample representing 0.75 g of total hydrazines was weighed accurately into a 100-ml volumetric flask containing 50 ml of chilled isopropanol. This was mixed well and 10 ml of glacial acetic acid was added in small portions. The solution was diluted to volume with isopropanol and exactly 2 ml transferred to an empty 200-ml volumetric flask. To this was added 0.11 ml of salicylaldehyde. The flask was tightly stoppered and placed in a 60° water bath for 15 min. When the flask was removed from the bath and cooled, it was brought to volume with chloroform. If the sample was presumed initially to contain only hydrazine, exactly 1 ml of this solution was diluted to 100 ml with chloroform and the absorbance determined at 325 mμ. For a sample containing only UDMH, 2 ml was diluted to 100 ml and read at 293 and 325 mμ. For a mixture, 2 ml was diluted to 100 ml and absorbance measurements made at 293, 325, and 360 mμ. If the qualitative nature of the sample presented for analysis is unknown, it should be treated as a mixture.

RESULTS AND DISCUSSION

Experimental conditions

Since 1 mole of hydrazine requires 2 moles of salicylaldehyde whereas 1 mole of UDMH needs only 1 mole of salicylaldehyde for complete reaction, variation in the amount of aldehyde to be added is possible. The amount of salicylaldehyde added in this analytical procedure is sufficient to be about 10% in excess of that required for complete reaction even in the case where the sample is entirely hydrazine. Should the sample be entirely UDMH, the larger excess of aldehyde will not interfere in the analysis.

Because of the nature of the analytical reaction and of the products formed, it was found necessary to use a mixed solvent system. When analysis was attempted using chloroform as the solvent, the results obtained indicated that the reaction was only 75% complete even after prolonged heating at 60°. However, when isopropanol was employed, the reaction was greatly facilitated and heating at 60° for 15 min assured the quantitative formation of the desired products. All dilutions of the reaction mixture were made using only chloroform because the products were not sufficiently soluble in isopropanol.

Spectral characteristics

The ultraviolet spectra of chloroform solutions of salicylaldazine, salicylaldehyde 1,1-dimethylhydrazone and salicylaldehyde are shown in Fig. 1. With the exception of salicylaldehyde, the spectra were obtained from freshly synthesized and purified samples. The molar absorptivities at wavelengths representing the maximum absorption for each of the compounds are reported in Table I. The constancy of the results confirmed the adherence of these systems to Beer's law over the range of concentrations studied. For the hydrazine derivative, this range was from $9.0 \cdot 10^{-6}$ M to $3.9 \cdot 10^{-5}$ M which corresponds to concentrations of hydrazine from 0.29 µg/ml to 1.25 µg/ml. In the case of the UDMH adduct, the range was $4.0 \cdot 10^{-6}$ M to $7.5 \cdot 10^{-5}$ M corresponding to a concentration of UDMH ranging from 0.24 µg/ml to 4.52 µg/ml.

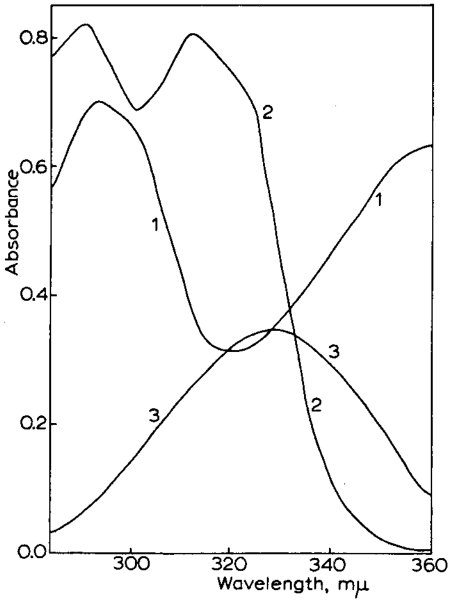

Fig. 1. Ultraviolet absorption spectra. (1) Salicylaldazine $2.7 \cdot 10^{-5}$ M; (2) salicylaldehyde dimethylhydrazone $6.0 \cdot 10^{-5}$ M; (3) salicylaldehyde $9.9 \cdot 10^{-5}$ M.

TABLE I

MOLAR ABSORPTIVITIES

Compound	*293 mµ*		*325 mµ*		*360 mµ*	
	Mean	*Std. dev.*	*Mean*	*Std. dev.*	*Mean*	*Std. dev.*
Salicylaldazine[a]	25,800	130	11,900	85	23,800	136
Salicylaldehyde dimethylhydrazone[a]	14,500	21	12,900	85	109	6.8
Salicylaldehyde[b]	750	11	3,475	27	706	6.5

[a] Calculations based on 8 determinations.
[b] Calculations based on 10 determinations.

Neither the spectrum nor the molar absorptivities of salicylaldehyde agree precisely with previously published results[14]. It was necessary to redetermine the molar absorptivities on this compound at least monthly or whenever a fresh lot of salicylaldehyde was required.

Hydrazine

The results of the spectrophotometric analysis of 7 samples containing only hydrazine are shown in Table II; (H), the quantity equivalent to the molar concentration of hydrazine in the final dilution, was calculated by solving the simultaneous equations:

TABLE II

DETERMINATION OF HYDRAZINE

Hydrazine taken (g)	*Hydrazine found (g)*	*Recovery of hydrazine (%)*
0.7774	0.7628	98.1
0.6279	0.6314	100.6
0.7942	0.7916	99.7
0.7244	0.7307	100.9
0.6419	0.6506	101.4
0.6419	0.6442	100.4
0.6419	0.6378	99.4
	Mean	100.1
	Std. dev.	1.1

TABLE III

DETERMINATION OF 1,1-DIMETHYLHYDRAZINE

UDMH taken (g)	*UDMH found (g)*	*Recovery of UDMH (%)*
1.1490	1.1227	97.7
1.1490	1.1258	98.0
1.1490	1.1288	98.2
1.3060	1.2548	96.1
1.2782	1.2488	97.7
1.0794	1.0567	97.9
1.2299	1.1888	96.7
1.2299	1.1918	96.9
1.1940	1.1438	95.8
1.1940	1.1498	96.3
	Mean	97.1
	Std. dev.	0.9

$$A_{325} = 11{,}900\ (H) + 3{,}475\ (S)$$

$$A_{360} = 23{,}800\ (H) + 706\ (S)$$

In these equations, A_{325} and A_{360} indicate the absorbances of the final dilution at 325 and 360 mμ respectively and (S) is the molar concentration of salicylaldehyde. Examination of Table II indicates excellent accuracy and good precision for this method.

1,1-Dimethylhydrazine

Table III shows the results obtained from the analysis by this spectrophotometric method of 10 samples containing only UDMH; (U), the quantity equivalent to the molar concentration of UDMH in the final dilution, was calculated by solving the following equations:

$$A_{293} = 14{,}500\ (U) + 750\ (S)$$
$$A_{325} = 12{,}900\ (U) + 3{,}475\ (S)$$

Examination of the data presented in Table III indicates good precision but shows values lower than those of the reference titrimetric method[7]. This may be rationalized by recognizing that frequently occurring basic impurities in UDMH are determined by the acid–base method, but not by the salicylaldehyde spectrophotometric method[15].

Mixtures of hydrazine and 1,1-dimethylhydrazine

Mixtures containing varying proportions of hydrazine and UDMH were prepared by combining accurately weighed quantities of the individual compounds. The results of the spectrophotometric analysis of 22 samples are given in Table IV. Since the over-all absorbance at any wavelength is the sum of the individual absorbances of each of the three compounds present in the solution, it was necessary to use a system of three equations in order to calculate the results. These equations are:

$$A_{293} = 25{,}800\ (H) + 14{,}500\ (U) + 750\ (S)$$
$$A_{325} = 11{,}900\ (H) + 12{,}900\ (U) + 3{,}475\ (S)$$

TABLE IV

ANALYSIS OF HYDRAZINE–1,1-DIMETHYLHYDRAZINE MIXTURES

Taken		*Found*		*Percentage recovery*	
Hyd (g)	*UDMH (g)*	*Hyd (g)*	*UDMH (g)*	*Hyd*	*UDMH*
0.2109	0.7292	0.2083	0.7055	98.8	96.8
0.2131	0.5137	0.2115	0.5013	99.3	97.6
0.2131	0.5137	0.2115	0.5013	99.3	97.6
0.2131	0.5137	0.2115	0.5013	99.3	97.6
0.2131	0.5137	0.2099	0.5043	98.5	98.2
0.2131	0.5137	0.2099	0.4983	98.5	97.0
0.2914	0.6814	0.2868	0.6634	98.4	97.4
0.2518	0.5900	0.2484	0.5704	98.7	96.7
0.2631	0.6046	0.2612	0.5914	99.3	97.8
0.3324	0.3353	0.3301	0.3392	99.3	101.2
0.3324	0.3353	0.3269	0.3392	98.3	101.2
0.3324	0.3353	0.3269	0.3302	98.3	98.5
0.3324	0.3353	0.3253	0.3362	97.9	100.3
0.3253	0.3217	0.3157	0.3242	97.1	100.8
0.3555	0.3088	0.3445	0.3032	96.9	98.2
0.3030	0.3623	0.2981	0.3602	98.4	99.4
0.4752	0.2791	0.4615	0.2783	97.1	99.7
0.3855	0.2132	0.3750	0.2113	97.3	99.1
0.4274	0.2049	0.4150	0.2050	97.1	100.0
0.5454	0.2421	0.5384	0.2432	98.7	100.5
0.5454	0.2421	0.5416	0.2462	99.3	101.7
0.5454	0.2421	0.5416	0.2420	99.3	100.0
			Mean	98.4	99.0
			Std. dev.	0.8	1.6

$$A_{360} = 23{,}800\ (H) + 109\ (U) + 706\ (S)$$

The use of determinants proved to be the most convenient method of solving these equations for (H) and (U). In simplified form the final equations are:

$$(H) = [A_{293}\ (8.132) - A_{325}\ (9.462) + A_{360}\ (37.93)] \cdot 10^{-6}$$

$$(U) = [-A_{293}\ (-69.23) + A_{325}\ (0.3399) - A_{360}\ (75.22)] \cdot 10^{-6}$$

These equations are likewise valid when applied to samples containing only one of the hydrazines. However, if only a single hydrazine is present, the simpler methods of calculation given in the preceding sections are more convenient.

The data in Table IV indicate somewhat lower recovery values for hydrazine in mixtures than for hydrazine alone. Examination of the final equations used for calculation of hydrazine and UDMH indicates that a decrease in the absorbance at 360 mμ will be reflected as a decrease in hydrazine but an increase in UDMH concentration. The predominant absorbance contribution at 360 mμ is that of salicylaldazine. This leads to the conclusion that the measured absorbance values for this derivative apparently are uniformly lower than expected. Calculations employing the final equations for (H) and (U) indicate that a determinate error of -0.60% in an absorbance reading at 360 mμ will yield, on the average, depending on the sample size, an error of -0.5% in the hydrazine and $+1.8\%$ in the UDMH concentration. It is therefore imperative that the absorbance readings, particularly at 360 mμ, be made with the greatest possible accuracy.

It may be noticed that the standard deviation for hydrazine analysis is relatively constant, whether in a mixture or alone, whereas that for UDMH is substantially greater in the analysis of mixtures than in the determination of the single compound. These deviations are not entirely unexpected when the spectral complexities of a 3-component system are considered. For example, UDMH is measured by the absorption properties of its derivative at 293 mμ. Although this is the most suitable wavelength for this measurement, the molar absorptivity of the hydrazine derivative at this point is greater (25,800) than that of the UDMH compound (14,500). As a result, the absolute random deviations in the absorption intensities of both derivatives contribute additively to the deviation of the over-all measured absorbance. This situation is not the same at 360 mμ where the hydrazine derivative is measured since its molar absorptivity is much greater than that of either of the other absorbing species.

Other hydrazine derivatives

Attempts were made to adapt this method of analysis to other methylated hydrazine derivatives. Synthesis of the 1-methylhydrazone of salicylaldehyde yielded a rather unstable product indicating that the reaction was not analytically suitable for the determination of 1-methylhydrazine. In the case of 1,2-dimethylhydrazine, this method was not applicable owing to the absence of a primary amino nitrogen which is necessary to permit the desired reaction with salicylaldehyde[16].

It is expected that extension of this procedure to other monoalkyl or 1,1-dialkyl derivatives should be possible. No work involving these compounds was carried out here.

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SUMMARY

A rapid, sensitive spectrophotometric method for the determination of hydrazine and 1,1-dimethylhydrazine, separately or in mixtures of varying proportions, is described. The analysis is based on the well-known reaction of these compounds with salicylaldehyde to form, in the case of hydrazine, a symmetrical azine, or with 1,1-dimethylhydrazine, a hydrazone. Absorbance measurements were made in the ultraviolet at wavelengths characteristic of the derivatives and of salicylaldehyde; the results were calculated by means of simultaneous equations. The procedure is sensitive to concentrations of hydrazine as low as 0.3 μg/ml and of 1,1-dimethylhydrazine as low as 0.25 μg/ml. This corresponds to initial sample solutions having a concentration of 3.0 mg of hydrazine and 1.25 mg of 1,1-dimethylhydrazine per ml.

RÉSUMÉ

On décrit une méthode spectrophotométrique rapide et sensible pour le dosage d'hydrazine et de diméthyl-1,1-hydrazine, séparément ou dans des mélanges de proportions variées. L'analyse est basée sur la réaction de ces composés avec le salicylaldéhyde pour former respectivement une azine symétrique ou une hydrazone. Les mesures d'absorption sont faites dans l'ultraviolet aux longueurs d'onde caractéristiques des dérivés et du salicylaldéhyde. Sensibilité: 0.3 μg/ml d'hydrazine et 0.25 μg/ml de diméthyl-1,1-hydrazine. Ceci correspond à des solutions initiales d'échantillon de 3 mg/ml d'hydrazine et 1.25 mg/ml de diméthyl-1,1-hydrazine.

ZUSAMMENFASSUNG

Es wird eine schnelle, empfindliche spektralphotometrische Methode zur Bestimmung von Hydrazin und 1,1-Dimethylhydrazin, einzeln oder in variierenden Mischungsverhältnissen, beschrieben. Die Analyse beruht auf der bekannten Reaktion dieser Verbindungen mit Salicylaldehyd. Die Absorptionsmessungen wurden im Ultravioletten bei charakteristischen Wellenlängen der Derivate und des Salicylaldehyds durchgeführt. Mit dem Verfahren lassen sich noch Konzentrationen von 3.0 mg/ml Hydrazin und 1.25 mg/ml 1,1-Dimethylhydrazin bestimmen.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH 2-NAPHTHOHYDROXAMIC ACID

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In a recent investigation of the reactions of a large variety of hydroxamic acids with metal ions[1,2], it became apparent that vanadium(V) has a high degree of reactivity with most of them. In particular, 2-naphthohydroxamic acid in methanol gives an intense and stable red-orange color with vanadium. This metal is a widely occurring element often in trace concentrations, and is found in plants, soils, clays, animal tissue and bone, and in many steels and non-ferrous alloys. 2-Naphthohydroxamic acid was synthesized for our study; its analytical properties have not been reported. It was therefore decided to examine the color reaction between vanadium(V) and 2-naphthohydroxamic acid and to develop a new reagent for the spectrophotometric determination of vanadium.

Several hydroxamic acids have been used for the analysis of vanadium, among them benzohydroxamic acid[3-6], N-phenylbenzohydroxamic acid[7-9], and N-cinnamoyl-N-phenylhydroxylamine[10]. Other frequently used reagents for vanadium include diphenylbenzidine[11] and cupferron[12]. The high sensitivity of 2-naphthohydroxamic acid for vanadium and the usefulness and simplicity of the reaction in analyzing for vanadium in a variety of materials indicates that it should compare favorably with those reported in the literature.

Study of the complex

2-Naphthohydroxamic acid exists as pale pink crystals, only slightly soluble in water but freely soluble in organic solvents. At a concentration of 0.05% (w/v) in methanol, the compound in solution is colorless, stable, unaffected by light, heat, oxygen, and carbon dioxide, and shows no absorption at 450 mμ, using a 1-cm cell.

Vanadium(V) and 2-naphthohydroxamic acid react to form a stable red-orange complex in methanol.

Figure 1 shows the absorbance curve of this complex in the visible region.

The absorption intensity of the complex and the wavelength of maximum absorbance vary with the acidity of the solution, as shown in Fig. 2. For purposes of sensitivity and simplicity, the peak at 450 mμ (curve 4) was selected rather than the 478 mμ (curve 3) or 500 mμ (curve 2) peaks. At wavelength 450 mμ a reproducible color intensity is obtained between pH 2.0 and 4.0*.

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* Since the reaction was carried out in methanol, with only a very small amount of water present, the true pH of the solution could not be determined; hence the acidity values observed throughout the investigation are pH-meter readings rather than actual pH values.

Solutions of the complex are stable to light for at least a week, and show no visible deterioration over a period of months. The complex forms almost instantaneously; the presence of a small rate effect is indicated by the fact that absorption is 4% higher when the vanadium solution is added to a reagent solution than when the reagent is added to vanadium. Variation in temperature (15°–35°) has a negligible effect on the color system.

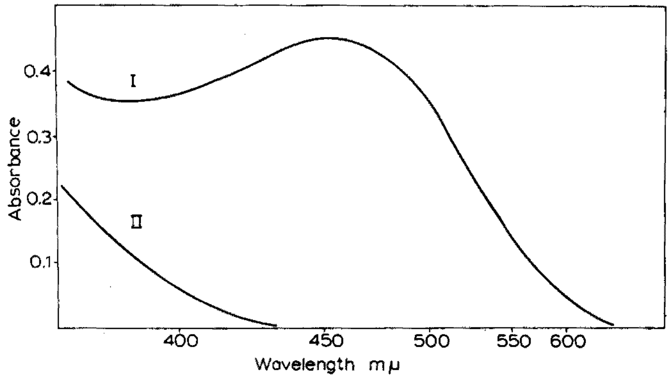


Fig. 1. (I) Vanadium–2-naphthohydroxamic acid complex *vs.* water (5 p.p.m. V); (II) 2-naphthohydroxamic acid *vs.* water.

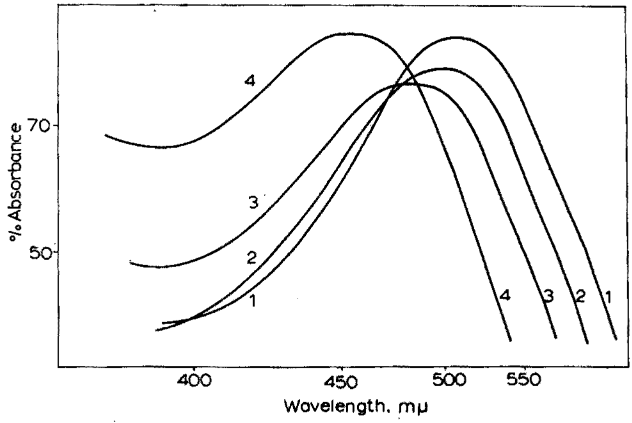


Fig. 2. pH-effect, vanadium–2-naphthohydroxamic acid complex (10 p.p.m. V). (1) pH 0.13; (2) pH 0.55; (3) pH 1.36; (4) pH 3.21.

The intensity of the complex in methanol solution is independent of the water concentration within the range 2–20% water. Outside this range absorption decreases considerably. Presumably a small amount of water is necessary to promote ionization of the reagent, and dissociation of the complex occurs as the water content increases. Also, a high reagent concentration is necessary for full color development; an excess of at least 20-fold by weight is required for maximum absorption. This is another indication that the complex is considerably dissociated.

2-Naphthohydroxamic acid reacts with vanadium(IV) as well as with the pentavalent ion, but the complex thus formed is only 12% as intense as the one containing vanadium(V). It is therefore necessary to oxidize the vanadium solutions before forming the complex; this was accomplished by heating with bromine water.

The complex obeys Beer's law over the range 1–10 p.p.m. vanadium. The absorbance at 10 p.p.m. was so great that no data were obtained at higher concentrations. The optimum concentration range is 2–7 p.p.m., corresponding to the absorbance range 0.2 to 0.7.

Under the conditions established, the sensitivity of the reagent is 0.009 μg V/cm^2 (for log $I_0/I = 0.001$), using a 1-cm cell. A standard deviation calculation gave a value for *sigma* equal to ± 0.006 abs. unit; this is equivalent to ± 0.08 p.p.m. V.

Considerable interference with the color reaction occurs from the presence of foreign ions, chiefly because of reactions of the ions with 2-naphthohydroxamic acid. Other causes of interference are reaction of foreign ions with vanadium(V), the presence of strongly colored foreign ions and reaction of foreign ions with constituents of the reaction medium. It was found that no interference was caused by the alkali metals, the alkaline earth metals, zinc, zirconium, cadmium, chloride, bromide, or

TABLE I

LIMITS OF CONCENTRATION OF INTERFERING IONS

(V, 5 p.p.m.)

Ion	*Concn. (p.p.m.)*	*Ion*	*Concn. (p.p.m.)*
Ti^{4+}	10	F^-	5
Cr^{3+}	30	I^-	100
Mn^{2+}	100	CO_3^{2-}	25
Co^{2+}	50	SCN^-	100
Cu^{2+}	100	HPO_4^{2-}	50
Sb^{3+}	5	SO_3^{2-}	100
Ce^{4+}	25	SO_4^{2-}	100
Cs^{6+}	200	Acetate	5
Pt^{4+}	100	Tartrate	5
Hg^+	10	Citrate	10
Hg^{2+}	150		

TABLE II

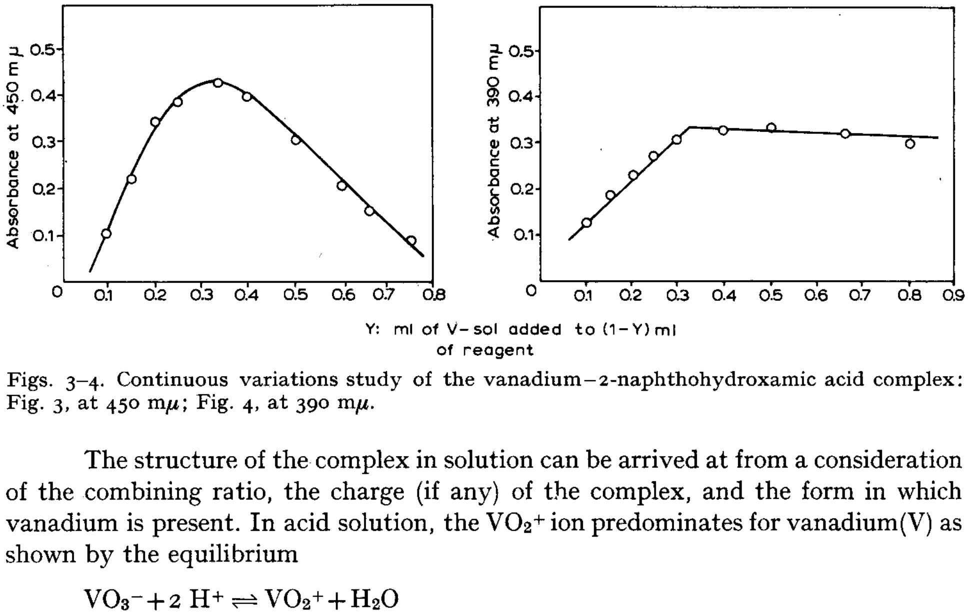
INTERFERENCE OF DIVERSE IONS

(V, 5 p.p.m.)

Ion	*p.p.m.*	*% Error*	*Ion*	*p.p.m.*	*% Error*
Ti^{3+}	50	− 24	Th^{4+}	5	−60
Al^{3+}	25	− 9	W^{6+}	10	−10
Cr^{3+}	100	− 27	Os^{6+}	150	−12
Co^{2+}	100	+ 15	Hg^{2+}	200	+ 9
Cu^{2+}	200	+ 31	Tl^{3+}	5	− 8
Nb^{3+}	100	− 67	BO_3^-	25	−89
Mo^{6+}	25	− 95	CO_3^{2-}	50	−59
Sn^{2+}	25	−100	NO_2^-	10	−75
Sn^{4+}	10	− 21	F^-	25	−88
Sb^{3+}	15	− 6	CrO_4^{2-}	10	+12
Ce^{4+}	50	+ 21	MnO_4^-	5	+11

nitrate ions. Interference occurred from the presence of any of the following: Al^{3+}, Fe^{3+}, Nb^{3+}, Ag^{+}, Sn^{2+}, Sn^{4+}, W^{6+}, Tl^{3+}, Th^{4+}; BO_3^{-}, NO_2^{-}, MnO_4^{-}, CrO_4^{2-} and oxalate. Between the extremes of interference are found the ions which can be tolerated in limited concentrations. They are listed in Table I, with the concentration of each which can be present without causing interference. Table II shows the extent of the interferences caused by various ions. (At a concentration of 5 p.p.m. vanadium and a large excess of reagent, a deviation in absorbance of 0.005 was arbitrarily taken to indicate an interference.)

The combining ratio of vanadium and 2-naphthohydroxamic acid proved difficult to determine. The high degree of dissociation of the complex made the HARVEY AND MANNING slope ratio technique[13] inapplicable, and caused ambiguous results when the mole ratio method of YOE AND JONES[14] was used. The VOSBURGH AND COOPER[15] modification of JOB's method of continuous variations[16], when applied at 2 wavelengths, indicated that the complex in solution consists predominantly of 2 molecules of 2-naphthohydroxamic acid for each atom of vanadium. Figures 3 and 4 are graphs of the data obtained by this method.

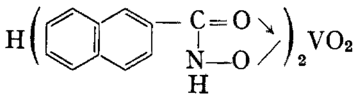


Figs. 3–4. Continuous variations study of the vanadium–2-naphthohydroxamic acid complex: Fig. 3, at 450 mμ; Fig. 4, at 390 mμ.

The structure of the complex in solution can be arrived at from a consideration of the combining ratio, the charge (if any) of the complex, and the form in which vanadium is present. In acid solution, the VO_2^{+} ion predominates for vanadium(V) as shown by the equilibrium

$$VO_3^{-} + 2\,H^{+} \rightleftharpoons VO_2^{+} + H_2O$$

If the formula R_2V is correct, a negatively charged complex should result. To verify this, solutions of the complex were passed through anion-exchange and cation-exchange columns, respectively; it was found that the complex is not strongly retained by either resin. Thus the complex is evidently a neutral species. The extractability, in organic solutions, of other vanadium–hydroxamic acid complexes bears this out. Hence it is postulated that a hydrogen ion is also involved in the complex formation, either in the form of one unionized hydroxamic acid molecule or of a proton ionically bonded to the $[R_2V]^{-}$ ion. The strongly alcoholic medium in which the complex is formed would tend to suppress removal of the hydrogen ion. Thus the structure of the complex, under the established conditions, is probably



The bonding involves three $3d$ orbitals and one $4s$ orbital, and the shape of the complex should therefore be tetrahedral.

Separation and determination of vanadium(V)

In view of the large number of ions which interfere with the reaction between vanadium(V) and 2-naphthohydroxamic acid, some method of separating the vanadium was necessary. Special attention was focussed on the removal of iron(III), which causes by far the most serious interference. Ion-exchange separation was eventually selected as a rapid and simple means of separation. A considerable amount of work in the field of anion-exchange separations in alcoholic media has been performed by KORKISCH *et al.*[17-22]; one of these studies[18] involves the separation of vanadium and nickel from copper and iron, and this method was adapted in our work to provide a satisfactory separation of vanadium. In a medium consisting of 10% 12 *M* hydrochloric acid and 90% methanol, vanadium(V) is not retained on Dowex-1, while iron(III) is held on the resin. Table III, showing the analysis of synthetic vanadium–iron samples, indicates the effectiveness of the separation. Recovery of vanadium from the column was found to be reproducible only in the range 1 to 7 p.p.m.; up to 7 p.p.m. a graph of absorbance *versus* vanadium concentration is linear, falling off slightly beyond this point. It is probable that this vanadium loss is due to reduction by the resin column and retention of vanadium(V).

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

V taken (p.p.m.)	*Fe taken (p.p.m.)*	*V found (p.p.m.)*	*V taken (mg)*	*Fe taken (mg)*	*V found (mg)*
0	0	0	0	2.5	0
2.00	100	2.01	0	5.0	0
2.00	200	1.99	0.100	100	0.104
4.00	100	4.01			
4.00	200	4.03			
8.00	400	7.96			

A further complication was found due to the high ionic strength of solutions which had been passed through the resin column, neutralized, and boiled with bromine water. The color of the vanadium complex was observed to fade on standing for several hours. From a time study of this effect it was found that the intensity of the color passes through a maximum less than an hour after mixing and then slowly diminishes. Color fading is greater, the more bromine water is used, presumably because of the larger amount of bromide ion thereby formed in solution. Hence it was necessary to measure the absorbance of the colored solutions between 30 and 40 min after the reagent was mixed with the vanadium solution, to achieve accurate results.

As a test of the method, five National Bureau of Standards samples were

TABLE IV

ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

Sample	*N.B.S. value (%)*	*New method (%)*
#58, Spiegeleisen	0.012, 0.012	0.0123
		0.0121
		0.0120
		0.0121
	Av. 0.012	Av. 0.0122
#66, Ferrosilicon	0.003–0.005	0.0037
		0.0040
		0.0038
		0.0040
	Av. 0.004	Av. 0.0039
#67, Manganese metal	0.17–0.19	0.198
		0.192
		0.197
		0.194
	Av. 0.19	Av. 0.195
#117, Ferrotitanium	0.05–0.08	0.037
		0.038
		0.036
		0.038
	Av. 0.07	Av. 0.037[a]
#132, steel	1.60–1.68	1.53
		1.52
		1.50
		1.55
		1.50
	Av. 1.64	Av. 1.52

[a] The high iron/vanadium ratio in this sample required that each aliquot be passed through the resin column twice. This, and interference caused by titanium ions which were not retained on the column, probably accounts for the low vanadium value.

analyzed. The results proved satisfactory (Table IV). The standard deviation was obtained for N.B.S. sample No. 67; a value of ±0.009 was found.

Experimental procedure

Dissolve a weighed sample, selected to provide 20–175 μg of vanadium in a 1–5 ml aliquot of the final solution, and transfer to a volumetric flask. Nitric acid should be used in the course of dissolving the sample to insure that all iron and vanadium ions are in their highest oxidation states. Take a 1.00- or 5.00-ml aliquot of the solution, depending on the vanadium concentration; evaporate to dryness, and add 1 ml of 12 *N* hydrochloric acid and 9 ml of methanol. Pass this solution through a column packed with Dowex 1-X8 (50–100 mesh) resin at about 0.5 ml per min. Discard the first 2 ml of effluent, collect the remainder in a beaker and wash the column with three 4-ml portions of wash solution (10% 12 *N* HCl/90% methanol), collecting the wash liquid in the same beaker. Add 15 *N* ammonia solution to this solution dropwise until the pH is between 3 and 6; approximately 1.5 ml is usually required. Next add bromine water dropwise until a permanent color is obtained. Care should be taken not to add more bromine than necessary; less than 1 ml should be sufficient. Boil the solution over low heat on a hot plate until the bromine color is discharged and the volume is less than 15 ml. After the solution has cooled, transfer it to a 25-ml volumetric flask containing 5 ml of a 0.05% 2-naphthohydroxamic acid solution in methanol. (A white precipitate may form in the beaker upon cooling, but it dissolves as the beaker is washed out with methanol.) Make the solution up to volume with methanol, mix thoroughly, and allow to stand for 30–40 min. Read its absorbance at 450 mμ against a water blank. Determine the vanadium concentration from a calibration curve, and calculate the percent vanadium in the sample.

Note. A resin bed of about 18 cm in length and 5 mm in diameter is satisfactory for most analyses. For an iron or steel sample containing less than 0.08% vanadium a larger amount of resin is needed.

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SUMMARY

2-Naphthohydroxamic acid in methanol gives an intense and stable red-orange color with vanadium(V), sensitive to 0.009 μg V/cm², for log $I_0/I = 0.001$ abs. unit at wavelength 450 mμ. The value for σ is ± 0.006 a.u., equivalent to ± 0.08 p.p.m. V. The colored complex obeys Beer's law over the range 1–10 p.p.m. vanadium. The absorbance (in 1-cm cell) at 10 p.p.m. was so great that no data were obtained at higher concentrations. Under the conditions of the reaction, the combining ratio of vanadium and 2-naphthohydroxamic acid appears to be 1 to 2. Optimum conditions for the use of 2-naphthohydroxamic acid as a spectrophotometric reagent for vanadium-(V) were established; the procedure was applied to the determination of vanadium in steels and non-ferrous alloys with good precision and accuracy.

RÉSUMÉ

L'acide 2-naphtohydroxamique en solution dans le méthanol donne avec le vanadium(V) une coloration orange rouge intense et stable. La loi de Beer s'applique de 1 à 10 p.p.m. de vanadium (longueur d'onde 450 mμ). Les conditions sont données pour un dosage spectrophotométrique du vanadium à l'aide de ce réactif. Ce procédé peut être appliqué au dosage du vanadium dans les aciers et alliages non-ferreux avec une bonne précision et une bonne exactitude.

ZUSAMMENFASSUNG

2-Naphthohydroxamsäure in Methanol ergibt bei 450 mμ eine intensive und stabile rot-orange Färbung mit Vanadin(V). Der gefärbte Komplex gehorcht im Bereich von 1–10 p.p.m. V dem Beerschen Gesetz. Bei den beschriebenen Reaktionsbe-

dingungen scheinen sich Vanadin und 2-Naphthohydroxamsäure im Verhältnis 1:2 zu binden. Es werden die optimalen Bedingungen für die Verwendung von 2-Naphthohydroxamsäure als spektralphotometrisches Reagenz für Vanadin angegeben. Das Verfahren wurde zur Bestimmung von Vanadin in Stählen und Nichteisenlegierungen mit guter Reproduzierbarkeit und Richtigkeit angewandt.

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GRAVIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF MERCURY WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

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N-Benzoyl-N-phenylhydroxylamine (BPHA) was introduced by SHOME[1] and has been applied in various fields of analytical chemistry by SHOME and many other workers[2]. In the present work the reagent was found to be suitable for the gravimetric and spectrophotometric determination of mercury(II). The metal forms a yellow precipitate with BPHA in aqueous solution which can be dried at 102–108° and mercury can then be determined by direct weighing of the complex. The mercury precipitate is very sparingly soluble in common organic solvents, but mercury can be extracted with a solution of the reagent in chloroform. The extract, which is yellow in colour, follows Beer's law at 340 mμ in the concentration range 5–52 μg of mercury per ml. Although mercury(I) does not form any precipitate with BPHA in aqueous solution, it can be extracted incompletely into chloroform producing a greenish yellow colour under conditions similar to those for mercury(II).

EXPERIMENTAL

Apparatus

A Karl Zeiss spectrophotometer, Model PMQ II with 1-cm quartz cells, was used for all absorbance measurements. A Cambridge Bench Model pH Meter equipped with glass and calomel microelectrodes was used for the pH measurements.

Reagents

Standard mercury solution. A standard mercury solution was prepared by dissolving mercury(II) nitrate (G.R., E. Merck) in 0.1 *N* nitric acid. The mercury content was determined by the periodate method.

Diverse ion solutions. Solutions of diverse ions were prepared by dissolving known amounts of pure compounds in distilled water. Acids were used where required to prevent hydrolysis of the metal ions.

Reagent solutions. For the precipitation of mercury a 1% solution of BPHA in ethanol was prepared. For the extraction of the metal 400 mg of recrystallized BPHA were dissolved in 50 ml of redistilled chloroform.

All reagents used were of A.R.quality. Solutions used for pH adjustment were 10% sodium acetate, 2 *M* nitric acid and 2% sodium hydroxide solution.

GRAVIMETRIC DETERMINATION OF MERCURY

The mercury(II) complex with BPHA is bright yellow in colour and is only slightly soluble in alcohol, ether, chloroform, carbon tetrachloride and ethyl acetate. It is soluble in dioxane, benzene and tetrahydrofuran (and tends to decompose) and dissolves freely in mineral acids. The complex sublimes slowly above 110° and decomposes at 119–120°. Analysis showed that the complex contains 32.05% Hg and 4.51% N; the theoretical values for $Hg(C_{13}H_{10}O_2N)_2$ are 32.09% and 4.48% respectively.

In tests to establish the optimum conditions for quantitative precipitation, it was found that 2.5–3 times the theoretical amount of BHPA was necessary in the pH range 3.0–6.0.

Procedure

Dilute a mercury(II) nitrate solution to 125–150 ml and adjust the pH of the solution to about 4 by addition of sodium acetate. Heat to 50–60° and add 15–20 ml of ethanolic BPHA solution. Digest the yellow precipitate on a water bath for 30 min with occasional stirring. Filter the precipitate on a No. 3 sintered crucible, wash with hot water and then with 15–20 ml of 20% ethanol. Dry at 105 ± 3° for 1 h, cool in a desiccator and weigh.

Typical results are shown in Table I.

TABLE I

DETERMINATION OF MERCURY BY DIRECT WEIGHING OF MERCURY–BPHA COMPLEX

Hg taken (mg)	*Hg found (mg)*	*Error (mg)*	*Hg taken (mg)*	*Hg found (mg)*	*Error (mg)*
10.80	10.76	−0.04	21.60	21.49	−0.01
10.80	10.77	−0.03	21.60	21.60	0.00
16.20	16.21	+0.01	32.40	32.42	+0.02

TABLE II

SEPARATION OF MERCURY FROM DIVERSE IONS

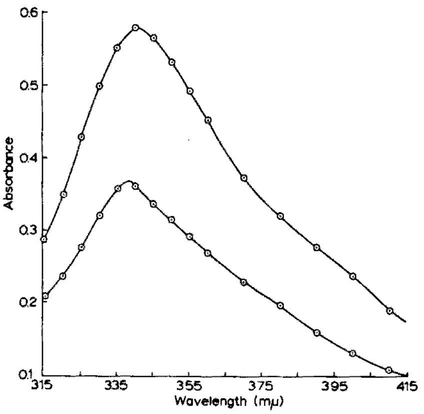
Hg taken (mg)	*Foreign ion added (mg)*	*Hg found (mg)*	*Hg taken (mg)*	*Foreign ion added (mg)*	*Hg found (mg)*
16.2	Zn^{2+}(10)	16.22	16.2	In^{3+}(10)	16.20
10.8	Zn^{2+}(15)	10.85	10.8	In^{3+}(20)	10.78
16.2	Cd^{2+}(12)	16.21	16.2	Bi^{3+}(8)	16.19
10.8	Cd^{2+}(20)	10.85	10.8	Bi^{3+}(20)	10.83
16.2	Ag^{+}(10)	16.22	16.2	Sb^{3+}(12)	16.19
10.8	Ag^{+}(15)	10.86	10.8	Sb^{3+}(24)	10.81
16.2	Tl^{+}(11)	16.20	16.2	Sn^{4+}(8)	16.20
10.8	Tl^{+}(16.5)	10.86	10.8	Sn^{4+}(16)	10.85
16.2	Co^{2+}(8)	16.19	16.2	As^{5+}(10)	16.19
10.8	Co^{2+}(12)	10.84	10.8	As^{5+}(20)	10.82
16.2	Ni^{2+}(7)	16.18	16.2	Mo^{6+}(9)	16.19
10.8	Ni^{2+}(14)	10.85	10.8	Mo^{6+}(12)	10.75
16.2	Pb^{2+}(9)	16.20	16.2	W^{6+}(12)	16.20
10.8	Pb^{2+}(18)	10.83	10.8	W^{6+}(24)	10.85

Effect of diverse ions

Mercury was determined by the above method in mixtures containing known amounts of mercury(II) nitrate and Zn, Cd, Ni, Sn(IV), In, Tl, Sb (as their sulphates), Co, Pb, Ag, Bi (as their nitrates), potassium arsenate or sodium tungstate. Addition of sodium potassium tartrate was necessary to mask the interference of Bi, As, Sb or W, sodium citrate to mask Co, Ni, Cd, Pb or Ag, and sodium oxalate to mask tin. The optimum pH for precipitation of mercury in the presence of these ions was 3.5–4.0. Mercury could be separated from zinc by precipitation at pH 3.0. Thallium(I) did not precipitate during the determination of mercury but addition of sodium fluoride was necessary to mask indium. Molybdenum could be separated from mercury by prior precipitation with BPHA from 1 *N* acidic medium. Ammonium ion did not interfere below pH 5.0, nor did phosphate or borate, but mercury could not be precipitated in the presence of chloride, cyanide or EDTA. The amounts of diverse ions which could be tolerated are shown in Table II.

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MERCURY

Mercury could be extracted from aqueous solution with a solution of BPHA in chloroform. The absorbance curve for the complex is shown in Fig. 1; it can be seen that the wavelength of maximum absorption shifts slightly towards higher wavelength as the amount of mercury(II) increases. All measurements were made at 340 mμ.



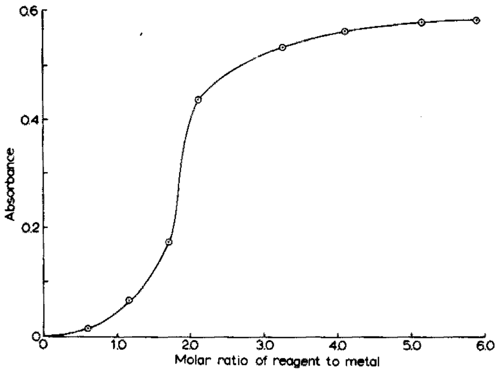


Fig. 1. Absorbance curves of mercury(II)–BPHA complex in chloroform. (a) 27.0 μg/ml mercury; (b) 43.2 μg/ml mercury.

Fig. 2. Composition by mole ratio method applied to mercury(II)–BPHA complex.

The complex is stable at room temperature (30°) for about 4.5 h, after which period the absorbance gradually decreases, although Beer's law is obeyed even after 24 h. At lower temperatures (5–10°), there is no appreciable change in absorbance even after 1 week.

Procedure

Place an aliquot of the mercury solution in a 100-ml graduated separatory funnel and dilute to 30–40 ml with distilled water. Adjust to pH 6.2 by addition of sodium acetate solution and add BPHA solution in chloroform in three 4-ml portions, shaking strongly for about 20 min after each addition. Transfer the chloroform layers to a 25-ml volumetric flask and dilute to the mark with chloroform. Measure the absorbance at 340 mμ against a reagent blank prepared in the same way.

Effect of variables

Mercury solutions containing 1.08 mg Hg were adjusted to different pH values with sodium acetate, nitric acid or sodium hydroxide and taken through the above procedure, the pH of the aqueous layer being checked after extraction. It was found that extraction began at pH 2.8 and was quantitative in the pH range 6.1–7.4; the pH for 50% extraction was 4.8.

The total time of extraction was varied between 30 min and 5 h: the optimum time was about 1 h.

The optimum reagent concentration was found to be 0.04 *M*; concentrations from 0.005 to 0.2 *M* were tested. At concentrations above 0.02 *M*, the absorbance remained essentially constant but below 0.01 *M* extraction was incomplete even with extraction times of 5 h.

Range and sensitivity

The mercury–BPHA complex obeyed Beer's law in the range 5–52 μg of mercury per ml at 340 mμ. According to Sandell's recommendation[3], the optimum range is 15–52 μg Hg per ml.

TABLE III

EFFECT OF DIVERSE IONS

(Mercury(II) taken = 1.08 mg)

Foreign ion	*Source*	*Tolerance limit (mg)*	*Foreign ion*	*Source*	*Tolerance limit (mg)*
Ag^+ [a]	$AgNO_3$	10	W^{6+} [b]	Na_2WO_4	20
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	2	U^{6+} [a]	$UO_2(NO_3)_2 \cdot 6H_2O$	20
Pb^{2+} [a]	$Pb(NO_3)_2$	10	La^{3+} [a]	$La(NO_3)_3$	20
Cd^{2+}	$CdSO_4 \cdot 8/3H_2O$	1	V^{5+}	$NaVO_3$	10
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	1			
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	1	Cl^-	NaCl	Interferes
Bi^{3+} [a]	$BiONO_3$	10	CN^-	KCN	Interferes
Sb^{3+} [a]	$Sb_2(SO_4)_3$	20	F^-	NaF	>100
As^{5+} [b]	$KH_2AsO_4 \cdot H_2O$	20	SO_4^{2-}	$Na_2SO_4 \cdot 10H_2O$	>100
Fe^{3+}	$Fe(NO_3)_3$	10	Ox^{2-}	Oxalic acid	>100
Ti^{4+} [c]	$Ti(SO_4)_2$	10	PO_4^{3-}	$Na_2HPO_4 \cdot 12H_2O$	20
Zr^{4+} [c]	$ZrOSO_4$	10	BO_3^{3-}	H_3BO_3	20
Th^{4+} [a]	$Th(NO_3)_4$	20	Cit^{3-}	Citric acid (also Na-salt)	>100
Sn^{4+} [d]	$Sn(SO_4)_2$	20	$Tart^{4-}$	Tartaric acid (also Na-K-salt)	>100
Mo^{6+} [a]	$Na_2MoO_4 \cdot 2H_2O$	20	$EDTA^{4-}$	EDTA (disodium salt)	Interferes

[a] Citrate added as masking agent.
[b] Tartrate added as masking agent.
[c] Fluoride added as masking agent.
[d] Oxalate added as masking agent.

The molar extinction coefficient was found to be 2693 ± 10. The sensitivity of the reaction based on Sandell's notation[3] was 0.075 μg/cm^2.

Nature of complex

Figure 2 shows the results of the mole ratio method. The maximum colour formation was attained so long as there was a 5-fold or greater molar excess of the reagent. Mercury may form more than one complex with BPHA, the stabilities of which hinder the precise determination of the formula by spectrophotometry; however, the 1:2 complex, as found in gravimetry, seems probable and the higher reagent concentration is needed to prevent slight dissociation of the complex.

Effect of diverse ions

The tolerance limits for various anions and cations are given in Table III. The figures represent the concentration of foreign ion which caused an error of less than 2% in the absorbance reading. Iron(III) and vanadium(V) were removed by a preliminary extraction at pH *ca.* 2.0 and copper at pH 3.8 using a 0.01 *M* reagent solution; mercury was subsequently extracted from the aqueous phase at pH 6.2. Zinc in amounts greater than 1 mg interfered by forming an emulsion with the extract.

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SUMMARY

N-Benzoyl-N-phenylhydroxylamine (BPHA) is suggested for the gravimetric determination of mercury(II) at pH 3.0–6.0; the precipitate, $Hg(C_{13}H_{10}O_2N)_2$, is dried at 105° and weighed. Separation from NH_4^+, Pb, Bi, Sb, As, Cd, Sn, etc. is possible, but chloride, cyanide and EDTA interfere. Mercury(II) can also be extracted with a BPHA solution in chloroform: the extracted mercury complex is yellow and shows an absorbance maximum at 340 mμ. The optimum concentration range for determination is 15–52 μg Hg/ml, the molar extinction coefficient is 2693 ± 10 and the sensitivity is 0.075 μg/cm^2. Interferences are similar to those found in the gravimetric method.

RÉSUMÉ

On propose la N-benzoyl-N-phénylhydroxylamine pour le dosage gravimétrique du mercure(II) au pH 3.0–6.0; le précipité $Hg(C_{13}H_{10}O_2N)_2$ est séché à 105° et pesé. Une séparation d'avec NH_4^+, Pb, Bi, Sb, As, Cd, Sn, etc. est possible, mais les chlorure, cyanure et EDTA gênent. On peut procéder également à une extraction dans le chloroforme; le complexe de mercure extrait est jaune et présente un maximum d'absorption à 340 mμ. Concentration optimum: 15–52 μg Hg/ml; coefficient d'extinction molaire: 2693 ± 10; sensibilité: 0.075 μg/cm^2. Mêmes interférences que pour la méthode gravimétrique.

ZUSAMMENFASSUNG

N-Benzol-N-phenylhydroxylamin (BPHA) wird für die gravimetrische Be-

stimmung von Quecksilber(II) vorgeschlagen. Beim pH-Wert 3.0–6.0 wird $Hg(C_{13}H_{10}O_2N)_2$ gefällt, bei 105° getrocknet und anschliessend gewogen. Die Trennung von NH_4^+, Pb, Bi, Sb, As, Cd, Sn, usw. ist möglich; Chlorid, Cyanid und EDTA stören. Quecksilber(II) kann auch mit BPHA in Chloroform extrahiert werden. Der extrahierte Quecksilberkomplex ist gelb und zeigt ein Absorptionsmaximum bei 340 mμ. Der optimale Konzentrationsbereich für die Bestimmung liegt zwischen 15 und 52 μg Hg/ml, der molare Extinktionskoeffizient beträgt 2693 ± 10 und die Empfindlichkeit 0.075 μg/cm². Die Störungen sind ähnlich denen, wie sie bei der gravimetrischen Methode gefunden wurden.

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CATALYTIC MICRODETERMINATION OF MERCURY

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Mercury exerts a strong catalytic effect on the reaction of ferrocyanide with water to form aquopentacyanide which forms a violet complex with nitrosobenzene[1]. The overall reaction is summarized as follows:

$$[Fe(CN)_6]^{4-} + C_6H_5NO \rightarrow [Fe(CN)_5(C_6H_5NO)]^{3-} + CN^- \qquad (1)$$

If the absorbance of the violet product, $[Fe(CN)_5(C_6H_5NO)]^{3-}$, is measured at a fixed reaction time, mercury can be determined from suitable working curves[1-3]. In these procedures inaccuracies are introduced in the absorbance measurement and/or time measurement.

To simplify and automate the mercury determination, a reaction-rate method that provides a digital readout value shortly after starting the reaction has been developed. The method utilizes the chemical system shown in eqn. (1) and the type of automatic spectrophotometric reaction-rate system recently used for the determination of glucose[4] and iodine[5]. In this method the times required for reaction (I) to proceed to a small fixed extent (as given by a preselected change in the output voltage of a photoconductive circuit) are measured automatically with an electronic timer switched by a sensitive amplifier–relay combination, and are related directly to the mercury concentration.

The automatic procedure is simple, accurate and rapid. The sample is pipetted into the reaction cell containing buffer and nitrosobenzene, potassium ferrocyanide is injected to start the reaction, the start button is pressed and the data are read off a dial shortly after the start. Amounts of mercury in the range 0.25–2.5 μg were determined with relative errors of about 1 to 2% and measurement times of only 15–120 sec.

The automatic reaction-rate measurement method was tested for the determination of mercury in inorganic and organic mercurial compounds and in pharmaceutical preparations. Results obtained with pure compounds agreed within 1 to 2% with the theoretical values and results obtained with pharmaceutical preparations were within the range assigned to those preparations.

The time required for reaction (1) to proceed to a small fixed extent (equivalent to a change in absorbance of about 0.04 unit) depends not only on the mercury concentration but also on pH, temperature, and the concentrations of ferrocyanide and nitrosobenzene. By adjusting the conditions the reaction is made pseudo first-order with respect to mercury.

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A composite reagent containing the acetate buffer and nitrosobenzene was unstable so the two reagents were added separately.

Mercury salts are slowly adsorbed on glass[6] and therefore the very dilute working standards were prepared daily.

After initiation of the reaction, a minimum premeasurement time of 5–10 sec was desirable to ensure thorough mixing of the reagents. The premeasurement time was controlled by the setting of the comparator zero adjust, larger settings resulting in larger premeasurement times. The appropriate setting was determined experimentally by running the more concentrated mercury solution. For example, the zero adjust was set at 5.40 for the 0.1–1.5 p.p.m. of mercury range. A higher comparator setting, 6.40, was necessary for the range 2.0–10 p.p.m. of mercury, where the reaction was faster. Whenever new conditions were selected or a new experimental set up was used, the zero adjust had to be determined only once. The zero adjust setting could be varied, but that decided upon had to be duplicated carefully from sample to sample, to secure starting of measurement time at the same concentration of the reactants.

The reaction rate has a large temperature coefficient and therefore the reaction was carried out in a thermostatted cell at $40 \pm 0.05°$. Temperature was controlled by circulating water from a constant temperature bath at $40 \pm 0.05°$ through the water-jacket surrounding the reaction cell. To minimize heat losses, the transfer of the reagents from the water bath to the reaction cell was done as quickly as possible. If a large number of samples are to be run routinely, automatic handling of these solutions may be preferable. To ensure thermal equilibrium in the reaction cell, the mixture was stirred for 2 min before starting the reaction by the addition of the ferrocyanide solution.

Although the rate of the reaction under selected conditions was proportional to the mercury concentration, the working curves (straight lines) obtained by plotting reciprocal of readout *vs.* mercury concentration did not pass through the origin. Therefore working curves were established by using several standards.

EXPERIMENTAL

Instrumentation

The basic instrumental components were the same as those used for determination of glucose except that a 1 kΩ resistor was substituted for the 820 Ω resistor previously used[4].

Reagents

All solutions, except of nitrosobenzene, were prepared with deionized water from reagent-grade materials. The ferrocyanide and the nitrosobenzene solutions were kept in glass-stoppered amber bottles.

Nitrosobenzene (Aldrich Chemical Co., Milwaukee, Wisc., U.S.A.). 0.5% solution in 95% ethanol.

Mercury standards. Stock solution I. 0.8984 g of mercuric bromide dissolved in 1 l of water. This solution contained 500 p.p.m. of mercury.

Working solution II. 20 ml of stock solution I were diluted to 1 l. This solution contained 10 p.p.m. of mercury. It was prepared weekly.

Working standard III. Standards containing 0.25, 0.5 and 1 p.p.m. of mercury were prepared from the 10 p.p.m. solution by appropriate dilution. They were prepared daily.

All working standards, reagent solutions and samples were kept in a water bath at 40° before use.

Procedure

Preparation of equipment. Switch the Spectro-Electro titrator to the Spectro position about 2 h before the measurements are started to ensure good stability from the light source. Dial the 525 position on the filter wheel and throw the polarity switch to position 1. A few minutes before the measurements are started, turn the comparator unit to *on* and the range selector switch to PNP ± 0.01 V.

Measurement step. Set the comparator Zero Adjust control at 5.40. Pipet *quickly* 1.00 ml of buffer pH 4.1 solution (0.5 *M* acetic acid–0.5 *M* acetate) and 2.00 ml of sample or standard mercury solution into the reaction cell in the order given. Inject into the reaction cell 0.100 ml of nitrosobenzene solution with a 0.1-ml Hamilton microliter syringe. Throw the comparator reagent selector switch to position 1 to start the stirring and adjust the Spectro balance control so that the meter needle is at the center. Set the comparator Zero Adjust at 4.50, and 2 min after the start of the stirring, inject 0.100 ml of 0.1 *M* potassium ferrocyanide solution using a 0.1-ml Hamilton microliter syringe and press *at once* the start button on the model Q-RR reaction-rate adapter. The analysis is completed automatically and the number on the readout dial is recorded. Empty the cell by inserting an aspirator tube and rinse twice with water. Repeat the procedure for each analysis.

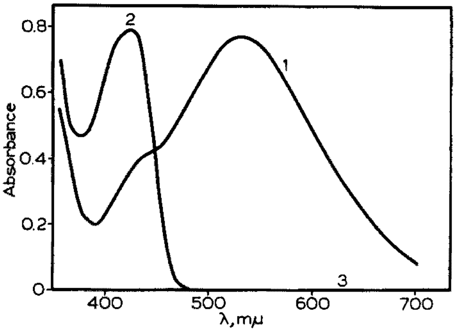
Preparation of mercury samples. The size of the sample chosen may be varied according to mercury content. If the mercurial compounds or the pharmaceutical preparations contain more than 0.2% mercury, weigh approximately 50.0 mg of sample. Transfer the sample into a 250-ml beaker, add 20 ml of bromine water, cover the beaker with a watch glass, and heat the contents on a sand bath until no odor of bromine can be detected. If a precipitate remains, filter and dilute the filtrate to the mark in a 100-ml volumetric flask. This solution contains about 1 p.p.m. of mercury if the mercury content of the sample is 0.2% and can be used directly for the measurement step. If the solution contains more than 1.5 p.p.m. of mercury, it should be brought to the range 0.3 to 1.5 p.p.m. (preferably to about 1 p.p.m.) by appropriate dilution with water. Smaller amounts of sample can be used if microbalances are available. In the case of pharmaceutical preparations containing less than 0.2% mercury, weigh more than 50 mg of sample or dissolve the sample in a smaller volume of water.

Calculations. The concentration of the final solution is read directly in p.p.m. of mercury from a working curve obtained by plotting linearly reciprocal times *vs.* mercury concentrations of the standards. The mercury content of the sample is calculated from the concentration of the final solution by multiplying by the appropriate dilution factor.

RESULTS AND DISCUSSION

The spectrophotometric response of the photocell was rapid, and reliable measurements could be made within a few seconds after the start of the reaction. It was found that the first run after a long exposure of the photocell always gave shorter measurement times and therefore, before a series of measurements was started, one standard solution was run and the readout value discarded.

From the absorption spectra (Fig. 1) it can be seen that the absorption maximum of the product $[Fe(CN)_5(C_6H_5NO)]^{3-}$ is at 527 mμ and that the reactants, $K_4Fe(CN)_6$ and C_6H_5NO, do not absorb at this wavelength. A 525-mμ band was selected for measurements by dialing the nominal 525-mμ second order interference filter. Curve 1 was taken after the reaction had gone to completion.



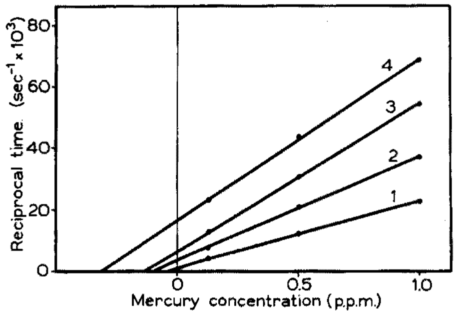
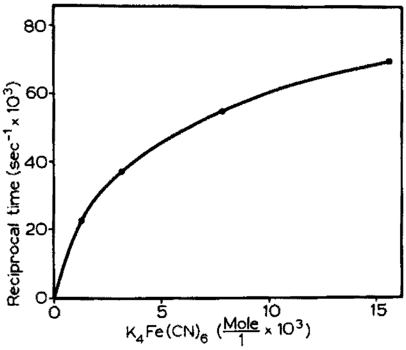


Fig. 1. Absorption curves. Concentration of reactants as under procedure. (1) $[Fe(CN)_5(C_6H_5NO)]^{3-}$, Hg 1.5 p.p.m.; (2) $K_4Fe(CN)_6$; (3) C_6H_5NO.

Fig. 2. Working curves for mercury with various concentrations of potassium ferrocyanide. (1) $1.25 \cdot 10^{-3}$; (2) $3.12 \cdot 10^{-3}$; (3) $7.81 \cdot 10^{-3}$; (4) $1.56 \cdot 10^{-2}$ *M*. Blank: (1) 0.06; (2) 0.09; (3) 0.14; (4) 0.32 p.p.m. mercury.



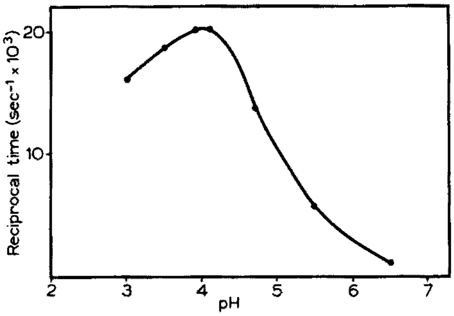


Fig. 3. Effect of concentration of potassium ferrocyanide on reaction rate in mercury determination. Other conditions as under procedure; Hg 1.0 p.p.m.

Fig. 4. Variation of reaction rate with pH. Other conditions as under procedure; Hg 0.5 p.p.m.

The rate of the catalyzed as well as that of the uncatalyzed reaction depends on the concentration of the ferrocyanide. This is shown in Figs. 2 and 3 where the blank increased from 0.06 to 0.32 p.p.m. of mercury as the ferrocyanide concentration increased from $1.25 \cdot 10^{-3}$ *M* to $1.56 \cdot 10^{-2}$ *M*. A ferrocyanide concentration of $3.12 \cdot 10^{-3}$ *M* was selected for the standard assay, so that measurement times did not exceed 2 min for the 0.1 p.p.m. mercury sample.

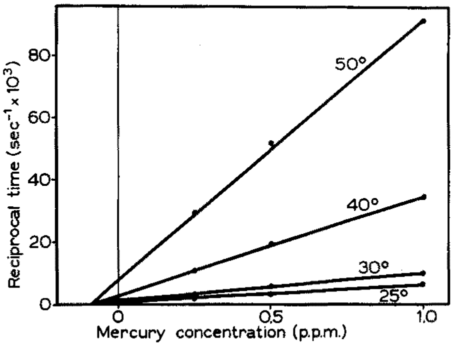
Variation in nitrosobenzene concentration showed that the reaction rate increased when the concentration of the nitrosobenzene in the final solution was increased from zero to about $6 \cdot 10^{-4}\,M$. Small variations in the concentration of nitrosobenzene had no effect on the reaction rate in the range chosen for the analysis ($1.46 \cdot 10^{-3}\,M$).

When other aromatic nitroso compounds were substituted for nitrosobenzene, the measurement times increased considerably, *e.g.* measurement times obtained with *p*-nitrosodimethylaniline were about 4 times larger than those obtained with nitrosobenzene.

Aqueous nitrosobenzene solutions decompose upon standing, and they have to be prepared daily[3]. It was found that solutions of nitrosobenzene in ethanol were stable for several months. Measurement times were the same with fresh and with a 2-month-old alcoholic solution of nitrosobenzene.

It was necessary to keep a constant ionic strength in all cases because the catalytic effect of mercury decreased with an increase in ionic strength of the solution. Thus, measurement times were about the same when the acetate buffer used was 0.14 to 0.28 *M*, but they increased by 9% when the buffer used was 0.5 *M*. Although the reaction showed a negative salt effect, a 0.5 *M* buffer was chosen for the assay to secure better buffering capacity. With such a buffer, measurement times obtained with a fresh ferrocyanide solution were the same as those obtained with a 2-month-old ferrocyanide solution, whose pH had increased to 9 because of hydrolysis.

Figure 4 illustrates the influence of the pH on the rate of the reaction with all other conditions as described for the procedure. The optimum pH lay in the range of pH 3.9 to 4.2; a pH of 4.1 was chosen.



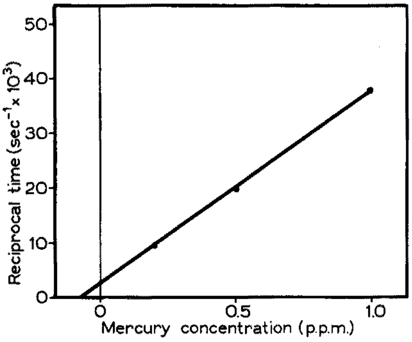


Fig. 5. Effect of temperature on reaction rate in mercury determination.

Fig. 6. Working curve for mercury determination.

The rate of the reaction is also increased by ultraviolet light[3]. However, no difference in measurement times was observed when a UV cut-off filter was placed in front of the interference filter. Since the effect of the ultraviolet light was negligible over the small period required for a measurement, the determination of mercury was made under ordinary light conditions.

The effect of temperature on the rate of the reaction is shown in Fig. 5. From Arrhenius plots of log $1/t$ *vs.* reciprocal of absolute temperature, the activation energy was calculated to be 21.4 kcal/mole (t = measurement time).

A working curve for the 0.1 to 1.0 p.p.m. mercury range is shown in Fig. 6. The abscissa intercept (blank) is a function of the uncatalyzed reaction and the mercury contamination of the reagents. Under the conditions of the procedure, the blank range over a period of 4 months was 0.06 to 0.09 p.p.m. of mercury. For the given set of conditions, the reaction was pseudo first-order with respect to mercury up to 3 μg of mercury (2 ml of 1.5 p.p.m. solution). Above 3 μg of mercury the reaction order with respect to mercury increased gradually. The working curve should be rechecked every 3 h.

Analysis of aqueous mercury solutions of known concentrations gave the results shown in Table I. The accuracy and precision for aqueous solutions containing 0.25 to 2.5 μg mercury in a total volume of 3.2 ml were 1–2%.

TABLE I

AUTOMATIC RESULTS FOR AQUEOUS MERCURY SOLUTIONS

Reciprocal time ($sec^{-1} \cdot 10^3$)	*Mercury in 2-ml sample (μg)*		*Relative error (%)*
	Taken	*Found*[a]	
9.4	0.400	0.402	+0.5
16.0	0.800	0.786	−1.7
24.6	1.200	1.240	+3.3
32.1	1.600	1.620	+1.3
46.5	2.500	2.490	−0.4

[a] From straight line working curve.

TABLE II

AUTOMATIC RESULTS FOR MERCURIAL COMPOUNDS TREATED WITH BROMINE WATER

Sample	*Mercury in 2-ml sample (μg)*		*Relative error (%)*
	Reported	*Found*	
Mercuric iodide	2.00	1.98	−1.0
Mercurous chloride	2.00	2.00	—
Mercurous sulfate	2.00	2.00	—
Phenylmercuric chloride	2.00	1.96	−2.0
Phenylmercuric nitrate	2.00	1.98	−1.0
Merbromin (mercurochrome)	2.00	1.99	−0.5
Merbromin (mercurochrome)	1.00	0.98	−2.0
Thimerosal (merthiolate)	2.00	1.98	−1.0
Chlormerodrin (neohydrin)	2.00	2.06	+3.0
Mercurophylline sodium (mercuzanthin)	2.00	2.02	+1.0
Mercaptomerin sodium (thiomerin)	2.00	1.98	−1.0
Mercuhydrin sodium (meralluride sodium)	2.00	1.98	−1.0
Thimerosal tincture[a]	2.00	2.20	+10.0
Merbromin (2% solution)[a]	2.00	1.98	−1.0
Chlormerodrin (tablet)[a]	2.00	2.12	+6.0
Meralluride (tablet)[a]	2.00	2.05	+2.5
Meralluride (injection)[a]	2.00	2.00	—
Nitromersol (metaphen)[a]	1.40	1.51	+7.9

[a] Pharmaceutical preparations.

Application of the method

Several mercurial compounds and pharmaceutical preparations were analyzed to establish the validity of the method. The results obtained show the accuracy of the procedure (Table II). The values obtained for 5 reagent-grade mercurial compounds (the first 5 samples listed in Table II) agreed within about 1% with the theoretical values. Even insoluble compounds, such as Hg_2Cl_2 and HgI_2, were completely dissolved after treatment with bromine water (larger amounts of bromine water were required for such compounds). Results obtained for 2 organic mercurial antiseptics (thimerosal, merbromin) and 4 mercurial diuretics (chlormerodrin, mercuzanthin, thiomerin, meralluride) checked closely with values given by the manufacturers. Results obtained for 5 pharmaceutical preparations (the last 6 samples in Table II) were within the range given by the manufacturer.

A modified procedure was used for the analysis of mercurial ophthalmic ointments (HgO and $HgCl_2$). The samples were treated with ether and water, acidified with hydrochloric acid, and the aqueous layer was treated with bromine water. Results were within the assigned range for the HgO but were low for the $HgCl_2$.

TABLE III

RECOVERY OF MERCURY ADDED[a] TO ORGANIC MERCURIAL COMPOUNDS

Sample	*Mercury in 2-ml sample (µg)*				*Recovery (%)*
	Originally present[b]	*Added*	*Total*	*Found*	
Phenylmercuric chloride	0.98	1.00	1.98	1.96	98
	0.49	1.50	1.99	1.99	100
Merbromin (mercurochrome)	0.50	1.50	2.00	1.96	97
Mercurophylline sodium (mercuzanthin)	1.01	1.00	2.01	2.05	104
	0.50	1.50	2.00	2.00	100
Meralluride sodium (mercuhydrin sodium)	1.00	1.00	2.00	1.97	97
	0.50	1.50	2.00	1.98	99
				Average recovery	99.3

[a] Mercury added as mercuric bromide.

[b] Average of 2 determinations.

In Table III data are given to show the recovery of mercury, which has been added to 4 organic mercurial compounds. The recovery of mercury varied from 97 to 104% with an average of 99.3%.

Interferences

The effect of various metals that might interfere in the determination of mercury was investigated. Silver, platinum and gold, which catalyze the reaction in the same manner as mercury, interfered seriously. The catalytic effect of gold was found to be about one-fifth that of mercury. Iodide reduced the concentration of mercury and caused negative errors; thus, 1 µg of iodide in the presence of 2 µg of mercury caused a negative error of 7%. Metal ions which form insoluble salts with ferrocyanide interfered seriously. It was found that most of the interfering ions could be masked with EDTA. Since EDTA reacts with mercury, whenever EDTA was added to the samples, exactly the same amount of EDTA was also added to the mercury standards. The procedure was modified as follows. After the addition of the mercury standard or of the sample, 0.100 ml of 0.25 M EDTA was injected into the reaction cell. Working curves obtained with EDTA had a smaller slope than those obtained without EDTA. Table IV gives the maximum amount of interfering ions which could effectively be masked with $7.24 \cdot 10^{-3}$ M EDTA, with relative errors of 1 to 2%.

TABLE IV

EFFECT OF INTERFERING IONS IN THE PRESENCE OF $7.4 \cdot 10^{-3}$ M EDTA

Mercury taken (μg)	*Additional ions (μg)*	*Mercury found (μg)*	*% Error*
2.00	50 Cu^{2+}	2.03	+1.5
2.00	50 Ni^{2+}	2.05	+2.5
2.00	10 Fe^{3+}	2.01	+0.5
2.00	50 Fe^{3+}	2.04	+2.0
2.00	2 Fe^{2+}	2.02	+1.0
2.00	20 Fe^{2+}	2.06	+3.0
2.00	8 Zn^{2+}	1.98	−1.0
2.00	40 Mn^{2+}	2.04	+2.0
2.00	150 Pb^{2+}	2.00	—
2.00	150 Mg^{2+}	1.97	−1.5
2.00	80 Cd^{2+}	2.00	—
2.00	30 Pt^{4+}	1.96	−2.0

Although the work reported here deals with the determination of mercury in mercurial compounds and in pharmaceutical preparations, the applicability of the method is more general. A basic procedure and general considerations for the determination of mercury are given, so that the method can be adapted to many specific cases—*e.g.* urine, blood, atmosphere, pulp, paper.

The author is indebted to Miss P. GANCARZ for technical assistance. This research was supported in part by the National Institutes of Health, Public Health Service, Research Grant GM 11039-02.

SUMMARY

An automatic spectrophotometric reaction-rate method is described for the microdetermination of mercury. The method is based on the catalytic effect of mercury on the reaction of ferrocyanide with nitrosobenzene. The time required for production of a small fixed amount of the violet product as given by a preselected change in the output voltage of a photoconductive circuit, is measured automatically and related directly to the mercury concentration. The possibility of masking interfering ions with EDTA was examined. Amounts of mercury in the range 0.25–2.5 μg were determined with relative errors of 1–2% in measurement times of only 15–120 sec. Results obtained with mercurial compounds, treated with bromine water, were

within 1–2% of the theoretical values and results obtained with pharmaceutical preparations were within the range assigned to those preparations.

RÉSUMÉ

Une méthode spectrophotométrique automatique est décrite pour le microdosage du mercure. Elle est basée sur l'effet catalytique du mercure sur la réaction ferrocyanure–nitrosobenzène. On mesure le temps nécessaire pour obtenir une quantité déterminée du produit violet. On a examiné également la possibilité de masquage d'ions gênants, au moyen d'EDTA. On peut ainsi doser des teneurs en mercure de 0.25 à 2.5 μg avec une erreur relative de 1 à 2%, en 15–120 secondes.

ZUSAMMENFASSUNG

Für die Mikrobestimmung von Quecksilber wird eine automatische spektralphotometrische Methode zur Bestimmung der Reaktionsgeschwindigkeit beschrieben. Die Methode beruht auf dem katalytischen Effekt des Quecksilbers auf die Reaktion von Eisen-(II)-cyanid mit Nitrosobenzol. Die für die Bildung eines violetten Produkts benötigte Zeit wird automatisch gemessen und direkt zur Quecksilberkonzentration in Beziehung gesetzt. Die Möglichkeit störende Ionen mit AEDTE zu maskieren, wurde geprüft. 0.25–2.5 μg Quecksilber wurden mit einem relativen Fehler von 1–2% bei Messzeiten von nur 15–120 Sek bestimmt. Ergebnisse, welche mit Quecksilberverbindungen erhalten wurden, wichen nur 1–2% von den theoretischen Werten ab.

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MICRODETERMINATION OF MOLYBDENUM BY AN AUTOMATIC REACTION-RATE METHOD

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Several kinetic methods have been developed for the determination of molybdenum[1-6]. In this paper, an automatic reaction-rate method is presented for the microdetermination of molybdenum. The method utilizes the chemical system shown in eqn. (1) and the type of automatic spectrophotometric reaction-rate system used for the determination of glucose[7].

$$H_2O_2 + 3\ I^- + 2\ H^+ \rightarrow 2\ H_2O + I_3^- \quad (1)$$

The time required for reaction 1 to produce a small fixed amount of triiodide and therefore for the absorbance to increase by a preselected amount—as given by a preselected change in the output voltage of a photoconductive circuit—is measured automatically and related directly to molybdenum concentration.

The method is rapid, sensitive and accurate. By means of a sensitive measurement system[7], measurements are completed automatically within 10–120 sec with very small changes in reactant concentrations. Microamounts of molybdenum in the range 0.036 to 2.5 μg can be determined with relative errors of about 2%.

EXPERIMENTAL

Instrumentation

The basic instrumental components were the same as those used previously[7] except that a 100 kΩ Helipot was substituted for the 5 kΩ Helipot and a 1 kΩ resistor for the 820 Ω resistor.

Reagents

All reagents were prepared in double-distilled water from reagent-grade materials.

Molybdenum standards. Dissolve 0.1840 g of ammonium paramolybdate tetrahydrate in 1 l of water. This solution contains 100 p.p.m. of molybdenum. Prepare working standards by appropriate dilution.

All working standards, reagent solutions and samples were kept in a water bath at 30±0.05° when used.

Procedure

Preparation of equipment. Switch the Spectro-Electro titrator to the Spectro position at least 1 h before the measurements are started to insure good stability from the light source. Dial the 525 position on the filter wheel and place the Corning No. 5860 filter in the auxiliary holder; this setting allows measurement at 365 mμ. Throw the polarity switch to position 1. A few minutes before the measurements are started, turn the comparator unit to *on* and the range selector switch to PNP ±0.01 V.

Measurement step. Method 1 (for the range 10–150 p.p.b. of molybdenum). Set the comparator Zero Adjust control at 5.20. Pipet 3.00 ml of sample or standard molybdenum solution into the reaction cell. Inject (with a 0.25-ml syringe) 0.25 ml of 0.05 *M* sulfuric acid and 0.100 ml of 0.07 *M* potassium iodide solution using a 0.1-ml Hamilton microliter syringe into the cell. Throw the comparator reagent selector switch to position 1 to start the stirring and adjust the Spectro balance control so that the meter needle is at the center. Set the comparator Zero Adjust at 4.50, and 1 min after the start of the stirring, inject 0.100 ml of 0.005 *M* hydrogen peroxide solution (prepared each day) with a 0.1-ml Hamilton microliter syringe and press *at once* the start button on the model Q-RR reaction-rate adapter. The analysis is completed automatically and the number on the readout dial is recorded. Repeat the procedure for each analysis.

Method 2 (for the range 100–1000 p.p.b. of molybdenum) is similar except that the Zero Adjust is set first at 6.50, and then, after the meter needle has been adjusted at the center by the Spectro balance control, at 3.50.

RESULTS AND DISCUSSION

Basic considerations concerning contamination, temperature control, premeasurement times and preparation of working curves were similar to those previously reported[8].

The triiodide formed in the reaction has an absorption maximum at 353 mμ, but the narrow band at 365 mμ was selected because the absorptivity is not much less than that at 353 mμ, whereas the instrument response is considerably greater.

The rate of both the catalyzed and the uncatalyzed reaction depends on the hydrogen ion concentration. For the catalyzed reaction, the reciprocal time reaches a maximum at *ca.* 0.01 *M* sulfuric acid and then decreases gradually as far as 0.10 *M*; in the absence of acid, the reaction is extremely slow. In a study of the effect of the hydrogen ion concentration on the rate of the uncatalyzed reaction the blank increased from 7 p.p.b. to 24 p.p.b. of molybdenum as the sulfuric acid concentration increased from 0.0036 to 0.0543 *M*. For the procedure described the concentration of sulfuric acid in the measured solution is 0.0036 *M*, which was selected so that the blank would be kept small and measurement times would be in the range 10–120 sec. Measurement times were the same when hydrochloric acid was substituted for sulfuric acid.

Although the reaction is first order with respect to iodide, under the experimental conditions there is a direct relationship between iodide concentration and reciprocal times only when the iodide concentration exceeds 0.0015 *M*. Measurement times decrease as the iodide concentration increases, but large iodide concentrations should be avoided because of the increase in the rate of the uncatalyzed reaction; the blank increased from 7 to 12 p.p.b. of molybdenum when the iodide concentration was increased from 0.002 to 0.004 *M*. A 0.002 *M* potassium iodide concentration was chosen as a compromise between velocity and blank.

The effect of variation in the hydrogen peroxide concentration was similar to that of iodide. The blank increased from about 6 to 75 p.p.b. of molybdenum when the concentration of hydrogen peroxide in the final mixture increased from 0.64 to $25.6 \cdot 10^{-4}$ *M*. A concentration of $1.4 \cdot 10^{-4}$ *M* hydrogen peroxide was chosen.

The reaction has a relatively small temperature coefficient of about 2%. The blank increases as the temperature increases. A thermostatted cell at 30±0.05° was used.

TABLE I

RESULTS FOR AQUEOUS MOLYBDATE SOLUTIONS

Molybdenum in 3-ml sample (µg)		*Relative error*	*Molybdenum in 3-ml sample (µg)*		*Relative error*
Taken Range A[b]	*Found*[a]		*Taken Range B*[b]	*Found*[a]	
0.036	0.034	−5.6	0.30	0.29	−3.3
0.090	0.090	—	0.90	0.93	+3.3
0.240	0.241	+0.4	1.20	1.20	—
0.360	0.364	+1.1	2.10	2.14	+1.9
			2.55	2.54	−0.4

[a] From straight-line working curve.
[b] Ranges A and B run according to Methods 1 and 2, respectively.

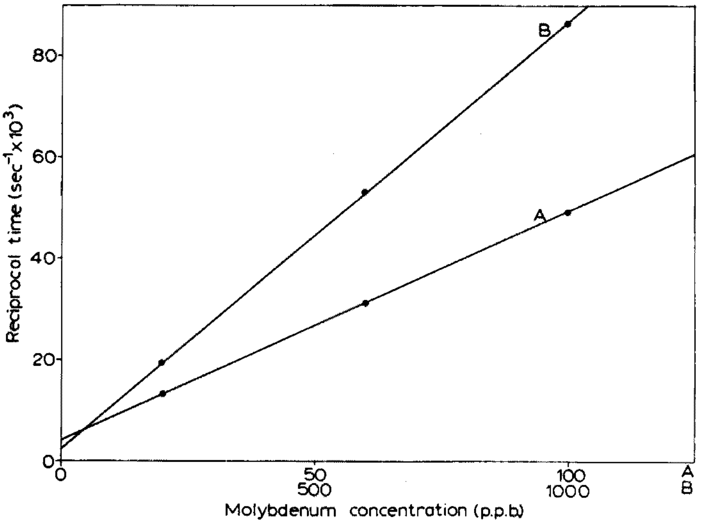

Fig. 1. Working curves for molybdenum determination. $3.6 \cdot 10^{-3}$ *M* H_2SO_4; $2.0 \cdot 10^{-3}$ *M* KI; $1.4 \cdot 10^{-4}$ *M* H_2O_2; 30°.

Large deviations in ionic strength have no effect on the rate of the reaction; measurement times remained the same when the ionic strength of the final solution was increased with the addition of zinc chloride from 0.013 to 0.230.

Results for the determination of molybdenum in pure aqueous molybdate solutions are given in Table I. The data indicate that molybdenum in the range 0.036–2.5

μg (3-ml samples of solutions containing 12–850 p.p.b. of molybdenum) could be determined with relative errors of about 2%. Typical working curves are shown in Fig. 1. Ten replicate determinations were made at the 60 p.p.b. of molybdenum level using the recommended procedure; the relative standard deviation was ±2.4%.

Interferences

Reducing or oxidizing agents should be eliminated before the measurements. The hydrogen peroxide–iodide reaction is catalyzed by other ions[9], which can be considered as interfering ions. Some ions interfere by forming complexes with molybdenum thus reducing its catalytic activity, and others by forming complexes or precipitates with iodide thus reducing its concentration in the final mixture.

To investigate the influence of interfering ions Method 1 was modified as follows: after the addition of a molybdenum standard (60 p.p.b.), 0.25 ml of water or of the solution of the examined ions was injected into the reaction cell. In the case of strongly alkaline solutions, the pH was decreased to less than 7 by the addition of sulfuric acid, before studying the effect on the reaction rate. The following ions did not affect the rate of the reaction even when their concentration exceeded that of molybdenum by several thousand times: ammonium, barium, cobalt(II), magnesium, manganese(II), nickel, potassium, sodium, strontium and zinc (in the case of barium and strontium, hydrochloric acid was substituted for sulfuric acid). Table II shows the effect of interfering ions. Of all the ions which decrease the rate of the reaction oxalate exerts the strongest inhibiting action. The possibility of determining microamounts of chromium(VI) on the basis of its catalytic effect is being examined.

TABLE II

EFFECT OF VARIOUS IONS ON MOLYBDENUM DETERMINATION AT A CONCENTRATION OF $6.25 \cdot 10^{-7}$ *M* (60 p.p.b.)

Ion	*Source*	*Ratio of added ion concn. to Mo concn.*	*Ion*	*Source*	*Ratio of added ion concn. to Mo concn.*
A[a]			*B*[b]		
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	0.15	$C_2O_4^{2-}$	$K_2C_2O_4$	1.1
WO_4^{2-}	Na_2WO_4	0.70	Citrate	Potassium citrate	1.3
Ce^{4+}	$Ce(SO_4)_2$	1.3	Tartrate	Potassium bitartrate	5
VO^{2+}	$VOSO_4$	1.3	EDTA	Na-EDTA	66
Zr^{4+}	$ZrOCl_2$	2.7	Hg^{2+}	$HgBr_2$	110
Fe^{2+}	$FeSO_4$	11	Cd^{2+}	$CdSO_4$	110
Fe^{3+}	$Fe(NO_3)_3$	32	Lactate	Lithium lactate	130
Th^{4+}	$ThCl_4$	80	F^-	NaF	210
UO_2^{2+}	$UO_2(NO_3)_2$	110	Ag^+	$AgNO_3$	270
SeO_3^{2-}	H_2SeO_3	130	Br^-	KBr	930
Cu^{2+}	$Cu(NO_3)_2$	530	$H_2PO_4^-$	KH_2PO_4	2700
Y^{3+}	$Y(NO_3)_3$	2700	$HAsO_4^{2-}$	Na_2HAsO_4	4000
			SiO_3^{2-}	Na_2SiO_3	6600

[a] These ions in the stated ratio caused a positive relative error of less than 5%.
[b] These ions in the stated ratio caused a negative relative error of less than 5%.

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SUMMARY

An automatic reaction-rate method is described for the microdetermination of molybdenum; the method is based on the hydrogen peroxide–iodide reaction which is catalyzed by molybdenum. The effect of reagent concentrations was studied and the maximum tolerable amounts of interfering ions were determined. Procedures for the determination of 0.01–0.15 µg and 0.1–1.0 µg molybdenum per milliliter are given; 0.036–2.5 µg of molybdenum could be determined with relative errors of about 2%.

RÉSUMÉ

On décrit une méthode automatique pour le microdosage du molybdène; elle est basée sur la réaction peroxyde d'hydrogène–iodure, catalysée par le molybdène. On a examiné l'influence des concentrations de réactifs, ainsi que celle d'ions étrangers. On peut doser ainsi 0.036 à 2.5 µg de molybdène avec une erreur relative d'environ 2%.

ZUSAMMENFASSUNG

Es wird eine Mikrobestimmung von Molybdän beschrieben, bei der automatisch die Reaktionsgeschwindigkeit zwischen H_2O_2 und J^- ermittelt wird, welche durch Molybdän katalysiert wird. Der Einfluss der Reagenzkonzentrationen wurde untersucht und der maximal zulässige Anteil störender Ionen bestimmt. Es werden Verfahren zur Bestimmung von 0.01 bis 0.15 µg und 0.1–1.0 µg Mo/ml angegeben. 0.036–2.5 µg Mo können mit einem relativen Fehler von etwa 2% bestimmt werden.

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THE AUTOMATIC DETERMINATION OF FLUORIDE IN SEA WATER AND OTHER NATURAL WATERS

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With the increasing spread of fluoridation of drinking waters the importance of reliable methods for the determination of fluoride in such waters needs little emphasis. The recent discovery[1,2] that fluoride is not a conservative element in the deep waters of certain parts of the oceans stresses the need for an increase in our knowledge of the distribution of this element in the marine environment. The pressure of work in both water-board and marine laboratories necessitates the automation of analytical methods; this paper gives a brief account of an automatic method for the determination of fluoride in natural waters. The manual method developed by GREENHALGH AND RILEY[3] was found to be readily adaptable to the AutoAnalyzer. In this procedure, the sample is treated with a buffered reagent containing the lanthanum chelate of 1,2-dihydroxyanthraquinonyl-3-methylamine-N,N-diacetic acid[4,5] (alizarin fluorine blue); and in the presence of fluoride a blue colour is developed which attains its maximum intensity at pH 4.5. The method is free from most of the anionic and cationic interferences which are troublesome in methods depending on the bleaching of lakes of zirconium, thorium and other elements. The AutoAnalyzer manifold shown diagrammatically in Fig. 1 gave satisfactory results with this reagent with both saline and non-saline waters in the range 0–1.5 μg fluoride/ml. GRASSHOFF[6] has also developed a method based on this reaction for the analyses of sea water.

EXPERIMENTAL

Reagents

Lanthanum–alizarin fluorine blue reagent for use with sea water. Add 0.24 g of alizarin fluorine blue to a solution containing 0.5 ml of concentrated ammonia solution and 15 ml of 6.7% (w/v) ammonium acetate. After the reagent has dissolved, filter the solution through a small Whatman No. 1 paper into a 1-l graduated flask containing a solution of 41 g of anhydrous sodium carbonate (A.R.) and 30 ml of glacial acetic acid in 300 ml of water. Add 500 ml of acetone slowly with swirling. Dissolve 0.2 g of lanthanum oxide (spectrographic grade) in 12.5 ml of 2 *M* hydrochloric acid, warming gently to assist dissolution, and mix with the aqueous acetone solution. Dilute to 1 l with distilled water. The reagent is stable for at least one week.

Lanthanum–alizarin fluorine blue reagent for use with fresh waters. The reagent is prepared as above with the exception that 70 ml of glacial acetic acid instead of 30 ml, is added in the preparation of alizarin fluorine blue solution.

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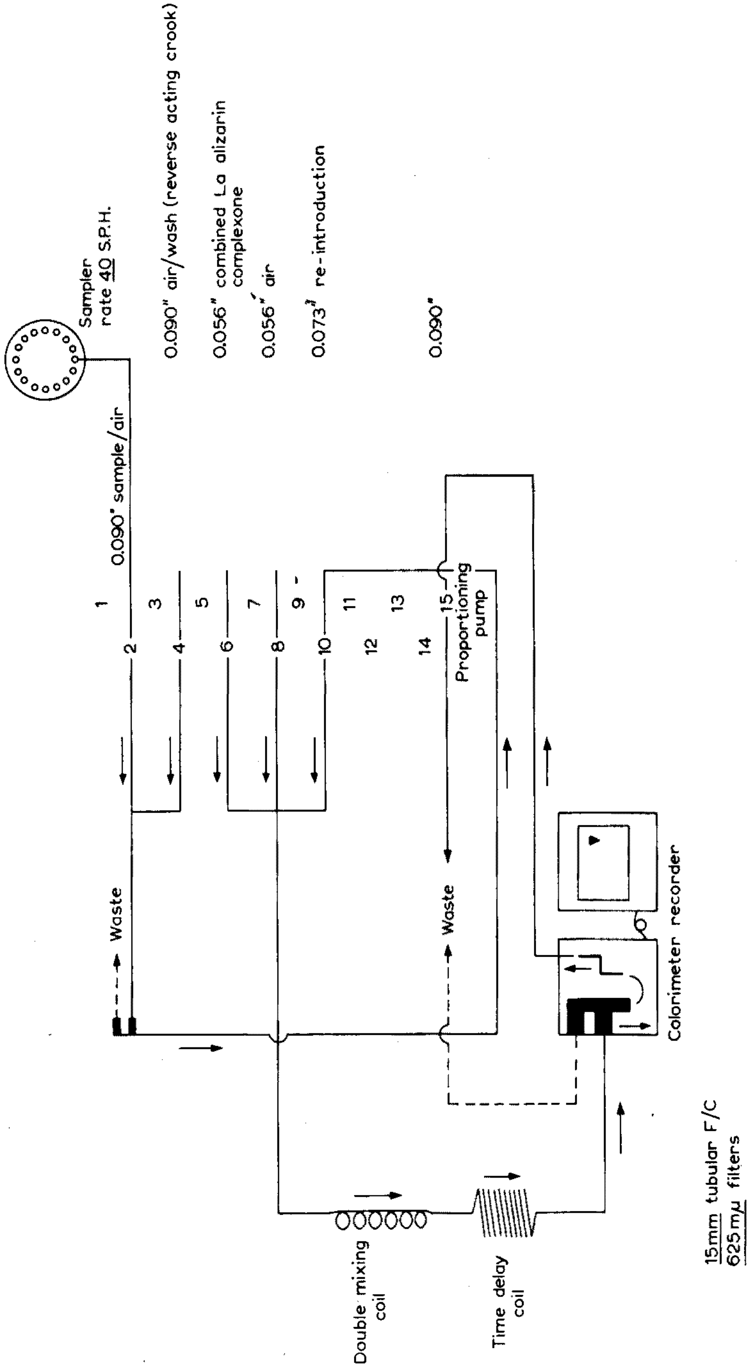


Fig. 1. AutoAnalyzer flow diagram for determination of fluoride.

Stock standard sodium fluoride solution (1 mg F/ml). Dissolve 2.210 g of reagent-grade sodium fluoride in *ca.* 100 ml of water containing 1 ml of 0.1 *M* sodium hydroxide and dilute to 1 l. Prepare a working standard solution containing 1.0 μg F/ml daily by dilution of this stock solution.

Artificial sea water. Artificial sea water is prepared as described by LYMAN AND FLEMING[7] without the addition of sodium fluoride.

Sodium chloride 23.47 g, magnesium chloride 4.98 g, sodium sulphate 3.91 g, calcium chloride 1.10 g, potassium chloride 0.66 g, sodium bicarbonate 0.19 g, potassium bromide 0.09 g, boric acid 0.03 g, and strontium chloride 0.02 g, were dissolved in 1 litre of distilled water.

Procedure

The AutoAnalyzer manifold used is shown schematically in Fig. 1.

As far as possible where the reagent is present glass or polyethylene tubing is used for connections owing to the action of acetone on solvaflex tubing. For pumping the reagent "acidflex" tubing is used, but it must be renewed daily; alternatively, if many samples are to be analyzed the reagent should be added by means of a displacement bottle. The sampler plate carries forty 10-ml sample cups. Cups containing 0.1 *N* acetic acid solution are alternated with the samples to be analyzed. A reverse-acting crook is used to flush the system with 0.1 *N* acetic acid solution and to prevent an excess of air being pumped as samples are being changed. The sampling rate is set at 40 per h.

The samples are pumped from the cups through 0.090″ i.d. tubing, and then passed through a debubbler to remove the excess air introduced through the reverse-acting crook. The sample is reintroduced using 0.056″ tubing and is then segmented with air, and mixed with the appropriate reagent both introduced through 0.056″ pump tubing. After the solution has been mixed by passing it through a single mixing coil, colour development is allowed to proceed to completion for 15 min in a half-time-delay coil. The solution is passed through a debubbler to remove segmenting air and then through a 1.5-cm flow cell in a phototube colorimeter which is fitted with an interference filter showing its maximum transmission at 625 mμ. The effluent from the cell is pumped to waste through 0.090″ tubing. Owing to the intense red colour of the reagent it is necessary to interpose a neutral density filter (density 0.2) in the compensating beam of the colorimeter.

Analysis of non-saline waters

At the beginning of each series of analyses of non-saline waters, the system should be allowed to run continuously on distilled water plus reagents; when stability has been attained the instrument should be set to read 100% transmission. At the end of a series of analyses the baseline should be checked using distilled water. The instrument should be calibrated using standard fluoride containing 1.0 μg F^-/ml. The manifold shown in Fig. 1 will give a linear response up to fluoride concentrations of 1.6 μg F^-/ml. If samples having greater fluoride concentrations are to be analyzed regularly, the bore of the sample pumping tubing should be reduced; distilled water should be pumped at an appropriate rate in order to compensate for reduction of the sample pumping rate. If only a few samples having relatively high fluoride contents are to be examined it is preferable to dilute them to bring their concentrations below

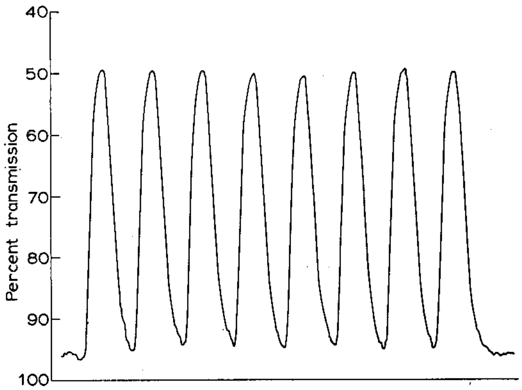
1.5 µg F^-/ml and then to analyze them as described above. The apparent pH of the effluent from the colorimeter cell should be in the range 4.45–4.85.

Analysis of sea waters (chlorinity range 12–20$^{0}/_{00}$)

The instrument should be set to 100% transmission while pumping a 0.1 *N* acetic acid solution. The method should be calibrated either (*1*) with a fluoride solution containing 1.0 µg F^-/ml in 0.1 *N* acetic acid solution: the optical densities found for the samples should be multiplied by 1.02 to correct them for salt error; or (*2*) by using an artificial sea water both alone, and spiked with 1.0 µg F^-/ml: in this instance the difference between the two optical densities gives an optical density increment for 1.0 µg F^-/ml which can be used for the calculation of fluoride concentrations of samples from their optical densities by direct proportion. For the analysis of samples having chlorinities below 12$^{0}/_{00}$ the method described for the analysis of non-saline samples should be used.

RESULTS

Replicate calibration runs were carried out on both distilled water and artificial sea water spiked with fluoride. The results of these experiments (Figs. 2 and 3) show that symmetrical AutoAnalyzer traces were obtained and that in each instance Beer's law was obeyed up to a fluoride concentration of *ca.* 1.5 µg/ml. Above this concentration, the increment of optical density per µg of fluoride decreased markedly. The range of linear response can be extended by increasing the strength of the reagent; however, this leads to an increase in the optical density of the blank, which leads to a decrease in the signal/noise ratio in the recorder and this in turn reduces the precision of the method. It is therefore recommended that if samples are likely to give optical densities above 0.4 they should be suitably diluted. Alternatively the size of the sample



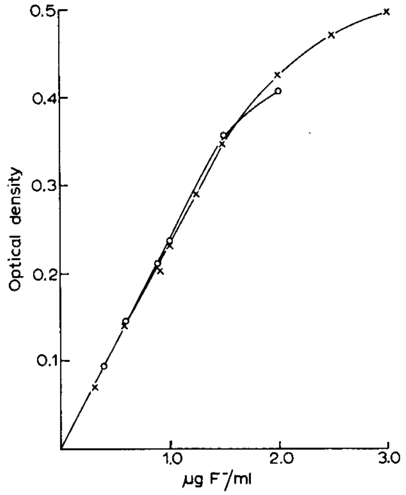


Fig. 2. AutoAnalyzer trace for replicate determinations of fluoride in sea water (Cl = 19.0$^{0}/_{00}$).

Fig. 3. Calibration curves for determination of fluoride in distilled water and artificial sea water. (o) distilled water; (×) artificial sea water.

pumping tube should be reduced and distilled water should be added at such a rate that the ratio of solution to reagent is maintained at the normal level.

As will be seen from Fig. 3 the sensitivity of the method is slightly depressed by the presence of sea salts. This error amounts to *ca.* 2% at a chlorinity of 19.00‰.

The precision of the method was checked by carrying out replicate analyses (10) on Liverpool tap water and on surface water from the Irish Sea (Cl = 19.0‰). These were found to contain 0.18 ± 0.01 and 1.21 ± 0.01 μg F$^-$/ml respectively. The accuracy of the method was checked by carrying out replicate analyses on an artificial sea water which had been spiked with known concentrations of fluoride (1.00 ± 0.01 and 1.25 ± 0.01 μg/ml); these showed the presence of 1.00 and 1.25 μg F$^-$/ml respectively after correcting for traces of fluoride already present.

Interferences

The effects of a number of cations and anions on the determination of fluoride by the lanthanum–alizarin fluorine blue method have been investigated by GREENHALGH AND RILEY[3]. From their results it seems probable that little or no interference will be caused by the major ions present in sea waters and other natural waters. Serious interference may be caused by aluminium at concentrations above 20 μg/l and by iron(III) and copper at concentrations greater than 200 μg/l.

SUMMARY

A Technicon AutoAnalyzer has been used for the determination of 0–1.5 μg fluoride/ml in sea water and other natural waters. Photometric measurement is made on the blue complex formed by reaction with the chelate formed between lanthanum and alizarin fluorine blue. The method has a coefficient of variation of *ca.* 0.9% at a fluoride level of 1.5 μg/ml.

RÉSUMÉ

Les auteurs décrivent un procédé automatique pour le dosage du fluorure (0–1.5 μg/ml) dans l'eau de mer et d'autres eaux naturelles. La mesure photométrique est basée sur le complexe bleu, formé par la réaction lanthane–bleu d'alizarine–fluor. Le coefficient de variation est d'environ 0.9% pour des teneurs en fluorure de l'ordre de 1.5 μg/ml.

ZUSAMMENFASSUNG

Der Technicon Auto-Analyzer wurde zur Bestimmung von 0–1.5 μg F$^-$/ml in Seewasser und anderen natürlichen Wässern benutzt. Photometriert wurde der blaue Komplex des Chelats, das zwischen Lanthan und Alizarinfluoridblau gebildet wird. Die Methode besitzt einen Variationskoeffizienten von etwa 0.9% bei 1.5 μg F$^-$/ml.

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LE DOSAGE DE TRACES DE CUIVRE DANS L'ARSENIC TRES PUR PAR ACTIVATION NEUTRONIQUE

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Le problème du dosage de traces de cuivre dans l'arsenic est particulièrement difficile en raison des faits suivants.

(*a*) La période du radioisotope engendré par l'élément matriciel (As) est double de celle donnée pour l'élément recherché (Cu) : $^{64}Cu: T^{\frac{1}{2}} = 12.8$ h et $^{76}As: T^{\frac{1}{2}} = 26.4$ h.

(*b*) Les sections efficaces de capture neutronique sont peu différentes, soit $\sigma_{(As)} = 4.2$ barns et $\sigma_{(Cu)} = 2.69$ barns.

(*c*) Les pics intéressants pour la mesure par spectrométrie-γ ont des énergies voisines: 511 KeV pour cuivre et 560 KeV pour l'arsenic.

Il en résulte que les activités spécifiques des 2 éléments sont du même ordre de grandeur et que la séparation du cuivre devra s'effectuer sans attendre, en réalisant un facteur de décontamination radiochimique, pour l'arsenic, d'au moins 10^8.

DONNÉES NUCLÉAIRES

La réaction d'activation de l'arsenic aux neutrons thermiques,

$$^{75}As + {}^{1}_{0}n \xrightarrow{(\sigma a = 4.2)} \gamma + {}^{76}As$$

donne un émetteur β^- et γ de période 26.4 h dont les caractéristiques de rayonnement sont:

β^- (E en MeV)	γ (E en MeV)
2.97 (50%)	0.56 (100%)
2.41 (31%)	1.19 (21%)
1.76 (16%)	0.64 (20%)
0.39 (2.5%)	2.05 (4%)
	1.41 (2%)

Les réactions parasites n−α, n−p, et n−2n sur l'élément matriciel ne gênent pas dans ce cas, car aucune ne donne du cuivre.

De même, la capture neutronique par le cuivre donne les réactions:

$$(a)\quad ^{63}Cu + {}^{1}_{0}n \xrightarrow{(\sigma a = 2.69)} \gamma + {}^{64}Cu$$

Il s'agit d'un émetteur β^+, β^-, γ et K de période 12.8 h avec

β^+ (E en MeV) 0.66 (19%) K: 42%
β^- (E en MeV) 0.57 (39%) γ: (E en MeV) 1.34 (0.5%)

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(*b*) $^{65}\text{Cu} + {}^{1}_{0}\text{n} \xrightarrow{(\sigma a = 0.56)} \gamma + {}^{66}\text{Cu}$

Il s'agit d'un émetteur β^- et γ de période 5 min seulement, peu approprié à notre problème étant donné la distance qui nous sépare du réacteur. On remarquera que le rayonnement vraiment caractéristique de ^{64}Cu à 1.34 MeV vient d'une transition fort peu probable (0.5%).

Aussi, dans le spectrogramme, est il en pratique plus efficace d'utiliser le pic 511 KeV résultant des recombinaisons de positrons à condition de réaliser un degré adéquat de pureté radiochimique.

PRINCIPE DE LA MÉTHODE PROPOSÉE

Après une irradiation de l'ordre de 24 h, les activités du cuivre et de l'arsenic ont atteints respectivement 75% et 50% de la saturation.

L'arsenic (quelques décigrammes) est dissout par le brome; on ajoute quelques centigrammes de cuivre inactif comme entraîneur et on hydrolyse à l'état d'arséniate en passant en milieu ammoniacal.

Le cuivre demeure ainsi sous forme de cations ammoniés, tandis que l'arsenic est essentiellement sous forme d'anions arséniates.

En principe, à ce stade, une résine échangeuse anionique, sous forme OH, retiendra la totalité de l'arsenic tout en laissant passer le cuivre.

En vue de limiter au maximum l'éparpillement d'activités importantes (ordre du dixième de curie), nous procédons toutefois, dans le récipient d'attaque, à une première précipitation de la majeure partie de l'arsenic sous forme d'un arséniate peu soluble (NH_4^+, Mg^{3+}, Ba^{2+} ou Pb^{2+}...) qu'on filtre.

Après passage du filtrat sur la colonne anionique adéquate, la solution contient encore une faible fraction de l'arsenic (10^{-3} à 10^{-5}) dont l'activité masque néanmoins celle du cuivre.

La décontamination doit donc être nettement plus poussée, et parmi les méthodes essayées avec un certain succès, nous citerons les précipitations répétées d'arséniate de baryum, les électrolyses soit en milieu ammoniacal après réduction à l'état Cu^+ par l'hydroxylamine soit en milieu sulfurique, le passage sur de nouvelles colonnes, tant anioniques que cationiques, la coprécipitation sur l'hydroxyde ferrique, la méthode des sulfosels solubles que nous avons finalement retenue.

PARTIE EXPÉRIMENTALE

Irradiations

L'arsenic ainsi que le fin fil de cuivre servant de référence ont été logés, pour l'irradiation, dans 2 tubes de quartz emboités l'un dans l'autre.

Le poids des échantillons, sous forme d'un ou de deux cristaux d'arsenic, était normalement de l'ordre de 140 mg; en vue de vérifier la validité du procédé expérimental adopté finalement, nous avons également fait irradier une série d'échantillons avec des ajouts dosés de cuivre; ce dernier a été déposé sur le cristal d'arsenic sous forme de solution de chlorure cuivrique, suivi de l'évaporation du solvant (10 à 100 ng de Cu).

Il s'écoulait généralement de 1 à 2 jours entre la fin de l'irradiation (BR1 de Mol) et l'attaque chimique.

Appareillage

L'appareil servant à dissoudre l'arsenic et à précipiter la majeure partie de l'arséniate est représenté sur la Fig. 1.

Sa forme particulière, notamment son fond large et légèrement cônique, résulte de l'expérience acquise lors des travaux préparatoires[1,2]; il permet d'une part une attaque avec le minimum de brome en excès et d'autre part un mélange facile des solutions aqueuses avec le tribromure d'arsenic qui est fort dense ($d = 3.54$).

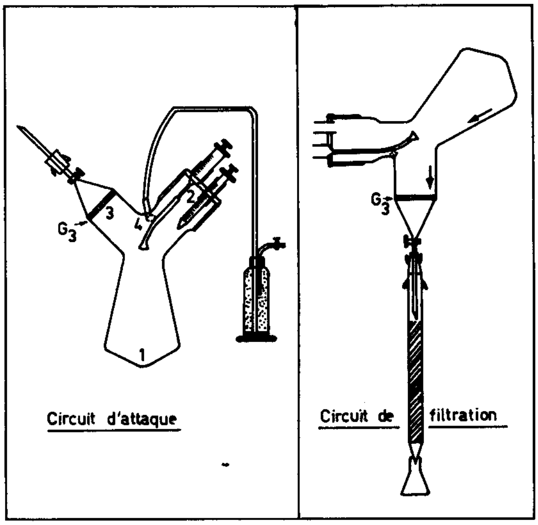

Fig. 1. L'appareil servant à dissoudre et à filtrer.

C'est essentiellement un récipient réactionnel à 3 branches faisant entre elles des angles d'environ 120°, qui peut pivoter autour d'un axe perpendiculaire au plan du dessin. Il est exécuté en pyrex soigneusement recuit.

La branche no 1 constitue le récipient de mise en solution et de précipitation.

La branche no 2 est fermée par un large bouchon à rodage externe (B45), qui est pourvu de 2 embouchures pour seringues à réactifs: dans la première vient s'insérer la seringue en verre contenant le brome; dans la seconde s'adaptent les embouchures de seringues en "plastique"; le conduit capillaire se prolonge à l'intérieur par un effilement coiffé d'une soupape en polyéthylène (tuyau applati à chaud) qui s'ouvre momentanément sous la pression de l'injection.

La branche no 3 sert à la filtration; elle est munie d'un disque de verre fritté de porosité G 3, d'un robinet et d'un rodage s'adaptant à la colonne de chromatographie.

Enfin, près du centre de rotation de l'appareil se trouve une petite tubulure latérale qu'un tuyau en plastique relie à un flaçon de garde. Celui-ci est garni d'un tampon d'ouate légèrement imbibé de glycol dans le but de retenir les aérosols, et de grains de chaux afin d'hydrolyser et de retenir toute trace éventuelle de tribromure d'arsenic.

L'appareil est posé sur un axe horizontal autour duquel il peut pivoter et occuper trois positions repérées: normale, agitation, renversée.

L'axe est lui-même soudé à un solide bâti en cornières servant de support stable à l'ensemble et à une épaisse brique de verre dense pour l'observation au travers de la protection en briques de plomb.

Traitement chimique

Les étapes successives sont les suivantes: (*1*) la mise en solution de l'arsenic dans le minimum de brome, (*2*) l'hydrolyse à l'état d'arséniate et sa précipitation, (*3*) la filtration et le passage sur colonne anionique sous forme hydroxyde, (*4*) la décontamination finale.

L'étape qui a nécessité le plus d'essais et de mises au point est la décontamination finale qui doit être simple et suffisante: c'est la méthode classique basée sur le sulfosel soluble d'arsenic suivie de l'électrolyse du cuivre en milieu acide qui a donné les meilleurs résultats.

Mode opératoire. L'arsenic (±140 mg) est introduit par l'ouverture de la branche no 2, on referme et on munit le couvercle de la seringue en verre contenant du brome (environ 0.5 ml), on injecte; l'attaque est terminée après 15 min.

On introduit par la seconde entrée de la branche no 2 successivement les autres réactifs avec des seringues en "plastique" à savoir: 4 ml d'eau pour hydrolyser le tribromure d'arsenic, 3 ml d'une solution saturée de soude pour détruire l'excès de brome, 5 ml d'une solution contenant 1 g de $BaCl_2$ (précipitation), 2 ml d'ammoniaque concentrée, 8 ml d'une solution de chlorure ou de nitrate de cuivre contenant de 40 à 50 mg d'élément entraîneur.

On laisse alors sédimenter le précipité d'arséniate de baryum un quart d'heure, puis on bascule lentement l'appareil en position de filtration, on y fixe la colonne chromatographique (diamètre 15 mm, longueur utile 13 cm), remplie de résine anionique Dowex 1 type 10 (100/200 mesh) sous forme hydroxyde. Il importe que la résine soit entièrement imbibée d'eau et surmontée d'un petit volume de solution (amorçage de l'écoulement). Au sortir de la colonne, l'activité résiduelle de la solution cupro-ammoniacale est suffisamment faible pour permettre les manipulations ultérieures sans protection spéciale.

On ajoute à la solution 20 à 30 mg d'arséniate sodique, puis quelques millilitres d'une solution chaude de sulfure sodique fraîchement préparée; CuS précipite en laissant l'arsenic en solution. Le précipité est floculé 10 min au bain-marie, filtré sur papier, lavé au sulfure sodique chaud, puis à l'eau, redissous sur filtre par l'acide nitrique 6 N et le filtrat est évaporé presqu'à sec, avec acide sulfurique, en creuset de platine.

Le cuivre est alors électrolysé, normalement, dans le creuset servant de cathode (15 min à 200 mA), puis pesé pour connaître le rendement chimique et enfin redissous quantitativement par quelques gouttes d'acide nitrique concentré en vue des mesures d'activité.

MESURES

L'activité et le spectre-γ du cuivre sont comparés aux données d'une prise aliquote (1/1000) d'une solution du cuivre étalon (1 à 2 mg d'un fil de cuivre de 2/10 de mm de diamètre).

L'appareil ayant servi à ces mesures est un spectromètre multicanal (TMC-256 chenaux). associé à un cristal à puits (NaI (Tl)) de 3 × 3 pouces.

Afin de rendre négligeable les erreurs dues aux statistiques de comptage, les spectres ont été enregistrés pendant un temps suffisamment long (environ 200 min).

Dans cette série d'essais, les mesures de surface du "photo-pic" à 511 KeV, ont été effectuées de la manière suivante: après accumulation du spectre dans la mémoire de l'analyseur, le fond continu en est immédiatement soustrait par une nouvelle mesure de même durée, sans l'échantillon, avec le signe négatif. L'examen visuel permet de fixer les limites, c'est à dire les canaux entre lesquels on effectue la somme des nombres de coups du pic 511 KeV.

RÉSULTATS

Nous avons fait ainsi l'analyse de 2 lots d'arsenic électroniquement purs; tous les échantillons à l'exception du no 5 contiennent des ajouts connus de cuivre. Le Tableau I en résume les résultats.

TABLEAU I

L'ANALYSE D'ARSENIC ÉLECTRONIQUEMENT PUR

Echantillon no.	*Poids de l'échantillon As (mg)*	*Ajout de Cu (µg)*	*Cu retrouvé (µg)*	*Différence (µg)*	*Teneur en Cu dans As (p.p.m.)*
Lot no 1					
1	142.7	0.02	*0.042*	0.022	0.154
2	139	0.10	0.132	0.032	0.23
3	142.6	0.05	**0.072**	0.022	0.154
4	140.2	0.01	0.039	0.029	0.207
	Moyennes pour 140 mg d'arsenic			0.026_1	0.18_6
Lot no 2					
5	136	—	0.022_8	0.023	0.16_9
6	141	0.01	0.038	0.028	0.19_8
7	139.5	0.04	0.067_5	0.027_5	0.19_8
8	138	0.03	0.062	0.032	0.23_3
9	139.4	0.02	*0.041*$_5$	0.021_5	0.154
10	145.8	0.05	**0.070**$_5$	0.020_5	0.14
	Moyennes pour 140 mg d'arsenic			0.025_5	0.18_2

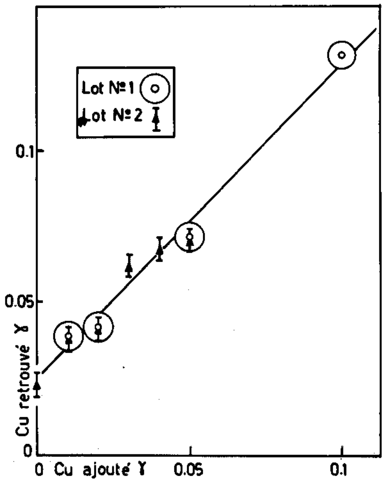

Fig. 2. Courbe de dosage de cuivre ajouté.

L'écart-type σ, pour une mesure, calculé sur l'ensemble des résultats et sur la moyenne totale de 0.184 p.p.m. est de 0.033.

Si la dispersion paraît élevée, il faut considérer qu'à ces teneurs une plus grande précision est rarement requise.

D'ailleurs, si l'on compare les 2 lots en fonction de la même quantité de cuivre ajouté, les chiffres sont nettement plus voisins (valeurs soulignées dans le Tableau).

De plus, le fait de trouver une droite de pente 1 sur la Fig.2 montre bien que la méthode proposée est valable; l'ordonnée à l'origine nous fournit la valeur la plus probable pour la quantité de cuivre dans l'arsenic. Cette teneur est de 0.184 p.p.m. ±0.011.

REMERCIEMENTS

Les auteurs sont redevables et reconnaissants à l'Institut Interuniversitaire des Sciences Nucléaires pour les crédits ayant permis cette recherche.

Nous remercions également et tout spécialement Monsieur le Directeur du Centre Nucléaire de Mol, ainsi que les membres de son personnel qui nous ont facilité la tâche lors des irradiations et des premières manipulations radiochimiques.

RÉSUMÉ

Le dosage par activation de traces de cuivre (<p.p.m.) dans l'arsenic n'est pas possible par spectrométrie-γ non-destructive à cause de la proximité des 2 isotopes utilisés, du point de vue périodes et spectres. La séparation du cuivre et sa décontamination sont basées sur les opérations suivantes: attaque par le brome, hydrolyse, précipitation de l'arséniate de baryum, passage de la solution cupro-ammoniacale sur une résine anionique, séparation des dernières traces d'arsenic par les sulfosels et récupération du cuivre par électrolyse. Les quantités de cuivre dosées se situent entre 20 et 100 ng.

SUMMARY

The determination of traces of copper (< p.p.m.) in arsenic is impossible by non-destructive γ-spectrometry because of the similarity in the half-lives and spectra of the two isotopes used. The proposed separation and decontamination of copper are based on the following operations: bromine attack, hydrolysis, precipitation of barium arsenate, anion exchange, separation of copper as sulfide and recovery by electrolysis. Amounts of copper in the range 20–100 ng can be determined.

ZUSAMMENFASSUNG

Die Bestimmung von Spuren Kupfer (<p.p.m.) in Arsen mit der Gammaspektrometrie ist unmöglich wegen der Ähnlichkeit der Halbwertszeiten und Spektren der zwei verwendeten Isotope. Die vorgeschlagene Trennung und Dekontamination des Kupfers beruht auf folgenden Operationen: Angriff durch Brom, Hydrolyse, Fällung mit Bariumarsenat, Anionenaustausch, Trennung des Kupfers als Sulfid und Rückgewinnung durch Elektrolyse. Das Kupfer kann in dem Bereich von 20–100 ng bestimmt werden.

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THE ANALYSIS OF DINITROTOLUENE ISOMER MIXTURES BY NUCLEAR MAGNETIC RESONANCE

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The dinitrotoluenes (DNT's) are important commercial compounds, being intermediates in several large scale manufacturing processes, *e.g.* in the production of polyurethane foams where large quantities of toluene diisocyanates are made from the dinitrocompounds via the diamines. The dinitrotoluenes are normally produced directly by the nitration of toluene itself, and the reaction product consists of a mixture of the 2,4- and 2,6-DNT's together with smaller amounts of the 2,3- and 3,4-isomers. Traces of the 2,5-isomer can also be present. It is often important to know the proportions of these isomers especially when the dinitrotoluenes are process intermediates, but hitherto no satisfactory single method has been available for a full quantitative analysis.

It has been shown that the mass spectra of the various dinitrotoluene isomers are all slightly different and mass spectrometry has been used to detect the isomers in a mixture qualitatively[1]. Infrared spectroscopy can be used to obtain the ratio of the two main components, the 2,4- and 2,6-isomers, quite accurately, but the minor components of the mixture are not detected. Further information can be obtained by reducing the dinitrotoluene isomer mixture to the diamines and carrying out the standard colorimetric tests: (*a*) using a diketone to give the *o*-diamine content, which determines the sum of the 2,3- and 3,4-isomers in the original DNT, and (*b*) using iron(III) chloride for the *p*-diamine content arising from any 2,5-DNT originally present. The current work arose from an attempt to discover whether the analysis of dinitrotoluene isomer mixtures could be done quickly and easily by NMR spectroscopy.

EXPERIMENTAL

Apparatus

A Varian A.60 spectrometer was used with tetramethylsilane as an internal reference. Chemical shifts are quoted in δ units, *i.e.* p.p.m. downfield from T.M.S.

Chemicals

99.5% $CDCl_3$ was obtained from Ciba (ARL) Ltd. Samples of all the dinitrotoluene isomers were available elsewhere in this Department and the NMR spectra themselves were used as a check for impurities.

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RESULTS AND DISCUSSION

Reference spectra in $CDCl_3$ were obtained for the pure 2,4-, 2,6-, 2,3-, 2,5- and 3,4-DNT isomers. A range of concentration from 5–50% (w/v) was covered. The results are shown in Table I. The aromatic proton chemical shifts and coupling constants are given where these are readily obtainable from the spectra, but no attempt has been made to resolve complex splitting patterns; for instance, for the ABC system in 2,3-DNT only the overall chemical shift range is quoted. Mononitrotoluenes (*o*- and *p*-) were also examined since these compounds are of course, intermediates in the formation of the dinitrotoluenes and values for 50% (w/v) solutions in $CDCl_3$ are given. For completeness, values are also given for 3,5-DNT, although this isomer is not normally produced during the nitration of toluene.

TABLE I

NMR DATA FOR SOME MONO- AND DINITROTOLUENES IN $CDCl_3$ SOLUTION

	Concn.	*δ p.p.m.*						*J (c/s)*
	(%, w/v)	CH_3	H_3	H_4	H_5	H_6	H_2	
2,4-DNT	50.1	2.77	8.75		8.41	7.72		$J_{56} = 8.7$
	20.5	2.76	8.78		8.37	7.65		$J_{35} = 2.4$
	13.7	2.75	8.80		8.37	7.64		
	5.1	2.74	8.81		8.36	7.59		
2,6-DNT	48.7	2.56	8.04	7.61				$J_{34} = 8.2$
	20.2	2.58	8.03	7.56				
	10.1	2.59	8.02	7.55				
	5.1	2.59	7.99	7.53				
3,4-DNT	57.0	2.56			7.88	[7.45–	7.75]	$J_{56} = 8.6$
	20.8	2.56			7.88			
	10.4	2.55			7.88			
	5.2	2.55			7.88			
	2.8	2.55			7.88			
2,3-DNT	50.0	2.44		[7.30	–	8.25]		
	25.0	2.44						
	5.0	2.44						
2,5-DNT	42.2	2.72	[8.1	–	8.6	]		
	4.5	2.72						
o-MNT	50.0	2.58	[7.1	–	8.0	]		
p-MNT	50.0	2.46	8.07				7.31	$J_{23} = 8.6$
3,5-DNT	~10	2.65		8.84		[	8.40]	$J_{24} = 2.7$

Four-component mixtures

An examination of the aromatic proton chemical shift values in Table I shows that it is possible to estimate the amount of 2,4-isomer in the usual mixture of 2,4-, 2,6-, 2,3- and 3,4-dinitrotoluenes, produced by direct nitration of toluene, by means of the doublet due to H_3 which in this isomer lies at lower field than all the other aromatic protons. However, the remaining aromatic protons give a complex system of overlapping signals and further analysis cannot be done easily using this band. At first sight, it does not seem possible to use the methyl group resonances to estimate the 4 components. The figures in Table I for the pure compounds indicate that in a mixture of isomers, the methyl proton peaks of the 2,4- and 2,3-isomers should be adequately separated whereas those of the 2,6- and 3,4-isomers might overlap or be separated by only a few cycles depending upon the concentration. However, Fig. 1 — a typical spectrum obtained from a synthetic mixture of the 4 components in $CDCl_3$ (50%, w/v) — shows that under these conditions the methyl proton peaks of the 2,6- and 3,4-isomers are more widely separated than the pure component spectra indicate, and an estimation of the 4 components becomes possible. The separation of the 2,6- and 3,4-isomer methyl proton peaks in fact increases as the total concentration of the solution increases and hence a standard concentration of 50% (w/v) was chosen. This relatively high total concentration is also useful in that it enables the minor components to be estimated more accurately. Even when the total concentration of the solution is kept constant, small variations in the position of the 3,4-isomer

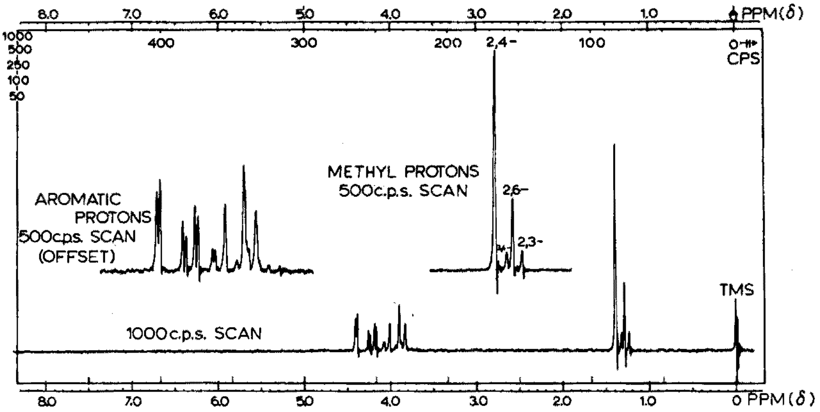

Fig. 1. Typical spectrum of a mixture of 2,4-, 3,4-, 2,6- and 2,3-dinitrotoluene isomers in $CDCl_3$ at 60 Mc/s.

TABLE II

METHYL PROTON CHEMICAL SHIFT CHANGES WITH RELATIVE CONCENTRATIONS FOR DNT ISOMER MIXTURES IN $CDCl_3$

(total concentration 50%, w/v)

Mole % by weight			*δ CH_3*		
2,4-	*3,4-*	*2,6-*	*2,4-*	*3,4-*	*2,6-*
16.71	73.05	10.24	2.75	2.59	2.56
10.22	65.74	24.04	2.76	2.59	2.56
6.71	54.26	39.03	2.76	2.60	2.57
18.47	34.71	46.82	2.76	2.62	2.56
48.08	4.86	47.06	2.76	2.62	2.56
79.34	3.42	17.24	2.76	2.63	2.56
78.77	1.07	20.16	2.78	2.64	2.57
81.19	0.72	18.09	2.78	2.65	2.57

methyl proton peak are observed as the relative concentrations of the isomers change. Table II shows this effect in a series of 2,4-, 2,6- and 3,4-DNT mixtures in $CDCl_3$ at a constant total isomer concentration of 50% (w/v). It can be seen that the movement of the 3,4-isomer methyl proton peak increases the separation of the 3,4- and 2,6-isomer peaks as the amount of the 3,4-isomer present decreases. This is very favourable since in a nitration mixture the normal level of the 3,4-isomer is only 1–5%. The changes in the methyl proton peak positions for the other three isomers, 2,4-, 2,6-, and 2,3-DNT, are very small and the values in a mixture are very close to those of the pure components.

In order to test the accuracy with which analyses can be made using the methyl proton resonances, weighed mixtures of 3 and 4 components were prepared. The mixtures were then examined as solutions in $CDCl_3$ on an A.60 spectrometer under the following conditions: concentration 50% (w/v) (0.25 g of mixture in 0.5 ml of $CDCl_3$ is sufficient); Rf 0.2 mG; filter bandwidth 4.0 c/s; sweep width 250 c/s; sweep time 250 sec. It was found that in this series of similar compounds, direct measurement of the heights of the methyl proton peaks gave results which were more accurate, particularly for minor components, than the conventional peak area measurements performed by the electronic integrator of the A.60. Table III compares the mole percentages of the mixtures calculated from the weights with those derived from the heights of the methyl proton peaks. The agreement between the two sets of figures is quite good. A more detailed examination of the deviations in the values reveals the following: (*i*) for a component present below the 10% level, NMR overestimates by about 0.5% absolute; (*ii*) at the 10–50% level NMR gives results accurate to within

TABLE III

ANALYSIS OF DINITROTOLUENE ISOMER MIXTURES USING METHYL PROTON PEAK HEIGHTS IN $CDCl_3$ SOLUTIONS (50%, w/v)

Mole % by weight				*Mole % by NMR*			
2,4-	*3,4-*	*2,6-*	*2,3-*	*2,4-*	*3,4-*	*2,6-*	*2,3-*
10.22	65.74	24.04		11.2	62.7	26.1	
6.71	54.26	39.03		7.2	52.4	40.4	
16.20	50.26	33.54		16.9	48.7	34.4	
18.47	34.71	46.82		18.5	32.4	49.1	
39.07	11.63	49.30		38.2	11.2	50.6	
69.38	10.95	19.67		71.6	10.9	17.5	
59.24	8.98	31.78		57.4	9.1	33.5	
50.07	5.40	44.53		48.8	6.7	44.5	
18.57	5.16	76.27		19.0	6.1	74.9	
79.34	3.42	17.24		77.7	4.1	18.2	
77.91	2.16	19.93		75.5	2.7	21.8	
78.77	1.07	20.16		77.2	1.4	21.4	
81.19	0.72	18.09		79.2	0.8	20.0	
62.04	9.84	17.76	10.36	59.0	10.5	18.2	12.3
58.51	8.96	27.47	5.06	57.7	7.4	28.4	6.5
59.84	8.00	22.45	9.71	57.5	8.2	23.9	10.4
67.79	5.87	20.81	5.53	65.8	5.9	22.2	6.1
59.82	1.88	36.22	2.08	57.8	2.4	37.4	2.4

±1.5%, (*iii*) above the 50% level NMR tends to underestimate a component by about 2%.

2,5-Dinitrotoluene

The data for the pure isomers in CDCl$_3$ in Table I indicate that in a mixture the methyl proton peaks of the 2,4- and 2,5-isomers are expected to be close, and spectra of synthetic mixtures of the five DNT's confirmed this. The peaks for 2,4- and 2,5-DNT were found at 2.77 δ and 2.72 δ respectively in a CDCl$_3$ solution of 50% (w/v) total concentration. These figures vary by ±0.01 p.p.m. depending upon the relative isomer concentrations. Table IV shows the results of analyses of 5-component mixtures using the methyl proton peak heights. These results indicate that the 2,5-isomer can be estimated with the accuracies quoted above for 4-component mixtures provided that its concentration is above the 2% level. Below this level there is interference from the large peak due to the 2,4-isomer, which is normally the major component of nitration mixtures, and the 2,5-isomer is overestimated. In 5-component mixtures, the 2,4-isomer when above the 50% level tends to be underestimated by 3% rather than by 2% as in 4-component mixtures. The cause of the general underestimation of the major components by the NMR method is not known. Spectra run at lower Rf power showed no improvement, so that peak saturation effects do not appear to be the cause.

TABLE IV

ANALYSIS OF 5-COMPONENT DINITROTOLUENE ISOMER MIXTURES

Mole % by weight					*Mole % by NMR*				
2,4-	*2,5-*	*3,4-*	*2,6-*	*2,3-*	*2,4-*	*2,5-*	*3,4-*	*2,6-*	*2,3-*
49.88	10.04	9.96	20.20	9.92	48.1	11.1	9.0	20.7	11.1
59.94	5.00	5.08	25.06	4.92	56.5	6.4	5.5	26.5	5.1
47.12	1.96	1.92	47.04	1.96	43.8	2.9	2.1	48.9	2.3
79.27	0.96	0.96	17.81	1.00	76.0	2.4	1.5	18.8	1.3

Toluene

Any traces of residual toluene in the DNT isomer mixtures can be detected readily by the additional methyl proton peak which appears at 2.32 δ. As the amount of toluene increases progressively above the 10 mole % level, general upfield shifts are observed for the DNT methyl proton peaks. The peaks move upfield uniformly with the exception of that arising from the 3,4-isomer whose movement is greater than that of the others. However, overlap of the 3,4- and 2,6-isomer peaks does not take place until toluene forms about 30 mole % of the sample. The presence of enough toluene to interfere with the analyses of the DNT isomers is therefore extremely unlikely.

o- *and* p-*Mononitrotoluenes*

It is possible that residual mononitrotoluenes (MNT) could also be present with the DNT isomers in nitration mixtures. The chemical shift values of the pure compounds in CDCl$_3$ shown in Table I indicate that some interference might be expected, and tests on synthetic mixtures in $CDCl_3$ solution confirmed that the methyl proton peaks of *o*- and *p*-MNT were extremely close to those of 2,6- and 2,3-DNT respectively. In $CDCl_3$ solution, therefore, broadening of the 2,6- and 2,3-isomer peaks indicates the presence of some residual MNT's, but further analysis is not possible. In this case, however, use can be made of the changes in chemical shift of the methyl proton peaks caused by aromatic solvents. The upfield shifts resulting from the addition of toluene or benzene to $CDCl_3$ solution are far less marked for *o*- and *p*-MNT than for any of the DNT's.

TABLE V

METHYL PROTON CHEMICAL SHIFT POSITIONS AND MIXTURE ANALYSES FOR MONO- AND DINITROTOLUENES IN C_6H_6

Compound	*o-*	*2,4-*	*2,6-*	*2,5-*	*p-*	*2,3-*	*3,4-*
δ CH_3 in C_6H_6	*2.28*	*2.21*	*2.13*	*2.09*	*2.03*	*1.92*	*1.88*
% by wt.	13.54	37.10	18.43		12.05	9.27	9.16
% by NMR	13.9	36.1	19.1		11.4	11.2	8.3
% by wt.	23.69	32.89	18.36		9.57	10.98	4.53
% by NMR	22.7	32.1	18.8		8.6	13.2	4.6
% by wt.		49.94	20.18	10.15		9.83	9.90
% by NMR		47.5	22.4	9.8		11.4	8.8

Table V shows the methyl proton chemical shift positions of the 7 components in mixtures with benzene as solvent (50% (w/v) total concentration). All the peaks are now separated and 2 analyses of 6-component mixtures (*o*- and *p*-MNT with the 4 main DNT's) are shown. The last analysis in Table V is of a mixture of 5 DNT's in benzene to see whether the 2,5-isomer can be determined better than in $CDCl_3$ solution. The 2,5-isomer peak, which with $CDCl_3$ as solvent is 0.05 p.p.m. from that of the 2,4-isomer, is only 0.04 p.p.m. from that of the 2,6-isomer when benzene is used as solvent, so that no advantage is gained.

SUMMARY

NMR data are given for all the dinitrotoluene isomers. It is shown that the components in mixtures of these isomers produced for example, by the direct nitration of toluene, can be recognised readily by NMR. Quantitative analyses can be performed using the heights of the methyl proton peaks of the various isomers. The accuracy of the method and the effects of any residual toluene or mononitrotoluenes are discussed.

RÉSUMÉ

Les résonances magnétiques nucléaires sont données pour tous les isomères du dinitrotoluène. On peut ainsi reconnaître facilement les constituants de mélanges de ces isomères produits, par exemple, par nitration directe du toluène. Il est possible également d'effectuer des analyses quantitatives en mesurant les hauteurs des pics du proton méthyl des divers isomères.

ZUSAMMENFASSUNG

Es werden kernmagnetische Resonanzdaten für alle Isomeren des Dinitrotoluols angegeben. Es wird gezeigt, dass die Komponenten in Mischungen dieser Isomeren, wie sie z.B. durch direkte Nitrierung des Toluols erzeugt werden können, mit der kernmagnetischen Resonanz schnell wiedererkannt werden können. Durch Verwendung der Höhen des Methyl-Peaks der verschiedenen Isomeren können quantitative Analysen ausgeführt werden. Die Genauigkeit der Methode und die Einflüsse von zurückbleibendem Toluol oder Mononitrotoluol werden diskutiert.

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Anal. Chim. Acta, 35 (1966) 376–382

TRACE ANALYSIS WITH AUTOMATIC PRINTOUT BASED ON REACTION RATE MEASUREMENTS: DETERMINATION OF OSMIUM

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The measurement of reaction rates as an analytical tool has received considerable attention in recent years[1]. These efforts have resulted in methods which are competitive with common equilibrium methods with respect to simplicity, speed, and reliability. Rate methods applied to catalytic reactions often have the advantage of very high sensitivity[2]. In this paper an instrument is described which measures reaction rates simply and rapidly and provides automatic digital printout of concentration data. Results are reported for the determination of osmium in the 1–60 parts-per-billion (p.p.b.) range.

Osmium catalyzes the reaction between cerium(IV) and arsenic(III)[3]. Under controlled conditions the rate is proportional to the osmium concentration. The rate of decrease of cerium(IV) concentration is followed colorimetrically at 420 mμ.

The instrument measures the time between 2 preset points on the response curve[4], and performs a computation to provide a voltage proportional to the reciprocal of the time. This voltage is a function of the reaction rate and is linearly related to osmium concentration in the 1–60 p.p.b. range. It is easily calibrated in units of osmium concentration and read from a digital voltmeter (DVM) or printed on tape.

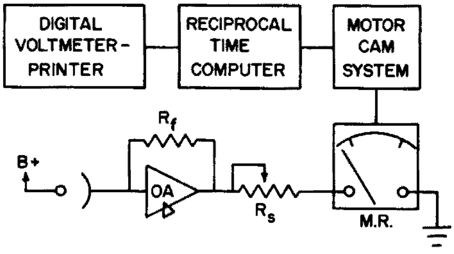
The measurement step is simple. It consists of cleaning the sample compartment, adding reagents and sample to the compartment and activating the start switch. The osmium concentration is printed out automatically. For the concentration range reported, measurement times vary between 15 and 150 sec and results are accurate to about 1%.

EXPERIMENTAL

Instrumentation

The general operational features of the instrument are easily understood from Fig. 1. Phototube current is converted to a voltage by the operational amplifier. This voltage, operating through R_s, drives the meter in the optical meter relay. The indicator on the meter relay changes continuously as the reaction proceeds. When the indicator reaches the first set point (zero time point), the meter relay activates the "motor-cam system" which in turn activates the "reciprocal time computer". The latter generates a voltage proportional to the reciprocal of the time elapsed after the indicator has passed the first set point. This voltage is indicated on the digital voltmeter. When the indicator reaches the second set point, the meter relay reactivates the motor-cam system which then performs several basic functions. It instantly deactivates the reciprocal time computer so that the voltage generated by it is representative of the reciprocal of the time required for the indicator to move between the first and the second set points. It activates the printer to print the voltage indicated on the digital voltmeter. It resets the reciprocal time computer and itself to the zero time condition.

In practice, the output from the digital voltmeter is calibrated in concentration units. The net result of the cycle described above is digital printout of concentration data.



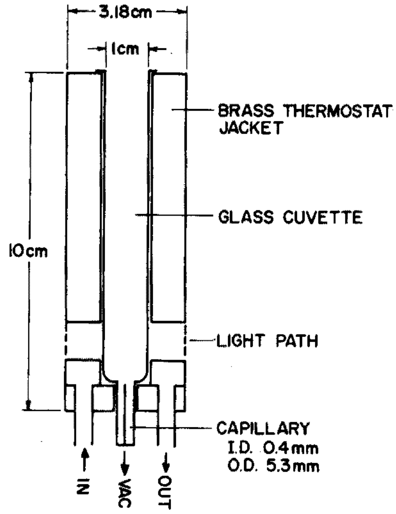


Fig. 1. Combined schematic-block representation of reaction rate instrument.

Fig. 2. Modified cell holder for Spectronic 20 colorimeter.

A modified transistor-stabilized Spectronic 20 colorimeter (Bausch and Lomb, Inc., Rochester, New York) is used for the transmittance measurements. Modification of the Spectronic 20 circuit has been described previously[5]. The cell holder shown in Fig. 2 permits circulation of water from a constant-temperature bath around the reaction cell. This holder is constructed from 2 brass cylinders to fit the sample well of the colorimeter. The capillary sealed at the bottom of the sample cell permits samples and wash water to be removed rapidly without contamination of the cell. The inlet and outlet tubes and the capillary extend through holes drilled in the plate at the bottom of the sample well. The colorimeter is mounted above a magnetic stirrer and the sample is stirred by a small stirring bar below the light path in the sample cell.

The remainder of the instrument is represented in Figs. 3 and 4. The Heath operational amplifier system (D. C. Heath Co., Benton Harbor, Mich.) is used in this work with OA3 being stabilized with a Philbrick Model K2P chopper amplifier (G. A. Philbrick Researches, Dedham, Mass.).

The phototube cathode is connected by shielded cable to J1 of Fig. 3. OA3 is the current-to-voltage converter with its gain selected by S3. In the work reported here the 10 MΩ resistor in position 3 was used. This arrangement provides about 1 V output for 100% T when no bucking current is applied from S2. Also in this work the series resistor R_s is kept at zero for the signal to provide a time interval ranging from

15–150 sec over 40 μA on the meter relay. Switch S4, S4′, in the position shown, permits the output from OA3 to be applied through the meter relay for automatic operation.

OA2 is the divider amplifier which generates an output proportional to reciprocal time. A potentiometer (P1 in Fig. 4) connected across the female Jones connector is driven at a constant rate by a synchronous motor; 0.5 V is applied, from the voltage

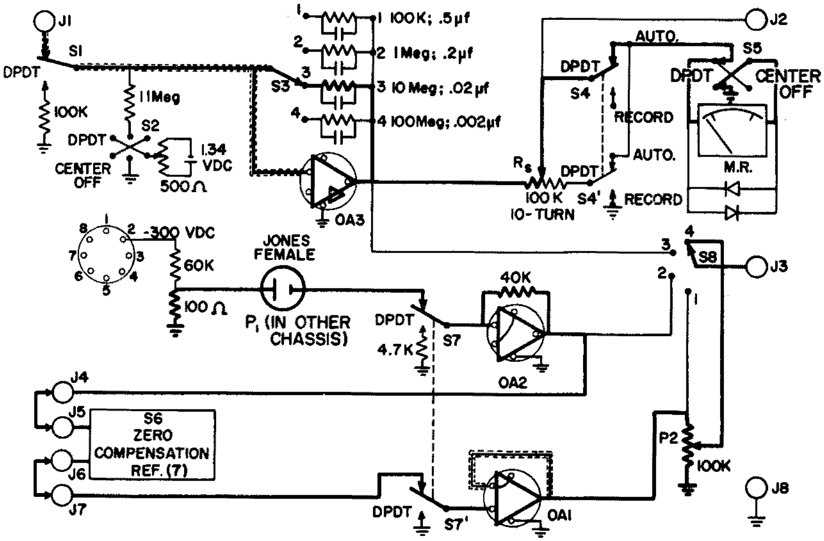


Fig. 3. Schematic diagram of amplifier and read-out circuit. M.R.—Assembly Products 503L, 100 μA, double set point.

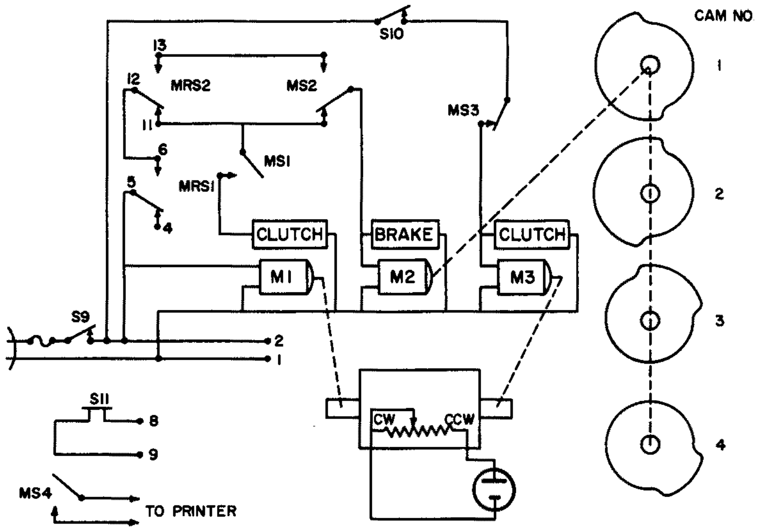


Fig. 4. Schematic diagram of motor-cam system. MS1–MS4, Robertson Snap Action Switch, SPDT, Type BRD2-LW228; M1, Hurst AR-SM, 4 rev./min; M2, Hurst PC-SM, 30 rev./min; M3, Hurst AR-SM, 30 rev./min; P1, Helipot, 100,000 AZH, ten turn, double shaft extension, 0.5% linearity; S11, Pushbutton, normally closed; Meter relay control module, Assembly Products, 903A.

divider from the −300 V power supply, through the potentiometer to the input of OA2. The operation of this system to measure reciprocal time has been discussed[6]. The output from this system is applied through the zero compensation system and follower amplifier (OA1) to the calibrate potentiometer P2. The output from P2 is applied through S8 to a digital voltmeter connected at J3.

The meter relay controls the operation of the motor-cam system represented in Fig. 4. The meter relay is connected to its control module (Assembly Products Inc., Chesterland, Ohio) via the 9-pin connector and cable provided by the manufacturer. Switches MRS1 and MRS2 in Fig. 4 represent the relays (low and high set points respectively) controlled by the meter relay. The Arabic numerals 1, 2; 4–6; 8, 9 and 11–13 refer to binding posts on the meter relay control module. M1, M2 and M3 represent synchronous motors. M2 drives the cam system through clockwise rotation. MS1–MS4 represent snap action switches operated by respective cams numbered 1–4.

Motors M1 and M3 are connected to the shaft of the potentiometer P1. Note that M1 operates continuously but is effective in driving the potentiometer only when its clutch is activated. The shafts of M1 and M3 rotate clockwise, and thus each drives the potentiometer shaft in opposite directions.

MS4 is connected to the remote control contacts of the printer. Each time MS4 is closed the printer is activated a single time.

The operation of the system is as follows. All contacts are shown in their "zero time" positions. The lever arms of MS1–4 are located at the tops of the respective cams. Power is applied to M3 and thus P1, looking from the left, is in its counter clockwise position so that the input resistance to OA2 (Fig. 3) is zero. It is assumed that when a reaction is proceeding the indicator on the meter relay is moving from left to right.

When the indicator reaches the first set point, MRS1 moves from 4 to 6 thus activating M2. As the cam system rotates it opens MS3, deactivating M3 and closes MS1 activating the clutch of M1. The result is that about 0.1 sec after the indicator reaches the first set point, M1 is driving P1 at a constant rate. After 180° rotation of the cam (about one second), MS2 moves to its closed position, deactivating M2 and stopping the cam.

The system remains in this state (with P1 being driven at a constant rate by M1) until the meter relay indicator reaches the second set point. When this occurs MRS2 moves from 11 to 13 reactivating M2. As the cam rotates, several things happen. MS1 is opened, deactivating the clutch of M1 and stopping the rotation of P1. MS4 is closed, signaling the printer to print the voltage on the digital voltmeter at that instant. After 90° rotation MS3 is closed activating M3 which resets P1 to its zero time position. After 180° rotation MS2 is moved back to the position shown on the diagram and M2 stops.

The meter relay contacts remain in positions 5–6 and 12–13 until the meter relay indicator falls below the two set points and S11 is opened momentarily. Thus S11 is the start switch which reactivates the instrument at the beginning of each run.

As a result of the above sequence of events, P1 has been driven at a constant rate during the time interval required for the meter relay to move between the two set points. The net result of the cycle described is that the time interval is determined, a voltage proportional to its reciprocal is printed out in digital form and the system is reset to its original position, ready for the next sample.

Several details of Figs. 3 and 4 remain to be discussed. In Fig. 3 switches S1, S7–S7′ and S8 permit amplifiers 1, 2 and 3 to be balanced easily.(When balancing OA3, S2 should be in the "center off' position.) The separate switch S1 was used to keep the input to OA3 as completely isolated from the remainder of the circuit as possible. The mercury cell and 11-MΩ resistor at the input to OA3 provides a current source variable up to about 0.13 μA which is useful for adjusting the output from OA3 to any desired level (usually zero volts) at zero time. S2 permits reversal of the polarity of the source and also has a center off position so the source can be removed from the circuit if desired. The capacitors in the feedback loop of OA3 filter out A.C. from the phototube circuit. S4–S4′ permits the meter relay to be removed from the circuit. A recorder connected to J2 will record the response curve continuously. The zero compensation system controlled by S6 has been discussed in detail previously. It is provided with jacks J5 and J6 so that it can be bypassed if desired.

Connections from components represented in Fig. 3 to the operational amplifier system are made by 5-pin female sockets plugged onto the 5-pin male plugs of the Heath amplifiers. The K2P stabilizing circuit is constructed to plug onto the Heath amplifier and also has its input and output connected to pins 1 and 3 respectively of a 5-pin male as indicated in Fig. 3.

It should be noted that the dashed feedback loop in OA1 is the conventional representation of a follower amplifier and does not represent an actual connection. The actual connection is between pins 1 and 2. All other connections are made internally by switching amplifier 1 to the follower position.

In Fig. 4, S9 applies line voltage to the circuit. S10 is included so that the reset function can be controlled manually if desired. This is used in the zero compensation and calibration steps. In addition it would be useful if a printer were not available and results were being recorded manually from a meter.

Reagents

All reagents were prepared in 2 *M* sulfuric acid and were made up with deionized water from a mixed-resin ion-exchange column. All of the reagents used were reagent grade unless otherwise indicated. The arsenic trioxide was recrystallized from hot 0.5 *M* sulfuric acid in an attempt to keep background iodine as low as possible. All solutions were stored in ground-glass-stoppered bottles.

Stock solutions of 0.125 *M* cerium(III), 0.125 *M* cerium(IV), 0.0625 *M* arsenic(III), and 0.0625 *M* arsenic(V) were prepared and standardized using conventional procedures. Two working solutions were prepared: one containing both Ce(III) and Ce(IV) at $2.5 \cdot 10^{-3}$ *M* and one containing both As(III) and As(V) at $1.25 \cdot 10^{-3}$ *M*.

The osmium solutions were prepared by dilution from a stock solution of 1.54 mg Os per milliliter in 2 *M* sulfuric acid. This stock solution was prepared by dissolving 1 g of OsO_4 (Engelhard Industries Inc., Newark, N.J.) in 500 ml of 2 *M* sulfuric acid. This solution was standardized by liberation of iodine from excess potassium iodide and subsequent titration with thiosulfate to an amperometric end-point. Sample solutions were prepared by diluting this stock solution with 2 *M* sulfuric acid. The dilutions were made fresh before each day's work.

Procedure

The operational amplifier unit, the Spectronic 20, and the digital voltmeter are permitted to warm up for a period of at least 30 min before the balancing and calibration procedures are started. The amplifiers are balanced as indicated above to give minimum offset. The reagents and samples meanwhile are all brought to constant temperature at 25.0° in a constant temperature bath.

The zero compensation and calibration operations are performed as described before[7] using osmium solutions with concentrations near the middle of the range to be determined.

The reagents, Os standards and samples are handled with tuberculin-type hypodermic syringes fitted with teflon needles (Hamilton KF18TF, Hamilton Co., Inc., Whittier, Calif.).

The measurement step involves 4 operations. The print identification number is set for the sample. Exactly 1.00 ml each of the cerium and arsenic working solutions are added to the reaction cell, followed by 0.50 ml of the osmium solution. The start switch is pressed momentarily. After the measurement is automatically completed and the results printed, the solution is removed and the reaction cell is rinsed with deionized water. The system is now ready for the next determination.

RESULTS AND DISCUSSION

The data shown in Tables I and II are reproduced from printed tapes. The

TABLE I

PRINTOUT DATA FOR AQUEOUS OSMIUM SOLUTIONS

Os conc. (p.p.b.)	*Digital Printout*			*Rel. error (%)*	*Rel. std. dev. (%)*
	# 1	*# 2*	*# 3*		
1.00	0.99	1.07	1.02	3.0	4.0
2.00	1.97	2.07	2.03	1.00	2.5
3.00	2.96	3.00	2.97	0.67	0.71
4.00	3.98	4.00	4.02	0.0	1.50
5.00	4.92	5.02	5.02	0.20	1.15
6.00	5.97	5.99	6.00	0.16	0.26
8.00	8.03	8.13	8.12	1.12	0.69
10.0	9.88	9.93	10.01	0.60	0.65

TABLE II

PRINTOUT DATA FOR AQUEOUS OSMIUM SOLUTIONS

Os conc. (p.p.b.)	*Digital Printout*			*Rel. error (%)*	*Rel. std. dev. (%)*
	# 1	*# 2*	*# 3*		
6.00	6.1	6.2	5.9	1.3	2.7
10.0	9.8	9.7	9.8	2.2	0.60
15.0	15.1	14.9	14.9	0.00	0.67
20.0	20.3	19.8	20.3	0.50	1.4
30.0	30.9	31.3	29.9	2.3	2.1
40.0	40.0	39.4	39.7	0.75	0.75
50.0	49.5	50.0	49.8	0.40	0.50
60.0	60.2	60.4	60.5	0.67	0.30

relative errors and relative standard deviations are presented along with the raw data.

Direct readout is achieved by this method only for systems in which a linear relationship exists between reaction rate and concentration of desired constituent. For osmium concentrations between 1 and 60 p.p.b. this requirement is fulfilled as indicated by the data in Tables I and II. However above 60 p.p.b. the rate *vs.* concentration curve becomes nonlinear, yielding low results. A nonlinear output system would be required to provide digital readout in this case. The reason for the observed nonlinearity is not evident at the present time.

According to the data of SAUERBRUNN AND SANDELL[3], the reaction velocity is nearly directly proportional ot the osmium concentration between 1 and 100 p.p.b. One major difference between their work and that reported here is the time interval over which the reaction was observed. Their measurements required between 1 and 70 min, while the data reported here were obtained in 15–150 sec. Also, differing conditions in reagent concentrations and in measurement techniques used in the experiments may be contributing factors. Further investigation into the kinetics of the reaction system is being undertaken to provide definitive answers to these differences.

Interfering substances such as iodine and ruthenium have been discussed[3] and methods presented for suitable elimination of their effects.

This investigation was supported in part by a David Ross XR Research Grant to one of us (R.L.H.) from the Purdue Research Foundation. The assistance of Mr. DAVID SNYDER and Mr. THOMAS MCCAIN in constructing the equipment is gratefully acknowledged.

SUMMARY

An instrument is described which measures reaction rates and converts the information to a voltage which is calibrated to read the concentration of the desired constituent. It is applied to the determination of trace amounts of osmium in solution, based upon catalysis of the Ce(IV)–As(III) reaction. The instrument is versatile, sensitive, and capable of high precision. After a short calibration procedure, it is necessary only to activate the instrument once between runs, and the concentration of sample is printed on tape automatically. Osmium is determined in the 1–60 p.p.b. range with relative standard deviations and accuracy of about 1%. At the lower end of the concentration range this corresponds to an error of about $2.5 \cdot 10^{-11}$ g of osmium. Measurement times range between 15 and 150 sec with average analysis times of 3–4 min per sample, including initial calibration and other manipulations.

RÉSUMÉ

Les auteurs décrivent un appareil permettant de mesurer des vitesses de réaction et de lire directement les concentrations des constituants à doser. Il peut être utilisé pour le dosage de l'osmium en solution, à l'état de traces (1–60 p.p.b.); la méthode est basée sur la réaction de catalyse Ce(IV)–As(III). La durée d'une mesure varie de 15 à 150 secondes, avec des temps moyens de 3 à 4 minutes pour l'analyse d'un échantillon, comprenant calibrage initial et autres manipulations.

ZUSAMMENFASSUNG

Es wird ein Instrument beschrieben, das Reaktionsgeschwindigkeiten misst, die Information in eine Spannung umwandelt und so nach Eichung die Konzentration des gewünschten Bestandteils angibt. Es wird für die Bestimmung von Spuren Osmium in Lösungen angewandt. Das Verfahren beruht auf der Katalyse der Ce(IV)-As(III)-Reaktion. Das Instrument ist vielseitig, empfindlich und sehr genau. Nach kurzem Eichen ist es notwendig, das Instrument nur einmal zwischen 2 Versuchen zu aktivieren; die Konzentration der Probe wird automatisch ausgedruckt. Osmium wird zwischen 1–60 p.p.b. mit einer relativen Standardabweichung und Genauigkeit von etwa 1% bestimmt. Am unteren Ende des Konzentrationsbereiches entspricht dies einem Fehler von etwa $2.5 \cdot 10^{-11}$ g Osmium. Die Messzeiten liegen zwischen 15 und 150 Sekunden bei einer durchschnittlichen Analysendauer von 3–4 Min pro Probe einschliesslich anfänglicher Eichung und anderer Manipulation.

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A FAST AND PRECISE HETEROMETRIC DETERMINATION OF THALLIUM(I) WITH SODIUM TETRAPHENYLBORATE

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The determination of small amounts of thallium is of considerable importance in industry as well as in the analysis of toxicological materials, and a large literature exists on this subject[1,2]. Attention has been drawn to thallium tetraphenylborate (TlTPB), which is quite insoluble, and 0.0166–0.0416 g of thallium were determined gravimetrically[3]. The solubility of TlTPB was determined by SIROTINA AND ALIMARIN[4] radiometrically, and at pH *ca.* 5 was found to be $6 \cdot 10^{-7}$ mol. Many metals form insoluble compounds with sodium tetraphenylborate, which may interfere with the precipitation of TlTPB. Thus, SPOREK AND WILLIAMS[5] cite the formation of insoluble compounds with Th, Ag, Hg(II), Cu(I) and Ce(IV); WENDLANDT[3] found interference in the presence of ammonium ion, K, Rb, Cs, Zn, Pt(IV), Sb(III) and Bi(III).

The heterometric determination of thallium(I) as presented in this paper appears to have the following advantages. Titrations can be done very rapidly, taking 3–4 min. The results are very reliable and the errors generally negligible. By exploiting the complex formation tendency of thallium(I) with pyrophosphate[6] and tripolyphosphate, about 0.75 mg of thallium in 20 ml of solution can be determined in the presence of a large excess of many bi- or polyvalent foreign metals.

EXPERIMENTAL

The instrumentation and working conditions were described previously[7].

Chemicals

Thallous nitrate (B.D.H. Ltd.), sodium tetraphenylborate (Hopkin & Williams Ltd.), sodium tripolyphosphate ($Na_5P_3O_{10}$; Westwaco Chemical Division, N.Y.) and sodium pyrophosphate (Baker Analyzed) were used. All other reagents were either chemically pure or analytical reagents.

Determination of thallium

An aqueous solution (20 ml) containing 3 ml of 0.005–0.0025 *M* thallium nitrate was titrated heterometrically with 0.005–0.0025 *M* sodium tetraphenylborate. To study the effect of pH, the titrated solutions contained also: 1 ml of *M* hydrochloric, nitric or acetic acid; 1 ml of *M* acetic acid and 1 ml of *M* sodium acetate; 1 ml of *M* sodium acetate; 1 ml of *M* disodium hydrogen phosphate; 3 ml of *M* sodium carbonate; 3 ml of *M* sodium hydroxide; or 17 ml of 0.05 *M* sodium tetraborate. To study the effect of neutral salts, the solutions contained 5 ml of *N* sodium sulphate, nitrate, or chloride. The effect of complexing agents was studied by addition of 3 ml of *M* sodium citrate, 3 ml of *M* sodium tartrate or 15 ml of 0.2 *M* EDTA. The solutions titrated in the presence of polyphosphate contained 3 ml of 0.005–0.00125 *M* thallium nitrate, 2–16 ml of 0.125 *M* sodium pyrophosphate or 1–8 ml of 0.25 *M* sodium tripolyphosphate diluted with water to 20 ml. Reverse titrations were also performed.

RESULTS AND DISCUSSION

Figure 1 shows the graphs obtained in some typical titrations. The titrations began with clear solutions, and precipitation commenced with the addition of the first drop of titrant. The maximum optical density (which gives an indication of the sensitivity of the titration) was about 0.5–0.7, depending on the amount of thallium present. The end-point of the titration always corresponded to the compound TlTPB (1:1), and the accuracy was ±3%. The sensitivity and the accuracy did not depend on the pH of the solution, whether a strong acid or strong base was present. Concentrated neutral salts, whether nitrate, sulphate or chloride, did not interfere with the results nor with the sensitivity of the titration. The sensitivity was not affected by the presence of excess of citrate, tartrate or EDTA, but the errors were higher (±6%).

The influence of the polyphosphates on the sensitivity of the titration was remarkable. Both sodium pyrophosphate and tripolyphosphate acted in the same way, increasing the maximum optical density considerably and thus allowing the

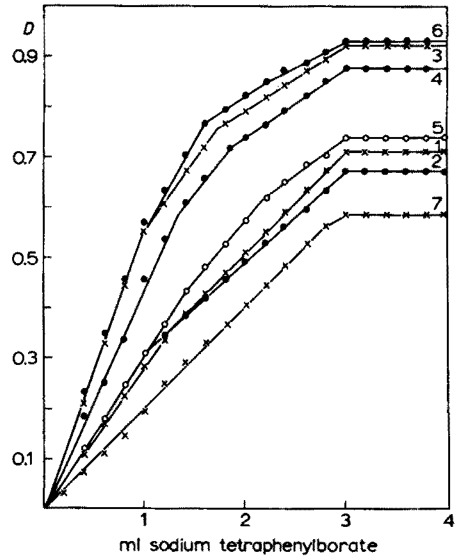

Fig. 1. (1) 3 ml 0.005 *M* $TlNO_3$ + 17 ml H_2O + *x* ml 0.005 *M* sodium tetraphenylborate (= TPB). (2) 3 ml 0.005 *M* $TlNO_3$ + 3 ml *M* NaOH + 14 ml H_2O + *x* ml 0.005 *M* TPB. (3) 3 ml 0.005 *M* $TlNO_3$ + 1 ml H_2O + 16 ml 0.125 *M* $Na_4P_2O_7$ + *x* ml 0.005 *M* TPB. (4) 3 ml 0.005 *M* $TlNO_3$ + 1 ml H_2O + 16 ml 0.125 *M* $Na_5P_3O_{10}$ + *x* ml 0.005 *M* TPB. (5) 3 ml 0.0025 *M* $TlNO_3$ + 1 ml *M* sodium acetate + 11 ml H_2O + 5 ml 0.125 *M* $Na_5P_3O_{10}$ + *x* ml 0.0025 *M* TPB. (6) 3 ml 0.005 *M* TPB + 12 ml H_2O + 5 ml 0.25 *M* $Na_5P_3O_{10}$ + *x* ml 0.005 *M* $TlNO_3$. (7) 3 ml 0.0025 *M* TPB + 17 ml H_2O + *x* ml 0.0025 $TlNO_3$.

determination of still smaller amounts of thallium. The results were more precise in the presence of the polyphosphates (the error was ±1.5%), and were almost independent of the amount of thallium present. The favourable effect of the polyphosphates was not disturbed by addition of sodium acetate or sodium hydroxide, but addition of sodium citrate reduced the maximum optical density to the values obtained without polyphosphate. No other complexing agent showed an effect as favourable as that of the polyphosphates. This may be attributed to a specific type of complexation of thallium(I) with the polyphosphates which promotes the formation of a heterometrically sensitive precipitate of TlTPB.

The reverse titrations corresponded well with the direct ones in all cases.

Titrations of thallium in the presence of foreign metals

From a previous study[8] it was known that most of the di- and polyvalent metals form soluble complexes with an excess of the sodium salts of pyro- or tripolyphosphate in neutral or basic solutions. Both phosphates exert a similar masking effect, but the tripolyphosphates are generally more soluble than the corresponding pyrophosphates.

To evaluate the addition of excess of polyphosphate for the masking of foreign metals in the determination of thallium with tetraphenylboron, series of titrations were performed as follows. The general composition of the solution titrated was: 3 ml of 0.0025 M thallium nitrate, a ml of p M aqueous salt solution of the foreign metal, 12 ml of 0.25 M sodium tripolyphosphate (or 16 ml of 0.125 M sodium pyrophosphate) diluted to 20 ml with water; this was titrated with a solution of 0.0025 M sodium tetraphenylborate.

The final concentration of the foreign salt in the analysed solution was as follows:

0.05 M: $CaCl_2$, $MgCl_2$, $ZnSO_4$, $MnSO_4$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Bi(NO_3)_3$, $AgNO_3$.
0.02 M: Na_2MoO_4, Na_2WO_4.
0.01 M: $NaVO_3$, $Th(NO_3)_4$.
0.0005 M: $PdCl_2$, $HAuCl_4$, H_2PtCl_6.

In the case of pyrophosphate, only half the above concentrations of foreign metal were used.

The results were as follows. In all cases, approximately the same maximum optical density value — 0.7 — was obtained, whether in the presence or absence of foreign metal. The titration time and the precision also remained unchanged in all cases. The above concentrations of foreign metals were not critical and higher concentrations could be present. The titrations in the presence of bismuth were done with added sodium citrate and the maximum optical density was lower. Cadmium was precipitated by pyrophosphate, and the titrations were carried out in presence of tripolyphosphate. Silver probably forms no complexes with the polyphosphates, so that the titrations were performed in the presence of sodium thiosulphate. Chromium(III) formed insoluble salts with both polyphosphates. The results of the titrations in the presence of mercury(II) (1 ml of 0.1 M $Hg(NO_3)_2$) were somewhat unusual[9]; mercury was precipitated by pyrophosphate, while in the presence of tripolyphosphate, mercury prevented the precipitation of thallium by tetraphenylborate. Also, no precipitate of thallium tetraphenylborate was obtained on addition of citrate to complex the mercury. A precipitate was obtained when halides were added to complex the mercury, but no calculated end-point could be obtained, and the density rose continuously.

On the basis of these studies, the following procedure is suggested for the determination of thallium(I). An aqueous solution (20 ml) containing 3 ml of 0.0025–0.00125 *M* thallium nitrate and *ca.* 7.5 ml of 0.25 *M* $Na_5P_3O_{10}$ (or *ca.* 15 ml of 0.125 *M* $Na_4P_2O_7$) is titrated with 0.0025–0.00125 *M* sodium tetraphenylborate.

SUMMARY

The heterometric titration of thallium(I) with sodium tetraphenylborate, at various pH values and in the presence of salts and different complexing agents, was studied; 1.5–0.75 mg of thallium(I) could be determined within 3–4 min, and the error was negligible. Of the complexing agents studied, sodium pyro- and tripolyphosphate had a specific influence, raising the sensitivity about 4-fold, and no interference was caused by the presence of 30–130-fold molar excesses of the following metals: Ca, Mg, Zn, Mn, Co, Ni, Fe(III), Al, UO_2(II), Cd, Cu(II), Pb, Bi(III), Ag, V(V), Mo(VI), W(VI) and Th. Pd, Au(III) and Pt(IV) did not interfere.

RÉSUMÉ

Les auteurs ont examiné le titrage hétérométrique du thallium(I), à l'aide de tétraphénylborate de sodium, en présence de sels et divers agents complexants. On peut doser ainsi 1.5–0.75 mg de thallium(I), en 3–4 minutes. Les pyro- et tripolyphosphates augmentent sensibilité et sélectivité: Ca, Mg, Zn, Mn, Co, Ni, Fe(III), Al, UO_2(II), Cd, Cu(II), Pb, Bi(III), Ag, V(V), Mo(VI), W(VI) et Th (en excès jusqu'à 30–130 fois la teneur en thallium); Pd, Au(III) et Pt(IV) ne gênent pas.

ZUSAMMENFASSUNG

Es wurde die heterometrische Titration von Thallium(I) mit Natriumtetraphenylborat untersucht bei verschiedenen pH-Werten und in Gegenwart von Salzen und unterschiedlichen Komplexbildnern. 1.5–0.75 mg Thallium(I) können innerhalb 3–4 Minuten bestimmt werden. Der Fehler ist vernachlässigbar. Von den untersuchten Komplexbildnern hatten Pyro- und Tripolyphosphat einen spezifischen Einfluss, indem sie die Empfindlichkeit etwa vervierfachten; dabei verursachte ein 30 bis 130 facher molarer Überschuss folgender Metalle keine Störungen: Ca, Mg, Zn, Mn, Co, Ni, Fe(III), Al, UO_2(II), Cd, Cu(II), Pb, Bi(III), Ag, V(V), Mo(VI), W(VI) und Th; Pd, Au(III) und Pt(IV) störten nicht.

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SHORT COMMUNICATIONS

A device for measuring spectral reflectance on thin-layer plates with a Zeiss spectrophotometer

The applicability of spectral reflectance to the quantitative analysis of thin-layer chromatograms has been described in several papers by FRODYMA, FREI *et al.*[1-4]. Measurements were carried out on powders scraped from the plate; a simple device for this has been described by FREI AND FRODYMA[5]. Indeed, the reflectance attachments supplied with commercial spectrophotometers are more fitted to the analysis of powdered materials or inert surfaces than for handling the fragile thin-layer chromatograms, especially when these are of the more convenient size (10 × 20, 20 × 20 cm^2).

For measuring spot reflectance on paper chromatograms HEBER[6] has proposed a device which consists essentially of a simple white integrating-sphere provided with 2 large circular openings and a photomultiplier. Currently, an apparatus of this kind is supplied by Zeiss optics, Oberkochen, Germany, as an attachment to the Zeiss PMQ II spectrophotometer. The main advantage of this device over the conventional reflectance attachments is the fact that the user is more free to adapt it to the problem at hand, *i.e.* to measurement of spot reflectance $(0,d)$ on thin-layer plates. An appropriate arrangement for this purpose is described below.

Apparatus

The device shown in Fig. 1 consists of a large frame (1), connected to a rigid bar (2) by means of two sliding rods (3). The frame contains two slots; in the front one the chromatographic plate is placed, the thin layer facing the light beam; in the other one an appropriate cover can be inserted to ensure reproducible background, *e.g.* a blackened metal plate or a stiff white paper. Horizontal and vertical movement of the frame are directed by two sliding rods, which improves rigidity and minimizes swinging during motion. Knobs (4) drive screws with a speed of 1 mm per revolution; this is coarse enough to allow rapid scanning of the plate, but it is also fine enough for comfortable adjustment to optimum reflectance.

A separate optical bench is used to carry the device, but this need not be carefully aligned with the total arrangement. Rotation of the frame at (5) and tilting of the bench with knobs (6) allow accurate positioning of the frame along the attachment housing. Reproducible setting is possible by letting the frame rest against the housing; at the same time this minimizes the distance between the thin layer and the inner sphere surface, which enhances the reflectance.

Since the rider can be moved to the end of the optical bench, the frame can be lowered down to the table surface. The impinging light beam strikes the plate at 18 cm above the table top. For measuring spots above this height the plate must be inserted upside down into the frame.

By varying the distance between the exit slit of the monochromator and the attachment the cross-section of the light beam at the thin layer increases from 1 × 1 cm^2 up to 3 × 3 cm^2. Smaller cross-sections can be obtained when an image of the exit slit is projected upon the thin layer with an additional lens (*e.g.* f = 5 cm). The exit slit is an image of the entrance slit, which is easily diaphragmed to any desired dimension. Thus it is possible either to measure the total spot reflectance[6] or to scan the spot with a small beam.

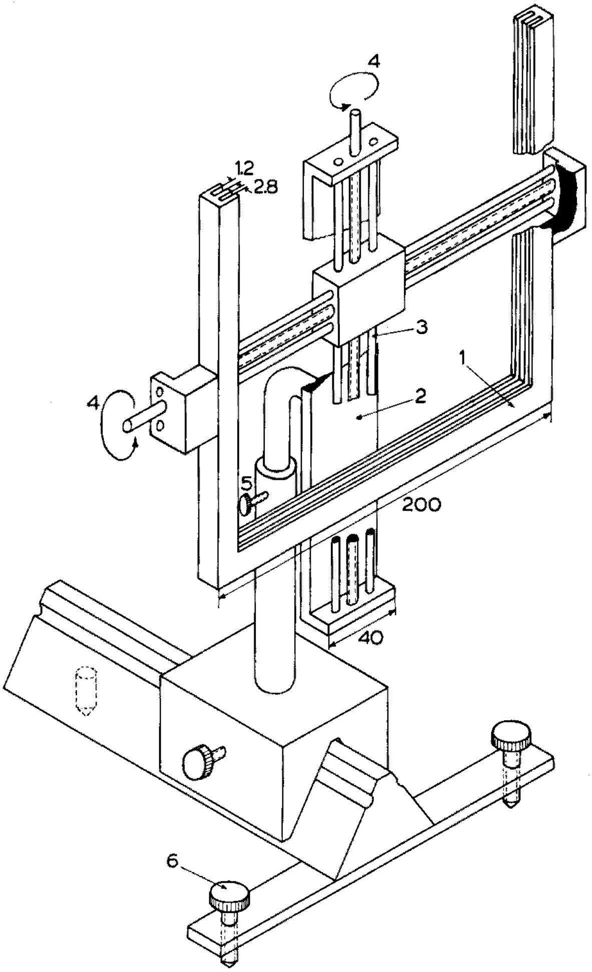

Fig. 1. Device for measuring spot reflectance. Dimensions in mm; for description see text.

Approximate coincidence of the spot and the light beam is easily ascertained when the cover plate is removed. After reinstalment of the cover, knobs (4) are turned to find the minimum reflectance (maximum absorption). When series of spots in one row or column are measured, the portion of white layer between spots is continually used as a reference for 100 % reflectance.

Spectral reflectance can be measured between 250 and 700 nm. For larger wavelengths the sensitivity of the photomultiplier is too small. For shorter wavelengths the reflectance of the white layer decreases rapidly and scattering of radiation becomes disturbing. The extension to the ultraviolet region of the spectrum should in many cases eliminate the use of coloring indicators and circumvent the inherent loss in precision.

Results

The device was tested by measuring the reflectance of azobenzene indicator dyes: Sudan Red (510 nm), Sudan Yellow (485 nm) and *p*-methoxyazobenzene (345 nm)[7]. The results obtained were comparable to those described by LIEU *et al.*[4]. With regard to the apparatus the following points should be mentioned.

(*a*) In reflectance a larger noise signal is measured than in transmittance. However, reflectance spectra are smoother than the corresponding transmittance spectra[6], so that relatively large slit widths are permissible, which makes it possible to reduce the amplification.

(*b*) With repeated settings of the complete device measurements could be reproduced to within 0.2 on a 100 unit scale. This is sufficient in view of the reproducibility of the chromatographic process[1,4].

(*c*) The limit of detection compares favourably with measurement in solution. For instance, spot reflectance of 99% (1% absorption) was obtained when chromatographing 5 μl of a solution of 1 p.p.m. of dye in benzene (5 ng dye absolute); in an ordinary 1-cm cuvet an absorption of 1% was reached for 3 ml of a 0.03 p.p.m. solution (100 ng absolute).

(*d*) Down to 300 mμ the reflectance of the thin layer (silicagel G) is equal to that of the inner surface of the Ulbricht sphere. The small distance between the plate and the sphere (2 mm) lowers the reflectance by 25%.

(*e*) With increasing distance between the plate and the attachment housing, the spot reflectance decreases, slowly at first, but rapidly for distances over 5 mm; reproducible setting of the frame is therefore crucial.

(*f*) When the optical system itself is sufficiently screened from outside light, a completely darkened room is not necessary, although excessive light is better avoided.

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Determination of phosphorus in organic compounds. Titration with lead nitrate

Phosphorus has often been determined titrimetrically by precipitating the orthophosphate salts of zinc, magnesium, thorium, or bismuth, dissolving the precipitate and titrating the metal ion with EDTA solution[1]. These methods, and the conventional titrimetric method involving the precipitation of a base phosphomolybdate suffer from the fact that the phosphate must be precipitated, filtered and redissolved before the final analysis.

Few direct titrations are available for phosphate and very few are suitable for micro amounts of phosphate. However, a few titrations with lead or cerium(III) solutions have been described for organic analysis (see ref.2). The method presented here utilizes the rapid "oxygen flask" method for decomposing the sample. After metal ions have been removed from the resulting solution by ion-exchange resin, the phosphate is titrated directly with 0.01 *M* lead nitrate solution in 80% acetone to a dithizone end-point. Sulfate causes serious interference; halides also require prior removal.

Apparatus

The oxygen flask apparatus used was a F & M model 141 Schoniger safety ignition unit with 500-ml and 1000-ml combustion flasks; ashless filter paper sample holders, and gelatin capsules were obtained from A. H. Thomas Co., Philadelphia.

Reagents

Dithizone indicator solution. Dissolve 10 mg of dithizone in 10 ml of acetone. Prepare fresh every 48 h.

Lead nitrate, 0.05 M. Dissolve 16.55 g of lead nitrate in water and dilute to 1 l. Standardize this solution by dissolving approximately 0.2 g of $Na_2HPO_4 \cdot 12H_2O$ in 5 ml of water and titrating according to the procedure. Prepare a 0.01 *M* lead nitrate solution by diluting 100 ml of this solution to 500 ml with acetone.

Preparation of ion-exchange column

Prepare a 15 × 1.5 cm column of Amberlite IR-120 resin (H-form, 20–50 mesh). Pass 20 ml of 20% (v/v) ammonium hydroxide through the column. Wash the column with distilled water until the effluent is neutral.

Procedure

Weigh out an amount of sample corresponding to approximately 1.0 mg of phosphorus and decompose in an "oxygen flask" containing 10 ml of 6% (v/v) ammonium hydroxide. Rinse the flask head and wall of the flask with distilled water into the flask. Boil the contents until the vapor no longer yields an alkaline reaction with a moist piece of pH-indicator paper. Do not evaporate to dryness.

Pass the sample solution through the cation-exchange column catching the effluent in a 150-ml beaker. Wash the flask with two 5-ml portions of distilled water, passing these through the column. Wash the column with 5 ml of distilled water.

Evaporate the solution to 15 ml and allow to cool. Add 0.8 ml of 2.0 *M* nitric acid, 0.4 ml of pyridine, 60 ml of acetone and 6 drops of dithizone indicator solution. Titrate with 0.01 *M* lead nitrate to a red color.

If fluoride is present, add 2 ml of concentrated nitric acid after boiling out ammonia and evaporate to a small volume on a hot plate. Continue the evaporation to dryness on a steam bath. Dissolve the residue in 1 ml of distilled water and evaporate again to dryness on a steam bath. Dissolve the residue in a few milliliters of water and continue as above.

Discussion and results

All of the phosphorus is converted to the pentavalent state in the "oxygen flask". Some of the phosphorus forms higher oxides such as pyrophosphate and must be boiled in the presence of ammonium hydroxide or nitric acid to form the orthophosphate. If this is not done low results and poor end-points will be obtained.

Cations other than alkali metals interfere by either reacting with the dithizone indicator or precipitating the phosphate; these cations are completely removed by the resin.

TABLE I

RESULTS OF PHOSPHORUS ANALYSES

Sample	*% P*		*Standard deviation*
	Calculated	*Found*	
Trioctylphosphate	7.32	7.21	0.05
Triphenylphosphine	11.81	11.71	0.14
Tri-*p*-tolylphosphate	8.79	8.77	0.01
Triphenylphosphate	9.50	9.53	0.03
Diphenyloctylphosphate	8.55	8.49	0.10

Anions such as the halogens interfere only when present in quantities greater than twice the molar quantity of phosphorus. Fluoride and sulfate interfere. Fluoride, and the other halogens when present in large amounts, are removed by evaporation to dryness; some orthophosphate is lost if the evaporation is carried out above 100°.

The pH and percentage of acetone must be carefully controlled, otherwise the end-point will be slow and difficult to detect. The optimum conditions at the end-point are 80% acetone and pH 4.0.

Some organophosphorus compounds were analyzed with satisfactory results (Table I).

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Composition, stability and structure of the vanadium(IV)–alizarin red S complex

The chromogenic properties of alizarin red S (Colour Index Mordant Red 3, C.I. 58005; sodium 1,2-dihydroxyanthraquinone-3-sulphonate) have often been utilized, particularly in spectrophotometric analysis. The zirconium–alizarin red S chelate has received particular attention (see, *e.g.*, refs. 1 and 2) because of its importance in the determination of fluoride. The colour changes of alizarin red S with change in pH have also been thoroughly studied[3,4].

A new chelate of vanadium(IV) with alizarin red S and a detailed investigation of the nature, composition and stability of the chelate are described in the present paper.

Reagents

Solutions of sodium alizarin-3-sulphonate and vanadyl sulphate (A.R., B.D.H.) were prepared in twice-distilled water. All other reagents used were of analytical grade. For adjustment of pH, dilute solutions of sodium hydroxide and sulphuric acid were used.

Apparatus

Spectrophotometric measurements were made with a Unicam SP 500 spectrophotometer and 10-mm glass cells. pH measurements were carried out with a L and N direct reading pH meter with glass and calomel electrodes.

Colour of the chelate

Colour formation was found to be instantaneous at room temperature and no effect was observed when the order of the mixing of the reagents was altered. The chelate was stable for 48 h.

Nature of alizarin red S with change in hydrogen ion concentration

The visible spectra (650–350 mμ) of pure alizarin red S solution (10^{-4} *M*) were examined over the pH range 4.2 to 12.0; the pH of the solutions was adjusted and the solutions were left for 30 min at 25° to attain equilibrium. With increase in pH, the wavelength of maximum absorbance shifts from 420 mμ at pH 1.4–5.3 (yellow) through 525 mμ at pH 5.7–9.5 (red) to 560 mμ above pH 10.6 (violet). This is essentially in accordance with the results of SARMA AND RAO[4].

Nature and stoichiometry of the chelate

In order to determine the nature of the vanadium(IV) complex which involves the mesomeric forms of the dye obtained in partially neutralized media, the method of VOSBURGH AND COOPER[5] was adopted. The results are shown in Fig. 1. The maximum wavelength for the chelate shifts to 490 mμ and there is a clear indication of the formation of only one complex under the conditions used.

To investigate the stoichiometric ratio of vanadium(IV) to alizarin red S in the chelate, JOB's method[6] was applied at pH 4.0 and 490 mμ. The results clearly showed

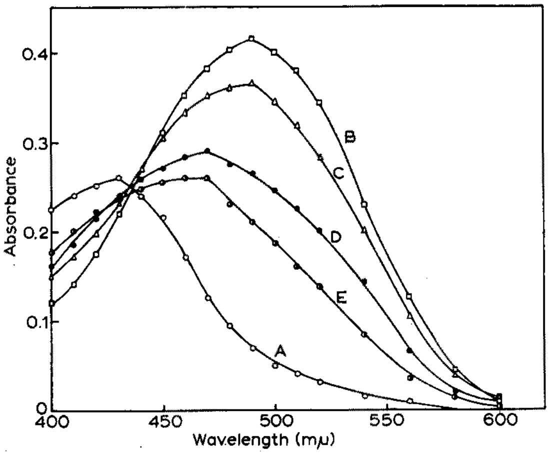


Fig. 1. Absorption spectra of vanadium(IV)–alizarin red S chelate. Nature of the complex formed: Total volume 50 ml; pH 4.0; development time 30 min; temperature 25°. Final concentration $M \cdot 10^4$.

VOSO₄	*Aliz.*	*Ratio V(IV):Aliz.*
A 0.00	1.0	0 :1.0
B 2.0	1.0	1.0:0.5
C 1.0	1.0	1.0:1.0
D 0.5	1.0	1.0:2.0
E 0.33	1.0	1 :3.0

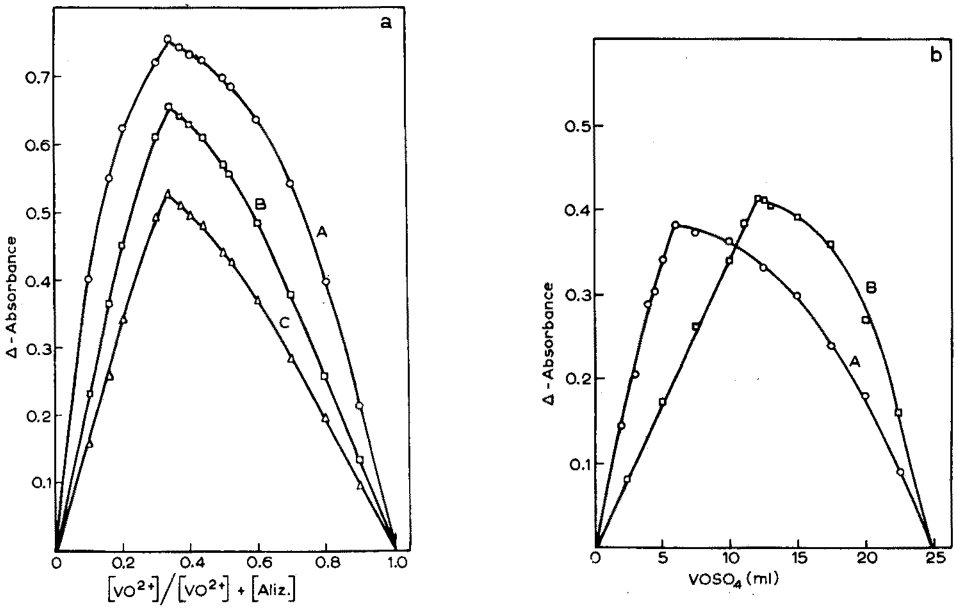


Fig. 2. (a) Determination of the composition of the chelate by the method of continuous variation at 490 mμ; pH = 4.0. Curve A, $5 \cdot 10^{-4}$ *M*; Curve B, $4.0 \cdot 10^{-4}$ *M*; Curve C, $3.33 \cdot 10^{-4}$ *M*. (b) Determination of the composition of the chelate by the method of continuous variation at 490 mμ; pH = 4.0. Curve A, $5.0 \cdot 10^{-4}$ *M*; Curve B, $2.50 \cdot 10^{-4}$ *M*.

the formation of a 1:2 vanadium(IV)–alizarin red S chelate when the concentrations of the vanadium(IV) and alizarin red S solutions were equal (Fig. 2a). The results shown in Fig. 2b were obtained for concentration ratios of alizarin red S to vanadyl sulphate of 0.5 (curve A) and 2.0 (curve B).

The stoichiometric composition of the chelate was also corroborated by the mole ratio method[7] (Fig. 3) and the slope ratio method[8] (Fig. 4).

The effect of pH on the stability of the chelate was recorded by measuring the absorbance of mixtures containing vanadyl sulphate and alizarin red S in a 1:2 ratio at different wavelengths. The complex was shown to be stable in the pH range 3.5–5.5.

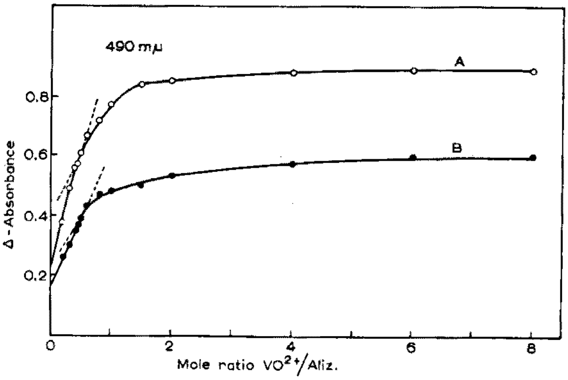


Fig. 3. Determination of the composition by the mole ratio method at 490 mμ; pH = 4.0. Final concentration of alizarin red S: Curve A, 2.0 · 10^{-4} M; Curve B, 1.33 · 10^{-4} M.

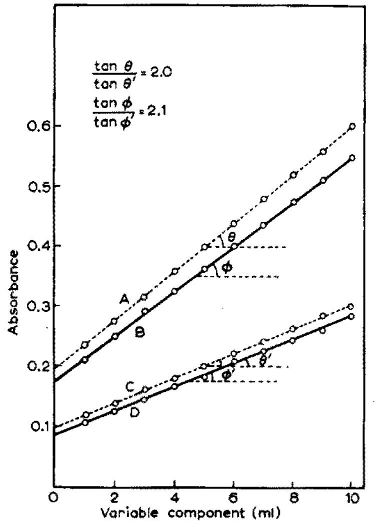


Fig. 4. Determination of the composition by the slope ratio method. Curve A, 490 mμ; Curve B, 500 mμ ($VOSO_4$ varying); Curve C, 490 mμ; Curve D, 500 mμ (Aliz. varying). 10 ml excess component (6.66 · 10^{-4} M) + x ml variable component (2.22 · 10^{-4} M) + (15 − x) ml of water.

Evaluation of the stability constant

The stability constant of the chelate was calculated by 3 different methods; the values obtained (Table I) are in close agreement with each other.

Possible structure of the chelate

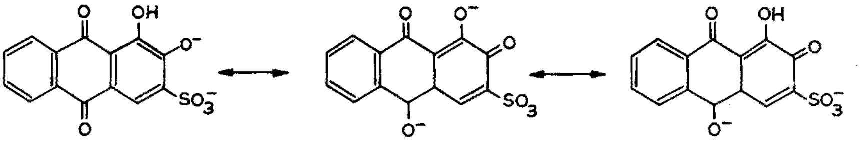
In a reaction with alizarin red S, the metal ion may be attached to the two phenolic oxygens, or to the quinoid oxygen and the α-phenolic oxygen.

TABLE I

STABILITY CONSTANTS OF VANADIUM CHELATE

Method	*log K*	*ΔG° (kcal)*
DEY AND MUKHERJI[9]	8.6 ± 0.4	−11.9 ± 0.4
Continuous variation	9.2 ± 0.6	−12.7 ± 0.6
Mole ratio	8.4 ± 0.2	−11.5 ± 0.2

Alizarin red S exists in 3 different structural forms depending on the hydrogen ion concentration. LARSEN AND HIROZAWA[1] have explained the half neutralisation of alizarin red S at pH 8.3 and subsequent shift to 525 mμ on the basis of the removal of the β-hydrogen which enhances the resonance in the molecule as follows:



A practically identical shift in the λ_{max} would be observed if the chelation of the metal ion with alizarin red S were due to the quinoid and α-phenolic oxygens when a resonance similar to the above would be possible. If the metal ion were attached by the 2 phenolic oxygens, resonance would not be possible, and the shift in the λ_{max} would probably be much smaller.

The vanadium(IV)-alizarin red S chelate investigated at pH 4.0 showed maximum absorbance at 490 mμ which is below the resonance level; the spectral evidence thus points to chelation through the two phenolic oxygens and not through the quinoid and α-phenolic oxygens. Further, chelation of vanadium(IV) through the phenolic oxygens would yield anionic complexes, and this was confirmed by ion exchange with the resin Amberlite IR-45(OH) and reconfirmed by electrolytic methods.

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Oxidimetry of iron(II) and the peroxide effect

According to BELCHER AND NUTTEN[1], MEINEKE[2] considered that slightly high results were obtained when iron(III) was reduced to iron(II) with tin(II) chloride and titrated with an oxidant after removal of excess of tin(II) by addition of mercury(II) chloride, and attributed this to slow reaction between the mercury(I) chloride precipitate and either the iron(III) produced or the oxidant used. For many years, students in chemistry at Aberdeen have compared the results obtained when iron(III) is reduced by the tin(II) chloride method and the zinc amalgam method; their results were invariably higher with the tin(II) reduction, which appeared to confirm MEINEKE's opinion.

A careful comparison of the 2 methods with each other and with the silver reductor method (modified to avoid errors from hydrogen peroxide[3]) showed that the tin(II) method gave essentially correct results whereas the amalgam method gave negative errors. It was further found that there was a small but definite amount of interaction between the mercury(I) chloride and iron(III). By inference it would be expected that mercury(I) chloride would also react with the oxidant used for the titration, but this interaction should not affect the results because it would be manifested as a "returning" end-point, and the first colour change could be taken as showing the equivalence point. The reaction between mercury(I) chloride and iron(III) was sufficiently slow for it to occur to a negligible extent during a normal titration. Investigation showed that when zinc amalgam was used in the presence of air, aerial oxygen was reduced to peroxide more quickly than the peroxide was reduced to water, and a steady state concentration of peroxide was obtained. The peroxide formed oxidised part of the iron(II) back to iron(III) even in the presence of the zinc amalgam. These findings were later found to have been anticipated by LIEBHAFSKY[4], and explain why the Japanese workers who first used amalgams as reductants[5] specified that the reduction must be made in an inert atmosphere. The inconvenience of using an inert atmosphere has led to doing the reduction in air and accepting the resultant negative error of about 1% as a tolerance on the method. The present investigation shows that peroxide will be produced whenever a two-phase reduction system is used in the presence of oxygen; in a one-phase system peroxide may be produced transiently, but is reduced to water by the excess of reductant that must be added if the reduction is a preliminary step to an oxidative titration. If a reductive titration was used it would be possible for peroxide to be produced in significant amount if the main reaction proceeded slowly.

Experimental

A standard solution of iron(III) was prepared by weight by dissolving pure iron in hydrochloric acid and oxidising with bromine water. The excess of bromine was removed by boiling. Weighed portions of the iron solution were reduced by the tin(II) chloride, silver reductor, and zinc amalgam methods, and titrated with a carefully standardised cerium(IV) solution. N-Phenylanthranilic acid was used as indicator in the tin(II) method, and ferroin for the other two. For amounts of iron ranging from 85 to 130 mg, the mean error was +0.16 mg for the tin(II) method and +0.12 mg for the silver reductor method, the standard deviations (15 results) being 0.10 mg for both methods. The spread of results is partly accounted for by the error in measuring the volume of titrant used in the titrations and in the standardisation of the titrant. The burette used was a precision burette[6] capable of delivering liquid with an error in volume of 0.01 ml. When the amalgam was used as reductant, the errors were variable and always negative, the average error being about −1 mg. The positive bias for the tin(II) and silver reductor methods is small enough to be negligible for most practical purposes.

When various amounts of tin(II) chloride were treated with an excess of mercury(II) chloride and the mixture was left in contact with iron(III) for various lengths of time, and then titrated with cerium(IV) added from a micrometer syringe (N-phenylanthranilic acid indicator), it was found that a 16-fold increase in the amount of mercury(I) chloride produced caused an additional consumption of 0.005 ml of 0.1 *M* cerium(IV) and a similar increase in consumption occurred when the mixture was allowed to stand for 64 min instead of 2. If any reaction takes place between mercury(I) chloride and iron(III) it does so very slowly, though to an extent that could just account for the positive bias observed. Blank tests with tin(II) chloride gave an average blank of 0.021 ml of 0.1 *M* cerium(IV), which was taken into account in calculating the results. The blank for the silver reductor was 0.03 ml of the same titrant. This blank (which must be *added* to the titre after deduction of twice the indicator correction[3]) was also taken into account. In work on the micro scale it had been found earlier that there was no bias in the results obtained by the silver reductor method[3].

It was found that if iron(II), free from detectable amounts of iron(III), was shaken in acidic solution with potassium thiocyanate in the presence of air, no oxidation took place in a period of 5 min, but if zinc amalgam was added and the shaking repeated, the red colour of the iron(III) thiocyanate complex rapidly appeared. If the air was displaced by carbon dioxide, the oxidation did not take place. When dilute sulphuric acid was shaken with zinc amalgam and air, and titanium(IV) was added to the aqueous phase, the yellow colour of the peroxytitanium(IV) complex appeared and could be used for measurement of the amount of peroxide produced. Similar results were obtained when copper wire, copper foil, mercury, lead, tin, bismuth, zinc, and silver were shaken with hydrochloric acid in the presence of air. Tin(II) chloride

TABLE I

PEROXIDE PRODUCED BY METALLIC REDUCTANTS FROM AERIAL OXYGEN

Time (min)	*Concentration of H_2O_2 (μg/ml) produced by*					
	Cu		*Hg*		*Zn/Hg*	
5	0.6	0.8	0.4	0.5	2.0	3.7
10	1.0	1.3	1.1	0.8	5.1	4.0
15	2.0	1.6	1.4	1.1	6.0	5.7
20	2.3	3.2	2.6	1.3	7.2	5.6
30	3.6	3.2	3.8	1.8	5.6	5.6
40	4.3	3.1	4.3	2.4	5.7	5.7
50					5.6	5.1
60	4.2	3.5	4.5	3.2	6.2	6.5
75	0.8	0.6	4.7	3.3		

produced a fleeting yellow colour under the same conditions, but iron(II) and iodide gave no coloration. The presence of peroxide was confirmed by the chemiluminescent reaction with luminol.

In further experiments, 100 ml of *M* hydrochloric acid were shaken mechanically with copper foil, mercury, and zinc amalgam in the presence of air. Aliquots were withdrawn at intervals and their peroxide content determined colorimetrically. Duplicate results are shown in Table I. It is evident that a steady state concentration of peroxide is reached when the rate of reduction of peroxide is equal to the rate of diffusion of oxygen into the solution and reduction of oxygen to peroxide. A measurable amount of peroxide is very rapidly produced. If a metal ion is reduced by zinc amalgam and the aqueous phase decanted, then if acid is shaken with the amalgam in the presence of air to wash out the remaining aqueous phase, peroxide will be produced in the washings and added to the titrant, resulting in a low titre. It was observed that the acid shaken with copper foil became green after some time, as a result of peroxide oxidation of the copper with an attendant fall in the peroxide concentration.

Discussion

The reduction potential for peroxide reduced to water is $+1.77$ V, which is considerably higher than the potential for the reduction of oxygen to water, $+0.68$ V, and it might be expected thermodynamically that the reduction to water would be the faster. There is a good mechanistic reason why this should not be so. In the reduction of oxygen to peroxide the mechanism is probably transfer of hydrogen atoms in an oxygen–water or oxygen–hydrion transition complex, whereas in the further reduction of peroxide to water the oxygen–oxygen bond must be broken in addition to the hydrogen atom transfer again required. The result is the build-up of peroxide in the solution. The amount of peroxide that can be produced in 100 ml of solution at 0.2 atm partial pressure of oxygen is equivalent to about 0.2 ml of 0.1 *N* oxidant, and could account for a negative bias of 1% in a 20-ml titre. For many routine purposes such an error can be tolerated, but for accurate work it is essential to conduct the reduction in an inert atmosphere and to remove aerial oxygen from the solutions beforehand.

We wish to thank Miss HELEN C. MCCULLOCH for performing some of the peroxide work.

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A Gran titration to determine the chlorinity of sea water

Determination of the chlorinity of sea water by potentiometric titration seems to have been first suggested by WEST AND ROBINSON[1] in 1941. The procedure was later examined by HINDMAN, ANDERSON AND MOBERG[2], HERRMANN[3], BATHER AND RILEY[4] and PROCTOR[5] in order to improve the accuracy of the titration procedure and to evaluate the errors. None of these authors have, however, used the Gran II method[6] for evaluating the equivalence point. As we believe that this method increases the precision of the titration irrespective of whether volume or weighing burets are used, we wish to report an experiment at Bornö station, which was carried out by 2 of our students, SIV GRIMVALL and LENNART JANSON, during a course in analytical chemistry.

Water sampled in Gullmarsfjord (57°N, 11°E) at Bornö from a depth of 20 m ($S = 29.82^0/_{00}$, temp. 10.29°) on the 19th of November 1965 was used for the titration. In a 100-ml beaker 5.01 g of sea water was diluted to 50 ml with distilled water. The emf was measured with a Radiometer pH Meter 25 with a scale expansion, which allowed the potential to be read to 1 mV and to be estimated to tenths of a mV. Polished silver rods were used as electrodes and the cell was as follows: Ag/diluted sea water/0.1 *M* KNO_3/0.1 *M* $AgNO_3$/Ag. The titrant, 0.1000 *M* $AgNO_3$, was delivered from an ordinary 25-ml buret and readings were taken after 15 ml as follows (volume in ml, potential in mV): 15 (407.5), 16 (405), 17 (402.5), 19 (391), 20 (382), 20.5 (377), 21 (371.2), 21.3 (367.5), 21.5 (364.9), 21.7 (360), 21.9 (357), 22.1 (354.5), 22.3 (349.5), 22.5 (344), 22.7 (337), 22.9 (327.3), 23.1 (311.3), 23.2 (300.5), 23.3 (282), 23.4 (219), 23.6 (161), 23.8 (144), 24 (134), 24.2 (127.8), 24.5 (119.5), 24.7 (114.8), 25 (110.3).

As the ionic strength and junction potential are practically constant in the vicinity of the equivalence point the emf is given by

$$E = E_0 - 58 \log [Ag^+]$$

The Gran II functions F_1 and F_2 for the titration with v ml of 0.1000 *M* $AgNO_3$ are derived as follows. The initial amount of chloride and bromide in the titration vessel is $m_{Cl} + m_{Br}$ mmoles. Before the equivalence point ($v < v_e$ ml) $AgNO_3$ removes Cl^- and Br^-, thus

$$(50 + v)([Cl^-] + [Br^-]) = m_{Cl} + m_{Br} - v \cdot 0.1000$$

At the equivalence point: $v_e \cdot 0.1 = m_{Cl} + m_{Br}$.
Introducing v_e, $[Ag^+][Cl^-] = 10^{-9.8}$ and $[Ag^+][Br^-] = 10^{-12.4}$ one obtains

$$[Ag^+]^{-1}(10^{-9.8} + 10^{-12.4}) = (v - v_e) \cdot 0.1/(50 + v)$$

Thus when $[Ag^+]^{-1} = 0$ then $v = v_e$. A quantity proportional to $[Ag^+]^{-1}$ is obtained from E as $[Ag^+]^{-1} = 10\exp(E - E_0)/58$. In Fig. 1 we have plotted the Gran II function $F_1 = (50 + v)10\exp(E - 300)/58$ against v together with the logarithmic diagram for the precipitation of silver chloride and silver bromide from sea water diluted 1:5. At $F_1 = 0$, $v = v_e = 23.33$ ml from which the chlorinity was calculated as follows.

$$v_e/1000 \cdot 0.1000 \cdot 107.868 \cdot 328.5233/5.01 = 16.50 \pm 0.03^0/_{00}$$

Independent measurements of the salinity with a gold-chain hydrometer gave $Cl = 16.51 \pm 0.02^0/_{00}$.

After the equivalence point ($v > v_e$ ml) the following relation is valid

$$(v - v_e) \cdot 0.1000 = [Ag^+](50 + v)$$

The Gran II function for this range is

$$F_2 = (50 + v) 10 \exp(200 - E)/58$$

The two functions intersect at P_e in the logarithmic diagram where $[Cl^-] = 10^{-4.9}$ ($= {}^1/_2 \log K_{s0}$), *i.e.* 0.01% of chloride is still untitrated. The extrapolation of F_1 to $[Cl^-] + [Br^-] = 0$ is therefore preferable although the difference is barely discernible.

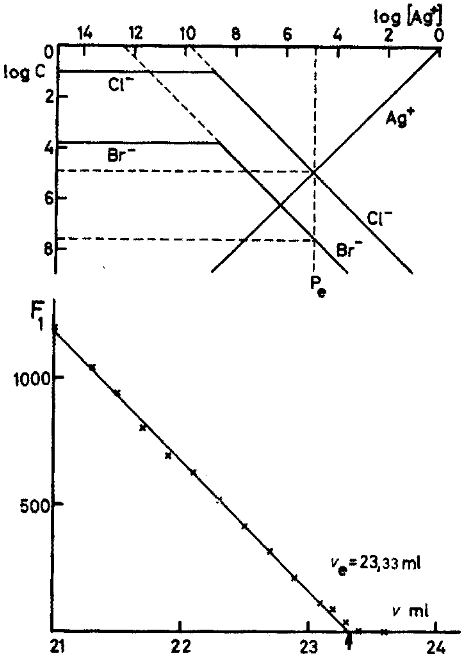

Fig. 1. Logarithmic diagram (above) and a Gran II plot (below) for the titration of $Cl^- + Br^-$ in sea water by Ag^+.

Notes. Sea water has a molality ratio of $Cl^-/Br^- \approx 10^{2.8}$ that corresponds closely to the ratio of the solubility products of the silver halides $10^{-9.8}/10^{-12.4} = 10^{2.6}$. Thus it can be seen from the logarithmic diagram in Fig. 1 that silver bromide starts to precipitate very soon after silver chloride when $[Ag^+]$ is increased. It has recently been shown[7] that Gran II plots also can be used for the evaluation of equivalence points in the potentiometric titration of the alkalinity and total carbonate of sea water.

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(Received December 8th, 1965)

Silver(II) oxide oxidation and spectrophotometric determination of chromium(III)

Chromium(III) in micro amounts can be quantitatively oxidized to chromium(VI) by oxidizing agents, such as potassium permanganate, potassium persulfate in acidic media, or perchloric acid[1]; the chromium(VI) obtained is determined by reading the absorbance of its complex with *s*-diphenylcarbazide at a wavelength of 540 mμ[1,2].

The present paper describes a simple, rapid and accurate method for this determination, using silver(II) oxide as oxidizing agent. Silver(II) oxide has been studied as an oxidizing agent in the titrimetric determination of chromium(III)[3] but, so far as is known, it has not been used in the colorimetric determination.

Apparatus

A "Hitachi–Perkin-Elmer" Model 139 spectrophotometer was used to read the absorbance.

Reagents

Silver(II) oxide was prepared by adding silver nitrate to an alkaline solution of potassium persulphate[4].

Standard chromium(III) solution (11.97 mg/l) was prepared by dissolving a weighed amount of spectroscopically pure metallic chromium (Johnson, Matthey and Co., Ltd.) in 5 ml of 1:1 sulfuric acid and then diluting it to 1 l with water.

Merck reagent-grade diphenylcarbazide was used. The water used was distilled from alkaline permanganate.

Procedure

Transfer an aliquot containing 10–100 μg of chromium to a 50-ml beaker. Add the proper amounts of acids to give 1 *N* nitric acid and 0.5 *N* sulfuric acid in a final volume of about 20 ml.

Add about 20 mg of silver(II) oxide in small portions, while stirring the solution until a brown colour appears[3]. Continue stirring for a further 15 min and then heat the solution to *ca.* 85° in order to destroy the excess of silver(II) oxide. The destruction is complete when the solution becomes colourless and clear. Cool the solution to room temperature, transfer the solution quantitatively to a 50-ml volumetric flask and add 1.0 ml of a freshly prepared 0.5% solution of diphenylcarbazide in acetone. Dilute to the mark with distilled water and allow to stand for 10–15 min. Read the absorbance at 540 mμ in a 1-cm cell, comparing it to a blank solution.

Read the amount of chromium(III) from a calibration graph prepared by following the above procedure.

Results and discussion

Both the quantitative oxidation of chromium(III) and the destruction of the excess of the reagent were carefully checked. The present study proved that silver(II) oxide can be used satisfactorily for accurate and precise spectrophotometric work. The media tried in the oxidation process were sulfuric and nitric acids; each was examined separately as well as in mixture, the maximum concentrations being 5 *N*. The optimal acidity for reproducible and accurate results was 1.5 *N*. The time required for the quantitative oxidation with silver(II) oxide and destruction of its excess was about 20 min. In order to find the time needed for colour development, the absorbances were read at intervals ranging from 5 min to 1 h after addition of diphenylcarbazide.

The calibration graph was prepared with known amounts of standard solution containing 10–100 μg of chromium(III). It was found to be linear, passing through the origin. For comparison, another calibration curve was prepared with known amounts of chromium (VI) from primary standard potassium dichromate by carrying out the above procedure. The two curves obtained were identical, which proves that the oxidation process is quantitative.

The precision of the method was estimated by calculating the standard deviation of the ratio of the absorbance to μg Cr for the calibration graph; a standard deviation of 0.6% was found.

The effect of interferences on the accuracy of the diphenylcarbazide method has been studied by other workers[1]. For the present method, it may be assumed that the effects of the interferences are similar to those mentioned previously[1].

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(Received December 20th, 1965)

BOOK REVIEWS

L. S. ETTRE, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965, xix + 164 pp., price $4.95.

One of the more striking developments of gas chromatography stems from the work of GOLAY, who proposed the use of coated capillary tubes as chromatography columns rather than narrow tubes containing a stationary phase supported on an inert powder, in order to attain greater resolving power. This book is concerned with the use of such volumes commonly known as capillary columns—although by using the term in the title, and by a plea in the text, the author tries to encourage the alternative descriptive term "open tubular columns".

The book outlines the theoretical principles underlying the use of this type of gas chromatography column and contrasts these with the principles of packed columns. It contains a valuable section on the preparation of the columns. This is followed by a description of the principal ancillary parts of the apparatus, such as the inlet system and the heating system for the column. Since the author's main preoccupation is the setting up of the column itself, detection practices are almost ignored. This does not detract from the value of the book.

The author has succeeded in setting out and illustrating the principles in a succinct and readable manner. He has avoided the dangers, that beset authors of books on techniques, of confounding the reader with a mass of detail relating to the many alternative practices that are often available. The book closes with a comprehensive (though unclassified) bibliography, complete to about the middle of 1964, which should enable the reader to find his way into the literature should he require further details.

C. R. PATRICK (Birmingham)

Anal. Chim. Acta, 35 (1966) 411

G. CHARLOT, *Rapid Detection of Cations and Anions*, 3rd revised Ed., translated by R. E. OESPER, Chemical Publishing Company, Inc., New York, 1965, 107 pp., price $ 5.00.

This English version of Professor CHARLOT's *Méthode d'Analyse Qualitative des Cations* contains tests for 36 cations and 24 anions. These tests can be used on solutions obtained by classical qualitative analytical separations, but simple procedures are described for the preparation of solutions for analysis. The value of this 3rd edition lies mainly in the new section devoted to tests for anions, although revision of the cation tests has led to the inclusion of certain superior procedures.

This is a very useful little book which students and teachers of chemical analysis will appreciate. Although qualitative testing may have lost some of its importance in industrial chemistry, nevertheless occasions arise when its use is unavoidable and this source book of simple and easily applied reactions should be on hand for such contingencies.

WILLIAM I. STEPHEN (Birmingham)

Treatise on Analytical Chemistry, Edited by I. M. KOLTHOFF AND P. J. ELVING with the assistance of E. B. SANDELL, *Part I, Theory and Practice, Vol. 6*, Interscience–J. Wiley and Sons, New York, 1965, xxiii pp. + p. 3347–4246, price 175 s.

La première partie de cet ouvrage important traite de la théorie et de la pratique en chimie analytique. Plusieurs volumes sont déjà en librairie dont le Volume 5 traite des méthodes optiques. Le Volume 6 qui vient de paraître complète le précédent. Il comprend les chapitres suivants: la spectroscopie d'émission par B. F. SCRIBNER ET M. MARVIN, la photométrie de flamme par B. L. VALLEE ET R. E. THIERS, la spectroscopie infrarouge par L. A. SMITH, la spectroscopie raman par E. J. ROSENBAUM, la diffraction électronique par J. H. REISNER, l'absorption neutronique par G. W. LEDDICOTTE, la réfractométrie et la dispersion par S. Z. LEWIN ET N. BAUER, la polarimétrie par W. S. STRUCK ET E. C. OLSON, la microscopie chimique par W. C. MCCRONE ET L. B. MCCRONE et la microscopie électronique par G. G. COCKS. Ces deux volumes donnent la gamme et la quasi totalité des méthodes optiques modernes. Il y manque cependant la spectrophotométrie d'absorption atomique qui sera peut-être traitée dans un prochain volume et nous l'espérons car elle prend en analyse minérale une importance grandissante. Nous ferons les mêmes critiques et les mêmes éloges que pour les autres volumes de cet ouvrage. Un certain manque de coordination entre les sujets traités, difficile à éviter car chacun d'entre eux a été confié à un ou plusieurs spécialistes distingués. Chaque sujet est traité avec une grande maîtrise, on y trouve les perfectionnements les plus modernes et la présentation est parfaite. De plus un effort a été fait pour ne donner que les bases essentielles à l'analyste. Les considérations trop théoriques et les détails de construction de l'appareillage ont été judicieusement laissés de côté. A la fin de chaque chapitre une bibliographie restreinte mais judicieusement choisie renvoie aux ouvrages et articles fondamentaux. Parmi les divers sujets traités nous avons examiné celui traitant de la photométrie de flamme. Il est parfait tant par son ordonnance que par la clarté des sujets exposés.

D. MONNIER (Genève)

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