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66

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Vol. **44**, No. **1**	January 1969	
Vol. **44**, No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45**, No. **1**	March 1969	
Vol. **45**, No. **2**	April 1969	
Vol. **45**, No. **3**	May 1969	**(completing Vol. 45)**
Vol. **46**, No. **1**	June 1969	
Vol. **46**, No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47**, No. **1**	August 1969	
Vol. **47**, No. **2**	September 1969	
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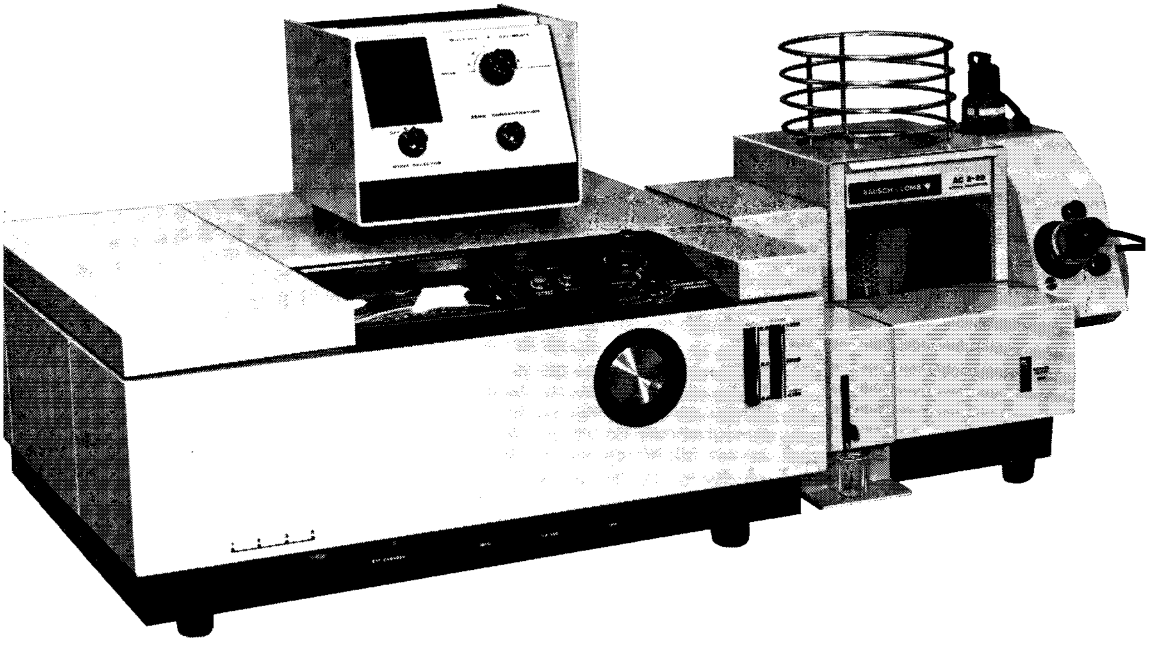

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Progress in Chromatography, Electrophoresis and Related Methods

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Chromatographic Reviews has for many years been a widely welcomed and successful series of books. However, since rapid publication is becoming more and more important, it was decided that Volume 9 and all subsequent volumes should appear in journal form. Volume 9 and Volume 10 have already appeared – the contents of Volume 10 and the titles of some of the reviews to be published in Volume 11 – are given below.

Contents of Volume 10 (1968)

no. 1
Dünnschichtchromatographie der Kohlehydrate (H. Scherz, G. Stehlik, E. Bancher und K. Kaindl)
Chromatographic analysis of plasmalogens (C. V. Viswanathan)
Chromatography of ureas and thioureas and related mammalian metabolites (L. Fishbein, H. L. Falk and P. Kotin)
Chromatography and electrophoresis of inorganic ions in fused salts (G. Alberti and S. Allulli)

no. 2
Chromatography of methylenedioxyphenyl compounds. I. Simple and pesticidal dericatives (L. Fishbein, H. L. Falk and P. Kotin)
Chromatographic detection of adulteration of oils and fats (V. V. S. Mani and G. Lakshminarayana)
The use of gas-liquid chromatography for the determination of thermodynamic properties (C. L. Young)

Some forthcoming titles to appear in Volume 11 (1969)

Chromatography of methylenedioxyphenyl compounds. II. Alkaloidal derivatives (L. Fishbein and H. L. Falk)
Chromatography of alkylating agents. I. Aziridinyl, nitrogen and sulfur mustards and related derivatives (L. Fishbein and H. L. Falk)
Chromatographic analysis of molecular species of lipids. A general survey (C. V. Viswanathan)

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 44, No. 1, January 1969

THE IDENTIFICATION OF METAL–PROTEIN COMPLEXES BY GEL CHROMATOGRAPHY AND NEUTRON ACTIVATION ANALYSIS

A method for the identification of protein–metal complexes in biological fluids by a combination of gel chromatography and neutron activation analysis is proposed. The distribution of protein–bound copper in human serum is studied as an example of the method.

D. J. R. Evans and K. Fritze,
Anal. Chim. Acta, 44 (1969) 1–7

APPLICATION OF A BETATRON IN PHOTONUCLEAR ACTIVATION ANALYSIS

The present study concerns the determination of fluorine, iodine, lead and mercury by means of the photonuclear activation technique with a betatron. The detection limits obtained for the elements in the above sequence were 3, 50, 400 and 15 μg respectively. The technique has been applied in the determination of iodine in pharmaceuticals. A rotating sample holder device was inserted in the bremsstrahlung beam of the betatron in order to ensure uniform irradiation of the samples.

D. Brune, S. Mattsson and K. Lidén,
Anal. Chim. Acta, 44 (1969) 9–14

ASPECTS OF LOW-TEMPERATURE IRRADIATION IN NEUTRON ACTIVATION ANALYSIS

Neutron irradiation of the sample while frozen in a cooling device inserted in a reactor channel is described for the determination of iodine in aqueous samples as well as of mercury in biological tissue and water. For the simultaneous irradiation of a large number of aqueous solutions the samples were arranged in a suitable geometry in order to avoid mutual flux perturbation effects. The influence of the neutron temperature on the activation process is discussed. Potential applications of the low-temperature irradiation technique are outlined.

D. Brune,
Anal. Chim. Acta, 44 (1969) 15–20

THE X-RAY FLUORESCENCE MEASUREMENT OF SURFACE URANIUM ON OXIDIZED FUEL ELEMENTS

When a uranium nuclear fuel material clad with an Fe–25Cr–4Al–1Y alloy is tested in an oxidizing environment at elevated temperatures, uranium diffuses through the clad and deposits on the surface of the specimen. A method has been developed whereby the amount of uranium per unit area on the surface of the specimen can be determined by X-ray fluorescence measurement. Synthetic specimens can be prepared by vapor-depositing uranium metal on Scotch tape and applying this tape to a solid piece of the alloy. The method described is accurate to $\pm 5\%$ relative and has a lower detection limit of about 30 μg U/(cm^2 × 150 μ).

E. A. Schaefer, P. F. Elliot and J. O. Hibbits,
Anal. Chim. Acta, 44 (1969) 21–28

ห้องสมุด กรมวิทยาศาสตร์
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THE DETERMINATION OF NICKEL IN HIGH-PURITY COBALT BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(in French)

Quantitative separation of nickel from cobalt has been achieved by means of a cation-exchange resin, Dowex 50-X8, in a 90% acetone–0.6 *M* hydrochloric acid medium. Nickel is then determined by atomic absorption spectrophotometry; the sensitivity of the method is increased by means of an ultrasonic spraying device. Under these conditions, 1 p.p.m. of nickel can be measured with an accuracy of *ca.* 20%.

G. UNY, M. BRULE AND J. SPITZ,
Anal. Chim. Acta, 44 (1969) 29–33

SUBSTOICHIOMETRIC ISOTOPE DILUTION ANALYSIS IN THE MICROGRAM AND SUBMICROGRAM RANGES BY PRECIPITATION REACTIONS ON FILTER PAPER

(in German)

A new microchemical variation of substoichiometric isotope dilution analysis by means of precipitation reactions on filter paper is described. The method is demonstrated for determinations of silver (precipitated as $^{110m}Ag_2S$), iron(III) (as $^{59}Fe_4[Fe(CN)_6]_3$) and iodide (as $Ag^{131}I$). Amounts of 0.1–40 μg can be determined with satisfactory accuracy. Essential conditions for the application of the method are discussed.

V. KRIVÁŇ, H. WEISZ UND D. KLOCKOW,
Anal. Chim. Acta, 44 (1969) 34–39

AN EXAMINATION OF THE EQUILIBRIUM BETWEEN H AND OH RADICALS AND OF RELATED EFFECTS IN TURBULENT HYDROGEN FLAMES AS USED IN FLAME SPECTROPHOTOMETRIC METHODS OF ANALYSIS

An examination of the relative radical and molecule concentrations in turbulent hydrogen flames as used in flame spectrophotometric methods of analysis has shown that they are in agreement with the equilibrium $H_2+OH \rightleftharpoons H_2O+H$. The flame profiles of the concentrations of H and OH radicals and of water vapour are described and discussed. The OH radical concentration reaches a maximum high in the flame. The emission from OH radicals in hydrogen–air flames, which is at a maximum low in the flame, is produced mainly by chemiluminescent excitation. The blue continuum in hydrogen–oxygen flames, which is produced by the combination of H and OH radicals, is spread throughout the flame. The influences of the evaporation of water from solutions atomised into the flame and of the expansion of the flame gases on the flame profiles of species in the flame are discussed.

D. J. HALLS AND E. PUNGOR,
Anal. Chim. Acta, 44 (1969) 40–50

SPECTROSCOPIC STUDIES OF THE CHROMOTROPIC ACID–NITRATE REACTION

Chromotropic acid is known to provide a specific and sensitive reagent for the detection of nitrate ion. The reaction is most sensitive in about 70% sulfuric acid. NMR studies indicated that the product was a mononitro derivative of chromotropic acid. The UV spectrum indicated that the product was a quinone compound. It is proposed that the structure of the product is a mononitro-quinone derivative of chromotropic acid in a polymerized sulfonyl form.

J. W. ROBINSON AND C. J. HSU,
Anal. Chim. Acta, 44 (1969) 51–58

THE EFFECT OF SUBSTITUENTS ON THE PROTONATION CONSTANTS OF MONO- AND BIS-AZO DERIVATIVES OF CHROMOTROPIC ACID

The protonation of 19 derivatives of mono- and bis-azochromotropic acid has been studied and the protonation constants determined. The effect of the substituents is described by comparison with different "zero" reagents. The relationship between the values of the protonation constants and the molar absorptivities of the protonated form of the reagents is discussed.

A. Muk and S. B. Savvin,
Anal. Chim. Acta, 44 (1969) 59–65

SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 2,3-DIAMINOPYRIDINE

Ruthenium, in solution as its high oxidation states, and 2,3-diaminopyridine react in concentrated acetic acid to give an indigo-blue product having an absorption peak at 572 nm. The color develops at room temperature, and the method is not highly sensitive to the concentration of the reagent nor to the development time. The optimum concentration range, for measurement at 1.00-cm optical path, is about 1–6 p.p.m. of ruthenium; the molar absorptivity is $1.2 \cdot 10^4$ l mole^{-1} cm^{-1}. A prior separation of ruthenium is necessary. Spectrophotometric methods established a 1:1 mole ratio in the color reaction. The product is predominantly in cationic form in acetic acid solution, and predominantly anionic in alkaline medium.

G. H. Ayres and D. T. Eastes,
Anal. Chim. Acta, 44 (1969) 67–72

DEPOLYMERISATION OF ZIRCONIUM IN SPECTROPHOTOMETRY WITH ARSENAZO III

The preparation of depolymerised solutions from various zirconium salts in the cold and on boiling, the depolymerisation of polymerised zirconium solutions, and the dissolution of precipitated zirconium hydroxide by hydrochloric acid, are described. The concentrations of the zirconium solutions are between 10^{-4} and 10^{-1} M. The minimum permissible concentrations of various acids are shown by depolymerisation curves. Zirconium was determined by spectrophotometry with arsenazo III in 8 N hydrochloric acid, and the interferences by sulphate, perchlorate, phosphate, fluoride and nitrate are described.

P. Pakalns,
Anal. Chim. Acta, 44 (1969) 73–83

SPECTROPHOTOMETRIC DETERMINATIONS OF IRON(III), TITANIUM(IV) AND VANADIUM(V) AND THEIR SEPARATION FROM EACH OTHER AND FROM OTHER IONS WITH 1-(*o*-CARBOXYPHENYL)-3-HYDROXY-3-PHENYLTRIAZENE

1-(*o*-Carboxyphenyl)-3-hydroxy-3-phenyltriazene is shown to be an excellent spectrophotometric reagent for the determination of iron(III), titanium(IV) and vanadium(V). Iron(III) forms an intense violet complex in presence of tartaric acid at pH 9.5 and titanium(IV) and vanadium(V) form yellow and green complexes, respectively, at pH 2.0. The wavelengths of maximum absorption of the complexes of iron(III), titanium(IV) and vanadium(V) in chloroform are 500, 430 and 410 nm, respectively. Beer's law is valid with optimum ranges 1.0–12.0 p.p.m. for iron(III), 0.5–4.0 p.p.m. for titanium(IV) and 1.0–6.0 p.p.m. for vanadium(V), where the relative errors are 2.78, 2.76 and 2.83%. The reagent forms 1:2 complexes with iron(III) and titanium(IV) and a 1:1 complex with vanadium(V), with instability constants of the order of 10^{-10}, 10^{-9} and 10^{-6}, respectively. Interfering effects of other anions and cations on the colour systems were studied; common complexing agents, such as fluoride, phosphate, citrate and tartrate when present even to the extent of 400 p.p.m. have no effect. A procedure for the separation and determination of iron, titanium and vanadium in presence of each other is described.

A. K. Majumdar and S. C. Saha,
Anal. Chim. Acta, 44 (1969) 85–93

ANALYTICAL APPLICATIONS OF PALLADIAZO AND ARSENAZO III TO THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

PART II. EXTRACTION OF DIFFERENT AQUEOUS COMPLEX SYSTEMS WITH QUATERNARY AMMONIUM SALTS AND DIPHENYLGUANIDINE CHLORIDE IN *n*-BUTANOL MEDIUM

The extraction characteristics of the palladium(II) complexes of arsenazo III and palladiazo were investigated at different pH values under conditions of both metal and ligand excess. Partition coefficients and concentration factors were estimated spectrophotometrically as a function of pH, volume of the organic phase and nature of the auxiliary organic cations introduced. Depending on the extraction conditions, the different complexes were extracted to very varying extents despite their consistently anionic nature. A summary of physicochemical data of interest for the complex systems is given. The two quaternary ammonium salts used gave very similar extraction results which differed sharply from those obtained with guanidine. A qualitative correlation of the spectra of the initial aqueous test solutions and their different organic extracts for 12 different systems is discussed; there is a strong chemical interaction between the extracted complex compounds and the organic cations of the extractant, so that nearly colorless ternary complexes may result. The suitability of some of the systems tested, for the direct extraction-spectrophotometric determination of palladium(II), is mentioned.

J. A. PÉREZ-BUSTAMANTE, C. MORELL GARCÍA AND F. BURRIEL-MARTÍ,
Anal. Chim. Acta, 44 (1969) 95–114

DISUBSTITUTED METHANES AS FLUORIMETRIC REAGENTS

PART I. DIBENZOTHIAZOLYLMETHANE

Disubstituted methanes, such as dibenzothiazolylmethane, react to form fluorescent species with metals through chelation to the thiazole nitrogens. A number of ions, such as hydrogen, sodium, potassium, form weakly fluorescent products but only zinc and lithium (with ionic radii of 0.72 and 0.71 Å respectively) form strongly fluorescent chelates at room temperature. Proton removal is not required for the formation of fluorescent species but stabler complexes, more resistant to the quenching action of water, are formed if a proton is removed from the methylene bridge. The reagent is slowly oxidized in ethanolic solutions, background intensity increases, and freshly prepared solutions are desirable for highest sensitivity. For zinc, the excitation and emission maxima are 410 nm and 450 nm respectively; 2 p.p.b. of zinc can be determined with a simple fluorimeter.

D. E. RYAN AND B. K. AFGHAN,
Anal. Chim. Acta, 44 (1969) 115–122

CHEMICAL PROPERTIES OF THE BIS-(2,3,5,6-TETRAKIS-(2′-PYRIDYL)PYRAZINE)-IRON(II) COMPLEX

2,3,5,6-Tetrakis(2′-pyridyl)pyrazine forms an iron(II) complex containing 2 moles of ligand for each mole of iron. In aqueous solution, the wavelength of maximum absorbance shifts from 575 nm to 590 nm when the complex solution is treated with strong acid. Both the protonated and non-protonated forms of the complex obey Beer's law over the range $8.95 \cdot 10^{-6}$–$5.37 \cdot 10^{-5}$ M, the molar absorptivities of the protonated and non-protonated complexes being 16,700 and 19,210 respectively. The overall stability constant of the iron complex was found to be 8.5 ± 0.3. There are 3 protons per molecule in the protonated form.

R. E. JENSEN, J. A. CARLSON AND M. L. GRANT,
Anal. Chim. Acta, 44 (1969) 123–128

COMPLEXIMETRIC DETERMINATION OF MERCURY(II) WITH *o*-(2-THIAZOLYLAZO)CRESOL AS INDICATOR

A direct EDTA titration method for mercury(II) ions with *o*-(2-thiazolylazo)cresol (TAC) as the metallochromic indicator at pH 7–8.3 is described. Sharp color changes from blue to yellow or red indicate the equivalence point. The indicator transition of TAC is discussed theoretically by using the formation constants of the mercury(II)–TAC chelate; the results obtained were confirmed experimentally by photometric titration.

F. Kai,
Anal. Chim. Acta, 44 (1969) 129–137

QUINOLINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE: A SELECTIVE AND SENSITIVE COPPER REAGENT

Quinoline-2-aldehyde-2-quinolylhydrazone (QAQH) allows a simple and rapid direct determination of less than 1 p.p.m. of copper. The red 2:1 QAQH to copper complex has a molecular extinction coefficient in benzene of $5.8 \cdot 10^4$ at the absorption maximum of 540 nm. Most metals (up to 500 μg) do not interfere in the determination of 35 μg of copper. Equivalent amounts of cobalt and twice as much nickel can be present; 15- to 20-fold excesses of these metals are allowable in acetone:water solutions and 0.01 μg of copper is detectable in this medium. Very small amounts of copper (1 p.p.b.) can be recovered from large sample volumes and determined directly.

G. G. Sims and D. E. Ryan,
Anal. Chim. Acta, 44 (1969) 139–146

THE GRAVIMETRIC DETERMINATION OF RHENIUM AS AMINE PERRHENATES

Various substituted 1-naphthylmethylamines have been studied as precipitants for the perrhenate ion. The perrhenate of the N-benzyl derivative is too soluble for analytical purposes, but both N-(*p*-chlorobenzyl)-1-naphthylmethylamine and di-(1-naphthylmethyl)-amine can be used, the latter being preferable, because of the greater permissible variation of conditions. This reagent is approximately equivalent to nitron in sensitivity and selectivity but has the advantage of being more easily prepared. *N*-Benzyl-1-naphthylmethylamine is a suitable precipitant for hexachlororhenate(IV), but there is no simple quantitative means of converting perrhenate to this ion, hence advantage cannot be taken of the improved conversion factor for rhenium. The pertechnetate ion also yields sparingly soluble salts with these amines.

M. H. B. Morton and W. I. Stephen,
Anal. Chim. Acta, 44 (1969) 147–152

AN INVESTIGATION OF BARIUM OXALATE BY COMBINED DERIVATOGRAPHIC AND THERMO-GAS ANALYSIS

The thermal decomposition of barium oxalate was investigated in a nitrogen atmosphere, by a combined derivatographic and thermo-gas analytical method. In contrast to studies conducted in air, a portion of the carbon monoxide formed in the nitrogen atmosphere during the decomposition of oxalate, undergoes further decomposition to yield carbon dioxide and carbon. At higher temperatures, the liberated carbon reacts with barium carbonate, and carbon monoxide and barium oxide are formed.

J. Paulik, F. Paulik and L. Erdey,
Anal. Chim. Acta, 44 (1969) 153–158

SEPARATION AND PURIFICATION OF BERYLLIUM BY THE FRACTIONAL SUBLIMATION OF BERYLLIUM ACETYLACETONATE

Solutions containing beryllium(II) in admixture with most common metals can be treated with acetylacetone to form the beryllium and various other acetylacetonates which precipitate. The precipitate is filtered, washed, dried and fractionally sublimed in a special sublimator. After sublimation with air as a carrier gas the beryllium acetylacetonate fraction is recoverable in high purity. Zinc is the only detectable contaminant by atomic absorption spectrometry but can be eliminated by masking with ammonium thiocyanate before the formation of the metal acetylacetonates. Beryllium fractions were checked for purity by atomic absorption spectrometry and found to contain less than 0.002% Zn after a single sublimation. The method appears to offer an excellent method of purification for beryllium if quantitative recoveries are not required.

E. W. Berg and A. D. Shendrikar,
Anal. Chim. Acta, 44 (1969) 159–164

THERMAL STUDIES OF BARIUM BROMATE

(in French)

Chemical, thermogravimetric, differential thermal, infrared spectroscopic and X-ray diffractometric analyses have been used to provide evidence for the existence of two crystalline forms of anhydrous barium bromate; a solid solution is formed during the thermal decomposition.

T. Dupuis and C. Rocchiccioli-Deltcheff,
Anal. Chim. Acta, 44 (1969) 165–173

STUDIES IN THE TETRAARYLBORATES

PART III. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE AND SODIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate were synthesized by a new *in situ* method. Both salts formed precipitates with potassium, rubidium and cesium ions, quaternary ammonium and protonated basic nitrogen compounds. Potassium tetrakis(*p*-trifluoromethylphenyl) borate was more insoluble than potassium tetraphenylborate while cesium tetrakis(*m*-fluorophenyl) borate was less soluble than cesium tetrakis-(*p*-fluorophenyl) borate. The salts formed with nitrogen-containing compounds offer possibilities for qualitative and quantitative analyses.

J. T. Vandeberg, C. E. Moore, F. P. Cassaretto and H. Posvic,
Anal. Chim. Acta, 44 (1969) 175–183

PRECIPITATION OF LEAD AS LEAD MOLYBDATE FROM HOMOGENEOUS SOLUTION

Lead molybdate can be precipitated in a granular form from a homogeneous solution by taking advantage of the long induction period for the formation of the precipitate in strong acid solution. The rate of precipitation is probably controlled by the rate at which the polymolybdate species depolymerize to yield simple molybdate ions. Although the bulk (>90%) of the precipitate forms at pH *ca.* 1.0, quantitative recovery requires final adjustment of the pH of the digested solution, either homogeneously (urea hydrolysis) or heterogeneously (dropwise addition of ammonia), to pH 3.0. Contamination by molybdic oxide occurs but both methods yield reliable results if the excess of molybdate is limited to 5% and the precipitate is ignited to 725°. Contamination by copper and cadmium was also studied.

C. C. Budke and L. A. Knecht,
Anal. Chim. Acta, 44 (1969) 185–192

COLLECTION OF TRACES OF SILVER ON PREFORMED *p*-DIMETHYLAMINOBENZYLIDENERHODANINE PRECIPITATES

Microgram or nanogram quantities of silver ion can be collected on 0.2–4 mg of preformed voluminous *p*-dimethylaminobenzylidenerhodanine precipitates from 50–2000 ml of 0.01–0.5 N nitric acid solution within 10 min. This separation method is successfully applied to the photometric determination of a few p.p.m. of silver in high-purity bismuth metal.

A. MIZUIKE AND K. FUKUDA,
Anal. Chim. Acta, 44 (1969) 193–198

PRECISE INTEGRATION OF VOLTAGE (CURRENT)–TIME FUNCTIONS WITH A FIXED FIELD D.C. MOTOR-COUNTER

Because of electrical and mechanical losses, the counting rate of a fixed field D.C. motor-counter integrator becomes less than linear with decreasing input voltage. This decay of the counting rate can be counteracted very simply by introducing a small, constant compensation voltage into the input circuit. When properly compensated, the integrator manufactured by Ether Ltd. (formerly Electro Methods Ltd.) is capable of measuring the time integral of current or voltage over a 20 to 1 range with an error of only $\pm 0.04\%$, and over a 200 to 1 range with an error of only about -0.1%.

J. J. LINGANE,
Anal. Chim. Acta, 44 (1969) 199–203

POLAROGRAPHY OF SULFUR DIOXIDE (SULFITE) IN AQUEOUS HYDROFLUORIC ACID

A well-formed polarographic wave exists for sulfur dioxide (sulfite) in aqueous hydrofluoric acid at a half-wave potential ($E_{\frac{1}{2}}$) of about -0.4 V *vs.* S.C.E. The characteristics of the wave are similar to those of the wave for sulfite in aqueous solutions of hydrochloric acid and of nitric acid. The relation of sulfite concentration (C) to diffusion current (i_d) is linear, and the wave is reproducible. Polarography in aqueous hydrofluoric acid media is indicated to be a suitable method for the detection and direct determination of sulfur dioxide. Possible significant applications of the method are to determine contaminative sulfur dioxide in hydrogen fluoride gas, in reagent-grade hydrofluoric acid and fluorosulfuric acid, and in the atmosphere.

H. P. RAAEN,
Anal. Chim. Acta, 44 (1969) 205–210

OSCILLOPOLAROGRAPHIC DETERMINATION OF INDIUM, LEAD AND CADMIUM IN A SUPPORTING ELECTROLYTE CONTAINING CUPFERRON

In a supporting electrolyte containing phosphate buffer pH 7, 10^{-2} M sodium thiosulphate and 10^{-2} M cupferron, lead(II), cadmium(II) and indium(III) give reversible, sensitive and well-defined incisions in the $dE/dt=f(E)$ curves (Q=0.40, 0.45, and 0.52 respectively). The limit of detection is $2\cdot10^{-6}$ M in each case and $2\cdot10^{-6}$–$5\cdot10^{-5}$ M of each cation may be determined. There are few serious interferences.

G. DONOSO N. AND M. A. SANTA ANA V.,
Anal. Chim. Acta, 44 (1969) 211–216

SEPARATION OF DICARBOXYLIC AND TRICARBOXYLIC ACIDS BY ANION-EXCHANGE CHROMATOGRAPHY IN MAGNESIUM ACETATE

An automatic method is described for the determination of acids containing two or three carboxyl groups. The acids are separated on an anion-exchange resin with magnesium acetate as the eluant and are determined colorimetrically by chromic acid oxidation.

L. BENGTSSON AND O. SAMUELSON,
Anal. Chim. Acta, 44 (1969) 217–223

THE DENSITY OF NITRIC ACID SOLUTIONS OF URANIUM AND URANIUM–ALUMINIUM ALLOYS

(Short Communication)

H. H. Ph. Moeken,
Anal. Chim. Acta, 44 (1969) 225–228

SORPTION OF PROTONATED COMPLEX ANIONIC SPECIES OF THE PALLADIAZO REAGENT ON CATION–EXCHANGE RESINS IN CONCENTRATED NEUTRAL SALINE MEDIA

(Short Communication)

J. A. Pérez-Bustamante and F. Burriel-Martí,
Anal. Chim. Acta, 44 (1969) 229–230

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(Short Communication)

V. Y. Armeanu and L. M. Baloiu,
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(Short Communication)

F. Will, III and C. Varsel,
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THE USE OF 5,7-DIBROMO-8-HYDROXYQUINOLINE FOR THE CONCENTRATION OF CERTAIN TRACE ELEMENTS FROM SEA WATER

(Short Communication)

J. P. Riley and G. Topping,
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A SIMPLE ONE-STEP METHOD FOR THE DETERMINATION OF α-HYDROXYAMINO NITROGEN

(Short Communication)

D. S. Galanos and E. C. Voudouris,
Anal. Chim. Acta, 44 (1969) 237–239

THE INDIRECT DETERMINATION OF SULFUR DIOXIDE BY ATOMIC ABSORPTION SPECTROMETRY AFTER PRECIPITATION OF LEAD SULFATE

(Short Communication)

S. A. Rose and D. F. Boltz,
Anal. Chim. Acta, 44 (1969) 239–241

DETERMINATION OF MERCURY(II) WITH *o*-(2-THIAZOLYLAZO)-4-METHOXYPHENOL AS SPECTROPHOTOMETRIC REAGENT AND METALLOCHROMIC INDICATOR

(Short Communication)

F. Kai,
Anal. Chim. Acta, 44 (1969) 242–246

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THE IDENTIFICATION OF METAL–PROTEIN COMPLEXES BY GEL CHROMATOGRAPHY AND NEUTRON ACTIVATION ANALYSIS

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(Received July 12th, 1968)

In recent years considerable attention has been focussed on the role of trace elements in biological systems. Trace metals in protein have attracted interest, since in combination with proteins, they often appear to function in some enzymic capacity essential to the health of the living organism. Many workers have determined the total amounts of various elements present in, say, whole blood or serum[1], while a few others have analysed specifically for protein-bound elements[2–5]. This paper proposes a new method for the identification of metal–protein complexes by a combination of gel chromatography and neutron activation analysis.

Although the technique of gel chromatography was introduced only recently, it has shown itself to be an excellent method for the fractionation of protein mixtures on the basis of molecular size. The gentle treatment of the proteins undergoing separation is one of the most important features of gel filtration, particularly in contrast with the somewhat harsher methods used previously. Such techniques as changes in ionic strength or pH always have associated with them the possibility of protein denaturation, or the complete break-up of the molecule into subunits. In gel chromatography the protein can be maintained in an environment very similar to that in nature and, in fact, the only real change in conditions lies in the dilution of the protein solution.

A number of workers have shown that macromolecules are eluted from cross-linked dextran or polyacrylamide gel columns in order of molecular size.

For globular proteins the elution volume is proportional to the molecular weight, whereas more elongated molecules show some deviation from this standard behavior. Hence unless the shape of the protein is known, it is not possible by gel filtration alone to do more than assign a limit to the molecular weight. A recent book by DETERMANN provides excellent coverage of gel chromatographic theory and practice[6].

With relatively few exceptions, the concentrations of individual metals in biological samples are extremely low. Consequently, most analytical techniques involve either concentration of the sample or measurements which are near the limits of detection for the method. Although neutron activation analysis cannot conveniently be used to determine some elements, for most metals it provides a method with very high sensitivity. Furthermore, contamination errors are reduced since contamination of the sample after irradiation is of no consequence.

The experiments reported here were designed to show the possibility of using a combination of gel chromatography and neutron activation analysis to identify metal–protein complexes in biological fluids, such as human serum. If the gel column is calibrated with "standard" proteins such a technique should also allow an estimation of the Stokes radius of the metallo–protein, thus further characterising the molecule. For these exploratory experiments it was therefore obviously advantageous to study a metal whose distribution in serum was already well known.

One of the most intensively studied protein-bound metals in serum is copper, which also has ideal neutron activation analysis properties (^{63}Cu is 70% abundant and has a 4.5-barn thermal-neutron capture cross-section to produce an isotope with a half life of 12.8 h). The normal serum copper concentration is 0.9–1.5 μg/ml and it is known that most of this ($\sim$90%) is present as ceruloplasmin, a glycoprotein with a molecular weight of approximately 160,000, containing 8 copper atoms per molecule. Most of the remaining 10% of serum copper is believed to be complexed with albumin. Ceruloplasmin-bound copper does not exchange with free copper and there is considerable evidence to show that incorporation of copper into ceruloplasmin occurs only in liver. Hence it is believed that the albumin merely carries recently ingested copper to the liver, and this is supported by evidence obtained through oral administration of ^{64}Cu. Two hours after ingestion the ^{64}Cu concentration in the plasma reached a maximum and the activity was found bound to serum albumin. After 24 h, virtually all the ^{64}Cu had been incorporated into ceruloplasmin. The physical and biological properties of ceruloplasmin were recently reviewed by SHEINBERG[7].

EXPERIMENTAL

Materials

Bio-Gel P-150 (Bio-Rad Laboratories, Richmond, California) was used for all gel columns. It should be noted that two different batches of Bio-Gel P-150 were used during this work. The first (#37473, 14/6/66) characteristically gave rise to serum protein chromatograms similar to those in Fig. 1 and Fig. 3, while the chromatograms produced by the second batch (#44613, 13/1/67) were as in Fig. 2. The flow rates of columns packed with gel from batch 44613 were significantly greater than those prepared from the older material whose properties appeared to be more those of Bio-Gel P-200 than P-150.

Analytical-grade reagents were used throughout and dissolved in deionised water. An exception was the eluting buffer (0.15 *M* ammonium acetate solution, pH 6.9) used in runs for subsequent neutron activation analysis. This solution was prepared from "Aristar" ultrapure ammonium hydroxide solution and "Aristar" acetic acid (B. D. H. Ltd.) diluted with deionised water, and stored in a polyethylene bottle.

All quartz ware used in activation analysis runs was washed in hot concentrated nitric acid for 24 h and rinsed thoroughly in deionised water before use.

Instrumentation

During a fractionation run the protein content of the eluate was monitored with an LKB Uvicord absorptiometer, and the effluent fractions were collected on an LKB Ultra-Rac fraction collector.

Irradiation of samples was carries out in the McMaster Reactor at a flux of $\sim 2 \cdot 10^{13}$ n/cm^2/sec.

The ^{64}Cu activity of each fraction after irradiation was measured either by γ-spectroscopy without prior chemical separation, with a Ge(Li) detector and a Nuclear Data 1024-channel pulse-height analyser, or by scintillation counting on a 3 × 3 in NaI(Tl) crystal and a Nuclear Data 256-channel analyser, following chemical separation.

Column preparation

Two cases may be distinguished here. The first involves the preparation of columms for the fractionation of serum containing biosynthesized ^{64}Cu-ceruloplasmin. In this case the gel was soaked in the 0.15 M ammonium acetate eluting buffer for 48 h and was then poured as a slurry into a glass column. After settling by gravity alone the gel bed was stabilised by washing with at least 10 column-volumes of eluting buffer.

The second method of column preparation was used for experiments in which the fractionated protein was to be subjected to neutron activation analysis. In this case, the column must be thoroughly cleansed of any impurities which might interfere in the analysis. This was achieved by swelling the dry gel in 0.1 M ammonium EDTA solution for 48 h before packing as above in a siliconised quartz column. After settling by gravity, the gel bed was washed with two column-volumes of 0.01 M sodium cyanide solution in 0.15 M ammonium acetate solution followed by washing with at least ten column-volumes of "ultra-pure" 0.15 M ammonium acetate solution. This solution was added from a quartz reservoir, to the column, through a Chelex-100 bed at a flow rate of approximately 10 ml/h for a column of 50 × 2.6 cm. After 3 column-volumes of the solution had passed through, the eluate was found to be free of sodium as indicated by a flame test.

Sample preparation and fractionation

For tracer experiments to test the feasibility of the technique, rats were injected with ^{64}Cu solutions. After 24 h, blood samples were taken, allowed to coagulate for 4 h and centrifuged to obtain serum.

For neutron activation analysis it was imperative that contamination of the sample be avoided. Consequently, the following procedure was adopted: a polyethylene cannula was inserted *ca.* 15 cm into the forearm vein of an adult male through an "Intracath" assembly. The needle was withdrawn, the cannula being left in place. Blood was allowed to drain through the cannula and the first 10 ml were rejected to allow adequate flushing of the system. Approximately 50 ml were then collected in quartz centrifuge tubes. This blood was maintained at 37° for 4 h, and then centrifuged at a slow speed to prepare serum. No evidence of hemolysis was observed.

The fractionation was carried out by allowing the buffer above the gel bed to run through until the surface was "dry". The serum sample (0.5–2 ml) was then applied to the surface with a quartz pipette. The serum was allowed to soak into the gel, and washed in further with two small portions (*ca.* 0.5 ml) of the buffer. The reservoir containing the "Aristar" ammonium acetate solution and the Chelex-100 was then attached to the top of the column and the elution proceeded in a normal manner.

Eluate fractions containing protein (monitored by UV absorption at 254 nm) for irradiation were collected in quartz capsules and frozen immediately in liquid air, in order to eliminate any interactions with the quartz. After freeze-drying, the samples were irradiated. Various irradiation times were used ranging from 2.5 h in oner un through to saturation in another.

Post-irradiation treatment

After a suitable cooling period the capsules were leached out with hot nitric acid containing copper carrier. The activity in this leach solution was counted directly when solid-state counting was used.

For scintillation counting, the leach from the capsule was added to concentrated sulfuric acid and boiled down to the evolution of fumes of sulfur trioxide. After cooling and neutralisation with concentrated ammonia solution, the copper, together with other metals, was absorbed onto Chelex-100. This step removed nearly all sodium contamination. The metals were washed off the chelating resin with dilute sulfuric acid solution and copper was extracted from the resulting aqueous solution at pH 2 as the cupferrate[8], which allows a separation of the copper from the other activities present in the original irradiated sample (mainly ^{24}Na, ^{82}Br, ^{56}Mn and ^{69}Zn). This procedure gives a chemical yield of *ca.* 95%.

Preliminary experiments with empty quartz irradiation capsules indicated that a comparatively small amount of copper activity was leached out of the quartz, but by carrying out the above procedure on samples of eluate collected just before the beginning of protein elution from the gel column, a blank for the whole determination was obtained. For a typical run this was found to be *ca.* 3 ng Cu/fraction, or if the copper content of 2 ml of serum was determined over 30 fractions, approximately 3% of the total copper. Small pieces of an aluminium–copper alloy (3.7% Cu) were used as irradiation standards.

RESULTS AND DISCUSSION

Tracer studies

Tracer experiments showed that the proposed method for the detection of metal–protein complexes was feasible. Figure 1 shows a plot of ^{64}Cu activity found in relation to the protein chromatogram. The three peaks in the protein distribution have been assigned by PORATH[9] as follows. The first peak contains the high-molecular-weight components of serum (α- and β-lipoprotein and α- and β-globulin), the centre peak 7S γ-globulin and the third peak albumin. Although the molecular weight of

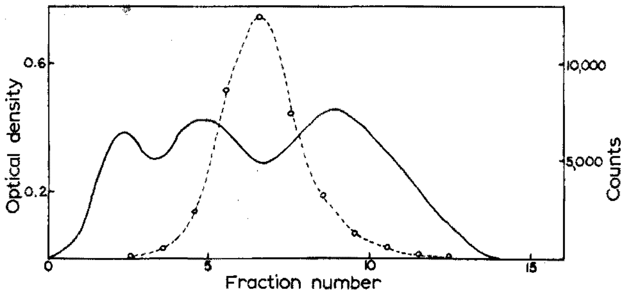

Fig. 1. Protein (solid line) and ^{64}Cu (broken line) distribution after fractionation of ^{64}Cu *in vivo* labelled rat serum on Bio-Gel P-150. Blood sample taken 24 h after administration of ^{64}Cu. 0.4 ml of serum applied to column 27 × 1.6 cm. Fraction size 2 ml. O.D. measured at 254 nm.

ceruloplasmin is known to be *ca.* 160,000, it can be seen that the copper activity peak occurs in a position corresponding to a molecular size considerably less than that of γ-globulin (mol. wt. ~150,000). However the ceruloplasmin molecule has an axial ratio of 11[7], and the apparent low molecular weight indicated by gel chromatography can be attributed to this asymmetry. KILLANDER[10] in the course of *in vitro* experiments involving the addition of ceruloplasmin to serum, observed the same relative positioning of the ceruloplasmin peak with respect to the γ-globulin and albumin peaks, after gel chromatography on Sephadex G-200.

No sign of ^{64}Cu activity was found in the albumin region, indicating that all of the injected copper had been incorporated into ceruloplasmin. An important feature of the preliminary experiments was the almost Gaussian-shaped activity elution curve. Such curves were observed even when the protein chromatogram was grossly distorted by overloading of the column, and this provided evidence that even when rather amorphous chromatograms are obtained the elution of an individual protein is essentially unaffected.

Activation analysis experiments

Figure 2 shows the protein elution curve for a typical human serum fractionation, together with the copper concentration in each fraction as determined by neutron activation analysis. Over 90% of the copper is contained in a single peak positioned between the γ-globulin and albumin peaks. Based upon evidence from the tracer work with ^{64}Cu, this peak is attributed to the ceruloplasmin content of the serum. A shoulder was found on the lower molecular size side of the ceruloplasmin peak in all four of the activation analysis runs carried out. This small quantity of copper (<10% of the total) occurs in the same position as the albumin in the protein chromatogram, and therefore presumably represents the albumin-bound copper.

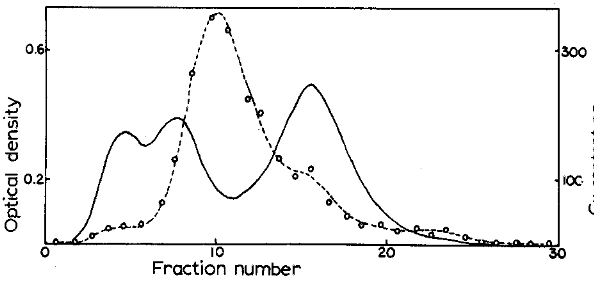

Fig. 2. Protein (solid line) and copper (broken line) distributions after fractionation of 2 ml of human serum on Bio-Gel P-150. Column 45 × 2.6 cm. Fraction size 2.5 ml. O.D. measured at 254 nm.

A smaller peak is visible before the main copper peak and this is probably due to contamination picked up during the gel chromatographic separation. Other work in this laboratory[11] has shown that fractionation of serum after *in vitro* addition of ^{64}Cu results in >99% of the activity being found in the albumin region of the protein chromatogram, but a small quantity of ^{64}Cu is found at the high molecular size end of the protein elution. In an early activation analysis run (Fig. 3), a copper peak comparable in size to the ceruloplasmin peak was observed at the beginning of the protein elution. A mass balance for copper indicated that this peak was due to contamination. Since the peak had the characteristic shape produced by gel chromatography of a single protein, and covered several fractions, the eluate must have been contaminated before the fraction collection stage of the procedure. However, the contamination must have occurred after application of the sample to the chromatographic column as there was virtually no enhancement of the albumin-bound copper peak. Consequently, the only explanation for this effect is the "scavenging" of traces of copper from the column by a high-molecular-weight protein in the serum. In subsequent work, a cyanide washing step was introduced during the column preparation to remove residual copper, and this appears to have the desired effect in almost eliminating this peak (see Fig. 2). Despite this argument the possibility that the first shoulder in Fig. 2 represents a high-molecular-weight copper–protein complex existing *in vivo* cannot be discounted.

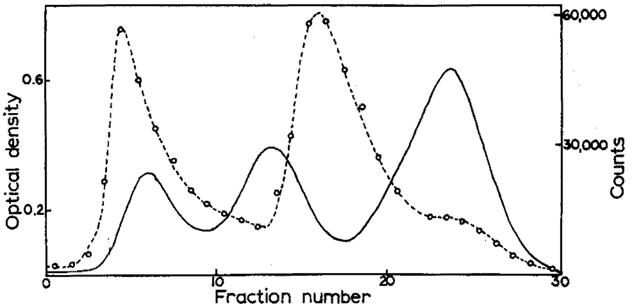

Fig. 3. Protein (solid line) and copper (broken line) distributions after fractionation of 2.5 ml of human serum on Bio-Gel P-150. Column 45 × 2.6 cm. Fraction size 2.5 ml. O.D. measured at 254 nm. Relative copper quantities determined by NAA and expressed as normalised counts/min. N.B. The high-molecular-weight copper peak is apparently due to contamination.

Apart from the sample "blanks" (experimental section) the possibility of the production of ^{64}Cu by any reaction other than ^{63}Cu(n,γ)^{64}Cu must be considered. The most likely other contributory process would be ^{64}Zn(n,p)^{64}Cu, and although preliminary experiments similar to those reported have shown that some zinc is bound in the albumin region of the protein chromatogram, the quantities found and the low cross-section for the (n,p) reaction make any such contribution to the ^{64}Cu activity negligible.

From the results reported here it is apparent that gel chromatography of a serum sample followed by neutron activation analysis, provides a simple and sensitive method for the detection and size identification of metal protein complexes. When such experiments are carried out in conjunction with *in vitro* labelling experiments the biosynthesised metallo–proteins are readily distinguished from complexes resulting from *in vitro* contamination of the sample. Obviously the method can be applied only to those elements which have favorable nuclear properties and are also protein-bound in quantities great anough to allow their detection. Some elements which could be well suited to such studies include zinc (although the best analytical technique here might be atomic absorption spectroscopy), manganese, aluminium, silver, gold and such non-metals as arsenic and bromine.

The authors wish to acknowledge the advice and valuable assistance given by Dr. N. Aspin, Hospital for Sick Children, Toronto, in arranging the preliminary *in vivo* labelling experiments, and by Dr. R. Kinlough, Department of Pathology, McMaster University, in performing the blood sampling for neutron activation analysis experiments.

Financial assistance from the National Research Council of Canada is also gratefully acknowledged.

SUMMARY

A method for the identification of protein–metal complexes in biological fluids by a combination of gel chromatography and neutron activation analysis is proposed. The distribution of protein-bound copper in human serum is studied as an example of the method.

RÉSUMÉ

On propose une méthode d'identification de complexes métal-protéines dans les liquides biologiques, par chromatographie sur gel et activation neutronique. Le partage du cuivre-protéine dans le sérum humain est choisi comme exemple.

ZUSAMMENFASSUNG

Es wird eine Methode zur Identifizierung von Protein–Metall-Komplexen in biologischen Flüssigkeiten vorgeschlagen, bei der die Gel-Chromatographie mit der Neutronenaktivierungsanalyse kombiniert wird. Als ein Beispiel dieser Methode wird die Verteilung von proteingebundenem Kupfer im menschlichen Serum untersucht.

REFERENCES

1 H. J. M. Bowen, *Trace Elements in Biochemistry*, Academic Press, London and New York, 1966.
2 S. R. Himmelhoch, H. A. Sober, B. L. Vallee, E. A. Peterson and K. Fuwa, *Biochemistry*, 5 (1966) 2523.
3 H. Sklavenitis and D. Comar, *I.A.E.A. Symposium on Nuclear Activation Techniques in the Life Sciences*, paper SM91/45, 1967.
4 C. W. Tang and R. H. Tomlinson, *I.A.E.A. Symposium on Nuclear Activation Techniques in the Life Sciences*, paper SM91/42, 1967.
5 K. Fritze and R. Robertson, *J. Radioanal. Chem.*, in press.
6 H. Determann, *Gel Chromatography*, Springer Verlag, Berlin, 1967.
7 I. H. Scheinberg, in J. Preisach, P. Aisen and W. E. Blumberg, *The Biochemistry of Copper*, Academic Press, London and New York, 1966.
8 N. H. Furman, W. B. Mason and J. S. Pekola, *Anal. Chem.*, 21 (1949) 1325.
9 J. Porath, in *Advances in Protein Chemistry*, Vol. 17, Academic Press, New York, 1962.
10 J. Killander, *Biochim. Biophys. Acta*, 93 (1964) 1.
11 K. Fritze and R. Gietz, *J. Radioanal. Chem.*, 1 (1968) 265.

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APPLICATION OF A BETATRON IN PHOTONUCLEAR ACTIVATION ANALYSIS

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(Received July 1st, 1968)

An extensive study of the determination of a large number of elements by means of photonuclear activation analysis has recently been carried out by ANDERSEN *et al.*[1].

With bremsstrahlung from a linear accelerator MULVEY *et al.*[2] analysed iodine in blood, and COOPER *et al.*[3] observed this element in thyroidea. They determined iodine by means of the nuclide ^{126}I with the half-life of 12.8 days, which is formed through the reaction $^{127}\mathrm{I}(\gamma,\mathrm{n})^{126}\mathrm{I}$. The application of photonuclear activation methods in rock analysis has been discussed by SULIN[4]. BASILE *et al.*[5] utilized a betatron in the determination of oxygen in various materials.

In the present study a betatron of common type was used as the irradiation facility. This machine yields a lower photon-flux density than a linear accelerator, and the detection limit for various elements is consequently lowered. However, the possibility of accomplishing the activation procedure is facilitated, inasmuch as a betatron is commonly located in large cities. Moreover, this machine has a great flexibility with regard to beam direction, which might be important in future studies of *in vivo* activation analysis. This technique has recently attracted great interest, and has been accomplished with thermal neutrons from a reactor[6-8] as well as with 14-MeV neutrons from a generator[9,10].

When the bremsstrahlung activation technique is used, certain disadvantages associated with *in vivo* neutron activation analysis, such as neutron attenuation and thermalization effects, are avoided.

For a great number of nuclides, the photonuclear reactions, achieved through (γ,n), $(\gamma,2\mathrm{n})$, (γ,p) and (γ,np) processes, exhibit resonances in cross-section behaviour in the energy region of *ca.* 12–25 MeV[11-14]. With the betatron suitable energy levels may easily be selected.

Photonuclear activation of samples of biological character yields several positron emitters from the macro element constituents, *e.g.* ^{11}C, ^{13}N, ^{15}O, ^{30}P and ^{31}S. In this sequence ^{11}C possesses the longest half-life (about 20 min). Consequently, such samples should be allowed to decay for some hours when longer-lived nuclides originating from trace quantities in the sample are desired to be determined.

The present study concerns the determination of iodine in pharmaceuticals as well as an investigation of the sensitivity for fluorine, lead and mercury. The determination of fluorine in small quantities is of interest in odontology, whereas determinations of lead and mercury are important in connection with pollution studies of air, water and food.

EXPERIMENTAL

Apparatus

A 35-MeV betatron constructed for medical purposes (Brown Boveri "Asklepitron 35") was used as the irradiation facility. This accelerator produces electrons of 35-MeV maximum energy at a current of about 1 μA. The electrons hit a platinum target (1.5 × 1.5 × 0.5 mm) and produce bremsstrahlung photons distributed in energy up to the electron energy; 32-MeV bremsstrahlung was used in the present study.

The bremsstrahlung is strongly peaked in the forward direction. Figure 1 shows the relative number of photons above 18.7 MeV per unit solid angle *versus* photon angle. The determination was made by means of the $^{12}C(\gamma,n)^{11}C$ reaction.

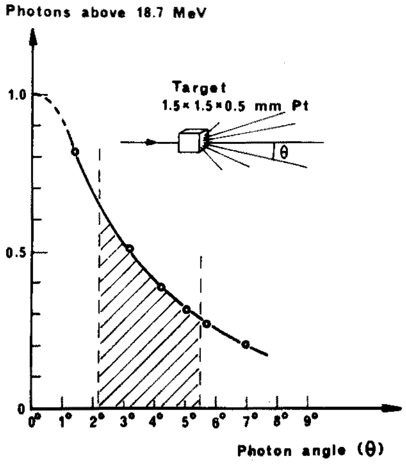

Fig. 1. Relative number of photons above 18.7 MeV per unit solid angle *versus* photon angle (forward direction).

In order to obtain a uniform irradiation of several samples it was necessary to rotate the samples during the irradiation procedure. Two rotating sample holder devices made of plexiglas were used in this investigation. One type contained positions for six 2.5-ml samples, and the other positions for ten 0.2-ml samples. In each case one of the samples constituted the standard. The samples were rotated at a velocity of one revolution per minute by a synchronous motor and were irradiated in the shaded field in Fig. 1 for 90 min (3 periods of 30 min, interrupted by 2 periods of 30 min each).

Figure 2 shows the experimental arrangement. The samples were placed as near the target as possible in order to obtain the maximal photon-flux density in the irradiation position. The distance between the target and the middle of the samples was 260 mm. The distance between the central line of the photon beam and the middle of the samples was 18 mm (*cf.* Figs. 1 and 2).

Determination of the photon-flux density

The photon-flux density in the irradiation position was determined by means of the $^{12}C(\gamma,n)^{11}C$ reaction in polystyrene discs. The induced ^{11}C activity was determined by comparing the counting rate in the annihilation peak from the polystyrene disc with a ^{22}Na standard source.

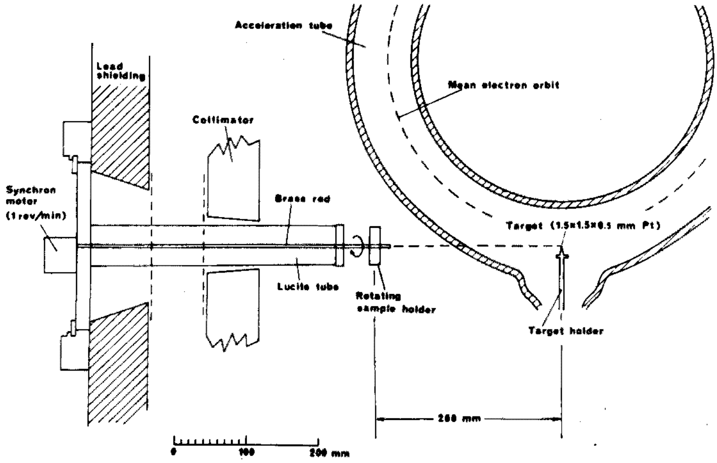

Fig. 2. The irradiation facility.

The ^{11}C activity (A) at the end of the irradiation of the polystyrene disc can be written as:

$$A = N\{1-\exp(-\lambda t_i)\}\int_{\text{th}}^{E_{\max}} \sigma(E)\,\phi(E)\,\mathrm{d}E \tag{1}$$

where N = number of nuclei,
$\sigma(E)$ = cross-section (cm^2) for the (γ,n) reaction at the photon energy E,
$\phi(E)$ = photon-flux density (cm^{-2}, sec^{-1}) at the photon energy E, per energy interval
t_i = irradiation time (sec),
λ = decay constant for ^{11}C (sec^{-1}).

The value of the integral in eqn (1) was determined experimentally. $\sigma(E)$ is well known in the energy region used[15]. The form of the bremsstrahlung spectrum as calculated by PENFOLD AND LEISS[16] was applied in the integration process. The flux density in the various energy intervals was determined with consideration of the shape of the theoretical bremsstrahlung spectrum[16] (Table I).

The photon flux density in the irradiation position can be increased by a factor of about two if the samples are placed very close to the central line of the photon beam (see Fig. 1). This can be done if only a few, small samples are irradiated. Other means of increasing the photon-flux density would be to use a bigger target or to irradiate the samples inside the acceleration tube[17]. Such modifications were difficult to achieve in this work, because the accelerator was in regular demand for other purposes with special requirements.

TABLE I

PHOTON FLUX DENSITY IN THE IRRADIATION POSITION

(32 MeV bremsstrahlung)

Photon energy (MeV)	*Photons/cm²/sec*	*Photon energy (MeV)*	*Photons/cm²/sec*
≥ 2	$1.8 \cdot 10^{10}$	≥ 18	$0.67 \cdot 10^{10}$
≥ 4	$1.7 \cdot 10^{10}$	≥ 20	$0.55 \cdot 10^{10}$
≥ 6	$1.5 \cdot 10^{10}$	≥ 22	$0.45 \cdot 10^{10}$
≥ 8	$1.3 \cdot 10^{10}$	≥ 24	$0.34 \cdot 10^{10}$
≥ 10	$1.2 \cdot 10^{10}$	≥ 26	$0.24 \cdot 10^{10}$
≥ 12	$1.1 \cdot 10^{10}$	≥ 28	$0.14 \cdot 10^{10}$
≥ 14	$0.92 \cdot 10^{10}$	≥ 30	$0.06 \cdot 10^{10}$
≥ 16	$0.79 \cdot 10^{10}$		

Temperature stability

The temperature stability in the irradiation position was determined by means of a thermocouple. The temperature increase was found to be less than 1° per 30-min irradiation time.

Measurements

The activity measurements were carried out by γ-ray spectrometry with a $3'' \times 3''$ well-type NaI(Tl) crystal connected to a Nuclear Data 128-channel pulse-height analyser.

Samples

The samples contained iodine in plasma solution at a concentration of (9.31 ± 0.21)mg/g according to the manufacturer (Pharmacia AB, Uppsala).

RESULTS AND DISCUSSION

With the present irradiation facility a detection limit of 50 μg was obtained for iodine; this may be of practical interest in pharmacy. This detection limit was obtained on irradiation of a pure compound containing iodine.

In the investigation of the iodine content of the samples, $(9.80 \pm 0.29^{*})$ mg iodine/g was obtained, which is essentially in agreement with the value reported by the manufacturer, as obtained by potentiometric titration.

The detection limits for the other elements studied, fluorine, lead and mercury, are given in Table II. The values given are based on an irradiation time of 90 min of pure compounds of these elements, measurement of the induced activity with a $3'' \times 3''$ well-type NaI(Tl) crystal and a counting time of 100 min.

The detection limit for fluorine, amounting to 3 μg, reveals the possibility of determining this element in teeth by means of the betatron. In analysis of materials containing sodium, the reaction ^{23}Na(γ,nα)^{18}F interferes with the fluorine determination. This reaction possesses an apparent threshold at 23 MeV[18]. If the activation process is done with 22-MeV bremsstrahlung this interference can be avoided[18].

The betatron could also be used for the determination of mercury in various biological materials. It is known that this element is accumulated in fish tissue, and

---

* Standard deviation of the single value.

TABLE II

DETECTION LIMIT FOR FLUORINE, IODINE, MERCURY AND LEAD

Element	*Photo-activation product*		*Photon energy measured (MeV)*	*Counts in full energy peak*[a] *(counts/min/g of element)*	*Detection limit*[b,c] *(μg)*
	Nuclide	*Half life*			
F	^{18}F	109.8 min	0.511 (194%)	$0.75 \cdot 10^6$	3
I	^{126}I	12.8 d	0.386 (34%)	$0.26 \cdot 10^5$	50
			0.667 (33%)	$0.14 \cdot 10^5$	100
Hg	^{197}Hg	65 h	0.077 (18%)	$0.37 \cdot 10^5$	50
	^{199m}Hg	43 min	0.158 (53%)	$0.22 \cdot 10^6$	15
Pb	^{203}Pb	52.1 h	0.279 (81%)	$0.89 \cdot 10^4$	400
	^{204m}Pb	67.2 min	0.375 (93%)	$0.40 \cdot 10^4$	800

[a] At the end of the irradiation.
[b] Mass of the stable element, which after the irradiation procedure increases the reading of the detector by an amount equal to 3 times the standard deviation of the background recorded in that time.
[c] Counting time 100 min.

in certain polluted waters, the mercury content of such tissues might amount to an order of 1 μg/g. However, analysis of this kind is more favourably accomplished by the common thermal neutron activation technique[19].

It does not seem possible to make a successful analysis of lead with the betatron.

The pharmaceutical samples were kindly provided by Pharmacia AB, Uppsala.

SUMMARY

The present study concerns the determination of fluorine, iodine, lead and mercury by means of the photonuclear activation technique with a betatron. The detection limits obtained for the elements in the above sequence were 3, 50, 400 and 15 μg respectively. The technique has been applied in the determination of iodine in pharmaceuticals. A rotating sample holder device was inserted in the bremsstrahlung beam of the betatron in order to ensure uniform irradiation of the samples.

RÉSUMÉ

Une étude est effectuée sur le dosage du fluor, de l'iode, du plomb et du mercure à l'aide d'une technique photonucléaire par activation, utilisant un bétatron. Les sensibilités obtenues pour les éléments ci-dessus sont respectivement 3, 50, 400 et 15 μg. Ce procédé est appliqué au dosage de l'iode dans des produits pharmaceutiques. Un dispositif rotatif est proposé pour assurer une irradiation uniforme des échantillons.

ZUSAMMENFASSUNG

Die vorliegende Untersuchung beschäftigt sich mit der Bestimmung von Fluor, Jod, Blei und Quecksilber mittels einer photonuklearen Aktivierung durch

ein Betatron. Die Empfindlichkeiten betrugen 3, 50, 400 bzw. 15 µg. Die Technik wurde bei der Bestimmung von Jod in Pharmazeutika angewandt. Um eine gleichmässige Bestrahlung zu erzielen, wurde die Probe auf einem rotierenden Präparathalter der Bremsstrahlung ausgesetzt.

REFERENCES

1 G. H. ANDERSEN, F. M. GRABER, V. P. GUINN, H. R. LUKENS AND D. M. SETTLE, *Nuclear Activation Techniques in the Life Sciences*, Proc. Symp. Amsterdam, 8–12 May 1967, Vienna, 1967, p. 99.
2 P. F. MULVEY, JR., J. A. CARDARELLI, M. ZOUKIS, R. D. COOPER AND B. A. BURROWS, *J. Nucl. Med.*, 7 (1966) 603.
3 R. D. COOPER, D. M. LINEKIN AND G. L. BROWNELL, *Nuclear Activation Techniques in the Life Sciences*, Proc. Symp. Amsterdam, 8–12 May 1967, Vienna, 1967, p. 65.
4 V. V. SULIN, *Soviet Advances in Nuclear Geophysics*, Consultants Bureau, New York, 1965, p. 129.
5 R. BASILE, J. HURÉ, P. LÉVÊQUE AND C. SCHUHL, *Compt. Rend.*, 239 (1954) 422.
6 J. ANDERSON, S. B. OSBORN, R. W. S. TOMLINSON, D. NEWTON, J. RUNDO, L. SALMON AND J. W. SMITH, *Lancet*, 2 (1964) 1201.
7 K. BODDY AND W. D. ALEXANDER, *Nuclear Activation Techniques in the Life Sciences*, Proc. Symp. Amsterdam, 8–12 May 1967, Vienna, 1967, p. 583.
8 J. M. A. LENIHAN, D. COMAR, R. RIVIERE AND C. KELLERSHOHN, *Nature*, 214 (1967) 1221.
9 C. K. BATTYE, R. W. S. TOMLINSON, J. ANDERSON AND S. B. OSBORN, *Nuclear Activation Techniques in the Life Sciences*, Proc. Symp. Amsterdam, 8–12 May 1967, Vienna, 1967, p. 573.
10 H. E. PALMER, W. B. NELP, R. MURANO AND C. RICH, *Phys. Med. Biol.*, 13 (1968) 269.
11 R. MONTALBETTI, L. KATZ AND J. GOLDEMBERG, *Phys. Rev.*, 91 (1953) 659.
12 R. L. BRAMBLETT, J. T. CALDWELL, B. L. BERMAN, R. R. HARVEY AND S. C. FULTZ, *Phys. Rev.*, 148 (1966) 1198.
13 D. O. HUNT, A. BRYNJOLFSSON AND R. D. COOPER, *Handbook of Photonuclear Reactions*, U.S. Army Natick Labs., Natick, Mass., Dec. 1963, (FD-1) (AD-428207).
14 I. C. NASCIMENTO, G. MOSCATI AND J. GOLDEMBERG, *Nucl. Phys.*, 22 (1961) 484.
15 W. C. BARBER, W. D. GEORGE AND D. D. REAGAN, *Phys. Rev.*, 98 (1955) 73.
16 O. W. BOCDANKEVICH AND F. A. NIKOLAEV, *Methods in Bremsstrahlung Research*, Academic Press, New York, 1966, p. 24.
17 L. V. CHEPAL, I. VITING AND B. A. CHAPYZNIKOV, *Pribory i Tekhn. Eksperim.*, 2 (1962) 23.
18 P. WILKNISS AND V. J. LINNENBOOM, *Proc. of the 2nd Conf. on Practical Aspects of Activation Analysis with Charged Particles*, Liege (Belgium), Sept. 21–22, 1967, p. 147.
19 D. BRUNE, *Acta Chem. Scand.*, 20 (1966) 1200.

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ASPECTS OF LOW-TEMPERATURE IRRADIATION IN NEUTRON ACTIVATION ANALYSIS

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Neutron, photon or charged particle activation of aqueous samples or biological tissues at low temperature offers various advantages in analysis. Thus, elemental losses from vaporization effects as well as contamination of the sample from the container surfaces can be eliminated[1]. This technique has proved favourable in a study of the normal distribution of mercury in human whole blood[2] and in the determination of various elements in water[3,4].

The present study concerns the determination of iodine in pharmaceutical solutions in the micro-to-milligram range, and the determination of mercury in fish and rainwater at the nano- to microgram level. The low-temperature irradiation technique is in this case adequate for an accurate analysis inasmuch as iodine is easily vaporizable, especially from acidic solutions. Iodine is also adsorbed to plastic containers. Vaporization effects of mercury are strongly pronounced for water solutions and seem to be dependent on the water quality[2].

In analyses of this kind, a large number of determinations are usually carried out simultaneously, which necessitates the irradiation of many samples in one operation. As regards neutron activation of several aqueous or tissue samples close together, mutual flux perturbation effects may occur, giving rise to heterogenous activation. Such disturbances can, however, be corrected for[4]. Similarly, a large aqueous or tissue sample gives rise to flux disturbances[4].

If a special geometrical arrangement is used during the multiple sample irradiation process, as here described, the mutual flux perturbation effect can be eliminated.

THE EFFECT OF NEUTRON TEMPERATURE ON THE ACTIVATION PROCESS

Neutron activation processes are generally carried out at neutron temperatures around 50°, whereas in the present study the activation process has been achieved at a temperature about 100° lower.

It is well known that the neutron flux as well as the absorption cross-section varies with the neutron temperature.

For a $1/v$ absorber (*e.g.* ^{127}I, ^{202}Hg) the absorption cross-section temperature dependence is given by the following relation:

$$\sigma_a = \sigma_0 (T_0/T)^{\frac{1}{2}} \tag{1}$$

where σ_a denotes the absorption cross-section at temperature T, and σ_0 the absorption cross-section at the temperature T_0 corresponding to a neutron velocity of 2200 m/sec. A temperature decrease of 100° corresponds to an increase of about 12% in the absorption cross-section value.

The activation rate, R, is proportional to the expression

$$R \sim \int \phi(E)\sigma_a(E)\mathrm{d}E \tag{2}$$

where $\phi(E)$ expresses the neutron flux per energy unit.

Considering the case of activation of a $1/v$ absorber, and assuming that the sample does not change the total neutron density, we then have

$$\sigma_a(E) = \sigma_0 v_0/v \tag{3}$$

$$\phi(E) = vn(E) \tag{4}$$

$$R \sim \int vn(E)\sigma_0(v_0/v)\mathrm{d}E = \int n(E)\sigma_0 v_0 \mathrm{d}E \tag{5}$$

$$\int n(E)\mathrm{d}E = n_{\mathrm{tot}} \tag{6}$$

$$R \sim \sigma_0 v_0 n_{\mathrm{tot}} \tag{7}$$

where v is equal to the neutron velocity ($v_0 = 2200$ m/sec), $n(E)$ expresses the neutron density per energy unit and n_{tot} denotes the total neutron density.

Thus the activation rate is proportional to the total neutron density and independent of the neutron temperature. In practical activation analytical work a flux monitor is sometimes used in order to facilitate the quantitative evaluations. With a monitor possessing a $1/v$-dependent activation cross-section, *e.g.* copper or cobalt, for which the above treatment is valid, the activation rate will be independent of the temperature.

However, in the determination of an element possessing resonances in the thermal region or very close to it, *e.g.* indium, the activation rate would vary with the neutron temperature. If a $1/v$ monitor is used in such cases instead of a standard, corrections for the temperature effect must be introduced.

The above discussion of the temperature effect also applies to rather complicated irradiation sample arrangements like that used in the present study, assuming the flux perturbation effects to be equal in samples, standard or monitor.

EXPERIMENTAL

Determination of the iodine

Iodine in pharmaceutical plasma solutions (containing 0.9% sodium chloride) in the concentration range 50 μg–50 mg/ml was determined in 0.5-ml samples. A sample arrangement for the simultaneous irradiation of sixty 0.5-ml samples is shown in Fig. 1. The holder is made of aluminium. The samples were solidified* in a deep-freeze refrigerator before being inserted in the cooling device for irradiation. In one series equal amounts of iodine (0.5 mg) were added to sixty 0.5-ml samples in order to investigate the mutual flux perturbation effect. In the irradiation position used, the thermal flux gradient was less than 0.5% per cm.

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* The solidification may also be carried out advantageously by freezing the samples in liquid nitrogen. However, this technique needs special care in order to avoid cracking of the containers.

The analyses were completed by γ-spectrometry by means of the nuclide ^{128}I, which was measured directly in the solution without prior chemical separations.

Determination of mercury

Aqueous samples such as rainwater, etc. (1–100 ml) or fish samples (pike) of 1–10 g contained in polyethylene bottles were solidified, like the aqueous iodine samples, in a deep-freeze refrigerator before being irradiated in the cooling device.

After the activation process the fish tissue was destroyed by immersion in concentrated nitric acid (about 20 ml/10 g of fish) and gentle heating for about 20 min in a flask connected to a reflux condenser. About 1 mg of mercury(II) nitrate was added as carrier. The pH of the solution was then adjusted to 1.5–2 by neutralisation with concentrated sodium hydroxide solution. The irradiated aqueous samples were also adjusted to the same pH region by acidification with nitric acid. The mercury activities were then separated from the bulk by means of mercury droplets with an isotopic exchange technique previously described by KIM AND SILVERMAN[5]. This technique has recently been modified[4]. The exchange time used depended on the volume of the solution[4]. The analysis was completed by γ-spectrometry by means of ^{203}Hg.

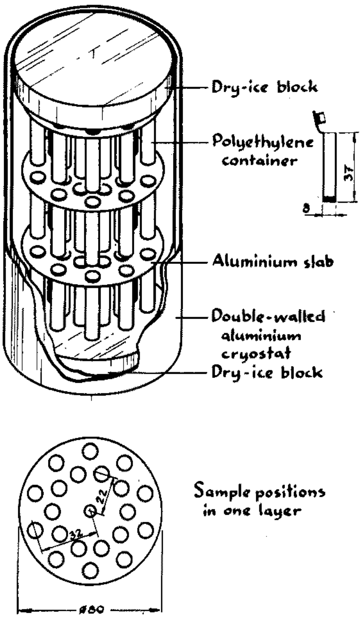

Fig. 1. Arrangement for simultaneous irradiation of 60 samples in 3 layers.

RESULTS AND DISCUSSION

Cooling devices

During these experiments dry ice was used as cooling medium in a doublewalled aluminium cryostat inserted in a central channel of a heavy-water moderated reactor (Rl). Operation of this device is simple and fairly inexpensive.

The irradiation time available is, however, limited inasmuch as continuous replenishment of the dry ice is rather complicated. With the present dry-ice cooling arrangement, temperatures of about $-40°$ were measured in solidified aqueous samples during the irradiation[3].

If the low-temperature irradiation is done with liquid nitrogen, longer irradiation periods can be attained and lower temperatures reached. In this context it may be mentioned that most of the liquid phase in tissues is solidified at or about $-20°$. The complete solidification of animal tissue, however, requires cooling to $\div 65°$ [6]. In the liquid nitrogen cooling devices*, nitrogen of extremely pure quality must be used within the radiation field in order to avoid explosions. Such explosions are assumed to originate from the decomposition of ozone formed from oxygen impurities in the nitrogen cooler[7,8].

With a liquid helium cooling technique, extremely low temperatures can be attained during the irradiation procedure[9-11].

The advantage of carrying out the irradiation of aqueous samples as well as biological tissues while frozen, in order to avoid the high pressures arising in the ampoules from radiolysis, which complicates the opening procedure, has been pointed out previously[1]. It should be mentioned that such pressures can be diminished by cooling the ampoules in liquid nitrogen before opening. This technique has found various applications for samples of biological origin[12,13].

The determinations of iodine and mercury

The geometrical arrangement for low-temperature irradiation of sixty 0.5-ml samples simultaneously is shown in Fig. 1. With this arrangement no mutual flux perturbation effects were observed. Normalized activities (of ^{128}I) in central and peripheral positions in each of 3 layers are given in Table I.

TABLE I

NORMALIZED ACTIVITIES (OF ^{128}I) IN EACH OF THE 3 LAYERS

(The values are mean values of 10 samples with standard deviation of the single value. The samples were geometrically arranged according to Fig. 1)

Layer	*Central position*	*Peripheral position*
Upper	0.97 ± 0.05	1.02 ± 0.05
Middle	0.98 ± 0.05	1.00 ± 0.05
Lower	1.00 ± 0.05	0.98 ± 0.05

It should be borne in mind that a 30-ml water sample which corresponds to the volume of the sixty 0.5-ml samples gives rise to a flux perturbation effect corresponding to an increase of the activity by about 25% in an irradiation position as used at present[4].

Iodine in the concentration range 25 μg–25 mg in the pharmaceutical solutions was determined with standard deviations of a single value of less than 5% without chemical separations.

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* Cooling devices for reactor operation are now commercially available.

As regards the determination of mercury, low-temperature irradiation combined with the fast isotopic exchange technique gave an overall yield of (98 ± 2*) % (for fish tissue or water). In a 70-ml rain-water sample, a mercury content of 0.33 ng/ml was measured. Correction for the flux perturbation effect was carried out by estimation of the flux advantage factor[4]. The mercury content in 3 pike was determined as shown in Table II.

TABLE II

DUPLICATE DETERMINATIONS OF MERCURY IN 3 PIKE

Sample no.	*Hg content in µg/g (wet material)*	
1	0.124	0.126
2	0.138	0.139
3	0.141	0.154

Potential applications of the low-temperature irradiation technique

The low-temperature activation technique seems to be of interest in the assay of various trace elements in enzyme samples. Drying of such samples of the order of 0.2 ml often leaves only a thin film on the container surface. The quantitative removal of the induced activities from this surface may be difficult without thorough rinsing of the container surface. In the determination of copper at the nanogram level in such samples at this laboratory, doubt arose concerning the interpretation of the result inasmuch as about equal copper activities could be extracted from empty quartz containers by rinsing with acids.

Moreover, the irradiation of aqueous samples and wet biological tissues while solidified by freezing finds applications in cases when it is desired that the destruction of the organic molecules in the samples should be minimized. Irradiation under such conditions in a suitable position of a thermal column would strongly suppress the radiation-induced chemical reactions which destroy the organic molecules.

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SUMMARY

Neutron irradiation of the sample while frozen in a cooling device inserted in a reactor channel is described for the determination of iodine in aqueous samples as well as of mercury in biological tissue and water. For the simultaneous irradiation of a large number of aqueous solutions the samples were arranged in a suitable geometry in order to avoid mutual flux perturbation effects. The influence of the neutron temperature on the activation process is discussed. Potential applications of the low-temperature irradiation technique are outlined.

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* Standard deviation of a single value.

RÉSUMÉ

Une étude est effectuée sur l'irradiation neutronique à basse température pour le dosage de l'iode dans des échantillons aqueux, de même que pour le dosage du mercure dans des tissus biologiques et dans l'eau. Lors d'une irradiation simultanée d'un grand nombre de solutions, les échantillons sont arrangés dans un ordre géométrique approprié afin d'éviter l'influence perturbatrice d'un flux mutuel. On examine l'effet de la température neutronique sur le processus d'activation.

ZUSAMMENFASSUNG

Die Bestrahlung von gefrorenen Proben mit Neutronen in einer Kühlanordnung im Reaktorkanal zur Bestimmung von Jod in wässrigen Proben und von Quecksilber in biologischem Gewebe und Wasser wird beschrieben. Zur gleichzeitigen Bestrahlung einer grossen Zahl von wässrigen Lösungen wurden die Proben in einer geeigneten Geometrie angeordnet, um Einflüsse durch gegenseitige Flussstörungen zu vermeiden. Der Einfluss der Neutronentemperatur auf den Aktivierungsprozess wird diskutiert. Mögliche Anwendungen dieser Tieftemperaturbestrahlungstechnik werden angegeben.

REFERENCES

1 D. BRUNE, Inaugural Dissertation, *Svensk. Kem. Tidskr.*, 78 (1966) 336.
2 D. BRUNE, *Acta Chem. Scand.*, 20 (1966) 1200.
3 D. BRUNE AND O. LANDSTRÖM, *Radiochim. Acta*, 5 (1966) 228.
4 D. BRUNE AND K. JIRLOW, *Radiochim. Acta*, 8 (1967) 161.
5 C. K. KIM AND J. SILVERMAN, *Anal. Chem.*, 37 (1965) 1616.
6 M. V. SUSSMAN AND L. CHIN, *Science*, 151 (1966) 324.
7 D. BRADLEY, *AERE-M683*, 1960.
8 P. T. WALKER, *AERE-M823*, 1961.
9 N. RIEHL, W. SCHILLING AND H. MEISSNER, *Research Reactor J.*, 3 No. 1 (1962) 9.
10 R. DOLL, H. MEISSNER, N. RIEHL AND W. SCHILLING, *Z. Angew. Phys.*, 17 (1964) 321.
11 H. MEISSNER, W. SCHILLING AND H. WENZEL, *Euro Nuclear*, 2 (1965) 277.
12 D. COMAR, C. LE POEC, M. JOLY AND C. KELLERSHOHN, *Bull. Soc. Chim. France*, (1962) 56.
13 D. BRUNE, K. SAMSAHL AND P. O. WESTER, *Clin. Chim. Acta*, 13 (1966) 285.

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THE X-RAY FLUORESCENCE MEASUREMENT OF SURFACE URANIUM ON OXIDIZED FUEL ELEMENTS*

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An Fe–25Cr–4Al–1Y alloy has sufficient oxidation resistance in an oxidizing environment to offer potential advantages as cladding material for uranium dioxide nuclear fuels. Preliminary investigations of its usefulness for this purpose indicated a core-clad reaction at elevated temperatures (750° and higher) which resulted in the appearance of a surface layer of uranium oxide[1]. The appearance of uranium oxide on the surface of the clad has been attributed to reduction of uranium dioxide in the core by aluminum metal, followed by diffusion of uranium metal to the clad surface where subsequent oxidation occurs.

A method was needed whereby the amount of uranium on the clad surface could be determined. Furthermore, it was necessary that this method be non-destructive in order to permit an evaluation of the effects of time and temperature on the core-clad reaction. Because of the foregoing, X-ray fluorescence was chosen as the most promising method for this analysis.

The problem involved the quantitative determination of uranium on the clad surface (or very near the surface) of test specimens with two different geometric surfaces: (*1*) a *die* specimen where measurements are made on a flat surface (item 4 in Fig. 1); and (*2*) a capsule specimen where measurements are made on a cylindrical surface (item 5 in Fig. 1).

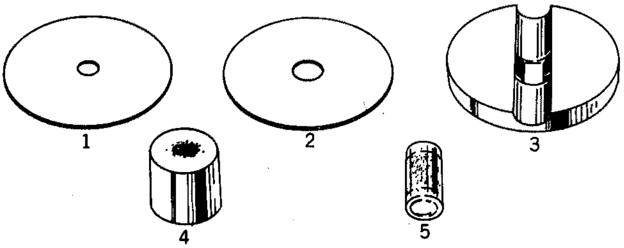

Fig. 1. Two-inch copper masks and test specimens. (Items 1, 2, 3) Masks with apertures of 1/4 in diameter, 3/8 in diam., and 7/16 × 1/4 in, respectively. (Item 4) Flat *die* specimen. The uranium intensity measurement was made on the flat clad surface directly over a 3/8 in diameter core. The clad thickness was 30–40 mils. (Item 5) Cylindrical *capsule* specimen. The uranium intensity measurement was made on the curved surface encapsuling a core 5/8 in in length and 3/8 in in diameter. The clad thickness was 30–40 mils.

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission, Contract AT(40-1)-2847.

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Four flat *die* specimens were available for destructive testing. After removing successive surface layers (1–2 mils) of three of these specimens, it was found that the uranium X-ray fluorescence measurements could be correlated with the amount of uranium remaining on the surface (more accurately, with the amount of uranium found to be within 6 mils of the surface, as this is estimated to be the extent of X-ray penetration in this alloy).

Therefore, a method was available for determining the amount of uranium on flat surfaces. However, this approach could not be taken with the cylindrical *capsule* specimens because lack of symmetry rendered the machining of these specimens impossible.

Electron microprobe examination of both flat *die* and cylindrical *capsule* specimens revealed that all, or nearly all, of the diffused uranium was present near the surface within 25 μ of the outermost edge. Because of the location of the uranium, it appeared that synthetic samples could be prepared by vapor-depositing uranium on Scotch tape. When this tape was backed with a flat piece of Fe–Cr–Al–Y alloy, a substitute for an actual *die* specimen was obtained. When the tape was wrapped around a cylindrical piece of Fe–Cr–Al–Y alloy, a substitute for an actual *capsule* specimen was obtained.

The masks shown in Fig. 1, items 1 and 3, respectively, were used and the X-ray fluorescent intensities of a synthetic sample were measured on the flat and then on the cylindrical surface. The ratio between the two measurements was found to be independent of the amount of uranium deposited on the Scotch tape. Inasmuch as it had been shown that the synthetic sample corresponded to actual specimens with respect to uranium location, it was postulated that this same ratio would exist with actual specimens. Thus a calibration curve for cylindrical *capsule* specimens could be prepared by means of measurements obtained from the synthetic specimens.

The suitability of this approach depended on the following points:

(*1*) that the majority of the uranium on tested specimens was located on the outer surface of the clad;

(*2*) that the distribution or location of uranium on the cylindrical *capsule* specimens was identical to that on the flat *die* specimens. This condition had to exist if experimental findings on flat surfaces were to be extended to curved surfaces;

(*3*) that the uranium X-ray fluorescent intensity *versus* uranium concentration curve for flat synthetic specimens approximated that obtained on the *analyzed die* specimens.

It was found that these requirements were fulfilled. Consequently, a non-destructive method for the determination of surface uranium on tested samples of Fe–Cr–Al–Y clad nuclear fuels containing uranium was developed.

EXPERIMENTAL

Norelco 100-kV constant potential X-ray spectrograph

All uranium intensity measurements were made with a LiF crystal and instrument settings of 90 kV and 25 mA. The scintillation detector was set at 665 V with an amplifier gain of 90%. The L_{α_1} 2θ value[2] was 26.14 with background measurements at 25.59 and 27.24. The uranium intensity was calculated as follows:

$$\mathrm{UL}_{\alpha_1}\ \text{intensity} = (\text{c/s at } 26.14) - [\tfrac{2}{3}(\text{c/s at } 25.59) + \tfrac{1}{3}(\text{c/s at } 27.24)].$$

Counting times were *ca.* 100 sec.

Since the test specimens were of two geometrical configurations, the use of a single copper mask was not feasible. Consequently, three masks, each having a different aperture, were employed. Test specimens and copper masks are shown in Fig. 1.

Fluorophotometer

A fluorimetric procedure, similar to that proposed by GUEST AND ZIMMERMAN[3], was employed to perform "solution" uranium determinations. Briefly, fragments of the clad were dissolved in *aqua regia* and evaporated several times with nitric acid to remove chloride ions. The metal nitrates were dissolved in saturated aluminum nitrate solution and the uranium extracted into a known volume of ethyl acetate. Aliquots of the extract were placed on pellets of 98 wt.% NaF–2 wt.% LiF and fused. The fluorescence of the resulting melt was measured. The ethyl acetate extraction was omitted if the specimen being analyzed was predominately uranium.

Mikros vacuum evaporator

This equipment was used to deposit uranium metal on Scotch tape. To prepare a vapor deposit, a piece of uranium metal was placed on a tungsten filament inside a bell jar. The jar was evacuated and the filament heated to vaporize the uranium. The vaporized uranium, upon leaving the immediate area of the filament, deposited on cooler surfaces. By placing the adhesive side of the Scotch tape facing the filament, a portion of the vaporized uranium adhered to the tape.

RESULTS AND DISCUSSION

Electron microprobe examination

A number of oxidized specimens, both flat *die* and cylindrical *capsule*, were cross-sectioned, and the electron beam of an electron-probe microanalyzer was traversed across the clad (30–40 mils thick). In all cases where the concentration of

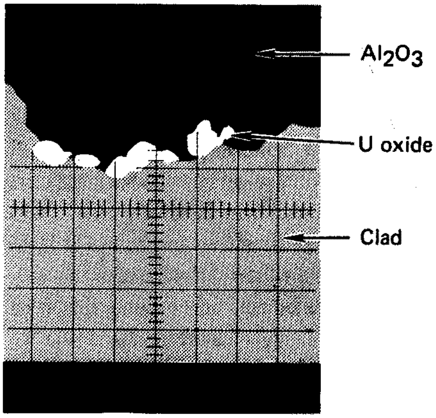

Fig. 2. Electron microprobe back-scattered electron image of clad surface (1780 ×).

TABLE I

URANIUM INTENSITY MEASUREMENTS OF FLAT DIE SPECIMENS AND FLAT SYNTHETIC SPECIMENS[a]

Sample		*Uranium intensity (c/s)*	*U found (μg)*[b]
Die specimen	1	206	23[c]
	2	919	95[c]
	3	2428	234[c]
	4	840	84[c,d]
Vapor deposit	1	64	5.1
	2	246	20
	3	270	23
	4	396	33
	5	425	38
	6	562	48
	7	653	51
	8	790	72
	9	851	74
	10	1159	103

[a] The diameter of the aperture was 0.25 in.

[b] Fluorimetric uranium analyses. All values normalized to an aperture of 0.25 in diameter.

[c] 1/4 in diam. × 6 mils in depth.

[d] Total clad analyzed.

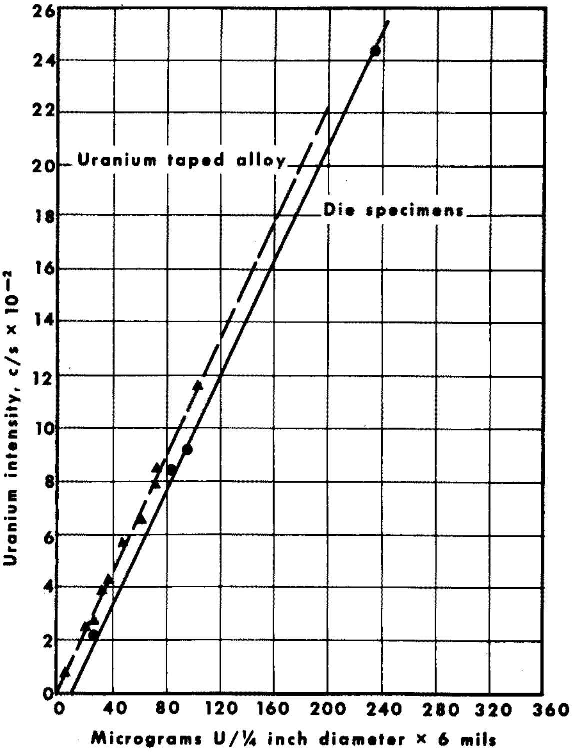

Fig. 3. Concentration–intensity curves of *die* specimens and uranium taped alloy.

diffused uranium in the clad had reached detectable levels (*ca.* 0.1%), uranium was found only on the surface of the clad directly under an aluminum oxide film which measured 1–10 μ in depth. A typical cross-section of the oxidized clad is shown in Fig. 2.

The tendency of the diffused uranium to accumulate on the clad surface suggested the possibility that synthetic specimens could be prepared by vapor-depositing uranium on Scotch tape backed with Fe–Cr–Al–Y alloy[4,5].

Chemical analysis and X-ray fluorescence measurement of die specimens

Four oxidized specimens, exhibiting a considerable spread in uranium intensity when measured on the X-ray emission spectrograph, were chosen for destructive testing in order to prepare a calibration curve. The specimens were chucked for a lathe in aluminum cylinders and rigidly cemented with plastic. The size of the aluminum cylinder was such that it could be fitted into the 2-in X-ray spectrograph sample holder. The purpose of such a mounting was to facilitate removal of the specimen for counting purposes after each pass of the cutting bit, without introducing the problem of repositioning the specimen when returned to the lathe. The clad alloy *not directly over the core* was removed (to a depth of 10 mils) and discarded. Clad fragments cut from the area directly over the core were trapped in the plexiglass container surrounding the bit area. The plexiglass container was fitted with a filter and vacuum connection to prevent loss of the fragments.

Three specimens were turned on the lathe and clad fragments collected at cutting intervals of 1–2 mils. A uranium intensity measurement was made after each cut until a depth of 6 mils had been removed. Further cuts would have exceeded the penetrating depth of the X-ray spectrograph's primary X-rays and consequently were not necessary. Furthermore, no count above background was obtained on any of these specimens after 6 mils had been removed. The fragments from each cut were analyzed by the fluorimetric procedure.

Comparison of the amount of uranium found in the fragments and the uranium intensity measurements indicated the following.

(*a*) Essentially all of the uranium was located within the first 1 mil of clad. This finding confirmed information gathered with the electron-probe microanalyzer.

(*b*) The lower limit of detection was about 10 μg of uranium in a volume measuring 1/4 inch in diameter by 6 mils.

(*c*) This lower limit of detection, combined with the fact that after the removal of 6 mils of clad the specimens gave no measurable count, indicated a maximum "solubility" of 1.7 μg of uranium in a volume measuring 1/4 inch in diameter by 1 mil.

A fourth specimen was analyzed for total uranium in the clad above the core. In this instance, the specimen was not milled, but rather, the entire clad 35 mils thick was isolated and analyzed. In order to compare the surface uranium content in this specimen with the milled specimens, the assumption was made that the clad was saturated with uranium to the extent of 1.7 μg of uranium per 1/4-in diameter by 1 mil (see (*c*) above). Uranium in excess of this amount was assumed to be deposited on the clad surface.

Data obtained on the four analyzed flat *die* specimens and also on synthetic specimens are presented in Table I. These data yield a calibration curve for flat *die* specimens and a curve for flat vapor-deposited uranium specimens as shown in Fig. 3.

It is apparent that the two curves shown differ by about 10 μg for the volume measured. This can be attributed to the fact that actual specimens had some uranium distributed in the clad below the surface, which was not the case with synthetic specimens. Note that the difference between the two curves correlates very closely with the calculated uranium "solubility".

The curves indicate that vapor-deposited uranium on Scotch tape represents a nearly ideal synthetic flat *die* specimen. Since electron-microprobe analysis showed an identical uranium concentration profile for flat *die* and cylindrical *capsule* specimens, it can be assumed that vapor deposits of uranium would also be ideal synthetic cylindrical *capsule* specimens.

Relationship between capsule and die specimens

A calibration curve developed for *die* specimens would not be directly applicable to *capsule* specimens since the curved surface of a capsule specimen would alter uranium intensity measurements if the same mask was employed. Ideally, one would prefer to machine the cylindrical *capsule* specimens in the manner previously described for flat *die* specimens. However, the specimens lack symmetry after fabrication, and no plan could be devised that would insure the removal of cladding of uniform depth around the specimen circumference.

An alternative approach is to use synthetic specimens and derive a relationship between the uranium intensity measurement obtained on the curved surface (aperture 7/16 × 1/4 in) and that obtained on a flat surface (aperture 1/4 in diam.). Table II shows typical values resulting from this approach.

The average count rrtio developed in Table II for synthetic specimens permits uranium intensity values obtained on a curved surface with a 7/16 × 1/4-in aperture to be converted to equivalent flat surface values for a 1/4-in diameter aperture by using the equation:

c/s with 1/4-in diam. aperture = c/s with 7/16 × 1/4-in aperture/1.91

It was postulated above that the same relationship will exist between oxidized flat *die* specimens and oxidized cylindrical *capsule* specimens as exists between the flat and curved surfaces of synthetic specimens. Thus, uranium intensity values obtained on cylindrical *capsule* specimens can be converted to theoretical 0.25-in diameter

TABLE II

URANIUM INTENSITY MEASUREMENTS OF FLAT AND CURVED SURFACED SYNTHETIC SPECIMENS

Tape no.	*Aperture size (diam. inches)*	*Uranium intensity (c/s)*[a]	*Aperture size (diam. inches)*	*Uranium intensity (c/s)*[b]	*Count ratio*[c]
2	0.25	246	7/16 × 1/4	470	1.91
4	0.25	396	7/16 × 1/4	770	1.94
6	0.25	562	7/16 × 1/4	1052	1.87
11	0.25	634	7/16 × 1/4	1201	1.89
12	0.25	771	7/16 × 1/4	1501	1.94
9	0.25	851	7/16 × 1/4	1624	1.90
					Av. 1.91

[a] Flat surface.
[b] Curved surface.
[c] c/s on 1/4-in diam. aperture taken as unity.

aperture intensities for flat surfaces. By means of these theoretical intensity values, uranium concentrations can then be read from the calibration curve for flat *die* specimens shown in Fig. 3.

The desirability of measuring certain flat *die* specimens with a copper mask of 3/8-in diameter aperture necessitated the development of a second uranium intensity count ratio relationship. The development of this ratio is shown in Table III. These data give rise to the following equation:

c/s with 1/4-in diam. aperture = c/s with 3/8-in diam. aperture/2.43

TABLE III

URANIUM INTENSITY MEASUREMENTS OF FLAT SURFACED SYNTHETIC SPECIMENS USING DIFFERENT SIZED APERTURES

Tape no.	*Aperture size (diam. inches)*	*Uranium intensity (c/s)*	*Aperture size (diam. inches)*	*Uranium intensity (c/s)*	*Count ratio*[a]
2	1/4	246	3/8	603	2.45
4	1/4	396	3/8	979	2.47
6	1/4	562	3/8	1374	2.44
7	1/4	653	3/8	1558	2.39
9	1/4	851	3/8	2025	2.38
					Av. 2.43

[a] c/s on 1/4-in diam. aperture taken as unity.

TABLE IV

CALCULATED COUNT RATIOS FOR MASKS OF VARIOUS APERTURE SIZES

Aperture size	*Aperture area (in^2)*	*Effective counting area*[a]	*Count ratio*[b,c]
1/4 in diam.	0.0491	0.03909	1
3/8 in diam.	0.1104	0.09517	2.43
7/16 × 1/4 in diam.	0.1094	0.0784	2.00

[a] Aperture area corrected for shading effects caused by mask thickness.
[b] Effective counting area of 1/4-in diam. aperture taken as unity.
[c] The experimental count ratios are 1:2.43:1.91.

The count ratio for masks with different aperture sizes can be calculated, if one takes into consideration the masking effect that the mask thickness has on the primary and secondary X-rays. The calculated ratios for masks employed in this paper are shown in Table IV.

The agreement between the experimental and calculated ratio for the 1/4-in and 3/8-in diameter apertures is excellent. A 5% discrepancy is indicated between the 1/4-in diameter and the rectangular aperture. The reason for the discrepancy is not readily apparent. However, the authors place more credence in the experimental ratio than in the calculated ratio, because of the problems associated with the determination of an effective counting area for a rectangular mask rotating about a 360° angle.

The authors acknowledge their indebtedness to H. S. EDWARDS for suggesting the use of vapor deposition as an auxiliary approach to the problem; D. K. Conley for the electron probe analyses; and J. R. Monday for designing the enclosed assembly for specimen milling.

SUMMARY

When a uranium nuclear fuel material clad with an Fe–25Cr–4Al–1Y alloy is tested in an oxidizing environment at elevated temperatures, uranium diffuses through the clad and deposits on the surface of the specimen. A method has been developed whereby the amount of uranium per unit area on the surface of the specimen can be determined by X-ray fluorescence measurement. Synthetic specimens can be prepared by vapor-depositing uranium metal on Scotch tape and applying this tape to a solid piece of the alloy. The method described is accurate to ±5% relative and has a lower detection limit of about 30 μg U/(cm^2 × 150 μ).

RÉSUMÉ

Lorsqu'un combustible nucléaire uranium, avec alliage Fe–25Cr–4Al–1Y, est testé dans un milieu oxydant à température élevée, l'uranium diffuse et se dépose sur la surface de l'étalon. Une méthode est proposée pour déterminer la teneur en uranium par unité de surface, par mesure de fluorescence aux rayons-X. On prépare des étalons en déposant de l'uranium métallique à l'état de vapeur sur une bande de scotch, on applique ce ruban sur l'alliage. Cette méthode est précise (±5% erreur relative) sa limite de détection inférieure est d'environ 30 μg U/(cm^2 × 150 μ).

ZUSAMMENFASSUNG

Wird ein Uran-Kernbrennstoff mit einer Fe–25Cr–4Al–1Y-Legierung umhüllt und bei erhöhten Temperaturen in oxydierender Umgebung geprüft, so beobachtet man eine Diffusion des Urans durch die Umhüllung zur Oberfläche der Probe. Es wurde eine Methode entwickelt, bei der mit Hilfe der Röntgenfluoreszenz der Urangehalt pro Einheit Oberfläche bestimmt werden kann. Durch Aufdampfen von Uran im Vakuum wurden synthetische Proben hergestellt. Die Methode besitzt einen relativen Fehler von 5% und hat eine Nachweisgrenze von etwa 30 μg U/(cm^2 × 150 μ).

REFERENCES

1 C. S. Wukusick, General Electric Co., NMPO, Evendale, Ohio, private communication.
2 M. C. Powers, *X-Ray Fluorescent Spectrometer Conversion Tables*, Phillips Electronics, Inc., Mount Vernon, N. Y., 1957.
3 R. J. Guest and J. B. Zimmerman, *Anal. Chem.*, 27 (1955) 931.
4 W. S. Horton and P. F. Elliot, *U.S. At. Energy Comm. Rept.*, *KAPL-M-WHS-6*, 1960.
5 M. C. Lambert, *U.S. At. Energy Comm. Rept.*, *HW-58967*, 1959.

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LE DOSAGE DU NICKEL DANS LE COBALT DE TRES HAUTE PURETE PAR SPECTROMETRIE D'ABSORPTION ATOMIQUE

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La spectrométrie d'absorption atomique constitue une méthode d'analyse couramment utilisée à l'heure actuelle pour le dosage des impuretés dans les métaux, les alliages et les composés métalliques. Elle présente l'avantage d'être à la fois sélective, sensible et facile à mettre en oeuvre. Nous avons cherché à appliquer cette méthode au dosage du nickel dans le cobalt de très haute pureté élaboré par fusion de zone. Il s'agit, dans ce cas, de déterminer de l'ordre d'une partie par million de nickel dans une matrice de cobalt.

La concentration en sels de la solution à pulvériser dans la flamme ne pouvant pas dépasser 40 g/l et la limite de sensibilité étant, pour le nickel, de l'ordre de 0.1 μg/ml avec un appareillage classique, la teneur minimale dosable est voisine de $2.5 \cdot 10^{-6}$. Il est donc indispensable d'effectuer une séparation préalable des deux éléments.

Etude de la séparation du nickel et du cobalt

En règle générale, la séparation du nickel et du cobalt est relativement délicate par suite de la similitude existant entre les propriétés chimiques des deux éléments. La nécessité de séparer le nickel d'une quantité de cobalt environ 10^6 fois supérieure complique encore sensiblement le problème.

Nous avons tenté d'effectuer cette séparation par échange d'ions en nous inspirant des travaux de KORKISCH ET AHLUWALIA[1]. Ces auteurs ont étudié systématiquement le comportement d'un grand nombre d'éléments en milieu acide chlorhydrique–solvant organique vis-à-vis d'une résine cationique. Les résultats obtenus au cours de cette étude permettent d'envisager la séparation du nickel et du cobalt par échange d'ions sur une résine cationique du type Dowex 50-X8 (100–200 mesh) en opérant en milieu acide chlorhydrique 0.6 *M*–acétone 90%. La présence d'acétone en forte concentration modifie notablement la stabilité des complexes et permet une meilleure élimination du cobalt. Le nickel, qui dans ces conditions n'est pas complexé par l'ion Cl^-, reste par contre fixé sur la résine.

La constante apparente d'échange est supérieure à 200.

Il convient cependant de remarquer que ces résultats ont été obtenus avec des solutions diluées. Or, il s'agit dans notre cas d'isoler le nickel contenu dans une solution concentrée de cobalt. Nous avons donc été conduits à reprendre partiellement cette étude en vue de définir le comportement du nickel en présence d'une grande quantité de cobalt. Nous avons dans un premier temps, déterminé le coefficient de partage du nickel en fixant la concentration en cobalt de la solution à 10 g/l et en utilisant la résine et le milieu préconisés par KORKISCH ET AHLUWALIA. Cette détermination a été effectuée par la méthode statique de mise à l'équilibre des deux phases. Une masse de résine préalablement traitée selon le mode opératoire décrit plus loin et dont le poids à sec est de 0.8 g est mise en équilibre avec 50 ml de la solution acide chlorhydrique–acétone contenant respectivement 2 mg de nickel et 500 mg de cobalt. Après 12 heures d'agitation et 24 heures de mise en contact, on détermine la quantité de nickel fixé sur la résine. Le coefficient de partage du nickel est, dans ces conditions, égal à 265.

Nous avons dans un deuxième temps, mesuré le volume du mélange acide chlorhydrique–acétone nécessaire pour éliminer la totalité du cobalt retenu sur la résine. Dans les conditions où nous avons opéré ce volume est égal à 5 volumes de colonne.

Nous avons enfin estimé le volume de rétention efficace du nickel, en utilisant une colonne de 12 mm de diamètre et de 100 mm de hauteur pour laquelle le volume de rétention théorique du nickel est de 1300 ml. Après avoir fait passer 350 ml d'une solution de chlorure de cobalt à 10 g/l de Co contenant également du nickel marqué et 150 ml du mélange acide chlorhydrique–acétone—soit environ 3 fois le volume nécessaire pour éliminer le cobalt retenu—nous n'avons pas constaté l'apparition de nickel dans l'effluent. L'ensemble de ces résultats montre que la séparation du nickel d'une matrice de cobalt est possible par échange d'ions en milieu acide chlorhydrique 0.6 *M*–acétone 90% sur une résine cationique.

Dosage du nickel

En appliquant pour la séparation du nickel et du cobalt le mode opératoire décrit, il est possible d'opérer avec 350 ml d'une solution contenant 10 g/l de cobalt. La prise d'essai initiale doit donc être de l'ordre de 3.5 g. Si après élution du nickel on concentre la solution recueillie de manière à obtenir finalement un volume de 20 ml la concentration en nickel de cette solution sera de l'ordre de 0.15 μg/ml, l'échantillon à analyser étant supposé contenir $1 \cdot 10^{-6}\%$ de nickel. Cette concentration est très voisine de celle correspondant à la limite de sensibilité que l'on peut espérer obtenir avec un spectromètre d'absorption atomique classique. Les mesures restent donc d'être très imprécises et il est souhaitable d'améliorer si possible la sensibilité de la méthode.

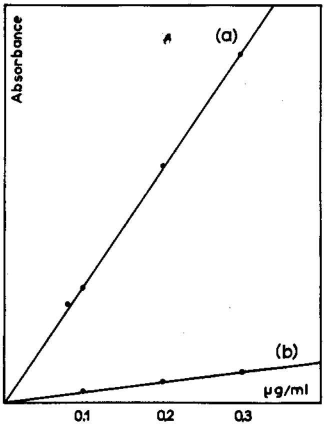
Nous avons montré dans une étude récente[2] que le remplacement du dispositif de pulvérisation pneumatique équipant normalement les appareillages commerciaux par un dispositif de pulvérisation par ultra-sons, permettait d'obtenir un gain de sensibilité très notable. Ce gain de sensibilité est dû, d'une part, à un accroissement du débit de la solution introduite dans la flamme, et d'autre part, à une diminution de la taille des gouttelettes constituant l'aérosol.

La Figure 1 représente les courbes d'étalonnage obtenues dans le cas du nickel avec les deux types de pulvérisation, en utilisant les conditions opératoires résumées ci-dessous.

Spectromètre	Hilger et Watts (modèle AA 2).
Lampe	Nickel (Hilger et Watts), I = 20 mA.
Longueur d'onde	2320 Å.
Fente	0.10 mm.
Brûleur	Laminaire.
Flamme	Air (1.1 l/min)–C_2H_2 (1.4 l/min).

La reproductibilité des mesures effectuées à l'aide de la pulvérisation par ultra-sons est bonne, ainsi que le montre, à titre d'exemple, l'enregistrement de la Figure 2.

Nous avons donc tout naturellement utilisé la pulvérisation par ultra-sons pour déterminer les concentrations en nickel inférieures à 0.2 µg/ml des solutions obtenues après séparation. Dans tous les autres cas nous avons utilisé la pulvérisation pneumatique.



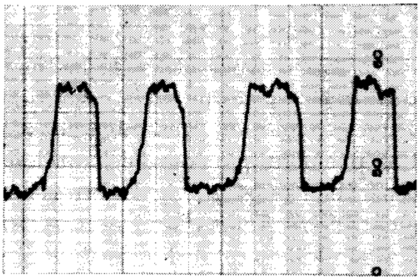


Fig. 1. Les courbes d'étalonnage. (a) Pulvérisation par ultra-sons; (b) pulvérisation pneumatique.

Fig. 2. La reproductibilité des mesures.

MODE OPÉRATOIRE

Dissolution de l'échantillon

On attaque 3.5 g d'échantillon par 15 ml d'acide nitrique concentré. Après avoir été amenée presque à siccité, la solution est reprise par 25 ml d'acide chlorhydrique 9 *N*. On répète encore deux fois cette opération. Le chlorure finalement obtenu est dissous dans 350 ml du mélange acide chlorhydrique 0.6 *M*–acétone 90%.

Séparation du nickel et du cobalt

Avant utilisation, la résine doit être purifiée. Après élimination des particules les plus fines par décantation, la résine est lavée avec une solution de citrate d'ammonium à 10%, puis avec de l'acide chlorhydrique 4 *N* et enfin avec de l'eau distillée. La résine est ensuite essorée à l'aide d'une trompe à eau.

La résine ainsi purifiée est alors mise en contact avec le mélange acide chlorhydrique–acétone, puis transvasée dans une colonne de 12 mm de diamètre intérieur. Avec 5 g de résine on obtient ainsi une colonne de 10 cm de hauteur. Après passage de 30 ml du mélange acide chlorhydrique–acétone destiné à la mise en équilibre, la colonne est prête à l'emploi. On fait alors passer la solution de cobalt. Le débit est de 1 ml/min.

Le cobalt retenu est élué par 60 ml du mélange acide chlorhydrique 0.6 *M*–acétone 90%. Le nickel fixé sur la résine est élué à son tour par 60 ml d'acide chlorhydrique 4 *N*.

Dosage du nickel

On amène la solution contenant le nickel à siccité afin d'éliminer l'acétone.

Les autres matières organiques éventuellement présentes sont détruites par addition de 20 ml d'acide perchlorique et 5 ml d'acide nitrique concentré. La solution obtenue est à nouveau amenée à siccité puis reprise par 20 ml d'acide chlorhydrique 0.5 *N*.

On procède enfin au dosage par spectrométrie d'absorption atomique en utilisant les conditions opératoires indiquées. Le dispositif de pulvérisation par ultra-sons est analogue à celui décrit précédemment[2].

L'étalonnage est effectué avec des solutions synthétiques obtenues par dilutions convenables d'une solution mère préparée par dissolution de nickel de très haute pureté.

RÉSULTATS

Nous avons utilisé la méthode de dosage décrite pour déterminer la concentration en nickel de trois échantillons de cobalt réputés de très haute pureté. Le Tableau I résume l'ensemble des résultats obtenus. Nous avons utilisé la pulvérisation pneumatique pour l'échantillon no. 1 et la pulvérisation par ultra-sons pour les échantillons nos. 2 ét 3. Les trois échantillons analysés contiennent donc respectivement $98 \cdot 10^{-6}$, $0.55 \cdot 10^{-6}$ et $1.05 \cdot 10^{-6}$ de nickel. La précision obtenue pour cette dernière valeur est de l'ordre de 20%.

TABLEAU I

DOSAGE DU NICKEL DANS LE COBALT DE HAUTE PURETÉ

Echantillon	*Prise d'essai (g)*	*Ni ajouté (μg/ml)*	*Blanc (μg/ml)*	*Ni trouvé (μg/ml)*	*Teneur et précision*
1	3.000	0	Non décelable	14.8	98.3
	3.000	0	—	14.8	97.5
	3.000	0	—	14.8	98.3
2	3.565	0	0.08	0.185±0.015	0.60±0.2
	3.780	0.5	0.075	0.675	0.50±0.2
3	3.471	0	0.145	0.335±0.015	1.1±0.2
	3.272	0.5	0.145	0.815	1.05±0.2

CONCLUSION

La spectrophotométrie d'absorption atomique constitue une méthode de dosage parfaitement bien adaptée à la détermination du nickel dans le cobalt de très haute pureté, et son emploi peut sans aucun doute être étendu à un grand nombre de cas analogues. Sa mise en oeuvre exige cependant, d'une part la séparation des traces de la matrice, et d'autre part, un accroissement de la sensibilité des spectromètres classiques. Les résultats obtenus au cours de cette étude confirment que la pulvérisation par ultra-sons occupe une place de choix parmi les différentes possibilités permettant d'obtenir un gain notable de sensibilité.

Il serait cependant illusoire de prétendre vouloir déterminer à l'aide de cette méthode, des concentrations inférieures à quelques dixièmes de p.p.m. En effet, à ce niveau de concentration, la contamination entraînée par les réactifs—même s'ils sont réputés très purs—devient prédominante et condamne de ce fait tout dosage.

RÉSUMÉ

On sépare quantitativement le nickel du cobalt par échange d'ions sur une résine cationique Dowex 50-X8 en milieu acétone 90%–acide chlorhydrique 0.6 *M*. Le nickel est ensuite dosé par spectrométrie d'absorption atomique. Afin d'améliorer la sensibilité on utilise un dispositif de pulvérisation par ultra-sons. Dans ces conditions, on dose $1 \cdot 10^{-6}$ de nickel avec une précision de l'ordre de 20%.

SUMMARY

Quantitative separation of nickel from cobalt has been achieved by means of a cation-exchange resin, Dowex 50-X8, in a 90% acetone–0.6 *M* hydrochloric acid medium. Nickel is then determined by atomic absorption spectrophotometry; the sensitivity of the method is increased by means of an ultrasonic spraying device. Under these conditions, 1 p.p.m. of nickel can be measured with an accuracy of *ca.* 20%.

ZUSAMMENFASSUNG

Es wird die quantitative Trennung des Nickels vom Kobalt mittels Dowex 50-X8 in 90%igem Aceton–0.6 *M* salzsaurem Medium beschrieben. Das Nickel wird mit der Atomabsorptionsspektrometrie bestimmt. Die Empfindlichkeit der Methode wird durch Ultraschallversprühung gesteigert. Unter diesen Bedingungen können 1 p.p.m. Nickel mit einer Genauigkeit von etwa 20% bestimmt werden.

BIBLIOGRAPHIE

1 J. Korkisch et S. S. Ahluwalia, *Talanta*, 14 (1967) 155.
2 J. Spitz et G. Uny, *Appl. Optics*, à paraître.

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SUBSTÖCHIOMETRISCHE ISOTOPENVERDÜNNUNGSANALYSE IM MIKRO- UND SUBMIKROGRAMMBEREICH DURCH FÄLLUNGSREAKTIONEN AUF FILTERPAPIER

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Die Isotopenverdünnungsanalyse gehört zu den besonders wertvollen radioanalytischen Methoden[1]. Bei ihrer einfachen Ausführungsform wird dem System eine bekannte Menge (m) der zu bestimmenden Komponente in radioaktiv markierter Form von bekannter spezifischer Aktivität (S_1) zugefügt. Ein Teil der zu bestimmenden Substanz wird aus dieser Mischung in reiner Form isoliert und dessen spezifische Aktivität (S_2) bestimmt. Die Berechnung der gesuchten Menge (x) der zu bestimmenden Komponente erfolgt nach

$$x = m\left(\frac{S_1}{S_2} - 1\right) \tag{1}$$

Die Bestimmung der spezifischen Aktivität S_2 des abgeschiedenen Reinstoffes ist ein Hindernis zur vollen Ausnutzung der Empfindlichkeit, welche die Radioaktivitätsmessungen eigentlich ermöglichen. Zur Ermittlung von S_2 ist es doch erforderlich, mindestens eine solche Menge des Reinstoffes zu isolieren, dass sie durch Wägen oder durch andere analytische Methoden bestimmbar ist.

Die Bestimmung der spezifischen Aktivität S_2 kann man jedoch durch Anwendung des substöchiometrischen Prinzips umgehen[2]. Dadurch gewinnt die Isotopenverdünnungsmethode in der Mikro- und Spurenanalyse sehr an Bedeutung. Bei der substöchiometrischen Isotopenverdünnungsanalyse werden sowohl aus der Lösung der radioaktiv markierten Substanz mit der spezifischen Aktivität S_1 als auch aus der durch Isotopenverdünnung entstandenen Lösung mit der spezifischen Aktivität S_2 beliebige aber stets gleiche Mengen des zu bestimmenden Elementes abgetrennt und unter identischen Bedingungen gemessen. Hierdurch ist es möglich, in Gleichung (1) anstelle der spezifischen Aktivitäten direkt die gemessenen Aktivitäten (Impulsraten) I_1 und I_2 einzusetzen.

Die reproduzierbare Isolierung jeweils gleicher, sehr kleiner Substanzmengen kann so erreicht werden, dass man den Lösungen immer die gleiche aber substöchiometrische Menge eines geeigneten Reagens zufügt. Die eigentliche Trennungsoperation kann durch Flüssig–flüssig-Extraktion[3], Ionenaustausch[4], elektrochemische Abscheidung[5] oder durch eine Kombination des Ionenaustausches mit Fällung[6]

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erfolgen. Bei einer mikrochemischen Variante der substöchiometrischen Isotopenverdünnungsanalyse durch Fällung werden der gefällte Anteil und die restliche gelöste Substanzmenge mit Hilfe des Ringofens voneinander getrennt und gemessen, wobei mit Eichkurven gearbeitet wird[7].

In der vorliegenden Arbeit wird eine neue mikrochemische Variante der substöchiometrischen Isotopenverdünnungsanalyse beschrieben, bei welcher Fällungsreaktionen auf Filterpapier durchgeführt werden. Die unbekannte Probelösung mit der zu bestimmenden Ionenart wird mit einer Lösung der gleichen, jedoch radioaktiv markierten Ionenart bekannter Konzentration und Aktivität durchmischt. Von dieser Mischung werden einige μl—entsprechend x μg des zu bestimmenden Ions $+m$ μg der gleichen Ionenart in markierter Form—auf die Mitte eines Rundfilters aufgetragen und hier mit einer substöchiometrischen Menge eines entsprechenden Fällungsreagens versetzt. Der nichtgefällte Anteil wird mit einer geeigneten Waschflüssigkeit kapillar in die äussere Zone des Rundfilters gewaschen und die Aktivität des im Zentrum zurückbleibenden Niederschlags (I_2) gemessen. In gleicher Weise wird mit der ursprünglichen Lösung der radioaktiv markierten Ionenart verfahren (Aktivität I_1). Die beiden so bestimmten Aktivitäten setzt man anstelle von S_1 und S_2 in Gleichung (1) ein und berechnet daraus die unbekannte Menge x.

EXPERIMENTELLER TEIL

Radionuklidlösungen

^{110m}Ag. Verdünnte salpetersaure Silbernitratlösung; Trägerkonzentration je nach Bestimmungsbereich 0.08–8 μg/μl; relative spezifische Aktivität 1,000–18,000 imp/min. μg.

^{131}J. Die ursprüngliche trägerfreie Lösung, welche Natriumkarbonat und Natriumthiosulfat enthielt, wurde mit Eisessig angesäuert und mit inaktiven KJ versetzt. Trägerkonzentration je nach Bestimmungsbereich 0.08–3 μg/μl; relative spezifische Aktivität 1,000–15,000 imp/min. μg.

^{59}Fe. Verdünnte salzsaure Eisen(III) chloridlösung; Trägerkonzentration je nach Bestimmungsbereich 0.028–2.1 μg/μl; relative spez. Aktivität 700–40,000 imp/min. μg.

Fällungsreagenzien

Für Silber. Jeweils frisch angesetzte Natriumsulfid-Lösungen mit *ca.* 0.066–0.2 μg S^{2-}/μl.

Für Jodid. Silbernitratlösungen mit 0.05–0.3 μg Ag^{+}/μl.

Für Eisen. Kaliumhexacyanoferrat(II)-Lösungen mit 0.06–0.6 μg $[Fe(CN)_6]^{4-}/\mu$l.

Messgeräte

Alle Aktivitätsbestimmungen erfolgten über Gamma-Messungen welche mit einem ESONE-Messplatz der Firma Prof. Berthold, Wildbad, sowie einem NaJ(Tl)-Kristall FH 421/24 (Frieseke u. Hoepfner) durchgeführt wurden.

Filtermaterialien

Rundfilter MN 2260 (5.5 cm Durchmesser) der Firma Macherey, Nagel u. Co., Düren. Für die Bestimmung von Eisen wurden die Rundfilter vor Gebrauch in der von WEST, LLACER UND CIMERMAN beschriebenen Weise[8] durch Waschen mit 0.05 N Salzsäure gereinigt.

Arbeitstechnik

Ein Volumen von 0.10 ml der Probelösung wird mit 0.10 ml der entsprechenden radioaktiven Standardlösung (welche das betreffende Ion in bekannter Konzentration enthält) durchmischt. Im Falle von Silber und Eisen werden einige μl (2–10) dieser Mischung in die Mitte eines Rundfilters aufgetragen und getrocknet. Anschliessend tüpfelt man mit 1 oder 2 μl der jeweiligen Fällungsreagens-Lösung nach. Die Konzentration dieser Lösung wird so gewählt, dass die zu bestimmende Ionenart auf dem Papier im Vergleich zum Fällungsreagens in mindestens 8–10 fachem Ueberschuss vorhanden ist. Im Falle des Jodids wird zuerst das Fällungsmittel, nämlich 1 oder 2 μl der Silbernitratlösung, und dann die Jodidlösung aufgebracht. Man lässt trocknen und wäscht mit Hilfe einer Kapillare die nichtgefällten Anteile Silber, Jodid oder Eisen mit 100–150 μl einer geeigneten Waschflüssigkeit–Ammoniaklösung (1:1) für Silber, 1-%ige NH_4NO_3-Lösung für Jodid, 0.05 N Salzsäure für Eisen—in die äussere Zone des Rundfilters. Als Unterlage für diese Auswaschoperation kann vorteilhaft das von WEST, LLACER UND CIMERMAN angegebene Zubehör zum Ringofen[8] verwendet werden. Nach dem Trocknen wird aus der Mitte des Rundfilters ein Scheibchen von 5–10 mm Durchmesser (S_p)—mit dem gefällten Anteil im Zentrum—ausgestanzt und zur Messung gebracht. Der Durchmesser des ausgestanzten Scheibchens richtet sich nach der Grösse des zentralen Niederschlagsfleckes (2–6 mm Durchmesser).

In der gleichen Weise wie eben beschrieben wird die radioaktive Standardlösung für sich allein behandelt (Scheibchen S_s). Weiterhin wird sowohl für die Standardlösung als auch für das Gemisch aus Standard- und Probelösung ein Blindwert ermittelt; dazu werden diese Lösungen den geschilderten Operationen *ohne* Zugabe des entsprechenden Fällungsreagens unterworfen (Scheibchen S_{bs} und S_{bp}). Aus statistischen Gründen werden die Messzeiten so gewählt, dass für die Scheibchen S_p und S_s mindestens 1200 Impulse und für die Scheibchen S_{bp} und S_{bs} mindestens 400 Impulse registriert werden. Für ein und dieselbe Bestimmung sollen alle 4 Scheibchen den gleichen Durchmesser besitzen.

Die Auswertung der Messergebnisse erfolgt nach

$$x = m\left(\frac{I_s - I_{bs}}{I_p - I_{bp}} - 1\right) \tag{2}$$

wobei I_s, I_{bs}, I_p, und I_{bp} die gemessenen Impulsraten der Scheibchen S_s, S_{bs}, S_p und S_{bp} sind. Die Grössen x und m sind die gesuchte bzw. bekannte zugegebene Menge der betreffenden Ionenart.

ERGEBNISSE UND DISKUSSION

Die mit Hilfe der geschilderten Arbeitstechnik gewonnenen Ergebnisse sind für Ag^+ in Tabelle I, für Fe^{3+} in Tabelle II und für J^- in Tabelle III zusammengestellt. Zur besseren Orientierung wird bei jeder Bestimmung die bekannte Standardmenge m angegeben. In der Mehrzahl der Fälle sind die relativen Fehler kleiner als 10%; es sei betont, dass es sich hier nicht um Mittelwerte aus mehreren Bestimmungen,

TABELLE I

ERGEBNISSE FÜR SILBER

Probe Nr.	*Menge m* (*μg*)	*Gefundene Menge x* (*μg*)	*Gegebene Menge* (*μg*)	*Abweichung Rel.* (%)
1	4.83	4.35	4.17	+ 4.31
2	4.83	8.07	8.34	− 3.47
3	4.83	13.80	12.60	+ 9.52
4	16.10	43.10	41.70	+ 3.35
5	8.05	21.00	20.80	+ 0.96
6	1.61	1.34	1.39	− 2.15
7	3.00	2.43	2.78	−12.58
8	0.80	0.65	0.70	− 7.14
9	0.40	0.33	0.35	− 5.71

TABELLE II

ERGEBNISSE FÜR EISEN-III

Probe Nr.	*Menge m* (*μg*)	*Gefundene Menge x* (*μg*)	*Gegebene Menge* (*μg*)	*Abweichung Rel.* (%)
1	0.14	0.09	0.12	−25.0
2	0.26	0.24	0.25	− 4.0
3	0.51	0.44	0.50	−12.0
4	0.26	0.79	0.75	+ 5.33
5	0.50	0.71	0.72	− 1.38
6	8.00	23.10	22.30	+ 3.58
7	2.50	5.20	5.55	− 6.30
8	0.72	2.03	2.10	− 3.33

TABELLE III

ERGEBNISSE FÜR JODID

Probe Nr.	*Menge m* (*μg*)	*Gefundene Menge x* (*μg*)	*Gegebene Menge* (*μg*)	*Abweichung Rel.* (%)
1	0.237	0.223	0.237	− 5.90
2	0.396	0.380	0.396	− 4.04
3	0.237	0.650	0.714	− 8.96
4	0.951	0.895	0.951	− 5.88
5	0.396	1.430	1.190	+20.16
6	0.792	5.550	5.540	+ 0.18
7	0.792	2.290	2.370	− 3.41
8	15.850	16.950	15.850	+ 6.94

sondern nur um Einzelbestimmungsresultate handelt. Um eine objektive Beurteilung der Methode zu ermöglichen, wurden für Submikrogrammengen der drei Ionenarten folgende Standardabweichungen ermittelt:

Silber: 0.7 ± 0.041 *μg* (17 Bestimmungen)
Eisen: 0.2 ± 0.016 *μg* (25 Bestimmungen)
Jodid: 0.62 ± 0.036 *μg* (19 Bestimmungen)

Wie die Ergebnisse in den Tabellen als auch die angegebenen Standardabweichungen zeigen, ist es möglich, mit dieser Variante der Isotopenverdünnungsanalyse kleine Mengen an Silber, Eisen oder Jodid mit befriedigender Genauigkeit zu bestimmen. Voraussetzung zum Erzielen guter Ergebnisse ist die vollständige Umsetzung des zugefügten Reagens mit dem zu bestimmenden Element auf dem Papier. Dies wird durch zwei Massnahmen gewährleistet: (*1*) Das zu bestimmende Element liegt in mindestens 8–10 fachem Überschuss im Vergleich zum Fällungsreagens vor; (*2*) Das aufgetragene Volumen der Reagenslösung ist so klein, dass die Fläche des Niederschlagsfleckes deutlich kleiner bleibt als der durch das Aufbringen der Probe- bzw. Standardlösung erzeugte Tüpfelfleck.

Es hat sich als notwendig erwiesen, von den beiden Partnern der Fällungsreaktion zunächst den kationischen und dann erst den anionischen Teil auf das Papier aufzubringen. Dies führt im Falle der Jodidbestimmung dazu, dass man erst die Reagenslösung ($AgNO_3$) und danach die Probelösung aufträgt. Vermutlich hängt dieser Tatbestand mit den Kationenaustauscheigenschaften des Filtermaterials zusammen. Weiterhin ist es empfehlenswert, den Tüpfelfleck der Lösung des zu fällenden Kations zunächst trocknen zu lassen, bevor man die Lösung des anionischen Reaktionspartners aufbringt.

Blindwerte kommen dadurch zustande, dass die nichtgefällten Anteile teilweise durch das Filtermaterial festgehalten werden und nicht ganz quantitativ in die äusseren Zonen des Rundfilters gewaschen werden können. Die Grösse der Blindwerte hängt von der spezifischen Aktivität und Konzentration der jeweiligen Lösungen sowie von der aufgetragenen Gesamtmenge ab und ist ausserdem von Ionenart zu Ionenart verschieden. Bei den hier geschilderten Untersuchungen lagen die Blindwerte relativ zu den jeweiligen Messwerten zwischen 1–15% für Silber, 7–31% für Eisen und 3–22% für Jodid. Wegen des Auftretens von Blindwerten müssen alle bei der Durchführung einer Bestimmung gemessenen Papierscheibchen (S_s, S_p, S_{bs}, S_{bp}) gleichen Durchmesser besitzen. Selbstverständlich ist in den Blindwerten auch der Untergrund enthalten.

Es können auch kleinere Volumina von Probe- und Standardlösungen miteinander gemischt werden, wenn dies erforderlich sein sollte; dann aber muss der Mischvorgang z. B. mit Hilfe von Blutmischpipetten erfolgen[7].

So wie hier an den Beispielen Silber, Eisen und Jodid beschrieben, können nach dem gleichen Prinzip der substöchiometrischen Fällung sicherlich auch andere Elemente bestimmt werden, falls sie schwer lösliche, gut auf Filterpapier haftende Niederschläge bilden.

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ZUSAMMENFASSUNG

Eine neue mikrochemische Variante der substöchiometrischen Isotopenverdünnungsanalyse durch Fällungsreaktionen auf Filterpapier wird beschrieben. Am Beispiel der Bestimmung von Ag^+ (gefällt als $^{110m}Ag_2S$), Fe^{3+} (gefällt als $^{59}Fe_4[Fe(CN)_6]_3$) und J^- (gefällt als $Ag^{131}J$) wird die Methode erläutert. Mengen von 0.1 bis zu etwa 40 μg konnten mit befriedigender Genauigkeit bestimmt werden. Notwendige Bedingungen für die Anwendung dieser Methode werden diskutiert.

SUMMARY

A new microchemical variation of substoichiometric isotope dilution analysis by means of precipitation reactions on filter paper is described. The method is demonstrated for determinations of silver (precipitated as $^{110m}Ag_2S$), iron(III) (as $^{59}Fe_4[Fe(CN)_6]_3$) and iodide (as $Ag^{131}I$). Amounts of 0.1–40 μg can be determined with satisfactory accuracy. Essential conditions for the application of the method are discussed.

RÉSUMÉ

On décrit une nouvelle variante d'analyse microchimique par dilution isotopique substoechiométrique au moyen de réactions de précipitation sur filtre. La méthode démontre qu'il est possible de déterminer l'argent (precipité sous forme de $^{110}Ag_2S$), le fer(III) (sous forme de $^{59}Fe_4[Fe(CN)_6]_3$ et l'iode (sous forme de $Ag^{131}I$). Il est possible de déterminer les quantités de 0.1 à 40 μg avec une précision satisfaisante. Les conditions essentielles pour l'application de cette méthode sont décrites.

LITERATUR

1 G. HEVESY UND R. HOBBIE, *Z. Anal. Chem.*, 88 (1932) 1.
2 J. RUŽIČKA UND J. STARÝ, *Atomic Energy Review*, 2 (1964) 3.
3 J. RUŽIČKA UND J. STARÝ, *Talanta*, 8 (1961) 228.
4 J. STARÝ UND J. RUŽIČKA, *Talanta*, 8 (1961) 775.
5 A. P. PELLA, A. R. LANDGREBE, J. R. DEVOE UND W. C. PURDY, *Anal. Chem.*, 39 (1967) 1781.
6 J. K. JOHANNESSON, *Analyst*, 92 (1967) 766.
7 H. WEISZ UND D. KLOCKOW, *Mikrochim. Acta*, (1963) 1082.
8 P. W. WEST, A. J. LLACER UND CH. CIMERMAN, *Mikrochim. Acta*, (1962) 1165.

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AN EXAMINATION OF THE EQUILIBRIUM BETWEEN H AND OH RADICALS AND OF RELATED EFFECTS IN TURBULENT HYDROGEN FLAMES AS USED IN FLAME SPECTROPHOTOMETRIC METHODS OF ANALYSIS

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A great deal of information on reactions and equilibria in hydrogen flames has been accumulated with pre-mix burners but this has not so far been extended to turbulent flames. The pre-mixed flame can be made uniform, one-dimensional and stable; moreover, the effect of entrained air can be practically eliminated by surrounding the flame under investigation with a sheath of nitrogen. Such a system[1-3] is very amenable to exact study of flame reactions. The results of such studies have been reviewed in a recent monograph[4]. A summary will be given here.

Hydrogen flames, supported by oxygen, consist principally of the following species H_2, O_2, H_2O, OH, H, O. Flames supported by air or oxygen–nitrogen mixtures will contain also nitrogen, of course. The concentrations of radicals produced in the reaction zone are far in excess[2,4,5] of the values defined by the equilibrium:

$$H + OH \rightleftharpoons H_2O \tag{1}$$

As the radicals pass into higher regions of the flame, they combine in the presence of third bodies such as oxygen, nitrogen or water molecules. If a metal atom is present as a third body, then chemiluminescence may be produced. The radical concentrations, even when in excess of their equilibrium values, have been shown to be related by the following equilibria[6].

$$H_2 + OH \rightleftharpoons H_2O + H \tag{2}$$

$$H_2 + O \rightleftharpoons OH + H \tag{3}$$

$$H + O_2 \rightleftharpoons OH + O \tag{4}$$

Of these, reaction (2) is the most important since hydrogen-rich flames are generally used and the oxygen radical concentration is then very small.

Hydrogen flames, in contrast to hydrocarbon flames[7], show a low spectral background[4,8,9], the principal emission being due to hydroxide radicals in the region of 3070 Å. Weaker emission is shown between 8000 and 12500 Å, which is due to the vibration–rotation system of water. In hydrogen–oxygen flames, a continuum is shown in the region 3400–6600 Å which gives rise to the blue colour of these flames. PADLEY[10] has proved that this is produced by the reaction:

$$H + OH \rightleftharpoons H_2O + h\nu \tag{5}$$

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The emission from OH is not entirely due to thermal luminescence. Chemiluminescence plays a considerable part in the excitation especially in cooler flames [3,11,12].

In practical analytical applications of flames—emission, atomic absorption and atomic fluorescence spectrophotometry—hydrogen flames are generally produced on direct atomiser-burners of the Beckman type, which produce turbulent flames. The properties of turbulent flames may be expected to differ in some respects since the reaction zone is not confined to a small well-defined zone as in the pre-mixed flame but is spread over a greater volume of the flame. Hence the high radical concentrations persist at greater heights in the flame. The object of the present study is to show that the principles developed for study of pre-mixed flames can be applied to these turbulent flames also, to show how the radical and water vapour concentrations vary in these flames, and to compare the results with those reported for pre-mixed flames.

EXPERIMENTAL

Apparatus

A Beckman DU spectrophotometer with the atomic absorption accessory was used. Only one of the burners (Beckman 4020) on the Turbulent Flow Burner accessory was employed in these investigations. The photomultiplier of the spectrophotometer detected radiation from a vertical area in the flame 0.8×0.4 cm^2.

The flow-rates of hydrogen and air or oxygen were monitored by rotameters connected in series with the gas supplies to the burner. When an oxygen–nitrogen mixture was used as the atomising gas, the oxygen supply was connected as usual to the gas-regulating unit of the instrument. A nitrogen cylinder with a two-stage regulator fed nitrogen to a rotameter, after which the nitrogen was mixed with the oxygen from the gas-regulating unit. The mixed gas flow-rate was read on a further rotameter. In this way it could be ensured that the total flow-rate was constant so that the rate of atomisation was unaffected and at the same time, the flow-rate of nitrogen (and hence $\%N_2$) could be measured.

The rotameters were calibrated *in situ* with a stopwatch and a gas-meter connected to the burner orifice.

Solutions

Reagent-grade chemicals were used.

Experimental techniques

Measurement of degree of evaporation of water. The extent of evaporation of water in the flame was followed by light scattering from the water droplets in the flame. The lamp-house backing plate of the DU spectrophotometer supporting a tungsten lamp and concave mirror, was placed so that light from the mirror passed through the flame at right angles to the optical axis of the instrument. A slit was placed between the mirror and the flame. The visible light scattered by the water droplets was measured by the spectrophotometer at a wavelength of 5000 Å with a slit width of 0.3 mm.

Measurement of OH radical concentration. The relative hydroxyl radical concentration was measured by an absorption method. A nickel hollow-cathode lamp which was found to give emission also in the region of the OH spectrum, was used as a source. The absorption measurements at 3094 Å were corrected for the emission from OH in the flame.

Measurement of temperature. This was carried out by the sodium D-line reversal method[4]. A tungsten filament lamp, calibrated with an optical pyrometer, was used as a source. A mask was placed over the lens between the burner and the spectrophotometer to reduce the area observed to that of the image of the filament.

Examination of the equilibrium (*2*). From eqn (2), the equilibrium constant may be expressed as

$$K = \frac{[H_2O]\ [H]}{[H_2]\ [OH]} = K_0\ e^{-\Delta H/RT} \tag{6}$$

To test this equilibrium, a fixed height in the flame was chosen (4 cm) where evaporation of atomised water was nearly complete and where the amount of excess hydrogen burnt was small. At this height, various functions representative of the species in the equilibrium were measured or calculated for six series of flames. In each series, the N_2/O_2 ratio was kept constant and readings at 5 different hydrogen flow-rates were taken. For the six series of flames, the total flow-rate of oxygen and nitrogen was kept constant, but the percentage of nitrogen in the mixture was varied, *viz.*

0 (100% O_2), 26, 41, 60, 76, 100% N_2

In all cases, measurements were made with water atomising into the flame (copper solution in the case of H radical determination).

The functions used for the species were:

$[H_2O] = \dfrac{I_{H_2O}}{c\ e^{-E/RT}}$ where I_{H_2O} = the intensity of emission from water at 9500 Å.

$[H] = \dfrac{I_{CuH}}{c'\ e^{-E'/RT}}$ where I_{CuH} = the intensity of emission from CuH at 4290 Å.

$[H_2] = c'' F_{xs}$ where F_{xs} = the difference between flow-rate of hydrogen and the flow-rate required for stoichiometry.

$[OH] = \dfrac{A_{OH}}{c'''}$ where A_{OH} = absorption by OH (see above).

c, c′, c″, c‴ are constants, E, E' are excitation energies.

When these values are substituted in eqn (6), an equation of the form (7) is obtained.

$$-\frac{b}{T} = c + \log \frac{I_{H_2O} \cdot I_{CuH}}{F_{xs} \cdot A_{OH}} \tag{7}$$

where b and c are constants.

Therefore if equilibrium (2) holds in the flame, a plot of log $(I_{H_2O} \cdot I_{CuH}/F_{xs} \cdot A_{OH})$ against $1/T$ should give a straight line.

RESULTS AND DISCUSSION

The evaporation of water in the flame

The amount of light scattered by water droplets was measured at various heights in the flame and compared with the amount of light scattered in the absence of a flame with only air passing through the burner to atomise the water (Fig. 1). An increase in hydrogen pressure had apparently little effect on the rate of evaporation, but decreased the amount of unevaporated water remaining in the flame. Evaporation is practically complete at a height of 4 cm in the flame.

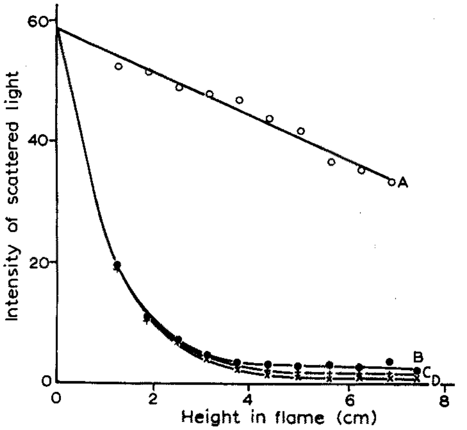
Visual observations of the illuminated water droplets in the flame were themselves of interest. The movement of the droplets showed the degree of turbulence in the flame. Some droplets pass right through the flame and join the air surrounding the flame whence they are sucked up again into the flame with the entrained air.

The expansion of the flame gases

The expansion of the flame gases should be considered because of the effect it has on the concentrations of species in the flame.

The hydrogen and support gas enter the burner at room temperature and at an average pressure of about 4 p.s.i.g. Within 1 cm from the nozzle, the temperature of these burning gases is raised to the final flame temperature. Such a rise in temperature causes a rise in pressure of the gases which then expand as gases pass higher into the flame until atmospheric pressure is approached.

By means of the gas laws, the reduction in volume from the combustion reaction being taking into account, an expansion factor of 7 was calculated for a stoichiometric hydrogen–oxygen flame. Such an expansion of the flame requires an increase in diameter of the flame of about 3 times, which agrees roughly with visual observation. Entrained air neglected in the above calculation, will also increase the expansion factor, especially for hydrogen-rich flames.



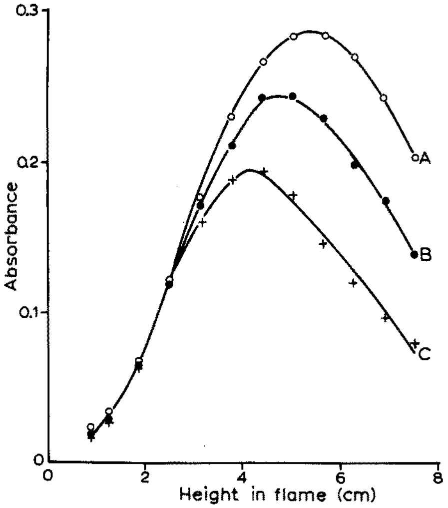


Fig. 1. The extent of evaporation of water in a hydrogen–air flame as determined by light scattering (A). Amount of light scattered in absence of flame (air only going through the burner). (B–D) amount of light scattered in presence of flame. Air flow-rate: 225 l/h, hydrogen flow-rate: (B) 540; (C) 650; (D) 750 l/h. Wavelength: 5000 Å. Slit width: 0.3 mm.

Fig. 2. The flame profile of absorption by zinc in the hydrogen–air flame at various hydrogen flow-rates: (A) 750; (B) 650; (C) 540 l/h. Air flow-rate: 225 l/h. Solution: 10^{-4} *M* Zn^{2+}. Wavelength: 2140 Å. Slit width: 0.2 mm. Lamp current: 37 mA.

Flame profile of zinc atom concentration

An examination of this profile (Fig. 2) is worthwhile, as it illustrates the phenomena of evaporation and expansion mentioned above.

The formation of zinc atoms from the atomised solution takes place through the evaporation of water from the droplets to give clotlets of a zinc salt from which zinc atoms are produced by thermal decomposition or by interaction with the flame components. In the lower part of the flame, the absorption from zinc atoms is independent of the hydrogen flow-rate. In this region, the rate of formation of zinc atoms may be assumed to be kinetically controlled by the rate of evaporation of water from the droplets. Since the rate of evaporation was shown to be independent of hydrogen pressure, the overall rate of production of zinc atoms is also independent of hydrogen pressure. When evaporation nears completeness, the rate of formation of zinc atoms becomes dependent on the flame composition. The increasing concentration of zinc atoms produced from the clotlets becomes counteracted at greater heights by the expansion of the flame gases. From Fig. 2, it would appear that the higher the hydrogen pressure, the lower is the rate of dilution. Similar features were found on the flame profiles of many other species.

Hydrogen radicals

The CuH emission method[13] was used to obtain relative hydrogen radical concentrations. In this method, the complete formation of copper atoms is assumed and so evaporation of the water and dissociation of the copper salt must be taken into

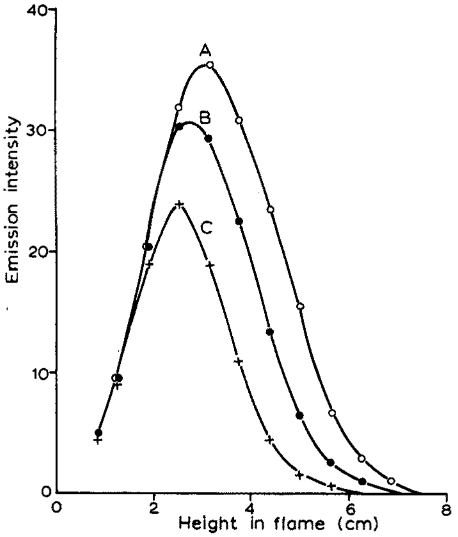


Fig. 3. The flame profile of emission by CuH in the hydrogen–air flame at various hydrogen flow-rates: (A) 750; (B) 650; (C) 540 l/h. Air flow-rate: 225 l/h. Solution: 10^{-2} *M* Cu^{2+}. Wavelength: 4290 Å. Slit width: 0.2 mm.

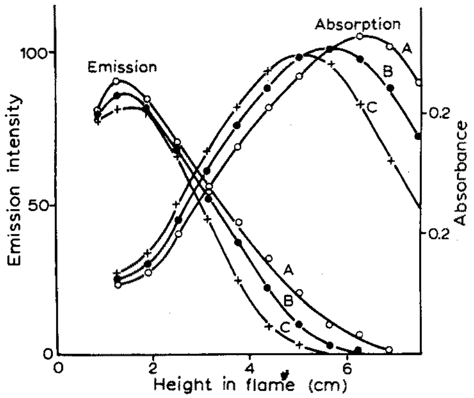


Fig. 4. The flame profiles of emission by excited OH radicals and of absorption by ground-state OH radicals in the hydrogen–air flame at various hydrogen flow-rates: (A) 750; (B) 650; (C) 540 l/h. Air flow-rate: 225 l/h. H_2O sprayed into flame. Wavelength: 3094 Å. Absorption: source: Ni lamp; current 25 mA; slit width: 0.05 mm. Emission: slit width: 0.2 mm.

account when the flame profile is considered (Fig. 3). However, by comparison with Fig. 2, it can be seen that the maximum hydrogen radical concentration occurs low in the flame and the radical concentration decreases rapidly with increasing height.

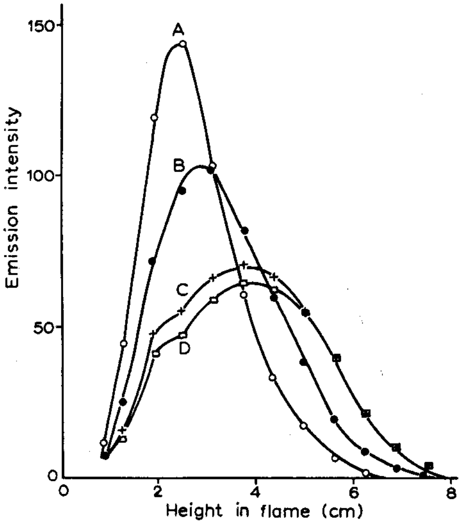
Hydroxyl radicals

The flame profiles of the concentration of OH radicals and of excited OH radicals are shown in Fig. 4.

The maximum OH radical concentration is shown quite high in the flame, in contrast to the maximum H concentration. The maximum OH concentration is, however, apparently very little affected by the hydrogen flow-rate. Up to a height of 5 cm in the flame, the OH concentration decreases with increasing hydrogen flow-rate as expected from equilibrium (2). Above this height, the differing rates of expansion of the flames become the controlling factor and the dependence is reversed.

The strong chemiluminescent excitation of OH is readily seen in Fig. 4, where the emission from OH bears practically no relationship to the ground-state OH concentration, although the temperature of the flame changes very little with height in the flame (Fig. 8). The emission from OH is also very little dependent on hydrogen pressure except at greater heights in the flame.

The chemiluminescent excitation of OH is even more clearly demonstrated in a hydrogen–oxygen flame (Fig. 5), where two peaks appear in the emission profiles for OH radicals. The hydrogen–oxygen flame is much hotter than the hydrogen–air flame and so the extent of thermal excitation of OH becomes comparable with that of chemiluminescent excitation. The lower peak corresponds to maximum chemilumines-



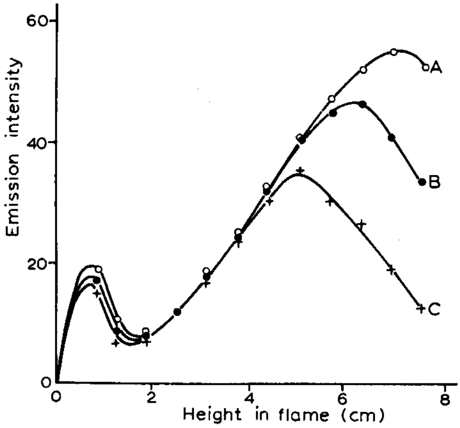


Fig. 5. The flame profile of emission by excited OH radicals in the hydrogen–oxygen flame at various hydrogen flow-rates: (A) 540; (B) 650; (C) 750; (D) 830 l/h. O_2 flow-rate: 150 l/h. H_2O sprayed into flame. Wavelength: 9500 Å. Slit width: 0.20 mm.

Fig. 6. The flame profile of emission from H_2O molecules in the hydrogen–air flame at various hydrogen flow-rates: (A) 750; (B) 650; (C) 540 l/h. Air flow-rate: 185 l/h. H_2O sprayed into flame. Wavelength: 9500 Å. Slit width: 0.20 mm.

cent excitation whereas that at higher flame heights corresponds to normal thermal excitation.

The increase of OH radical concentration with increasing height in the flame (Fig. 4) is not shown in pre-mixed flames, where an initial high radical concentration in the reaction zone decreases with increasing height in the flame[2,5]. Also it has been observed[14] in pre-mixed flames that the ratio of [OH] to [H] was independent of height for a given flame composition. This is a result of the relation:

$$\frac{[OH]}{[H]} = K_0 \frac{[H_2O]}{[H_2]} \tag{8}$$

which results from equilibrium (2).

In these turbulent flames, however, the ratio is obviously not constant and increases with increasing height in the flame. The increase in OH concentration is a result of the combustion of the excess of hydrogen by the entrained air. This is in agreement with the equation above, since the concentration of excess of hydrogen decreases with increasing height in the flame, because of its combustion with the increasing amount of entrained air entering the flame. Thus the ratio $[H_2O]/[H_2]$ increases and consequently there is a decrease in the H radical concentration and an increase in the OH radical concentration with increasing height in the flame.

Water vapour

Water vapour in the flame results not only from the evaporation of water atomised into the flame, but also from the combustion of the hydrogen. The concentration of water from evaporation would be expected from Fig. 1 to reach a maximum at a height of about 4 cm. However, the amount of water produced by combustion is more significant. For the case shown in Fig. 6, the amount of water produced by combustion can be calculated as 1.14 g/min if the combustion of the excess of hydrogen by the entrained air is temporarily neglected; the amount of water introduced by atomisation was only 0.77 g/min. Moreover, the concentration of water produced by combustion would be expected to increase with height as more of the excess hydrogen is burnt by the entrained air.

These observations are in agreement with the results shown in Fig. 6, which gives the flame profiles of the intensity of emission caused by the vibration–rotation system of water for three hydrogen–air flames. The intensity of the emission reaches a maximum high in the flame consistent with the increasing amount of water produced by the combustion of the excess hydrogen. Furthermore, the evaporation of water atomised into the flame apparently has very little influence in determining the flame profile.

The peak at low heights in the flame is presumably due to chemiluminescent excitation of the water molecules. In the region 2–5 cm, the water vapour content would appear to be practically independent of hydrogen flow-rate.

The blue continuum

In turbulent hydrogen–oxygen flames on the Beckman burner, a blue inner cylindrical zone begins to appear at a height of about 1 cm. The most intense colour is just above this, but after about a further 1 cm the colour begins to spread through the flame and becomes less intense. The flame profile of this continuum measured in the blue region at 4700 Å is shown in Fig. 7. The maxima shown at 2 cm correspond to the well-defined intense zone and the region above 3 cm to the more diffuse region. The intensity of the well-defined zone increases as stoichiometry is approached (*i.e.* as the hydrogen flow-rate is decreased). However, the greater the hydrogen flow-rate, the greater is the ratio of the intensity in the diffuse zone to the intensity in the well-defined zone.

PADLEY[10] observed in pre-mixed hydrogen flames that the intensity of the continuum was greatest in the reaction zone and the intensity decreased with increasing distance from the reaction zone. Since, from eqn (5),

$$I_{\text{continuum}} \propto [H]\,[OH] \qquad (9)$$

this decrease is to be expected as the concentrations of H and OH radicals both decrease on leaving the reaction zone. In turbulent flames, however, although [H] decreases with increasing height, [OH] increases, as was shown previously, and so the intensity of the continuum is appreciable at all heights in the flame.

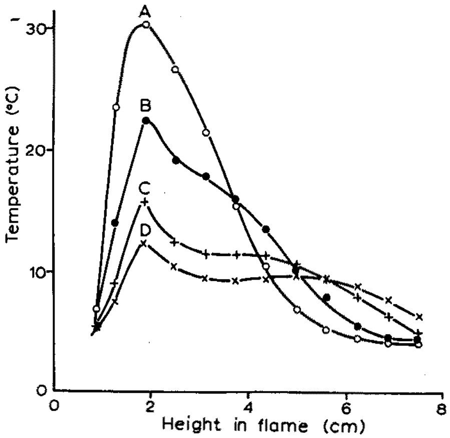


Fig. 7. The flame profile of the "blue continuum" in the hydrogen–oxygen flame at various hydrogen flow-rates: (A) 410; (B) 540; (C) 650; (D) 750 l/h. O_2 flow-rate: 125 l/h. H_2O sprayed into flame. Wavelength: 4700 Å. Slit width: 0.20 mm.

Fig. 8. The flame profile of temperature in the hydrogen–air flame at various hydrogen flow-rates: (A) 750; (B) 650; (C) 540 l/h. Air flow-rate: 170 l/h. Solution of NaCl sprayed into flame.

Temperature

The temperature at various points in the hydrogen–air flame as determined by sodium D-line reversal is shown in Fig. 8. There is no great variation in temperature over the whole of the flame. The greater the flow-rate of hydrogen, the more the temperature increases with increasing height in the flame as more of the excess of hydrogen is burnt. There is very little variation in the flame temperature with differing hydrogen flow-rates at lower heights in the flame.

The equilibrium $H_2 + OH \rightleftharpoons H + H_2O$

The values of the function log ($I_{CuH} \cdot I_{H_2O}/F_{xs} \cdot A_{OH}$) are plotted against $1/T$ in Fig. 9 for the six series of flames. The points are in agreement with a straight line except for the extreme cases, *i.e.* when 100% oxygen or 100% nitrogen is used as atomising gas. A large error may be expected in the function when 100% nitrogen is used, as the values of the intensities and absorption measured are very small compared with those in higher temperature flames. Error may also be expected in the hydrogen–oxygen flame as the measurement of temperature in this flame proved very difficult and also the continuum will cause an error in the values of the intensity of emission caused by water. However, the good agreement of the points with a straight line for the other four series shows that even in turbulent hydrogen flames, equilibrium (2) holds.

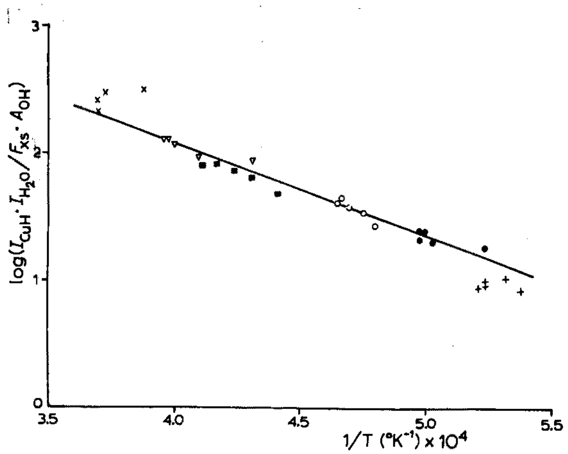


Fig. 9. The value of the function log ($I_{CuH} \cdot I_{H_2O}/F_{xs} \cdot A_{OH}$) plotted against 1/T for H_2–O_2–N_2 flames of various composition. Atomising gas: O_2+N_2. Percentage N_2: + 100, ● 76, ○ 41, ▽ 26, × 0%.

Conclusion

The principles found true for pre-mixed hydrogen flames can be applied also to turbulent flames as used in flame spectrophotometric methods of analysis. In particular, the equilibrium (2) can be used to explain the relative radical concentrations. Turbulent flames differ mainly in that combustion is not confined to a small zone as in the pre-mixed flame, but occurs also throughout the flame due to combustion of the excess hydrogen by the entrained air. Thus the OH radical concentration increases with increasing height in the flame and the blue continuum in the hydrogen–oxygen flame is spread throughout the flame.

It is hoped that such a knowledge of the basic properties of hydrogen flames will be useful in the elucidation of the processes involved in the production of metal atoms in these flames.

One of us (D. J. H.) is grateful for a scholarschip under the British Council–Hungarian Institute of Cultural Relations exchange scheme, and we are grateful to the Hungarian Optical Works (MOM) for financial help.

SUMMARY

An examination of the relative radical and molecule concentrations in turbulent hydrogen flames as used in flame spectrophotometric methods of analysis has shown that they are in agreement with the equilibrium $H_2+OH \rightleftharpoons H_2O+H$. The flame profiles of the concentrations of H and OH radicals and of water vapour are described and discussed. The OH radical concentration reaches a maximum high in the flame. The emission from OH radicals in hydrogen–air flames, which is at a maximum low in the flame, is produced mainly by chemiluminescent excitation. The blue continuum in hydrogen–oxygen flames, which is produced by the combination of H and OH radicals, is spread throughout the flame. The influences of the evaporation of water from solutions atomised into the flame and of the expansion of the flame gases on the flame profiles of species in the flame are discussed.

RÉSUMÉ

Un examen des concentrations relatives du radical et de la molécule dans des flammes turbulentes d'hydrogène, telles que celles employées dans les méthodes d'analyse par spectrophotométrie de flamme, à montré qu'elles sont en accord avec l'équilibre: $H_2+OH \rightleftharpoons H_2O+H$. Les profils des flammes sont décrits et discutés en ce qui concerne la concentration des radicaux H et OH et celle de la vapeur d'eau. La concentration du radical OH atteint une valeur maximale dans la flamme. L'émission, provenant des radicaux OH dans les flammes air-hydrogène, qui atteint une valeur minimale dans la flamme, est produite principalement par excitation chimi-luminescente. Le bleu continu, dans les flammes hydrogène-oxygène, qui est produit par la combinaison des radicaux H et OH, se répand à travers la flamme. On discute les influences de l'évaporation de l'eau provenant des solutions atomisées dans la flamme; on étudie également les influences de l'expansion des gaz de la flamme sur les profils des flammes obtenus avec les composés présents dans la flamme.

ZUSAMMENFASSUNG

Eine Prüfung der relativen Radikal- und Molekülkonzentrationen in turbulenten Wasserstofflammen, wie sie bei der Flammenspektralphotometrie verwendet werden, hat gezeigt, dass folgendes Gleichgewicht vorliegt: $H_2+OH \rightleftharpoons H_2O+H$. Es werden die Flammenprofile der Konzentrationen von H- und OH-Radikalen und des Wasserdampfs beschrieben und diskutiert. Die OH-Radikal-Konzentration erreicht ein Maximum oben in der Flamme. Die Emission von OH-Radikalen in Wasserstoff-Luft-Flammen, welche ein Maximum unten in der Flamme besitzt, wird hauptsächlich durch Chemieluminiszenzanregung erzeugt. Das blaue Kontinuum in der Wasserstoff-Sauerstoff-Flamme, welches durch die Kombination von H- und OH-Radikalen erzeugt wird, ist über die ganze Flamme verteilt. Die Einflüsse der Wasserverdampfung atomisierter Lösungen auf das Flammenprofil der Spezies in der Flamme werden diskutiert.

REFERENCES

1 P. J. Padley and T. M. Sugden, *Proc. Roy. Soc. (London)*, 248A (1958) 248.
2 W. E. Kaskan, *Combust. Flame*, 2 (1958) 229.

3 P. J. T. Zeegers, *Recombination of Radicals and Related Effects in Flames*, Thesis, University of Utrecht, 1966.
4 E. Pungor, *Flame Photometry Theory*, Van Nostrand, 1967.
5 W. E. Kaskan, *Combust. Flame*, 2 (1958) 286.
6 E. M. Bulewicz, C. G. James and T. M. Sugden, *Proc. Roy. Soc. (London)*, 135A (1956) 89.
7 V. A. Fassel and D. W. Golightly, *Anal. Chem.*, 39 (1967) 466.
8 A. G. Gaydon, *Quart. Rev.*, 4 (1950) 1.
9 E. Pungor and D. J. Halls, *Hung. Sci. Instr.*, in press.
10 P. J. Padley, *Trans. Faraday Soc.*, 56 (1960) 449.
11 W. E. Kaskan, *J. Chem. Phys.*, 31 (1959) 944.
12 M. Charton and A. G. Gaydon, *Proc. Roy. Soc. (London)*, 245A (1958) 84.
13 E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.*, 52 (1956) 1475.
14 R. W. Reid and T. M. Sugden, *Discussions Faraday Soc.*, 33 (1962) 213.

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SPECTROSCOPIC STUDIES OF THE CHROMOTROPIC ACID–NITRATE REACTION

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The spectrophotometric determination of nitrate with chromotropic acid has been known for several years[1,2]. The reaction provides a specific and sensitive spot test for nitrate[3] based on its reaction with a solution of chromotropic acid (1,8-dihydroxy-3,6-naphthalenedisulfonic acid) in strong sulfuric acid. In the presence of 70% sulfuric acid, as little as a microgram amount of nitrate ion produces the immediate appearance of a yellow color with chromotropic acid at room temperature. The reaction between chromotropic acid and nitrate is markedly influenced by the amount of sulfuric acid present in solution. Spectrophotometric studies[1,2] indicated that the yellow coloration obtained with chromotropic acid and nitrate was most intense in aqueous media containing 69–73% sulfuric acid. It was also indicated that one mole of nitrate reacted with one mole of chromotropic acid. But the exact chemical nature of the reaction was not clearly understood.

A further investigation of the reaction between chromotropic acid and nitrate at the optimum concentration (*i.e.* about 70%) of sulfuric acid by means of NMR has been carried out. Interpretation of the NMR spectra indicated that one mole of chromotropic acid reacted with one mole of nitrate in 70% sulfuric acid. The UV spectrum indicated the formation of a quinone during the reaction. It was concluded that a polymerized mononitro derivative of chromotropic acid was the chromophoric agent in the reaction.

EXPERIMENTAL

Reagents

Purified chromotropic acid. A saturated solution of disodium salt of 1,8-dihydroxy-3,6-naphthalenedisulfonic acid (Eastman Organic Chemicals, technical grade) was purified twice with decolorizing charcoal. The purified reagent was crystallized from the filtered solution by cooling and adding concentrated sulfuric acid. The white product was filtered under suction, washed several times with ethanol, and dried in a vacuum oven.

Standard nitrate solution. A stock nitrate solution was prepared by dissolving 0.825 g of analytical grade sodium nitrate in 1 ml of distilled water to give a 0.602 mg nitrate/μl solution.

Sulfuric acid. Concentrated sulfuric acid (du Pont Company) was found to be free from nitrate by testing with chromotropic acid.

Equipment

A Varian HA-60 MHz spectrometer was used to obtain the NMR spectra. A Beckman model DB spectrophotometer equipped with a Sargent recorder was used in the study of absorption spectrum.

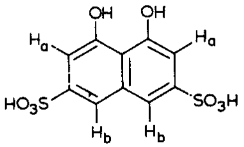
Procedure

The optimum concentration (70%) of sulfuric acid which gave the most sensitive result for the chromotropic acid–nitrate reaction was chosen as the reaction media. 25 mg of chromotropic acid were dissolved in 0.5 ml of 70% (v/v) sulfuric acid. The NMR spectra of the chromotropic acid–nitrate system were taken at various ratios of the two compounds.

RESULTS AND DISCUSSION

NMR spectra of chromotropic acid

In water. The structure of chromotropic acid is illustrated as follows:



The NMR spectrum is shown in Fig. 1. The assignments of the ring protons are indicated. The phenolic protons and the sulfonic acid protons are not evident in the spectrum because they exchange rapidly with water molecules in the solvent. In benzene the ring proton usually resonates at 7.26 p.p.m. The location of the H_a peak which is upfield compared to benzene at 7.13 p.p.m. is due to two effects: (*a*) the adjacent $-OH$ group which causes a diamagnetic shift, and (*b*) the adjacent $-SO_3H$ group which also causes a slight diamagnetic shift. The location of H_b peak which is downfield at 7.83 p.p.m. is due to three effects: (*a*) the $-OH$ group in *para* position which has about the same effect as in *ortho* position, (*b*) the $-SO_3H$ group which causes a slight diamagnetic

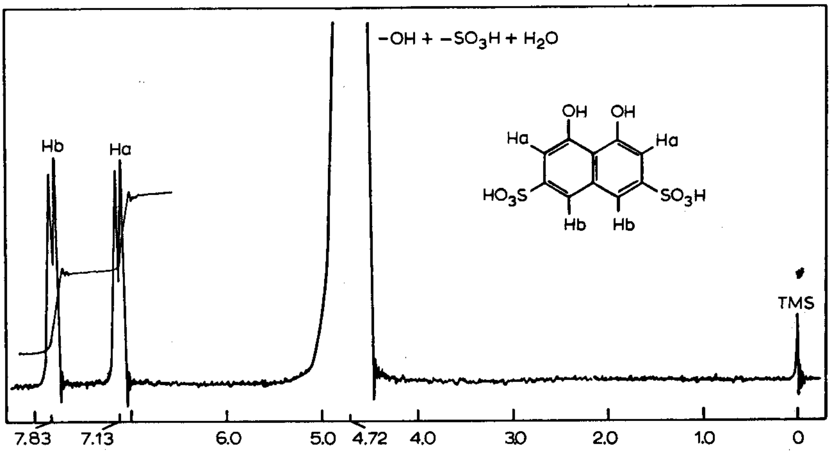


Fig. 1. NMR spectrum of chromotropic acid, 10% (w/v) in water.

shift, and (*c*) the neighboring phenyl group which causes a strong paramagnetic shift. The distance between these two peaks is 0.7 p.p.m. The splitting of each peak into a doublet is due to coupling between the ring protons. The equal area of the two peaks by integration indicates that each peak contains the same number of protons.

In dimethyl sulfoxide–D_6. In order to identify the phenolic proton peak, deuterated dimethyl sulfoxide was used as a solvent for chromotropic acid. The spectrum is shown in Fig. 2. The broad peak at 10.88 p.p.m. is due to phenolic proton resonance. Integration of the peaks for –OH, H_a, and H_b, showed that all three peaks had the same area. It can be concluded from this that each peak represents two protons.

In 70% sulfuric acid. The reaction of the chromotropic acid–nitrate system was studied at the optimum concentration of sulfuric acid[1,2]. The NMR spectrum of chromotropic acid in 70% (v/v) sulfuric acid is shown in Fig. 3. The water peak shifted

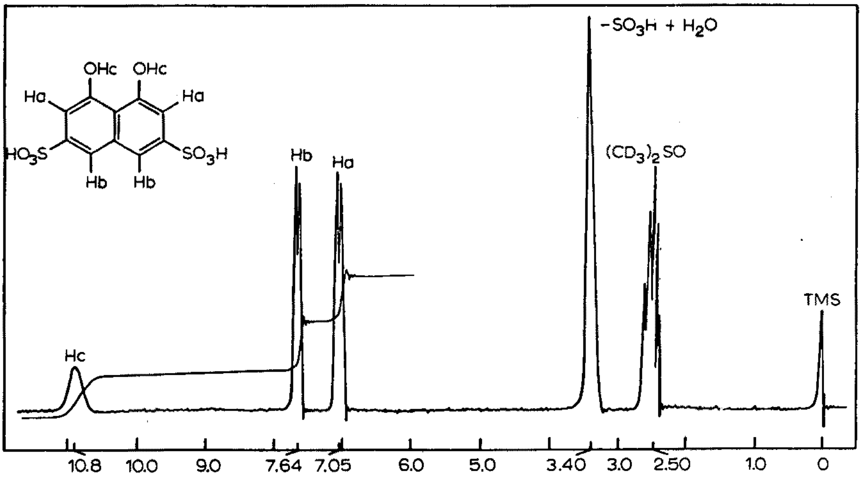


Fig. 2. NMR spectrum of chromotropic acid, 8% (w/v) in dimethyl sulfoxide –D_6.

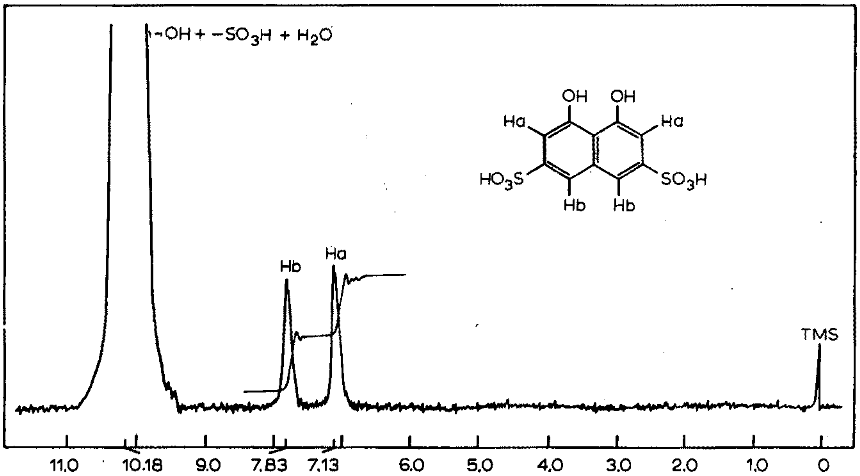


Fig. 3. NMR spectrum of chromotropic acid, 5% (w/v) in 70% sulfuric acid.

downfield in the strong acid media. The chemical shift of the ring hydrogens remained the same, but the spin–spin splitting was lost. Apparently the coupling between the protons decreased in the strongly acidic solution.

NMR spectra of the chromotropic acid–nitrate system in 70% sulfuric acid

Solution prepared by the addition of standard nitrate solution. The spectrum of the chromotropic acid in 70% sulfuric acid was recorded first. Without changing the instrumental settings, the spectrum of the chromotropic acid in 70% sulfuric acid was then recorded after the addition of standard nitrate solution. The process was repeated with increased nitrate addition. The results are shown in Fig. 4. Both H_a and H_b peaks were equally affected by the addition of nitrate solution indicating that neither ring hydrogen was attacked in preference to the other.

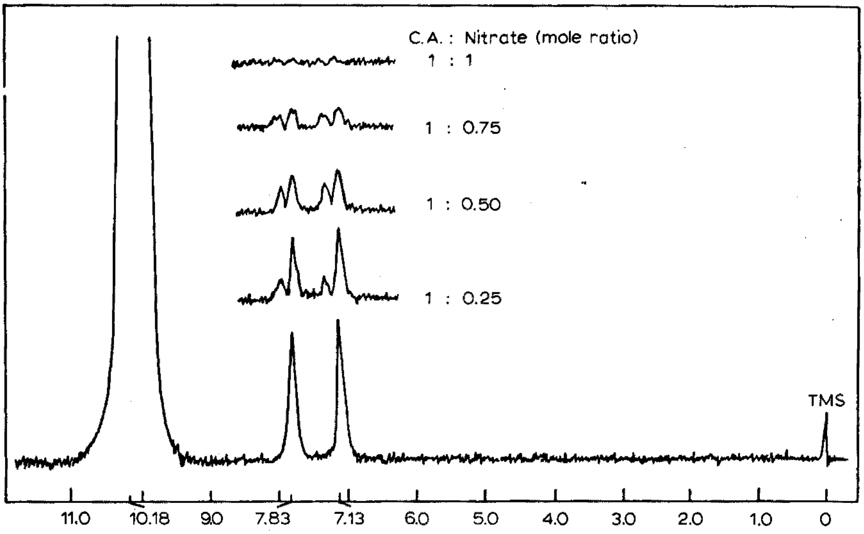


Fig. 4. NMR spectra of the chromotropic acid–nitrate system in 70% sulfuric acid: by the addition of sodium nitrate solution.

As the sodium nitrate concentration increased extra peaks became evident. These were attributed to the formation of the disodium salt of the chromotropic acid causing the ring hydrogens to resonate with a different chemical shift from the ring hydrogens in free chromotropic acid. The mixture of the disodium salt and the free acid resulted in the two spectra being superimposed and the appearance of 4 ring hydrogen peaks instead of two.

At mole ratio 1:1, the H_a and H_b peaks disappeared. Obviously both H_a and H_b protons in chromotropic acid are attacked simultaneously during the addition of nitrate solution. Also, the disappearance of the peaks when the ratio was 1:1 indicated that the product was a mononitrate.

Solution prepared by the addition of concentrated nitric acid. It was suggested that the appearance of the extra peaks in Fig. 4 was the result of the formation of disodium salt of the chromotropic acid. To check this hypothesis a study was made using nitric acid instead of sodium nitrate solution as a means of adding nitrate ion to the solution.

The results are shown in Fig. 5. The extra small peaks attributed to the sodium salt seen in Fig. 4 did not appear under these conditions. However, as before both H_a and H_b peaks disappeared at an equimole of nitrate to chromotropic acid. This evidence supported the theses that the extra peaks were brought about by the sodium present, rather than spin–spin splitting in a new compound.

NMR spectrum of the chromotropic acid–nitrate system in 10% sulfuric acid.
As already mentioned the reaction between chromotropic acid and nitrate is

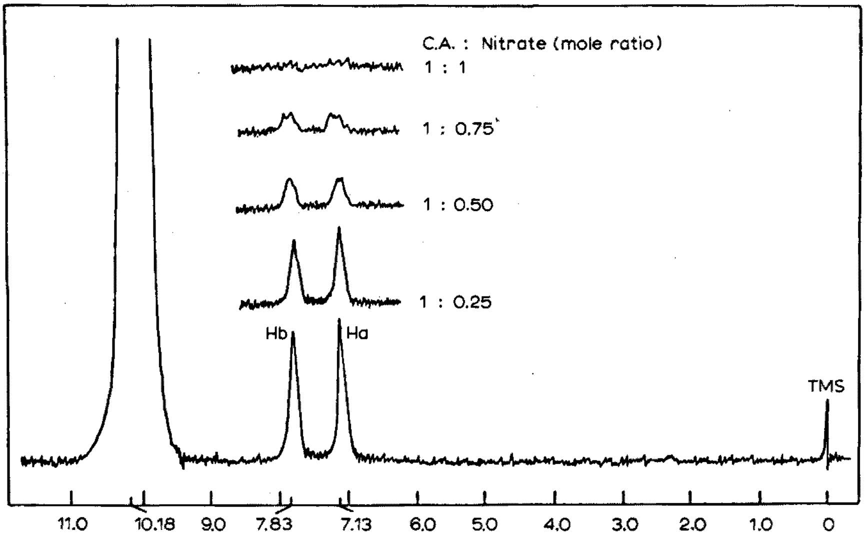


Fig. 5. NMR spectra of the chromotropic acid–nitrate system in 70% sulfuric acid: by the addition of concentrated nitric acid.

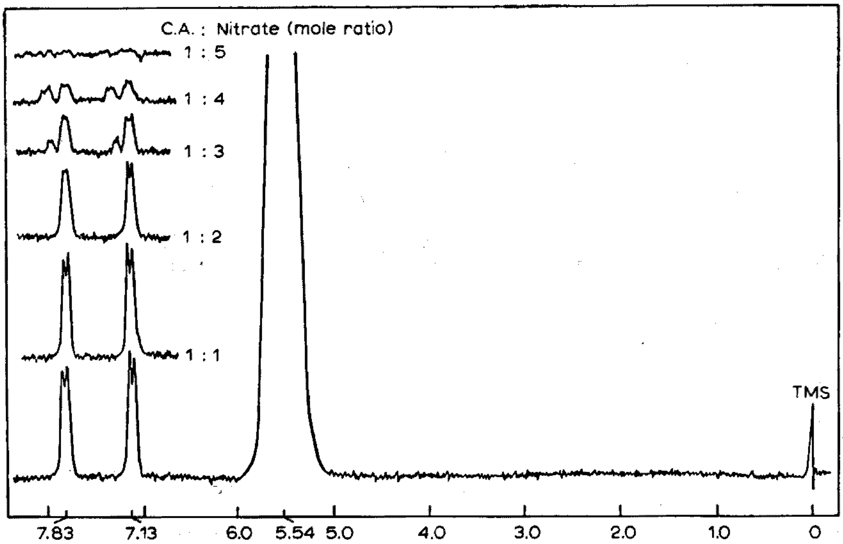


Fig. 6. NMR spectra of the chromotropic acid–nitrate system in 10% sulfuric acid.

markedly influenced by the amount of sulfuric acid present in the solution and the most sensitive reaction takes place at about 70% of sulfuric acid. For the purpose of comparison, a 10% sulfuric acid used as reaction media was also investigated (Fig. 6). It was observed that when the nitrate concentration was increased to a large excess, a slight decrease in the H_a and H_b peak intensities followed. At the mole ratio 1:3 (chromotropic acid/nitrate) two small extra peaks started to appear. At the mole ratio 1:5, both H_a and H_b peaks disappeared. The results indicated a reduced reaction between the nitrate ion and the chromotropic acid at this low acidity.

UV spectrum of the chromotropic acid–nitrate system in 70% sulfuric acid

In order to identify the product of the chromotropic acid–nitrate reaction at the mole ratio 1:1 in the presence of 70% sulfuric acid, a UV absorption spectrum was taken (Fig. 7). It is known that *p*-benzoquinone has a high intensity band near 2450 Å, a medium intensity band near 2850 Å, and a low intensity band near 4350 Å[4]. The spectrum obtained shows that the reaction product has a high intensity band near 2210 Å, a medium intensity band near 2590 Å, and a low intensity band near 4350 Å. Since these absorption bands of the product closely resemble those of *p*-benzoquinone, it can be concluded that the color product was a quinone compound.

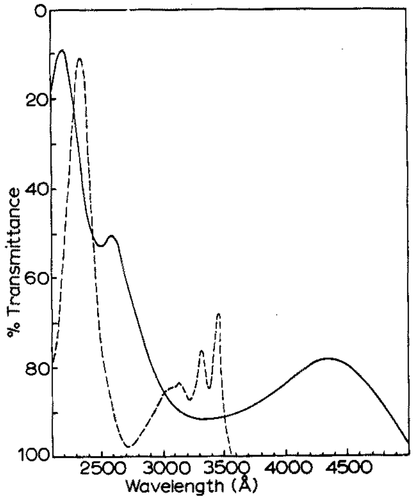
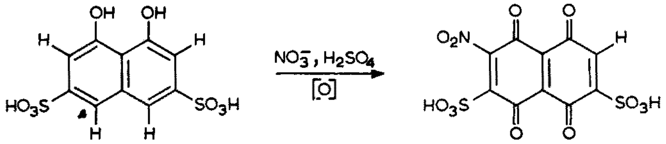


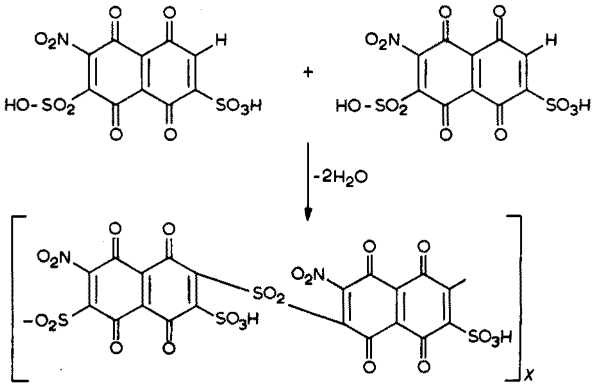
Fig. 7. UV absorption spectra: (–––) Absorption spectrum of chromotropic acid in 70% sulfuric acid; (——) Absorption spectrum of the chromotropic acid–nitrate system at mole ratio 1:1 in 70% sulfuric acid.

POLYMERIZATION

The NMR spectra indicated that the product of the chromotropic acid–nitrate reaction in 70% sulfuric acid was a mononitration compound. Since the nitrate solution present in strong sulfuric acid produced a nitronium ion (NO_2^+), the product would be a mononitro derivative of chromotropic acid. The UV spectrum indicated that the product had a quinone structure. Further, since the NMR spectra indicated that there were no hydrogens left on the ring system, a possible mechanism for the reaction is as follows:



(1)

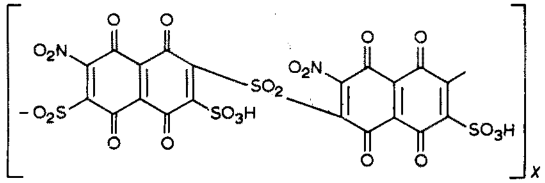


(2)

A polymerized sulfonyl derivative would satisfy the data obtained for the reaction. However, no experimental studies were undertaken to separate the product and to prove the presence of such a polymer.

CONCLUSION

NMR spectra indicated that the product of the reaction between chromotropic acid and nitrate in 70% sulfuric acid was a mononitro derivative of chromotropic acid and that all protons on the ring system after reaction disappeared. The UV spectrum indicated the product was a quinone compound. A proposed structure for the product of chromotropic acid–nitrate reaction in 70% sulfuric acid is as follows:



The compound is a mononitro-quinone derivative of chromotropic acid in a polymerized sulfonyl form.

SUMMARY

Chromotropic acid is known to provide a specific and sensitive reagent for the detection of nitrate ion. The reaction is most sensitive in about 70% sulfuric acid.

NMR studies indicated that the product was a mononitro derivative of chromotropic acid. The UV spectrum indicated that the product was a quinone compound. It is proposed that the structure of the product is a mononitro-quinone derivative of chromotropic acid in a polymerized sulfonyl form.

RÉSUMÉ

L'acide chromotropique est connu pour être un réactif spécifique et sensible pour l'identification des nitrates. La réaction est plus sensible dans l'acide sulfurique à 70% environ. Le produit formé est un mononitro-dérivé de l'acide chromotropique. Un spectre UV indique qu'il s'agit d'une quinone. On arrive à la conclusion que la structure de ce composé est un dérivé mononitro-quinone de l'acide chromotropique sous forme sulfonyle polymérisée.

ZUSAMMENFASSUNG

Chromotropsäure ist als spezifisches und empfindliches Reagenz zur Bestimmung des Nitrations bekannt. Die Reaktion ist sehr empfindlich in etwa 70%iger Schwefelsäure. Kernresonanzspektren zeigen, dass hier ein Mononitroderivat der Chromotropsäure auftritt. Aus dem UV-Spektrum ergibt sich eine Chinonverbindung. Für das Produkt wird die Struktur eines Mononitrochinon-Derivates der Chromotropsäure in einer polymerisierten Sulfonylform vorgeschlagen.

REFERENCES

1 P. W. West and T. P. Ramachandran, *Anal. Chim. Acta*, 35 (1966) 317.
2 T. P. Ramachandran, *Ph. D. Dissertation*, Louisiana State University, Baton Rouge, La., May 1966.
3 P. W. West and P. L. Sarma, *Mikrochim. Acta*, 4 (1957) 506.
4 R. West (Editor), *Chemical Applications of Spectroscopy*, Interscience, New York, 1956, p. 681.

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THE EFFECT OF SUBSTITUENTS ON THE PROTONATION CONSTANTS OF MONO- AND BIS-AZO DERIVATIVES OF CHROMOTROPIC ACID

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Azo derivatives of chromotropic acid are at present widely used for the photometric determination of more than 30 elements. These reagents are noted for their high sensitivity (the molar absorptivities of the metal complexes are in the 10^5 region) and the characteristic colour contrast on chelation (a bathochromic shift of 50–150 nm generally occurs). With some of these reagents, the complexation of readily hydrolysed elements (Zr, Th, Nb, etc.) proceeds in strongly acidic media, so that high selectivity is possible[1–3].

In recent years, several papers have been published on the physico-chemical properties of the reagents of this group and their metal complexes, and the effect of substituents on the sensitivity, selectivity and other analytical characteristics has been studied[2–6]. In these papers, the relation between the conditions of the chelation of the metal and the protonation of the reagent itself has been indicated[7,8]. It has been concluded that the protonation constant of the reagent, the $\mathrm{pH}_{\frac{1}{2}}$-value of the metal chelation reaction, and the solubility product of the metal hydroxide can be correlated in a relatively simple fashion. Relationships have also been found between the molar absorptivity of a complex and the $\mathrm{pH}_{\frac{1}{2}}$-value of the reaction involved, and between the molar absorptivity of the protonated form of the reagent and its protonation constant[8].

These results have shown that in investigations of the chelation processes of metals, it is necessary to know the essential characteristics of the reagent: the protonation constant, dissociation constants, absorption spectra of various reagent forms, etc.

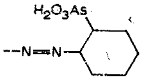
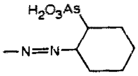
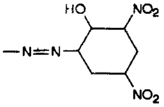
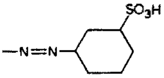
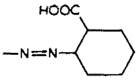
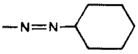
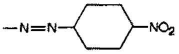
The effect of *meta* and *para* substituents on equilibrium constants can be expressed by Hammett's equation[9]. The attempt of some authors[10,11] to find an analogous dependence for the *ortho* substituents, by modifying Hammett's equation, has not given satisfactory results[12,13]. Some other authors have investigated the effect of the substituents on the change in electron density on the reaction group[14,15], but these methods are also unsatisfactory for *o*-substituents. MULLIKEN[16] and SAIDOV AND BAKSHIEV[17] have related the equilibrium constants to the oscillator strength of the absorption spectrum.

The reagents investigated in the present work are mostly *o*-substituents, so

TABLE I

VALUES OF PROTONATION CONSTANTS (K) AND MOLAR ABSORPTIVITIES (a_{HB}) OF PROTONATED FORMS OF MONO- AND BIS-AZO DERIVATIVES OF CHROMOTROPIC ACID

(R_1 = substituent in a benzene ring, closer to the reacting azo group;
R_2 = substituent in the position 7 of naphthalene)

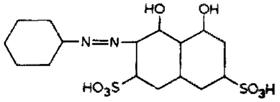
Reagent no.	*Name*	R_1	R_2	*log K*	$a_{HB} \cdot 10^{-4}$
1	Br-arsenazo	o-AsO_3H_2	Br	−7.2[b]	1.5
2	Arsenazo I	o-AsO_3H_2	H	−6.36[c]	2.5
3	—[a]	o-OH,m-,m'-NO_2	H	−6.36	1.8
4	Arsenazo III	o-AsO_3H_2		−5.04[d]	5.3
5	2-Azobenzene-chromotropic acid	H	H	−4.89	2.7
6	—	o-COOH	H	−4.87	2.5
7	Arsenazo-p-NO_2	p-NO_2		−4.23[b]	4.6
8	Arsenazo M	m-SO_3H	,,	−3.20[b]	6.6
9	Arsenazo B	H	,,	−2.72[b]	4.6
10	Arsenazo K	o-COOH	,,	−2.67	5.4
11	Picramine S	o-OH,m-, m'-NO_2		−2.67	5.4
12	Picramine M	m-SO_3H	,,	−1.63	8.4
13	Picramine K	o-COOH	,,	−1.36	6.1
14	Anthranilic M	o-COOH		−0.63	6.0
15	Anthranilic S	o-COOH		−0.30	6.6
16	2,7-Bis-(azobenzene)-chromotropic acid	H		−0.32	6.3
17	—	p-AsO_3H_2		−1.45	
18	—	H		−0.93	
19	—	H		−0.91	

[a] Reagents 3, 6, 17, 18 and 19 have no trivial name.
[b] Ref. 8.
[c] Ref. 7.
[d] Ref. 6.

that the use of Hammett's equation was excluded. To compare the protonation constants of the reagents and the effect of the substituents on their values, one of the investigated reagents was chosen as the "zero" reagent. The dependence of the molar absorptivity of the protonated form on the protonation constant of the reagent is discussed.

RESULTS

Protonation constants of 19 mono and bis-azo derivatives of chromotropic acid were determined. These reagents should be considered as the derivatives of 2-azobenzene-1,8-dihydroxynaphthalene-3,6-disulfonic acid (reagent 5 in Table I).



The protonation constants were determined by the spectrophotometric methods in perchloric or sulfuric acid, depending on the value of the constant[9,18,19]. The values of the constants and the molar absorptivities are given in Table I.

By choosing various "zero" reagents, log K/K_0 values were obtained for different substituents (Table II). The effect of the substituent on protonation of the azo group was studied with the assumption that, in the case of bis-azo compounds, the azo group protonated is attached to the benzene ring which does not possess another substituent, or any substituent present is "less acidic", *i.e.*, has little effect on the binding of protons to the azo group.

The last column of Table II contains values for log K/K_0 for different substituents. From these data, the effect of two substituents: R_1 and R_2 in reagent 5 (Table I) or both substituents in the benzene rings in reagent 16 (Table I), was calculated as the sum of both effects (Σ log K/K_0 from Table II). Table III shows the agreement of the calculated and experimental values.

DISCUSSION

Relation between protonation constants and molar absorptivities

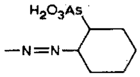
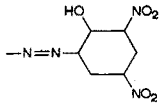
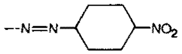
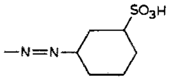
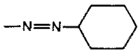
A direct relation between the protonation constants and the molar absorptivities can be observed. The molar absorptivity increases with increasing protonation constant (Fig. 1). This is a logical result of the simultaneous increase of the free energy of the protonation reaction ($\Delta F^0 = -RT \ln K$) and the increase of the transition energy of the electronic spectra expressed by oscillator strength ($f = k\int a\Delta\nu$). Figure 1 shows that all the investigated reagents can be classified in 3 groups.

Group I contains reagents with an arsonic acid group in the *o*-position in relation to the protonating azo group (reagents 1, 2, 4 from Table I). The effect of the arsonic acid group is considerable, so that the azo group is not easily protonated as is evident from the slope of curve I in Fig. 1. The arsonic acid group considerably reduces the basicity of the reagent, *i.e.* the value of the protonation constant.

Group II contains reagents which are protonated on the azo group without or with an *o*-carboxylic acid substituent in the adjacent benzene ring. The main effect on the value of the protonation constant is exerted by the substituent in position 7

TABLE II

EFFECT OF THE SUBSTITUENTS ON THE VALUE OF PROTONATION CONSTANTS EXPRESSED BY LOG K/K_0 (K_0 is a protonation constant for chosen "zero" reagent)

Substituent	*log K/K_0*								*log K/K_0*
	Reagent no.	*5*	*9*	*16*	*2*	*13*	*3*	*14*	
	log K_0	*−4.89*	*−2.72*	*−0.32*	*−6.36*	*−1.36*	*−6.36*	*−0.63*	
o-AsO_3H_2		−1.47	−2.32						−1.9
o-OH,*m*-,*m'*-NO_2		−1.47							−1.5
p-NO_2			−1.51						−1.5
(*o*-AsO_3H_2)'[a]						−1.36		−2.57	−2.0
(*o*-OH,*m*-,*m'*-NO_2)'						−1.31		−1.00	−1.2
Br[b]					−0.84				−0.8
(*p*-AsO_3H_2)'				−0.69					−0.7
(*p*-NO_2)'				−0.61					−0.6
m-SO_3H			−0.48						−0.5
(*m*-SO_3H)'				−0.31		−0.27			−0.3
o-COOH		+0.02	+0.05						0.0
	b	2.17			1.32				1.8
	b	3.53					3.69		3.6
	b	3.88							3.9
	b	3.96							4.0
	b	4.26							4.3
	b	4.59							4.6
o-COOH + (*o*-COOH)'[c]				0.02					0.0
o-AsO_3H_2 + (*o*-AsO_3H_2)'[c]				−4.72					−4.7
p-AsO_3H_2 + (*p*-AsO_3H_2)'[c]				−1.13					−1.1

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[a] Substituent marked (   )' is in a second benzene ring.
[b] Substituent in position 7 of naphthalene ring.
[c] Effect of substituents in both benzene rings.

TABLE III

COMPARISON OF THE CALCULATED AND EXPERIMENTAL VALUES OF LOG K/K_0

Reagent		*log K/K_0*			
No.	*Name*	*"Zero" reagent 5*		*"Zero" reagent 16*	
		Exp.	*Calc.*	*Exp.*	*Calc.*
1	Br-arsenazo	−2.31	−2.7	—	—
4	Arsenazo III	−0.15	−0.10	−4.72	−3.9
7	Arsenazo-*p*-NO_2	0.66	0.3	−3.91	−3.5
8	Arsenazo M	1.69	1.3	−2.88	−2.5
11	Picramine S	2.22	2.1	−2.35	−2.7
12	Picramine M	3.26	3.1	−1.31	−1.7

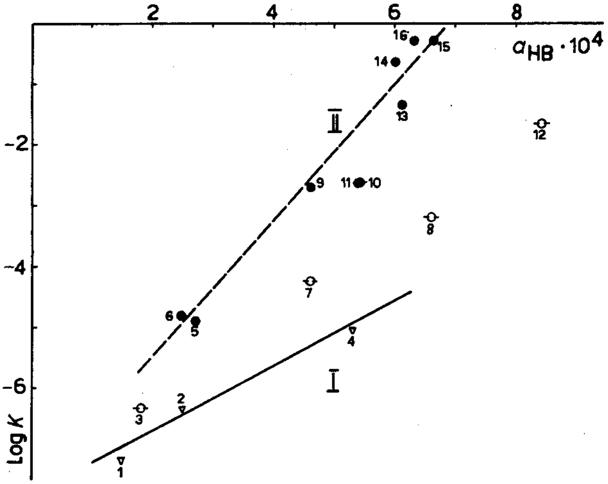

Fig. 1. Dependence of molar absorptivities of protonated forms of reagents on the value of protonation constants. ▽ reagents with *o*-AsO_3H_2, ● reagents without substituents or with *o*-COOH, ⊖ reagents with other substituents closer to the reacting azo group.

of the naphthalene nucleus. Except for the bromine substituent, all the other investigated substituents increase the basicity of the reagent. This is why the slope of curve II (Fig. 1) is greater than that of curve I.

Group III. This contains reagents 3, 7, 8, 11, 12, which lie between groups I and II; this is reasonable because, in addition to the substituents in position 7 of the naphthalene group, these reagents also possess substituents in the benzene ring closer to the reacting azo group. The effect of the latter substituents on the basicity of the reagent is less than that of the *o*-arsonic acid group.

The greatest decrease in the basicity of the reagent, and shift of its protonation to a strongly acidic medium, is exerted by *o*-substituents with a strong steric effect. The *o*-carboxy group, in spite of its position, does not affect the basicity of the reagent; this is clear from a comparison of the protonation constants of the following reagent pairs in Table I: reagents 5 and 6; 9 and 10; 15 and 16. These pairs include reagents without and with the *o*-carboxylic acid substituent.

Transition from mono-azo compounds to the corresponding symmetrical bis-azo compounds increases the basicity of the reagent, *i.e.* its protonation constant. The least increase appears in the group of arsenazo reagents, with respect to the effect of the arsonic acid group. The transition from arsenazo I to arsenazo III induces a change of $\Delta \log K = 1.32$; on transition from reagent 3 to reagent 11 (so-called "picraminic reagents"), the change of $\Delta \log K$ is 3.69. In the case of transition from mono-azo to bis-azo compounds without substituents in the benzene rings (reagents 5 to 16), the change in $\Delta \log K$ is 4.56.

Relation between protonation constants and reaction with metals

A shift of protonation to a more acidic medium also causes a shift of the reaction with metals, as observed earlier[7,8]. For example, the reactions of reagents of the arsenazo group (arsenazo I, arsenazo III, arsenazo-*p*-NO_2 and arsenazo M) with lanthanum are related to the protonation of the reagent itself. The reagent reacts with the metal in less acidic media as its basicity decreases.

The protonation constants (log K from Table I) and the $pH_{\frac{1}{2}}$-values for reaction of these reagents with lanthanum have the following values:

Reagent	*log K*	*$pH_{\frac{1}{2}}$*
Arsenazo I	−6.36	6.10
Arsenazo III	−5.04	1.95
Arsenazo-*p*-NO_2	−4.23	2.20
Arsenazo M	−3.20	1.25

This relationship is observed when the complexation and the protonation reactions have the same mechanism.

A preliminary knowledge of the value of the protonation constant of a reagent and the effect of each substituent on this value enables prediction of the optimal reaction conditions between the reagent and metals, and may allow the synthesis of new reagents with predicted properties.

SUMMARY

The protonation of 19 derivatives of mono- and bis-azochromotropic acid has been studied and the protonation constants determined. The effect of the substituents is described by comparison with different "zero" reagents. The relationship between the values of the protonation constants and the molar absorptivities of the protonated form of the reagents is discussed.

RÉSUMÉ

La fixation de protons de 19 dérivés des acides mono- et bis-azochromotropique a été étudiée et les constantes de fixation des protons ont été déterminées. L'effet des substituants est décrit par comparaison avec différents réactifs appelés "zéro". On discute la relation entre les valeurs des constantes de fixation des protons et les absorptions molaires des réactifs quand ces derniers sont dans la forme ayant fixé les protons.

ZUSAMMENFASSUNG

Es wurde die Protonisation von 19 Derivaten der Mono- und Bis-azochromotropsäure untersucht und die Protonisationskonstante bestimmt. Der Einfluss der Substituenten ist durch die Differenz zwischen dem Logarithmus der Protonisationskonstante der untersuchten und der "Null"-substanz (log K/K_0) gegeben. Die Abhängigkeit der Werte der Protonisationskonstante von der Molarabsorption der protonisierten Form wurde untersucht und diskutiert.

REFERENCES

1 S. B. Savvin, *Arsenazo III*, Atomizdat, Moscow, 1966.
2 S. B. Savvin, *Talanta*, 11 (1964) 1, 7.
3 S. B. Savvin and E. L. Kuzin, *Zh. Analit. Khim.*, 22 (1967) 1058.
4 L. A. Gribov, E. L. Kuzin and S. B. Savvin, *Zh. Analit. Khim.*, 22 (1967) 1790.
5 S. B. Savvin, E. L. Kuzin and L. A. Gribov, *Zh. Analit. Khim.*, 23 (1968) 5, 490.
6 A. Muk and R. T. Radosavljević, *Bull. Boris Kidrič Inst. Nucl. Sci. (Belgrade)*, 17 (1966) 1.
7 A. Muk and R. T. Radosavljević, *Croat. Chem. Acta*, 39 (1967) 1.
8 A. Muk, S. B. Savvin and R. F. Propistsova, *Zh. Analit. Khim.*, 23 (1968) 1277.
9 L. P. Hammett, *Physical Organic Chemistry*, McGraw Hill, New York, 1940, p. 186 and p. 267.
10 R. W. Taft, Jr., *J. Am. Chem. Soc.*, 74 (1952) 3120.
11 R. W. Taft, Jr., *J. Am. Chem. Soc.*, 75 (1953) 4231.
12 H. H. Jaffé, *Chem. Rev.*, 53 (1953) 191.
13 V. A. Palm, *Usp. Khim.*, 30 (1961) 1069.
14 F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, 42 (1959) 1877.
15 H. H. Jaffé, *J. Chem. Phys.*, 20 (1952) 279; 21 (1953) 415.
16 R. C. Mulliken, *J. Am. Chem. Soc.*, 72 (1950) 600.
17 G. V. Saidov and N. G. Bakshiev, *Dokl. Akad. Nauk SSSR*, 175 (1967) 1090.
18 H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, 80 (1958) 319.
19 T. G. Bonner and J. Phillips, *J. Chem. Soc.*, B, (1966) 650.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 2,3-DIAMINOPYRIDINE

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Although a wide variety of reagents for the spectrophotometric determination of ruthenium has been described[1], no procedure yet devised permits the determination of ruthenium in the presence of other platinum elements[2]. Interference from other metals is easily eliminated by distillation of ruthenium tetroxide after an appropriate oxidation from lower oxidation states. The ruthenium tetroxide is usually received in an aqueous solution of an appropriate reducing agent, and the chromogenic reaction is carried out therein.

In the present study, preliminary experiments showed that 2,3-diaminopyridine reacts with ruthenium in oxidation states III, IV, VI, VII, and VIII to give various colored solutions, depending upon the anion matrix, the solvent, and the hydrogen ion concentration of the solution. The reaction of ruthenium(III,IV) with 2,3-diaminopyridine, giving a red solution (absorption maximum at 510 nm), is essentially complete after heating the mixture at 100° for 30 min if the hydrogen ion concentration is 1.0–1.2 *F*. At pH greater than 1, the absorption peak occurs at 525 nm, but does not reach maximum absorbance until the pH is greater than that at which hydrolytic precipitation of hydrous oxides can occur. In both instances, the intensity and/or the wavelength of absorption were modified by many common anions.

Because of the virtual necessity, in practice, of separating ruthenium from other metals, attention was directed to the application of 2,3-diaminopyridine to ruthenium distillates containing ruthenium(VIII) or its reduction products ruthenium(VII,VI), *i.e.* perruthenate and ruthenate. The oxidation and distillation procedures and the receiving solution were essentially those given by LARSEN AND ROSS[3].

EXPERIMENTAL

Apparatus

Absorbance scanning was done with a Cary Model 14 spectrophotometer. Absorbance measurements at fixed wavelength were made with a Beckman Model DU spectrophotometer, using matched silica cells of 1.00-cm optical path. A Mettler microbalance, Type M-5, was used for weighings requiring a high degree of accuracy. The distillation equipment consisted of a 200-ml flask, fitted with a side tube to admit nitrogen gas, and connected to a water condenser the delivery end of which was connected to a 25-ml volumetric flask *via* a vacuum take-off adapter to allow exit of the sweep gas. Ground glass joints were used throughout. The receiving flask was surrounded by an ice bath. The apparatus was cleaned initially by distillation of several ml of perchloric acid, followed by thorough rinsing with distilled water. Subsequent cleaning was done with hot sodium hypochlorite solution followed by thorough rinsing with distilled water. Soap and detergents are to be scrupulously avoided because of possible introduction of reductants[3].

Reagents

2,3-Diaminopyridine (Aldrich Chemical Co.) was purified by heating 10 g of the material in dichloromethane, and filtering off insoluble matter. The orange-colored solution was scrubbed, three times in succession, with a small amount of decolorizing activated carbon, followed by filtration through filter paper overlaid with Celite filtering aid. The final filtrate was crystallized at ice-bath temperature; the solid was collected on a sintered glass funnel, and dried under vacuum. A 0.25% (w/v) solution was prepared by dissolving 0.125 g of reagent in 50 ml of glacial acetic acid; the solution, which is light-sensitive, was stored in a nonactinic bottle.

Ruthenium(III) chloride hexahydrate (A. D. Mackay, Inc.) was used to prepare a stock solution, *ca.* 0.005 *M*, by dissolving the salt in 10% hydrochloric acid. For standardization, 5-ml aliquots of the solution were evaporated to dryness, then reduced in hydrogen and weighed as metal.

All other reagents were A.C.S. reagent grade. Triple distilled water was used.

Oxidation and distillation

Before oxidation of the ruthenium, strong fuming of the solution with sulfuric acid is required to remove reductants. Various oxidants and receiving solutions have been used for osmium and ruthenium tetroxides[2]. Oxidation with sodium bismuthate in 3 *M* sulfuric acid[3,4] has the advantages of rapid quantitative yield and of not introducing volatile reduction products into the receiving solution. Strict cleanliness is required in order to avoid deposition of ruthenium oxides on the walls of the distillation apparatus.

First attempts at receiving the ruthenium tetroxide directly into an aqueous solution of the 2,3-diaminopyridine for color development were unsatisfactory, because of deposition of ruthenium dioxide on the tip of the delivery tube. By receiving the distillate in 1 *M* sodium hydroxide and finally forming the color with the reagent in concentrated acetic acid, a satisfactory method was developed.

Recommended procedure

Pipet 10 ml of solution containing 100–300 p.p.m. of ruthenium into the still flask. Add 20 ml of 3 *M* sulfuric acid, and evaporate to strong fumes on a hot plate. Cool, add water, and repeat the fuming. (If nitrate is present, add a 4-fold excess of 12 *M* hydrochloric acid and evaporate, before fuming with sulfuric acid, to prevent premature volatilization of ruthenium tetroxide.) Cool, and add water to make the acid concentration about 3 *M* in sulfuric acid. Place about 15 ml of 1 *M* sodium hydroxide in the receiving flask, set it in an ice bath, and connect it to the distillation apparatus. To the still flask add about 1 g of sodium bismuthate and 10 ml of 3 *M* sulfuric acid, and connect the flask to the condenser. Heat with a small flame for

15 min while nitrogen gas is passed through the apparatus at a rate of about 2 bubbles per sec. Allow the receiver and contents to stand overnight, and then dilute to volume with 1 *M* sodium hydroxide. Pipet an aliquot (up to 2 ml) of the solution into a 25-ml volumetric flask containing 3 ml of 2,3-diaminopyridine solution, and then dilute to volume with glacial acetic acid. Allow the color to develop for 3 h, then measure the absorbance of the indigo-blue solution at 572 nm against a reagent blank prepared similarly. Determine the ruthenium concentration from a previously prepared calibration graph.

The spectral curves of the ruthenium–2,3-diaminopyridine reaction product and of the reagent itself are shown in Fig. 1.

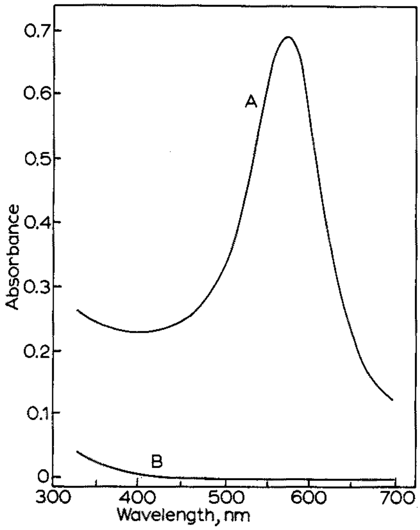

Fig. 1. Spectral curves. (A) Ruthenium + 2,3-diaminopyridine; (B) 2,3-diaminopyridine.

RESULTS

Calibration, range, and sensitivity

The ruthenium–2,3-diaminopyridine system conforms to Beer's law over the range investigated, namely, 0.6–7 p.p.m. (absorbance about 0.1 to 0.7). The optimum working range is about 1–6 p.p.m. of ruthenium. The molar absorptivity is $1.2 \cdot 10^4$ l mole^{-1} cm^{-1}, a sensitivity comparable to those of many other methods for ruthenium.

Effect of reagent concentration

Samples containing a fixed amount (2.34 p.p.m.) of ruthenium were developed and measured by the recommended procedure, except that the amount of reagent was varied. Full color development required about a 4-fold molar excess of reagent. Very large excesses of reagent produced a slight decrease in absorbance at 572 nm. At low ratios of reagent to ruthenium there was a bathochromic shift in the wavelength of the absorption maximum, corresponding to the variation of the reagent/Ru ratio in the range of ruthenium concentration recommended; this shift was less pronounced at high ratios of 2,3-diaminopyridine to ruthenium. In the recommended procedure the amount of reagent specified provides a reagent/Ru mole ratio of about 30–300 for the concentration range studied.

Effect of time

Absorbance readings of samples developed by the recommended procedure were started 15 min after the dilution step, and were continued at various time intervals thereafter. Although most of the color developed immediately upon addition of the reagent and acetic acid, the absorbance increased slowly with time. Typical results are shown in Table I. Concordant results were obtained by measuring the absorbance 2–4 h after dilution.

TABLE I

EFFECT OF TIME ON ABSORBANCE

Hours after dilution	*Absorbance at 572 nm*	*Hours after dilution*	*Absorbance at 572 nm*
0.25	0.470	3.0	0.498
0.50	0.482	4.0	0.500
1.0	0.488	5.0	0.508
2.0	0.497	24	0.520

Effect of solvent

In the preliminary investigation various solvents and additives were used in an attempt to stabilize the ruthenium–2,3-diaminopyridine product. Glacial acetic acid was found to be superior to aqueous solutions or other organic solvents.

Reproducibility

The precision of the method was tested by measuring the absorbance of 8 identical samples containing 2.34 p.p.m. of ruthenium developed by the recommended procedure. The mean absorbance was 0.294, with a standard deviation of 0.002.

Interferences

Inherent in the recommended procedure is the separation of ruthenium by distillation as ruthenium tetroxide. Osmium, if present, would be volatilized as osmium tetroxide during the sulfuric acid fuming[5]. The use of the nonvolatile sodium bismuthate, rather than other oxidants such as perchloric acid, sodium bromate, sodium hypochlorite, etc., eliminates any anion contamination of the receiving solution. A systematic investigation of interferences was therefore unnecessary.

STUDY OF THE REACTION

Because of the ease with which the higher oxidation states of ruthenium are reduced, it seemed plausible that the color developed in this method might be due to an oxidation product of 2,3-diaminopyridine. Separate solutions of the reagent were treated with peroxydisulfate, periodate, perchloric acid, hydrogen peroxide, and bromine. Only yellow- or brown-colored solutions resulted; none of the oxidized solutions approximated the color of the ruthenium–2,3-diaminopyridine product, nor subsequently gave the indigo-blue color upon addition of ruthenium solution. A redox reaction thus being ruled out, it was assumed that complex formation occurred, and spectrophotometric methods were applied to establish the stoichiometry of the complex.

Method of continuous variations

In this method[6] the total concentration of the two reactants (2,3-diaminopyridine + ruthenium) was held at a constant value ($4.8 \cdot 10^{-5}$ *F*) but the mole fraction of the reagent was varied in the different samples. In a plot of absorbance against mole fraction of 2,3-diaminopyridine, a sharp peak at 0.5 mole fraction indicated a 1:1 mole ratio of the reactants; moderate changes of slope also occurred at 0.33 mole fraction (corresponding to Ru: reagent = 2:1) and at 0.78 mole fraction (corresponding to Ru: reagent = 1:3 or 1:4).

Mole ratio method

In the method of YOE AND JONES[7], a series of samples was prepared containing a constant amount of ruthenium ($2.4 \cdot 10^{-5}$ *F*) and varying amounts of 2,3-diaminopyridine. In the plot of absorbance against mole ratio of reagent to ruthenium, the initial steep portion of the curve and the final flat portion of the curve extrapolated to an intersection at a mole ratio of 1:1. The experimental plot was highly rounded in the vicinity of this mole ratio.

Ion-exchange behavior

Ion-exchange columns were prepared, using Bio-Rad sulfonic type resin in the hydrogen form, and quaternary ammonium resin in the chloride form. An acetic acid solution of the ruthenium–2,3-diaminopyridine product was partially retained on the anion-exchange column, and very strongly retained on the cation exchanger. An alkaline solution of the reaction product was partially retained on the cation exchanger and very strongly held on the anion exchanger.

Attempts were made to isolate the reaction product for further characterization. All efforts to extract or to precipitate the product were unsuccessful.

Financial support provided by National Science Foundation grant GP 5454 is gratefully acknowledged.

SUMMARY

Ruthenium, in solution as its high oxidation states, and 2,3-diaminopyridine react in concentrated acetic acid to give an indigo-blue product having an absorption peak at 572 nm. The color develops at room temperature, and the method is not highly sensitive to the concentration of the reagent nor to the development time. The optimum concentration range, for measurement at 1.00-cm optical path, is about 1–6 p.p.m. of ruthenium; the molar absorptivity is $1.2 \cdot 10^4$ l mole^{-1} cm^{-1}. A prior separation of ruthenium is necessary. Spectrophotometric methods established a 1:1 mole ratio in the molar reaction. The product is predominantly in cationic form in acetic acid solution, and predominantly anionic in alkaline medium.

RÉSUMÉ

Le ruthénium en solution à l'état de ses degrés d'oxydation les plus élevés et la 2,3-diaminopyridine réagissent dans l'acide acétique concentré en donnant un produit de couleur indigo-bleue ayant un pic d'absorption à 572 nm. La couleur se développe à température ordinaire et la méthode n'est très sensible ni à la concentration du réactif, ni au temps de développement. Le domaine optimum de concentration, pour des mesures dans des cellules de 1.00 cm d'épaisseur est environ de 1 à 6 p.p.m. de ruthénium. L'absorption molaire est de $1.2 \cdot 10^4$ litre cm^{-1} $mole^{-1}$. Une séparation préalable du ruthénium est nécessaire. Les méthodes spectrophotométriques permettent d'établir que le rapport molaire est de (1:1) lors de la réaction colorée. Le produit prédomine sous forme cationique dans les solutions d'acide acétique et sous forme anionique en milieu alcalin.

ZUSAMMENFASSUNG

Ruthenium, welches in Lösung in seiner höchsten Oxidationsstufe vorliegt, und 2,3-Diaminopyridin reagieren in konzentrierter Essigsäure zu einem indigoblauen Produkt, das ein Absorptionsmaximum bei 572 nm besitzt. Die Farbe entwickelt sich bei Raumtemperatur und die Methode ist weitgehend unabhängig sowohl von der Reagenzkonzentration als auch der Entwicklungszeit. Der optimale Konzentrationsbereich für Messungen mit einer 1 cm-Küvette liegt bei etwa 1–6 p.p.m. Ruthenium. Die molare Extinktion beträgt $1.2 \cdot 10^4$ Liter Mol^{-1} cm^{-1}. Eine vorhergehende Abtrennung des Rutheniums ist erforderlich. Ruthenium verbindet sich mit dem Reagenz im Molverhältnis 1:1. In essigsaurer Lösung liegt vorwiegend die kationische, im alkalischen Medium die anionische Form vor.

REFERENCES

1 F. E. Beamish, *Talanta*, 12 (1965) 743.
2 F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon Press, New York, 1966.
3 R. P. Larsen and L. E. Ross, *Anal. Chem.*, 31 (1959) 176.
4 G. Kesser, R. J. Meyer and R. P. Larsen, *Anal. Chem.*, 38 (1966) 221.
5 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959, p. 700.
6 P. Job, *Ann. Chim. (Paris)*, (10) 9 (1928) 113.
7 J. H. Yoe and H. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 11.

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DEPOLYMERISATION OF ZIRCONIUM IN SPECTROPHOTOMETRY WITH ARSENAZO III

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The reagent arsenazo III[1] (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis [(azo-2)-phenylarsonic acid]) has been used to determine thorium, zirconium, hafnium and uranium(IV) in strong hydrochloric acid solutions[2]. Zirconium can be determined in 2–9 *M* hydrochloric acid without separation from most metals[3,4]. Small amounts of sulphate decrease, and large amounts of perchlorate increase, the absorbance of the zirconium–arsenazo III complex. Nitrate ion must also be absent because of oxidation of the dye when solutions are prepared in strong hydrochloric acid media.

Zirconium forms polymerised species readily and the rate of the formation of these species is dependent on the concentration of zirconium ions, the anions associated with the zirconium, the pH, the temperature, and the time of standing after dissolution[5–7]. PILKINGTON AND WILSON[8] studied the depolymerisation of zirconium in sulphate systems under the conditions required for a direct titration with EDTA and found that 0.1 *M* zirconium sulphate solutions could be depolymerised by boiling for 15 min with 5 *N* sulphuric acid. SINHA AND DAS GUPTA[9] found that 3 *N* nitric acid can be used to depolymerise zirconium solutions for titration with EDTA. BABKO AND GRIDCHINA[5] studied the rate of establishment of equilibrium between zirconium and xylenol orange in acidified zirconium chloride solutions.

It is important that zirconium ions in solutions which are prepared for spectrophotometric determination be depolymerised, otherwise low results will be obtained. A literature search on the spectrophotometric determination of zirconium showed that a variety of methods have been used for the preparation of zirconium solutions. Standard solutions have been prepared by dissolving zirconium salts in water[10,11]; in 0.01 *M*[12], 1 *M*[13], 6 *M*[2] and 10 *M*[14] hydrochloric acid; in 8 *M* nitric acid[15]; in 0.8 *M*[16] and 5 *M*[17] perchloric acid; and in 0.1 *M* and 4 *M* sulphuric acid[16]. Zirconium solutions have been heated to boiling in 2 *M*[3] and 4 *M*[18] hydrochloric acid before arsenazo III is added.

In the present work, the depolymerisation of zirconium as applied to spectrophotometry with arsenazo III has been thoroughly investigated. The areas of investigation were: (*1*) preparation of zirconium solutions in the cold; (*2*) polymerisation of zirconium solutions in various concentrations of acids on boiling; (3) depolymerisation of highly polymerised zirconium species with acids; and (*4*) dissolution of precipitated zirconium hydroxide by hydrochloric acid.

In this work the term "depolymerisation" refers to the condition where such zirconium species, after reaction with arsenazo III in 8 N hydrochloric acid, produced maximum absorbance. The depolymerisation curves obtained should, however, be usable when zirconium is determined with other reagents such as methyl thymol blue, alizarin S, phenylfluorone, arsenazo I and stilbazo[5,10].

EXPERIMENTAL

Polymerisation of zirconium solutions in the cold

Solutions containing 20 μg, 200 μg, 2 mg and 20 mg Zr/ml were prepared by dissolving zirconium oxychloride octahydrate and hydrated zirconium sulphate in water. Aliquots of 50 ml of each solution were transferred to a number of 100-ml volumetric flasks containing water and various amounts of acid totalling 45 ml. Water was added to volume and the solutions mixed. The zirconium was determined in solutions directly after mixing and after standing periods of 1, 3, 10 and 30 days. All the zirconium solutions were then diluted to contain 10 μg Zr/ml for spectrophotometric determination, and 3-ml aliquots were taken for analysis (see Appendix). The diluted solutions were prepared in 0.5 N hydrochloric acid, except where the original acidity was below 0.5 N in which case the hydrochloric acid concentration was maintained at the initial acid concentration.

Polymerisation of zirconium solutions with acids on boiling

Solutions containing 20 μg, 200 μg, 2 mg and 20 mg Zr/ml were prepared by dissolving zirconium salts in water. Aliquots (25 ml) of each of these solutions were transferred to a number of 250-ml beakers, the required amount of acids were added, and the solutions were diluted to 50 ml and covered with a watch-glass. The solutions were boiled gently for 30 min, the volume being kept constant by the addition of water. The solutions were diluted to contain 10 μg Zr/ml for spectrophotometric determination. The acid concentrations on dilution were maintained as in the case of polymerisation of zirconium solutions in the cold.

Depolymerisation of zirconium solutions

Solutions containing 20 μg, 200 μg, 2 mg and 20 mg Zr/ml were prepared from zirconium salts. Aliquots (25 ml) of each of these solutions were transferred to a number of 250-ml beakers, diluted to 50 ml, covered with a watch-glass and boiled for 30 min, the volume being kept constant by the addition of water, to produce highly polymerised species. Then various amounts of acids (10 N hydrochloric acid, 11.6 N perchloric acid and 18 N sulphuric acid) were added and the solutions boiled gently for 15 min to depolymerise zirconium, the volume being kept constant at the new level. The solutions were diluted to contain 10 μg Zr/ml for the spectrophotometric determination. The acid concentrations on dilution were maintained as in the case of polymerisation of zirconium solutions in the cold.

Dissolution of precipitated zirconium hydroxide in hydrochloric acid

Solutions containing 2 mg Zr/ml were prepared from zirconium salts. Aliquots of 50 ml were transferred to 250-ml beakers and diluted to 100 ml. Depolymerised zirconium oxychloride solutions were prepared by boiling with 1.5 N hydrochloric acid, 1 N sulphuric acid and 1 N perchloric acid for 5 min, and zirconium sulphate solutions were depolymerised with 2 *N* hydrochloric acid, 1 *N* sulphuric acid and 3.5 *N* perchloric acid by bringing the solutions to boil. Polymerised zirconium solutions were prepared by boiling zirconium oxychloride and zirconium sulphate solutions for 30 min. Ammonia was added to boiling solutions to precipitate zirconium hydroxide at pH 7 and the precipitate was digested for 15 min. The precipitation of zirconium hydroxide from solutions containing sulphate ion was carried out at pH 9. The filtered and washed zirconium hydroxide was dissolved in a measured amount of hydrochloric acid, and the solution was diluted to 100 ml with water and boiled for 15 min, the volume being maintained at a constant level. The solutions were diluted to contain 10 μg Zr/ml for the spectrophotometric determination, the acidity of the diluted solutions being maintained at 0.5 *N* hydrochloric acid.

Free acid

The free acid was determined by the method of MOSKOWITZ *et al.*[19]. To determine the acid deficiency of basic zirconium solutions, a known amount of 0.1 *N* hydrochloric acid in excess was added before the reagents and the excess of acid was backtitrated with 0.1 *N* sodium hydroxide.

RESULTS

Polymerisation of zirconium chloride solutions in cold

Figures 1, 2 and 3 show that zirconium oxychloride octahydrate on dissolution in water forms polymeric species, since the absorbance of the zirconium–arsenazo III complex is only 92% of the maximum value. After a standing period of 1 day the absorbance values increase slightly and thereafter decrease rapidly, showing that a steady polymerisation of basic zirconium chloride takes place.

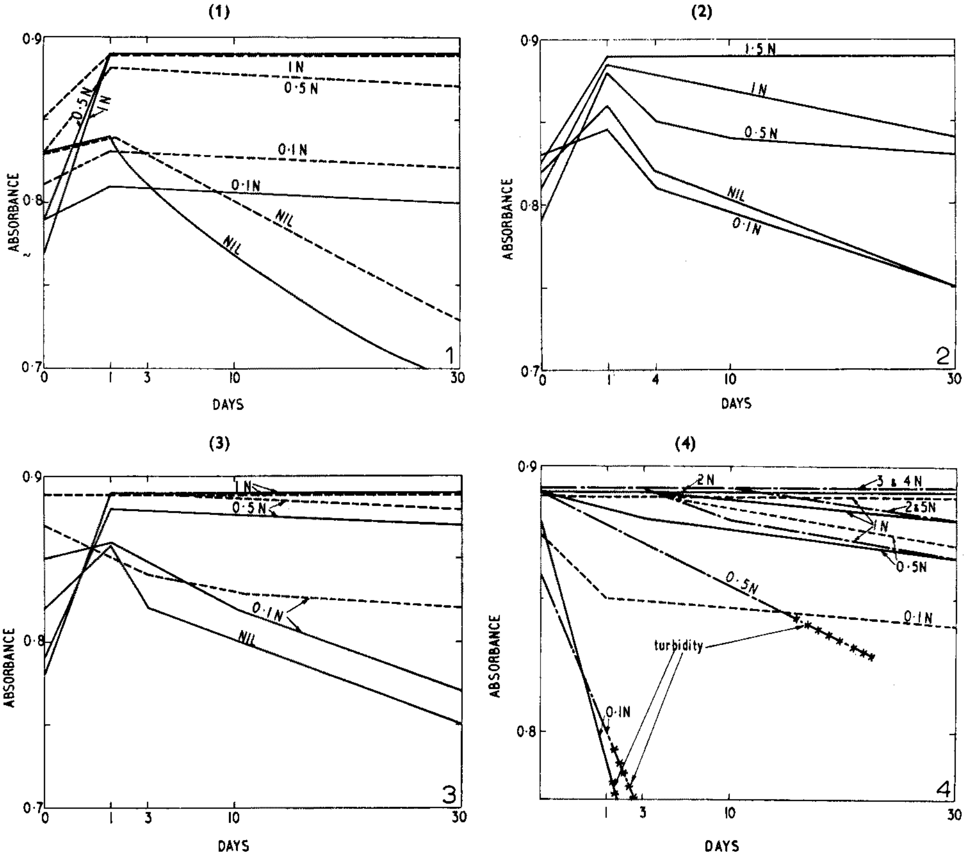
Zirconium solutions prepared from zirconium oxychloride in hydrochloric acid solutions of various strengths gave lower absorbances than solutions containing no hydrochloric acid when measured immediately after preparation. The maximum absorbances for each acid strength were obtained after standing for 24 h. The absorbances decreased on further standing when insufficient amounts of acids had been added to prevent the polymerisation of zirconium in solutions. Results indicate that the minimum concentrations of hydrochloric acid which are required to keep respectively 10^{-4}, 10^{-3} and 10^{-2} *M* zirconium oxychloride solutions from polymerisation are 0.5, 1 and 1.5 *N* (Figs. 1 and 2).

Experiments with perchloric acid gave similar results, but only 1 *N* perchloric acid was required to depolymerise 10^{-2} *M* solutions prepared from zirconium oxychloride. Also 1 *N* sulphuric acid depolymerised 10^{-2} *M* zirconium oxychloride solution (Fig. 3).

When solutions are prepared from zirconium oxychloride octahydrate by dissolving in hydrochloric and perchloric acids in the cold, even after dissolution in the appropriate amount of acid, solutions must be left to stand for 24 h before use. Solutions of zirconium oxychloride prepared in sulphuric acid can be used immediately (Figs. 1, 2 and 3).

Polymerisation of zirconium sulphate solutions in cold

Zirconium sulphate when dissolved in water polymerised very rapidly and a



Figs. 1–4. Polymerisation in acids on standing. Curves represent various concentrations of acids.
(1) $ZrOCl_2 \cdot 8H_2O$ in HCl, (——) 10 and (– – –) 100 μg Zr/ml.
(2) $ZrOCl_2 \cdot 8H_2O$ in HCl, 1000 μg Zr/ml.
(3) $ZrOCl_2 \cdot 8H_2O$ in $HClO_4$(——) and in H_2SO_4 (– – –), 1000 μg Zr/ml.
(4) $Zr(SO_4)_2 \cdot 4H_2O$ in HCl (————), in H_2SO_4 (– – –) and in $HClO_4$ (–.–), 1000 μg Zr/ml.

10^{-3} *M* solution became turbid after standing for 1 h. The required acidities to keep 10^{-2} *M* zirconium sulphate solutions from polymerisation are 2 *N* hydrochloric acid, 1 *N* sulphuric acid and perchloric acid in the range between 3 and 4 *N* only (Fig. 4).

Polymerisation of zirconium chloride solutions on boiling

Zirconium solutions were boiled with acids of varying strength to speed up the rate of polymerisation so as to ascertain the minimum acid concentrations at which depolymerised zirconium solutions were formed. A full range of experiments was carried out in the cold by dissolving zirconium oxychloride in varying strengths of hydrochloric acid (Figs. 1 and 2) and the same experiments were repeated simultaneously by boiling zirconium chloride solutions for 30 min (Fig. 5). Both sets of results showed excellent agreement, and in further experiments only the polymerisation of 10^{-2} *M* zirconium solutions by various acids in the cold was checked. The absorbance curves obtained on boiling were used to determine the minimum acidities required to obtain depolymerised zirconium solutions. A boiling time of 5 min at the appropriate acid concentration was found to be sufficient to obtain maximum colour when solutions were prepared from zirconium oxychloride octahydrate.

The results show that 2 *N* hydrochloric acid will produce depolymerised solutions prepared from zirconium chloride even at 10^{-1} *M* zirconium concentrations on boiling (Fig. 5). Perchloric acid (2 *N*) can also be used to prepare 10^{-1} *M* solutions from zirconium chloride (Fig. 6). The concentration of sulphuric acid must be 2.5 *N* to prepare 10^{-1} *M* solutions from zirconium oxychloride, although 10^{-2} *M* solutions can be prepared in 1 *N* sulphuric acid (Fig. 7).

Polymerisation of zirconium sulphate solutions on boiling

The results show that sulphuric acid is the most satisfactory for preparing solutions from zirconium sulphate. Even 10^{-1} *M* zirconium sulphate solution can be prepared in 2.5 *N* sulphuric acid to obtain a depolymerised zirconium solution (Fig. 8). When hydrochloric acid is used to depolymerise solutions prepared from zirconium sulphate, 3 *N* and 2 *N* hydrochloric acid is required for 10^{-1} *M* and 10^{-2} *M* zirconium solutions respectively (Fig. 9). The use of perchloric acid in the preparation of zirconium sulphate solutions is limited because of variations in the optimum perchloric acid concentration and the high degree of polymerisation, which is shown by formation of colloidal particles and turbidity in solutions. The concentration of perchloric acid must be between 3 and 4 *N* for 10^{-2} *M* zirconium sulphate solutions, but any concentration above 1 *N* perchloric acid may be used for 10^{-3} *M* zirconium sulphate (Fig. 10).

Polymerisation of zirconium perchlorate solutions

Zirconium oxychloride octahydrate was fumed with a calculated amount of perchloric acid so as to obtain zirconium perchlorate in various strength of perchloric acid on dilution. The solutions were polymerised as described in the Experimental part.

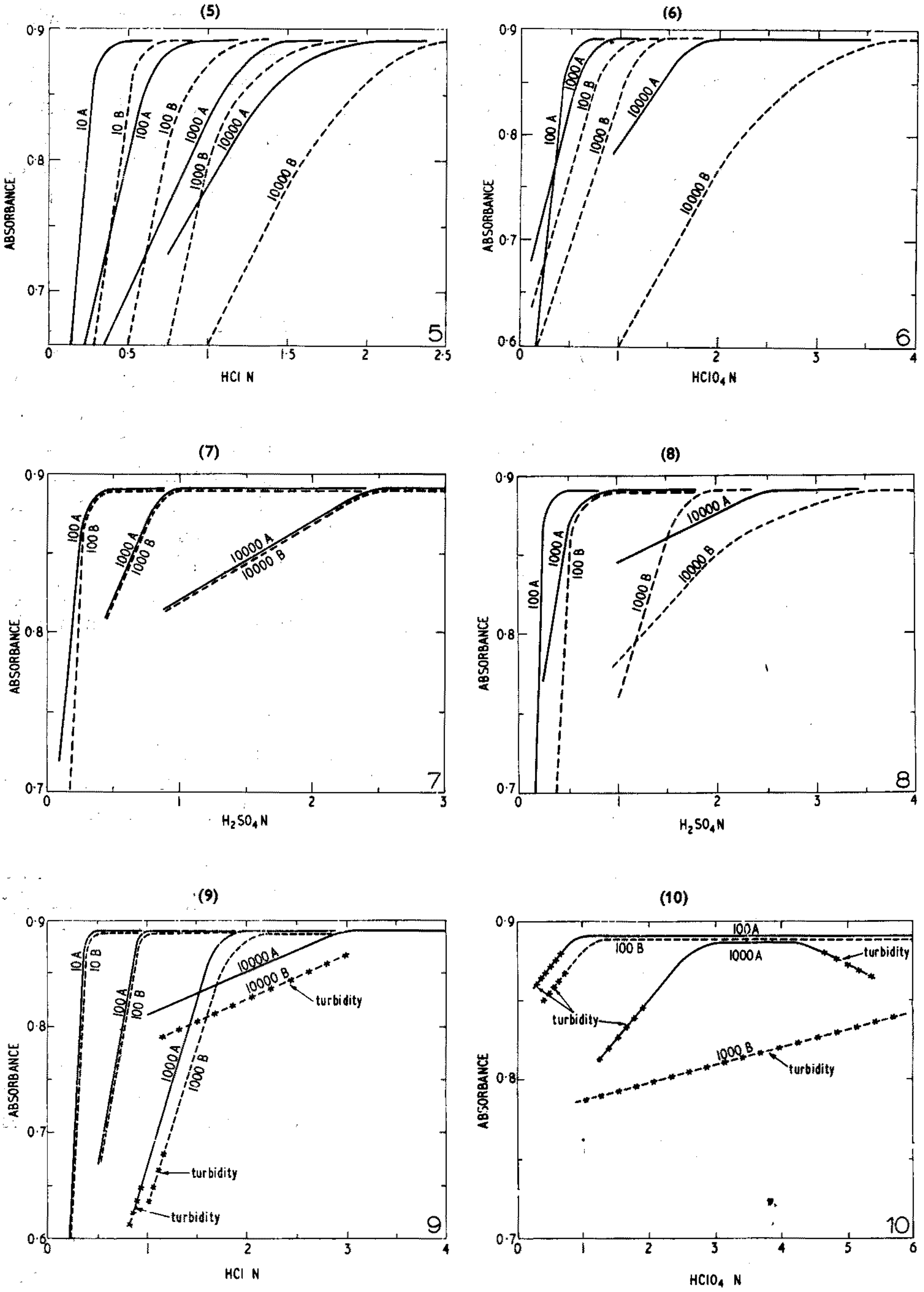
The results show that depolymerised zirconium perchlorate solutions can be obtained when the strength of perchloric acid is 2.5, 1.0 and 0.5 *N* for respectively 10^{-1}, 10^{-2} and 10^{-3} *M* zirconium solutions. (The polymerisation curves are similar to curves A in Fig. 7.)

Polymerisation and depolymerisation of zirconium nitrate solutions

Experiments with zirconium nitrate in the concentration range between 10^{-4} and 10^{-1} *M*, showed that the depolymerisation curves for zirconium nitrate solutions in hydrochloric and nitric acids are similar to those indicated in Fig. 5 (Curves A and B).

Depolymerisation of zirconium oxychloride solutions

Figures 5, 6 and 7 (Curve B) show that hydrochloric, perchloric and sulphuric acids can be used for the depolymerisation of highly polymerised zirconium oxychloride species. Solutions of 2.5 *N* hydrochloric and sulphuric acids will depolymerise up to 10^{-1} *M* zirconium oxychloride solutions. But 4 *N* and 1.5 *N* perchloric acids must be used to depolymerise 10^{-1} *M* and 10^{-2} *M* zirconium oxychloride solutions, respectively.



Figs. 5–10. Polymerisation and depolymerisation on boiling. (A) polymerisation after 30 min boiling, (B) depolymerisation after 15 min boiling. Numbers 10, 100, 1000 and 10000 denote μg amounts of Zr/ml or 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} M zirconium solutions, respectively.
$ZrOCl_2 \cdot 8H_2O$ with HCl (5), idem with $HClO_4$ (6), idem with H_2SO_4 (7).
$Zr(SO_4)_2 \cdot 4H_2O$ with H_2SO_4 (8), idem with HCl (9), idem with $HClO_4$ (10).

Depolymerisation of zirconium sulphate solutions

The only acid which will depolymerise highly polymerised zirconium sulphate solutions satisfactorily is sulphuric acid, and even then boiling with 3.5 N sulphuric acid for 15 min is required to depolymerise 10^{-1} M zirconium solutions (Fig. 8). Hydrochloric acid (2 N) may be used to depolymerise up to 10^{-2} M zirconium sulphate solutions (Fig. 9). Perchloric acid of 1.5 N and higher concentrations can be used to depolymerise 10^{-3} M zirconium sulphate solutions, but at higher zirconium sulphate concentrations a turbidity persists (Fig. 10).

Depolymerisation of basic zirconium sulphate solutions

Pilkington and Wilson[8] prepared 0.1 M zirconium sulphate solution at pH 1.8 and polymerised it at 90° for 30 min. In the present work, the free acid of the unpolymerised solution was determined and it was shown that 2 gramequivalents of

TABLE I

DEPOLYMERISATION OF POLYMERISED $Zr(OH)_2SO_4$ SOLUTIONS (pH 1.8)

	Zirconium recovery (%)			
Acidity	*H_2SO_4*[a]	*HCl*		*$HClO_4$*[b]
(N)	*10^{-1} M Zr soln*	*10^{-1} M Zr soln*	*10^{-2} M Zr soln*	*10^{-2} M Zr soln*
1	86.3	Ppt	Ppt	Ppt
2	—	Ppt	99	Ppt
3	95.8	96	100	Ppt
4	98.8	99	100	Ppt
5	100.0	100	100	Ppt
6	—	100	—	Hazy
7	—	—	—	Hazy
8	—	—	—	98
9	—	—	—	99
10	100.0	—	—	—

[a] Ref. 8.

[b] With 10^{-1} M Zr solution, a precipitate was formed at all perchloric acid concentrations.

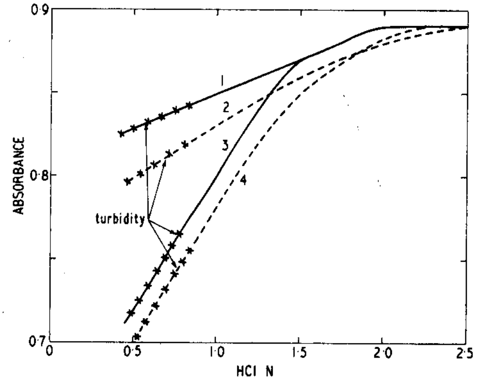


Fig. 11. Effect of HCl on the dissolution of $Zr(OH)_4$ (100 mg Zr/100 ml).
Solutions before precipitation: (1) $ZrOCl_2 \cdot 8H_2O$ depolymerised with 1.5 N HCl, 1 N H_2SO_4 and 1 N $HClO_4$, and $Zr(SO_4)_2 \cdot 4H_2O$ depolymerised with 2 N HCl and 3.5 N $HClO_4$; (2) $Zr(SO_4)_2 \cdot 4H_2O$ polymerised on boiling; (3) $Zr(SO_4)_2 \cdot 4H_2O$ depolymerised with 1 N H_2SO_4; (4) $ZrOCl_2 \cdot 8H_2O$ polymerised on boiling.

ammonia have been added to each mole of zirconium sulphate. Hydrochloric and perchloric acids were used to depolymerise these polymeric basic zirconium sulphate solutions; 5 *N* sulphuric[8] as well as 5 *N* hydrochloric acids may be used to depolymerise basic zirconium sulphate species, but perchloric acid even up to an acidity of 9 *N* does not depolymerise highly polymerised basic zirconium sulphate solutions completely (Table I).

Dissolution of precipitated zirconium hydroxide in hydrochloric acid

Precipitated zirconium hydroxide (100 mg Zr) when separated from depolymerised zirconium chloride, sulphate and perchlorate solutions can be dissolved completely on boiling for 15 min in 100 ml of 2 *N* hydrochloric acid. When precipitations are carried out from polymerised zirconium oxychloride or zirconium sulphate solutions, then 2.5 *N* hydrochloric acid is needed to dissolve and depolymerise 100 mg of zirconium as hydroxide in a volume of 100 ml (Fig. 11).

DISCUSSION

When standard zirconium solutions are prepared from zirconium oxychloride octahydrate the salt must be dissolved in acidic solutions. The relationship between the zirconium concentration and the required acid strength is given in Figs. 5, 6 and 7 (Curve A). The solutions prepared in hydrochloric and perchloric acids are ready for use either after standing for 24 h in the cold, or after a boiling time of 5 min. Zirconium oxychloride solutions prepared in sulphuric acid can be used immediately.

When standard zirconium solutions are prepared from zirconium sulphate tetrahydrate, the salt must be dissolved in acid to prevent a rapid polymerisation. The relationship between the zirconium concentration and the required acid strength is given in Figs. 8, 9 and 10 (Curve A). Provided that the correct amount of acid has been added, the standard solution can be used immediately.

To obtain stable zirconium perchlorate solutions it is necessary that 10^{-1}, 10^{-2} and 10^{-3} *M* solutions be prepared in respectively 2.5, 1 and 0.5 *N* perchloric acid.

When stronger zirconium solutions are diluted, the required normality of hydrochloric acid for the diluted solution can be obtained from Fig. 5 (Curve A), but the acidity must not be below 0.5 *N* in hydrochloric acid. The recommended order of addition is hydrochloric acid, sample aliquot and water.

When unknown zirconium solutions are analysed, a depolymerisation procedure must be followed by boiling the solutions with an acid for 15 min, and the relationship between the zirconium concentration and the required acid strength is as given in Figs. 5 to 10 (Curve B). On further dilution the required strength of hydrochloric acid is that given in Fig. 5 (Curve A).

When a highly polymerised acid-deficient zirconium sulphate solution is submitted for analysis, a 5 *N* hydrochloric acid solution (by addition of an equal volume of 10 *N* acid) must be used to depolymerise zirconium by boiling for 15 min (Table I).

Zirconium hydroxide (100 mg of Zr) can be dissolved and depolymerised in 100 ml of 2.5 *N* hydrochloric acid solution on boiling for 15 min (10^{-2} *M* Zr soln.).

Arsenazo III forms a 2:1 complex[20] with zirconium(IV), hence it is essential that zirconium species containing either hydroxy- or oxy-bonds are converted to the ionic form. X-Ray studies show that zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) in aqueous solutions forms species of a formula $[Zr_4(OH)_8 \cdot 16H_2O]\,Cl_8$[21]. The present results also show that a period of 24 h after the addition of hydrochloric and perchloric acids is required to revert these zirconium species to a simple aquo complex which can react subsequently in 8 N hydrochloric acid with arsenazo III (Figs. 2 and 3). It has been established[6] that the tendency to form complexes with zirconium decreases in the following order $SO_4^{2-} \gg NO_3^- > Cl^-$. The immediate use of zirconyl chloride solution when prepared in sulphuric acid can be explained by the strong tendency to form sulphate complexes which are stronger than the zirconium–hydroxy bonds (Fig. 3). Perchloric acid also forms acido complexes with zirconium[6]. The present results indicate that the zirconium–perchlorate complex is not as strong as the sulphate complex, because zirconyl chloride solutions cannot be used immediately after the dissolution of the salt in perchloric acid (Fig. 3). The difference in the rates of polymerisation in the same concentrations of hydrochloric and perchloric acids also indicates that a complex is formed between zirconium and perchlorate (Figs. 2 and 3).

APPENDIX

Spectrophotometric determination of zirconium with arsenazo III

Recommended procedure. Transfer an aliquot (not more than 4 ml) containing 10–30 μg of zirconium to a 50-ml volumetric flask. Add 1 ml of 1% ascorbic acid solution and 40 ml of 10 N hydrochloric acid. Cool in ice water. Add 3 ml of 0.12% solution of arsenazo III (Aldrich Chem. Co. Inc., U.S.A.), dilute to volume and mix. Read the absorbance in 1-cm cells at 665 nm against a reagent blank.

Discussion. The ascorbic acid was introduced to reduce any oxidising agents which could arise from sample preparation (fuming with perchloric acid) and to permit the determination in the presence of milligram amounts of nitrate. A maximum amount of 1 ml of 1% ascorbic acid can be added to the solution; higher concentrations of ascorbic acid tend to reduce the dye.

The interferences of sulphate, perchlorate, phosphate and fluoride ions in the spectrophotometric procedure are given in Table II.

Zirconium may be determined in solutions containing milligram amounts of nitrate, provided that a special technique is used. Solutions, before the addition of the dye, must be chilled and the absorbances read immediately after dilution to volume. The effect of standing time on the absorbance is shown in Table III.

TABLE II

THE EFFECT OF SULPHATE, PERCHLORATE, PHOSPHATE AND FLUORIDE IONS ON THE DETERMINATION OF ZIRCONIUM (30 μg Zr)

SO_4^{2-}		ClO_4^-[a]		PO_4^{3-}		F^-	
Added (mg)	*Recovery (%)*	*Added (g)*	*Recovery (%)*	*Added (mg)*	*Recovery (%)*	*Added (μg)*	*Recovery (%)*
10	100	1.0	100	5	99	5	98
25	99.5	2.0	102	10	88	10	96
50	98.5	3.0	104	25	52	20	94
100	95			50	30	25	93

[a] Added as $HClO_4$.

TABLE III

THE EFFECT OF STANDING TIME ON THE ABSORBANCE OF ZIRCONIUM IN THE PRESENCE OF NITRATE ION (30 μg Zr)

NO_3^- (mg)	Recovery (%) Measured immediately	After 10 min	After 30 min
62	100	100	100
124	100	99	98
186	100	98	96
248	100	98	93
310	100	98	Low
465	98	Low	—

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

SUMMARY

The preparation of depolymerised solutions from various zirconium salts in the cold and on boiling, the depolymerisation of polymerised zirconium solutions, and the dissolution of precipitated zirconium hydroxide by hydrochloric acid, are described. The concentrations of the zirconium solutions are between 10^{-4} and 10^{-1} *M*. The minimum permissible concentrations of various acids are shown by depolymerisation curves. Zirconium was determined by spectrophotometry with arsenazo III in 8 *N* hydrochloric acid, and the interferences by sulphate, perchlorate, phosphate, fluoride and nitrate are described.

RÉSUMÉ

On décrit une méthode de préparation de solutions dépolymérisées de divers sels de zirconium, à froid et à l'ébullition, ainsi que la dépolymérisation de solutions de zirconium polymérisées et la dissolution d'hydroxyde de zirconium précipité par l'acide chlorhydrique. Concentrations des solutions de zirconium 10^{-4} – 10^{-1} *M*. Les concentrations minima possibles des divers acides sont fournies par les courbes de dépolymérisation. Le zirconium est dosé spectrophotométriquement par l'arsénazo III en milieu acide chlorhydrique 8 *N*, on examine l'influence des sulfates, perchlorates, phosphates, fluorures et nitrates.

ZUSAMMENFASSUNG

Die Herstellung depolymerisierter Lösungen verschiedener Zirkoniumsalze in der Kälte und in der Hitze, die Depolymerisierung von polymerisierten Zirkoniumlösungen und die Auflösung von gefälltem Zirkoniumhydroxid durch Salzsäure wird beschrieben. Die Konzentrationen der Zirkoniumlösungen liegen zwischen 10^{-4} und 10^{-1} *M*. Die zulässige minimale Konzentration verschiedener Säuren wird durch Depolarisationskurven gezeigt. Zirkonium wurde spektralphotometrisch mit Arsenazo III in 8 *N* Salzsäure bestimmt. Die Störungen durch Sulfat, Perchlorat, Phosphat, Fluorid und Nitrat werden beschrieben.

REFERENCES

1 S. B. Savvin, *Dokl. Akad. Nauk SSSR*, 127 (1959) 1231.
2 S. B. Savvin, *Talanta*, 8 (1961) 673.
3 V. G. Gorynshina and E. V. Romanova, *Zavodsk. Lab.*, 26 (1960) 415.
4 V. I. Kuznetsov and A. A. Nemodruk, *Conference on Spectrophotometric Methods of Analysis*, Moskow, 1955, p. 46.
5 A. K. Babko and G. J. Gridchina, *Russ. J. Inorg. Chem.*, 7 (1962) 458.
6 A. S. Solovkin and S. V. Tsvetkova, *Russ. Chem. Rev.*, 31 (1962) 655.
7 L. M. Zaitsev and G. S. Bochkarev, *Russ. J. Inorg. Chem.*, 7 (1962) 411.
8 E. S. Pilkington and W. Wilson, *Anal. Chim. Acta*, 33 (1965) 577.
9 B. C. Sinha and S. Das Gupta, *Analyst*, 92 (1967) 558.
10 O. Guebeli and A. Jacob, *Helv. Chim. Acta*, 38 (1955) 1026.
11 R. B. Hahn, in I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 5, Interscience, New York, 1961, p. 78.
12 C. Dragulescu, T. Simonescu and S. Policec, *Talanta*, 11 (1964) 747.
13 A. Mayer and G. Bradshaw, *Analyst*, 77 (1952) 476.
14 E. Cerrai and C. Testa, *Anal. Chim. Acta*, 26 (1962) 204.
15 J. O. Hibbits, A. F. Rosenberg, R. T. Williams and S. Kallman, *Talanta*, 11 (1964) 1509.
16 K. L. Cheng, *Talanta*, 2 (1959) 61.
17 H. E. Zittel and T. M. Florence, *Anal. Chem.*, 39 (1967) 320.
18 S. V. Elinson and N. A. Mirzoian, *Zavodsk. Lab.*, 27 (1961) 798.
19 A. Moskowitz, J. Dasher and H. W. Jamison, *Anal. Chem.*, 32 (1960) 1362.
20 I. P. Alimarin and S. B. Savvin, *Pure Appl. Chem.*, 13 (1966) 445.
21 W. B. Blumenthal, *The Chemical Behaviour of Zirconium*, Van Nostrand, New York, 1958, p. 128.

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SPECTROPHOTOMETRIC DETERMINATIONS OF IRON(III), TITANIUM(IV) AND VANADIUM(V) AND THEIR SEPARATION FROM EACH OTHER AND FROM OTHER IONS WITH 1-(*o*-CARBOXYPHENYL)-3-HYDROXY-3-PHENYLTRIAZENE

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In a previous communication, the use of 1-(*o*-carboxyphenyl)-3-hydroxy-3-phenyltriazene as a new gravimetric reagent for the direct determination of titanium(IV) in presence of all other ions has been described[1]. The procedure involves the precipitation of titanium with an alcoholic solution of the reagent, but it has since been found that better results are obtained if first an ammoniacal solution of the reagent (just neutralised) is added to the solution at pH 7.0 (adjusted by ammonia) containing titanium, EDTA and other ions; the pH of the solution is then lowered to the proper value by the addition of dilute hydrochloric acid.

The present paper discusses the use of the reagent for the spectrophotometric determinations of titanium(IV), vanadium(V) and iron(III) and their separation from each other and from a large number of other ions.

With iron(III), the reagent forms in ammoniacal medium a pink complex which on extraction in chloroform shows an absorption maximum at 500 nm. Tartaric, oxalic or citric acid increase the intensity of the colour without causing any shift of the absorption maximum. In the presence of tartaric acid, the complex obeys Beer's law over the range 0.5–12.0 p.p.m. of iron; in the absence of tartaric acid the range is 1.0–16.0 p.p.m.; the optimum ranges, evaluated from the standard curves, are 1.0–12.0 p.p.m. and 2.0–16.0 p.p.m., respectively.

The golden-yellow solution obtained by extracting the titanium(IV) complex into chloroform in the pH range 1.0–3.5 has an absorption maximum at 430 nm. The colour system obeys Beer's law in the range 0.25–6.0 p.p.m. of titanium, the optimum range being 0.5–4.0 p.p.m.

The green vanadium(V) complex extracted into chloroform at pH 2.0–3.0, obeys Beer's law in the range 0.5–8.0 p.p.m. of vanadium, with the optimum range 1.0–6.0 p.p.m. at 410 nm, the region of its maximum absorption.

For the separation of these ions from each other, first the iron complex formed in presence of tartaric acid at pH 9.5 is extracted into chloroform. From the residual aqueous phase, adjusted to pH 1.0, the titanium complex is extracted into the same solvent, after the reduction of the vanadate present to the tetravalent state and its complexation with thiocyanate. Finally, from the residual solution, the vanadium(V) complex is extracted, at pH 2.0, into chloroform. Thus, all three elements are determined photometrically after extraction of their coloured complexes separately in chloroform.

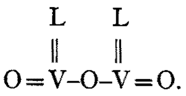
The sensitivities of the colour reaction of iron, titanium and vanadium are, respectively, 0.01126, 0.0038 and 0.0062 μg/cm^2.

The study of the composition of the complexes formed in solution indicates that iron(III) and titanium(IV) combine with the reagent in a ratio of 1:2 and that vanadium(V) gives a 1:1 complex. On isolation and analysis, the violet, shining crystals of the iron(III) complex and the green crystals of the vanadium complex were found to have the same metal–reagent ratios of 1:2 and 1:1, respectively, as in solution, like the titanium complex[1].

The iron(III) complex, $FeH(C_{13}H_9N_3O_3)_2$, with a magnetic susceptibility value of 6.02 B.M., decomposes at 212° and is slightly soluble in alcohol (and still less so in acetone, benzene, dioxan and chloroform) but very soluble in pyridine. However, on the addition of a drop or two of dilute ammonia or alkali, it is freely soluble in all the solvents mentioned.

The vanadium(V) complex, $V_2O_3(C_{13}H_9N_3O_3)_2$, which decomposes at 165°, is diamagnetic and is moderately soluble in ethanol and methanol, chloroform and dioxan (but only slightly soluble in water and benzene) and very soluble in pyridine.

Infra-red study shows that the asymmetric stretching frequency of the C=O group shifts to 1625 cm^{-1} in the vanadium complex and to 1610 cm^{-1} in the iron(III) complex. The O–H band of the reagent is destroyed and in the vanadium complex the V=O band appears at 997 cm^{-1}. This suggests the structure of the vanadium complex to be



$$\begin{array}{ccccc} & L & & L & \\ & \| & & \| & \\ O= & V & -O- & V & =O. \end{array}$$

In the iron and in the vanadium complexes the metal ions are hexa- and penta-coordinated, respectively, the ligand being tridentate.

EXPERIMENTAL AND RESULTS

Apparatus, reagents and solutions

A Hilger Uvispek spectrophotometer and Cambridge pH-meter were used for the measurements of absorption and pH, respectively.

Standard solutions of iron(III) as chloride, titanium(IV) as sulphate, and vanadium(V) as ammonium vanadate were prepared from analytically pure samples of resublimed iron(III) chloride, potassium titanyl oxalate and ammonium vanadate. The solutions prepared in doubly distilled water were standardised by recommended methods[2,3]. Standard solutions were subsequently diluted to obtain weaker solutions.

A 0.5% (w/v) reagent solution was prepared by suspending the pure reagent in water and dissolving it with the addition of a minimum amount of ammonia.

The solutions of various ions were prepared from analytical grade reagents and were standardised by the usual methods.

Absorbance curves

Iron(III). To an aliquot of the standard iron(III) solution containing 200 μg of iron(III) in a separating funnel, were added 1 ml of 2% tartaric acid solution and 2 ml of the reagent solution. The solution was then diluted with doubly-distilled water, and its pH adjusted with dilute ammonia solution, so that the final volume of the solution was 25 ml and the pH was 9.5. The violet-coloured complex was then extracted three times with 5-ml portions of chloroform. The extracts were collected in a 25-ml flask and diluted to the mark with the same solvent.

Titanium(IV). The solution containing 75 μg of titanium(IV) was mixed successively with 2 ml of the reagent solution and 10 ml of distilled water. Dilute hydrochloric acid was then added to adjust the pH to about 2.0 and then the solution was heated on a water-bath for about 5 min, cooled to room temperature, and transferred completely by washing with water, into a 100-ml separating funnel. From this aqueous solution (25 ml), the extraction was done as for iron(III).

Vanadium(V). The solution containing 100 μg of vanadium(V) was mixed with the reagent solution (2 ml), distilled water (10 ml) and hydrochloric acid to adjust the pH to 2.0. It was then transferred to a 100-ml separating funnel by washing with water. From this solution, after dilution to 25 ml, vanadium was extracted in the same way as for iron(III).

The absorbances of the coloured complexes were measured against the reagent blanks and the regions of maximum absorption for the systems with iron, titanium and vanadate were found to be at 500, 430 and 410 nm, respectively (Fig. 1).

Effect of pH, reagent, time and tartaric acid

The colour intensity of the systems remains the same in the pH ranges: 6.0–10.5 for iron(III), 1.0–3.5 for titanium(IV) and 2.0–3.0 for vanadate. The intensity decreases at pH values other than those referred to above.

A volume of 2 ml of the reagent solution suffices for the complete development of colour with 8.0 p.p.m. of iron or vanadate, and 2 p.p.m. of titanium. The addition of more reagent has no effect.

The colour of the iron system is stable for 72 h, while those of titanium and vanadate are stable for 7 days and 48 h, respectively.

Excess of tartaric acid has no effect on the colour system involving iron(III).

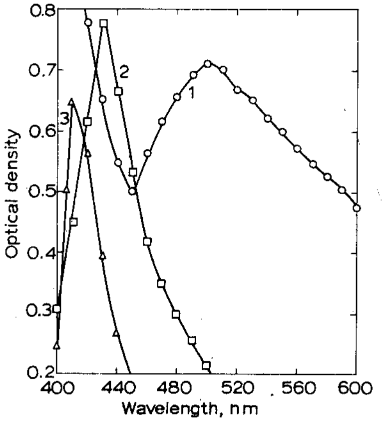


Fig. 1. Absorption spectra. (1) Fe(III), 8; (2) Ti(IV), 3; (3) V(V), 4 p.p.m.

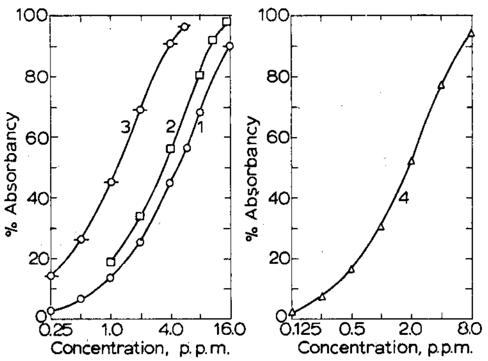


Fig. 2. Standard curves. (1) Fe(III) without tartaric acid; (2) Fe(III) with tartaric acid; (3) Ti(IV); (4) V(V).

The titanium(IV) system tolerates 12.5 ml of 2% tartaric acid but the vanadium(V) system cannot tolerate more than 1 ml.

Beer's law, optimum range, photometric error, sensitivity and molar extinction coefficient

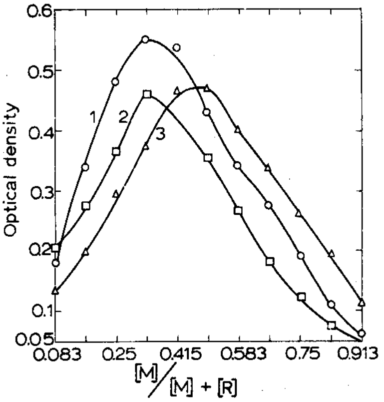
The iron, titanium and vanadate systems obey Beer's law over the ranges 0.5–12.0 p.p.m., 0.25–6.0 p.p.m. and 0.5–8.0 p.p.m., respectively. The iron system was measured in presence of tartaric acid. The optimum concentration ranges, as obtained from the curves drawn according to RINGBOM[4], are 1.0–12.0, 0.5–4.0 and 1.0–6.0 p.p.m., respectively (Fig. 2).

The relative errors per 1% absolute photometric error[5] for the systems are 2.78% for iron, 2.76% for titanium and 2.83% for vanadate. The sensitivities calculated[6] for $\log I_0/I = 0.001$ are 0.01126, 0.0038 and 0.0062 μg/cm^2, and the molar absorptivities are 4970, 12454 and 8255, respectively.

Composition of the complexes

The compositions of the iron, titanium and vanadate complexes were determined by JOB's method[7] of continuous variation and by the molar ratio method[8].

In the first method, equimolar solutions of the particular metal ion and the reagent were mixed in different proportions to a volume of 12 ml. After adjustment of the pH to proper values, the complexes were extracted into chloroform, as described for the study of the absorbance curves, and their absorbances were measured.



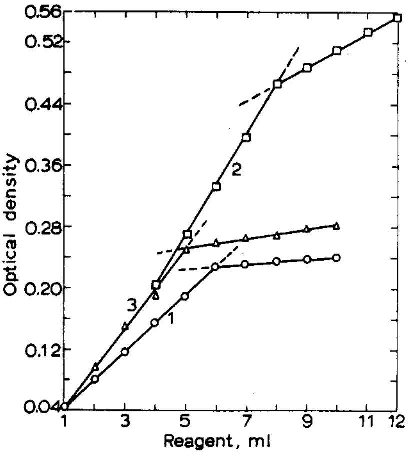


Fig. 3. Curves by Job's method (equimolar). (1) Fe(III) = reagent = $1 \cdot 10^{-3}$ M; (2) Ti(IV) = reagent = $2.5 \cdot 10^{-4}$ M; (3) V(V) = reagent = $5 \cdot 10^{-4}$ M

Fig. 4. Molar ratio method. (1) Fe(III) = reagent = $1 \cdot 10^{-3}$ M, 3 ml of Fe (III) soln used; (2) Ti(IV) = reagent = $2.5 \cdot 10^{-4}$ M, 4 ml of Ti(IV) soln used; (3) V(V) = reagent = $5 \cdot 10^{-4}$ M, 5 ml of V(V) soln used.

The peaks of the curves (Fig. 3) obtained by plotting optical densities against increasing amounts of metal ions, show that iron(III) and titanium(IV) combine with the reagent in the ratio of 1:2, while vanadium(V) forms a 1:1 complex.

For the molar ratio method, solutions at their optimum pH values were prepared, with varying ratios of moles of the reagent to moles of metal ion, keeping the concentration of the metal ion constant. From these solutions the metal complexes were extracted by the procedure described earlier and their absorbances measured at their maximum absorption regions against similarly treated reagent blanks. The curves (Fig. 4) show sharp breaks at metal:reagent mole ratios of 1:2 for titanium(IV) and iron(III), and 1:1 for vanadium(V).

Degree of dissociation and instability constant

The values of α, the degree of dissociation, were calculated from HARVEY AND MANNING's equation[9], $\alpha = (E_m - E_s)/E_m$, where E_m and E_s have their usual significances. The instability constants, evaluated from the equation, $K = (m\alpha c)^m (n\alpha c)^n / c(1-\alpha)$ with $m=n=1$ for vanadate, and $m=1$ and $n=2$ for titanium(IV) or iron(III), are $5.26 \cdot 10^{-10}$, $1.15 \cdot 10^{-9}$ and $7.61 \cdot 10^{-6}$ for iron, titanium and vanadate, respectively (Table I).

TABLE I

INSTABILITY CONSTANTS BY THE HARVEY–MANNING METHOD

Complex	E_m	E_s	C	α	K
Fe(III)	0.239	0.227	$1 \cdot 10^{-3}\,M$	0.05	$5.26 \cdot 10^{-10}$
Ti(IV)	0.552	0.465	$2.5 \cdot 10^{-4}\,M$	0.157	$1.15 \cdot 10^{-9}$
V(V)	0.284	0.251	$5 \cdot 10^{-4}\,M$	0.116	$7.61 \cdot 10^{-6}$

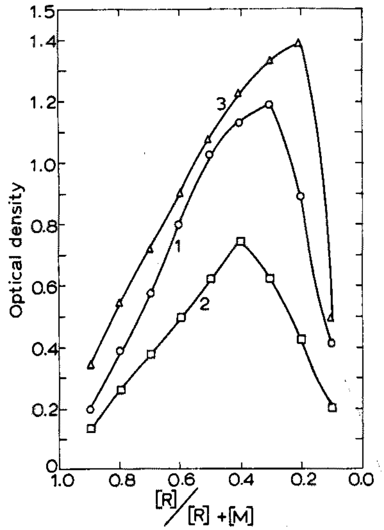


Fig. 5. Job's method of dissociation constant. (1) Fe(III) $= 1 \cdot 10^{-3}\,M$, reagent $= 5 \cdot 10^{-3}\,M$; (2) Ti(IV) $= 2.5 \cdot 10^{-4}\,M$, reagent $= 1 \cdot 10^{-3}\,M$; (3) V(V) $= 5 \cdot 10^{-4}\,M$, reagent $= 2.5 \cdot 10^{-3}\,M$.

From the absorption data (Fig. 5) for the chloroform extracts of non-equimolar solutions of metal ions and the reagent, at optimum pH-values, the instability constants were calculated from the equation[10]:

$$K = \frac{c^{m+n-1}\, p^{n-1}\, [(pm+n)x-n]^{m+n}}{m^{n-1}\, n^{m-1}\, (p-1)^{m+n-1}\, [n-(m+n)x]}$$

The values obtained are recorded in Table II.

TABLE II

INSTABILITY CONSTANTS BY THE JOB METHOD

Metal concn. (M)	*Reagent concn. (M)*	*m*	*n*	*p*	*x*	*K (at 25°)*
Fe(III), $1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	1	2	5	0.3	$2.84 \cdot 10^{-10}$
Ti(IV), $2.5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	1	2	4	0.4	$2.2 \cdot 10^{-9}$
V(V), $5 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	1	1	5	0.2	$8.3 \cdot 10^{-6}$

Effect of various ions

To evaluate the tolerance limits of different ions, solutions containing 8 p.p.m. of iron(III), 4 p.p.m. of vanadium(V) and 2 p.p.m. of titanium(IV) were prepared separately with varying quantities of other ions; the procedures followed for their determinations were as described above.

The iron system in presence of an excess of tartaric acid (250 mg) tolerates Cr^{3+} (20 p.p.m.), Mn^{2+} (10 p.p.m.), Cu^{2+} (10 p.p.m.), Ni^{2+} (4 p.p.m.), Co^{2+} (4 p.p.m.) and EDTA (100 p.p.m.). Even 400 p.p.m. of each of the ions, Sn^{2+}, Sb^{3+}, Bi^{3+}, Zr^{4+}, Th^{4+}, WO_4^{2-} and $C_2O_4^{2-}$ do not interfere.

With the vanadate system, the tolerance limits are: Cu^{2+} (10 p.p.m.), Ni^{2+} (200 p.p.m.), Co^{2+} (200 p.p.m.), Sn^{2+} (40 p.p.m.), Sb^{3+} (200 p.p.m.), Bi^{3+} (20 p.p.m.), Zr^{4+} (50 p.p.m.), Th^{4+} (200 p.p.m.), Cr^{3+} (400 p.p.m.), Mn^{2+} (400 p.p.m.), $C_2O_4^{2-}$ (40 p.p.m.), EDTA (40 p.p.m.) and WO_4^{2-} (200 p.p.m.).

The titanium(IV) system tolerates, in presence of tartaric acid (250 mg), Cu^{2+} (10 p.p.m.) and 400 p.p.m. each of Sn^{2+}, Sb^{3+}, Bi^{3+}, Zr^{4+}, WO_4^{2-}; there is no interference from EDTA (100 p.p.m.) and 400 p.p.m. each of Cr^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Th^{4+}.

There was no interference from 400 p.p.m. of other ions such as, NO_2^-, F^-, Br^-, I^-, $S_2O_3^{2-}$, SO_3^{2-}, PO_4^{3-}, AsO_4^{3-}, $C_4H_4O_6^{2-}$, citrate, MoO_4^{2-}, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, As^{3+}, Ag^+, Au^{3+}, Pd^{2+}, rare-earths, UO_2^{2+}, Se^{4+}, Te^{6+}, Ce^{3+} and Tl^{3+}, in any of the systems.

Separation of iron(III), titanium(IV) and vanadium(V)

For the separation of iron(III), titanium(IV) and vanadium(V) present in 25 ml of solution, iron(III) was first extracted, in the presence of tartaric acid, with chloroform at pH 9.5. The aqueous phase containing both titanium(IV) and vanadium(V) was then transferred to a beaker and the pH adjusted to 1.0–2.0 by the addition of dilute hydrochloric acid. About 0.5 mg of hydroxylamine hydrochloride was added and the mixture boiled for 2 min to reduce vanadium(V) to vanadium(IV); 5 ml of 5% ammonium thiocyanate solution and 2 ml of the reagent solution were then added, the pH was adjusted to 1.0 and the solution was heated for 5 min and then cooled to room temperature. The titanium(IV) complex was then extracted with chloroform after quantitative transference of the mixture into a separating funnel.

For the recovery of vanadium, V(IV) in the residual aqueous phase was oxidized with 0.1 *N* potassium permanganate solution and mixed with 2 ml of the reagent solution. The pH of this mixture was then decreased to 2.0 with dilute hydrochloric acid, the solution was transferred to a separating funnel, and vanadium was extracted into chloroform. The extracts containing the different metal chelates were diluted in separate 25-ml flasks to the mark with chloroform and their absorbances were measured against standards at the appropriate maximum absorption regions. The separation values are recorded in Table III.

TABLE III

SEPARATION OF IRON(III), TITANIUM(IV) AND VANADIUM(V)

Amounts present in the mixture (p.p.m.)	*Fe(III) found (p.p.m.)*	*Ti(IV) found (p.p.m.)*	*V(V) found (p.p.m.)*
8.0 Fe(III) 2.0 Ti(IV) 8.0 V(V)	7.96	1.98	7.899
4.0 Fe(III) 4.0 Ti(IV) 4.0 V(V)	3.944	3.992	3.949
8.0 Fe(III) 2.0 Ti(IV) 4.0 V(V)	8.034	1.988	4.052
8.0 Fe(III) 4.0 Ti(IV) 8.0 V(V)	8.056	4.012	7.918

Preparation of the iron and vanadium compounds

The solution obtained by adding a solution of hydrated iron(III) chloride (0.5 g in 20 ml of ethanol) to a solution of the reagent (1.0 g in 30 ml of hot ethanol) was kept overnight. The violet crystals that separated were filtered, washed with ethanol and dried at room temperature (Found: Fe 9.94%, N 14.72%; calculated for $FeH(C_{13}H_9N_3O_3)_2$: Fe 9.85%, N 14.82%).

To an acetone solution of the reagent (3.0 g in 60 ml) was added a solution prepared by dissolving ammonium vanadate (1.2 g) in 20 ml of boiling hot water with the addition of a few drops of dilute ammonia. Concentrated hydrochloric acid was next added dropwise until the brown solution turned greenish yellow. The solution was filtered and kept overnight. The deep green crystals that separated were filtered, washed successively with acetone and water and dried at room temperature. (Found: V 15.3%, N 12.7%; calculated for $V_2O_3(C_{13}H_9N_3O_3)_2$: V 15.45%, N 12.73%).

SUMMARY

1-(*o*-Carboxyphenyl)-3-hydroxy-3-phenyltriazene is shown to be an excellent spectrophotometric reagent for the determination of iron(III), titanium(IV) and vanadium(V). Iron(III) forms an intense violet complex in presence of tartaric acid at pH 9.5 and titanium(IV) and vanadium(V) form yellow and green complexes, respectively, at pH 2.0. The wavelengths of maximum absorption of the complexes of iron(III), titanium(IV) and vanadium(V) in chloroform are 500, 430 and 410 nm, respectively. Beer's law is valid with optimum ranges 1.0–12.0 p.p.m. for iron(III), 0.5–4.0 p.p.m. for titanium(IV) and 1.0–6.0 p.p.m. for vanadium(V), where the relative errors are 2.78, 2.76 and 2.83%. The reagent forms 1:2 complexes with iron(III) and titanium(IV) and a 1:1 complex with vanadium(V), with instability constants of the order of 10^{-10}, 10^{-9} and 10^{-6}, respectively. Interfering effects of other anions and cations on the colour systems were studied; common complexing agents, such as fluoride, phosphate, citrate and tartrate when present even to the extent of 400 p.p.m. have no effect. A procedure for the separation and determination of iron, titanium and vanadium in presence of each other is described.

RÉSUMÉ

Le 1-(*o*-carboxyphényl)-3-hydroxy-3-phényltriazène constitue un excellent réactif pour la spectrophotométrie du fer(III), du titane(IV) et du vanadium(V). Le fer(III) donne un complexe violet intense en présence d'acide tartrique au pH 9.5, le titane(IV) et le vanadium(V) forment respectivement des complexes jaunes et verts au pH 2.0. Les longueurs d'onde des absorptions maxima des complexes de fer(III), titane(IV) et vanadium(V) dans le chloroforme sont respectivement 500, 430 et 410 nm. La loi de Beer s'applique pour les concentrations 1.0 à 12.0 p.p.m. pour le fer(III), 0.5–4.0 p.p.m. pour le titane(IV) et 1.0–6.0 p.p.m. pour le vanadium (V). L'influence de divers ions est examinée, les agents complexants courants tels que fluorure, phosphate, citrate et tartrate (même jusqu'à 400 p.p.m.) ne gênent pas. On décrit une méthode de séparation et de dosage du fer, du titane et du vanadium les uns en présence des autres.

ZUSAMMENFASSUNG

Es wird gezeigt, dass 1-(*o*-Carboxyphenyl)-3-hydroxy-3-phenyltriazen ein ausgezeichnetes spektralphotometrisches Reagenz für die Bestimmung von Eisen(III), Titan(IV) und Vanadin(V) ist. Eisen(III) bildet einen intensiven violetten Komplex in Gegenwart von Weinsäure beim pH 9.5, Titan(IV) und Vanadin(V) bilden gelbe bzw. grüne Komplexe beim pH 2.0. Die Absorptionsmaxima der Komplexe liegen in Chloroform bei 500, 430 bzw. 410 nm. Das Beersche Gesetz wird befolgt in den optimalen Bereichen 1.0 bis 12.0 p.p.m. für Eisen(III), 0.5 bis 4.0 p.p.m. für Titan(IV) und 1.0 bis 6.0 p.p.m. für Vanadin(V). Die relativen Fehler betragen 2.78%, 2.76% bzw. 2,83%. Das Reagenz bildet 1:2-Komplexe mit Eisen(III) und Titan(IV) und einen 1:1-Komplex mit Vanadin(V) — mit Instabilitätskonstanten in der Grössenordnung von 10^{-10}, 10^{-9} bzw. 10^{-6}. Störende Einflüsse anderer Anionen und Kationen wurden untersucht; Fluorid, Phosphat, Citrat und Tartrat hatten bis zu einem Überschuss von 400 p.p.m. keinen Einfluss. Ein Verfahren zur Trennung und Bestimmung von Eisen, Titan und Vanadin wird beschrieben.

REFERENCES

1 A. K. MAJUMDAR AND S. C. SAHA, *Anal. Chim. Acta*, 40 (1968) 299.
2 A. I. VOGEL, *A Text Book of Quantitative Inorganic Analysis*, 3rd Edn., Longmans Green and Co., London, 1962.
3 G. CHARLOT AND D. BEZIER, *Quantitative Inorganic Analysis*, 3rd Edn., John Wiley, New York, 1957.
4 A. RINGBOM, *Z. Anal. Chem.*, 115 (1938/39) 332.
5 G. H. AYRES, *Anal. Chem.*, 21 (1949) 652.
6 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience Publ. Inc., New York, 3rd Edn., 1959.
7 P. JOB, *Compt. Rend.*, 180 (1925) 928; *Ann. Chim. (Paris)*, 9 (1928) 113.
8 J. H. YOE AND A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.
9 A. E. HARVEY JR. AND D. L. MANNING, *J. Am. Chem. Soc.*, 72 (1950) 4488; 74 (1952) 4744.
10 A. K. MAJUMDAR AND B. SEN, *Anal. Chim. Acta*, 8 (1953) 369.

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ANALYTICAL APPLICATIONS OF PALLADIAZO AND ARSENAZO III TO THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

PART II. EXTRACTION OF DIFFERENT AQUEOUS COMPLEX SYSTEMS WITH QUATERNARY AMMONIUM SALTS AND DIPHENYLGUANIDINE CHLORIDE IN *n*-BUTANOL MEDIUM*

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The favourable properties exhibited by the arsenazo III and palladiazo reagents for the spectrophotometric determination of palladium have been stressed in earlier papers[1]. The reaction of arsenazo III with palladium(II) has been investigated independently by SEN GUPTA[2]. These communications seem to constitute the literature on the analytical application of the reaction of palladium(II) with bisdiazoarsono derivatives of chromotropic acid. The possibility of extracting the complexes with quaternary ammonium salts or diphenylguanidine chloride was indicated qualitatively at an early stage of the investigations[1]. Quaternary ammonium salts, which are normally used as cationic surfactants, have been used recently by SARDIÑA *et al.*[3] for the extraction of complex uranyl tricarbonate from alkaline media, and by GINDIN *et al.*[4] for extraction of the platinum group metals from hydrochloric acid solutions; KARGER *et al.*[5] have used them for the extraction of some chromogenic–metallochromic organic reagents, such as methyl orange and rhodamine B, from aqueous solutions by means of octanol by resorting to the technique of "solvent sublation" (mass transfer process using gas bubbles). The use of diphenylguanidine chloride in alcoholic media was first proposed by KUZNETSOV AND SAVVIN[6] for the analytical extraction of various arsenazo–metal complexes, and this extractant system has become widely applied in connection with complexes formed by mono- and bisdiazoarsenazo reagents with many cations[7–12]. In especially favourable cases, the extraction of such complexes can be readily accomplished in alcoholic media even in the absence of voluminous organic cations[13–15], which are normally used to compensate for the electronegative charges exhibited by the arsenazo derivatives and their metal complexes, owing to the dissociation of the strongly acidic sulfonic groups present in their molecules. In such cases the use of appropriate alcohols (1-butanol, *iso*-octanol, amyl alcohol, etc.) suffices completely to remove the accentuated hydrophilic character of the arsenazo reagents and their metallic complexes, thus enabling their extraction into the organic phase.

It was felt that a quantitative investigation of the extraction behaviour of the palladium–arsenazo complexes with selected extractants was necessary before such

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methods could be adopted in connection with the spectrophotometric determination of trace amounts of palladium(II) in systems of the type investigated earlier[1]. A physicochemical investigation of the characteristics of these systems has indicated that complex formation is considerably more complicated than was initially assumed. The difficulties arise from the accentuated general complex-forming character of palladium, as well as from the presumably complex hydrolytic behaviour of the element caused by its very small ionic radius and relatively high polarizing power. In addition to marked difficulties arising from the competitive complexing nature of the different media used as buffer solutions in the present studies, further complications would be expected in the palladiazo– and arsenazo III–palladium(II) systems in the presence of chloride ions (all the palladium stock solutions used in these studies were prepared in hydrochloric acid solutions). Palladium undergoes stepwise complex formation with the chloride ligand to build four successive chloropalladite complex compounds whose apparent stability constants[16–20] are probably similar to some of the corresponding data for the palladiazo– or arsenazo III– palladium(II) complexes, especially when a large excess of chloride is present as in the acidic biphthalate buffer media used. Thus complications would be expected from the variable displacement by chloride of the equilibria established between the different arsenazo–palladium(II) species, and from the formation of arsenazo–palladium(II)–chloride mixed complex compounds.

No definitive picture of the hydrolytical phenomena of palladium is possible, because of the shortage of data dealing with the hydrolysis of chloropalladites[21], palladium chloride[22] and palladium(II)[23]. The role of polymeric palladium species in hydrolysis is even more obscure. It is thus extremely difficult to establish unequivocal conclusions about the actual composition of the different complex species formed by reaction of palladiazo or arsenazo III with palladium(II) or to obtain definitive quantitative physicochemical values.

THE PHYSICOCHEMICAL PROPERTIES OF THE COMPLEX SPECIES FORMED IN THE PALLADIAZO–Pd(II) AND ARSENAZO III–Pd(II) SYSTEMS

A detailed account of the data accumulated for these systems by means of instrumental techniques will be published later[24,25], when their full interpretation has been completed. However, some significant results obtained so far are summarized below.

A study of the absorbance *vs.* pH function with excess of palladium(II) present ($c_M > c_L$) (Fig. 1), gives a preliminary indication of the complicated characteristics of the two systems; the various types of complex formed are clearly of widely different kinetic character[24].

The spectrophotometric investigation of these systems with excess of ligand present ($c_L > c_M$) is in some cases much more complicated than when the metal is in excess ($c_M > c_L$), especially in the palladiazo–Pd(II) systems. The differences arise from various factors. There is uncertainty about the true "analytical equivalence" of the palladiazo and arsenazo III preparations synthesized. In the case of palladiazo[1], the secondary absorption band of the reagent ($\lambda_{max.} = 630$ nm) interferes seriously with the investigation of the complex species formed with palladium(II) when the ligand is in excess. Ill-defined, dubious and unexpected stoicheiometric ligand:metal ratios are obtained by the molar ratio and isomolar continuous variations methods. There is a stepwise formation of some complex species of limited kinetic stability which change extensively with time to yield various new species exhibiting very different spectrophotometric properties and stoicheiometries, so that in some cases a study of the fundamental properties of each particular complex species involved becomes very difficult. It is also probable that mixed arsenazo–Pd(II)–buffer ligand complexes are formed. Spectacular kinetic evolution of the wavelength of maximum absorbance and/or of the values of the corresponding molar absorptivities during the first hours as functions of pH, nature of the buffer media used and the size of the ligand excess[24,25] all complicate the interpretation of the system.

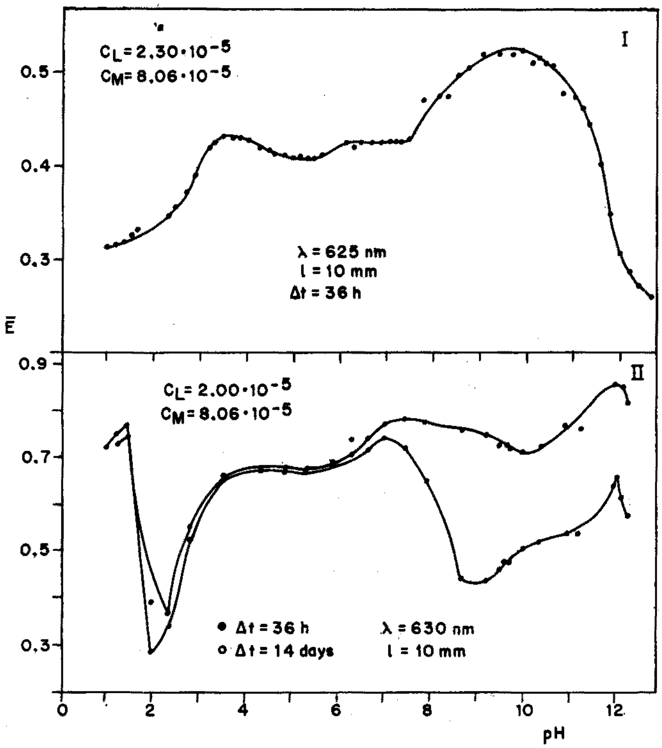

Fig. 1. Absorbance of complex solutions as a function of pH (palladium in excess). (I) Palladiazo–Pd(II) system; (II) arsenazo III–Pd(II) system.

The main uncertainty factor in the complex formation with palladium(II) appears to be caused by the secondary absorption band of palladiazo; this probably arises[26] from the coexistence of indeterminate proportions of various *cis-trans* stereoisomers, the existence of which has been generally postulated by BRODE[27] for bisdiazo dyes with two conjugated chromophoric centres. The appearance of a secondary absorption band in the visible region is not unique to the palladiazo reagent. An interesting sequence of phototropic and thermotropic phenomena has been found in aqueous unbuffered solutions of arsenazo III under appropriate conditions; two or even three absorption bands in the visible region (at 540–575, 600 and 650 nm) can be obtained.

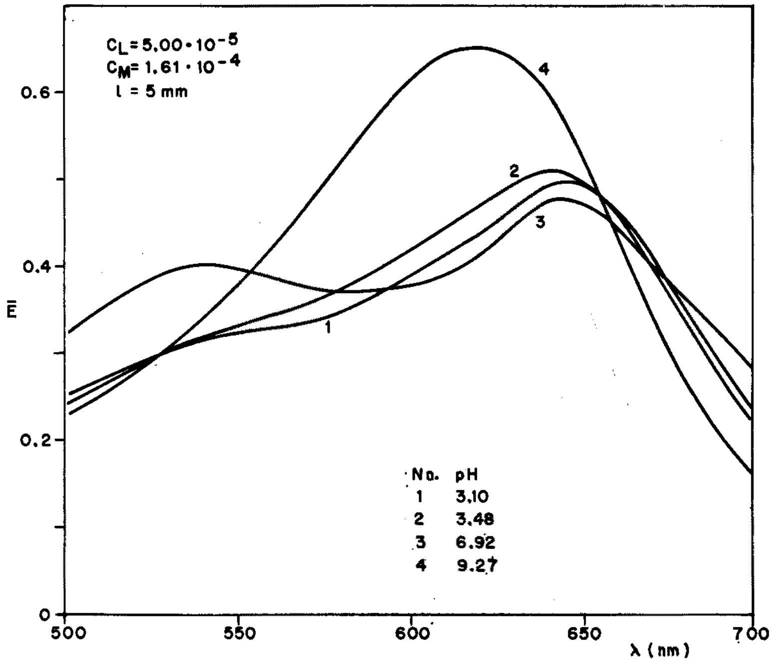

Fig. 2. Absorption spectra of aqueous solns of palladiazo–Pd(II) complex at different optimum pH values (palladium in excess).

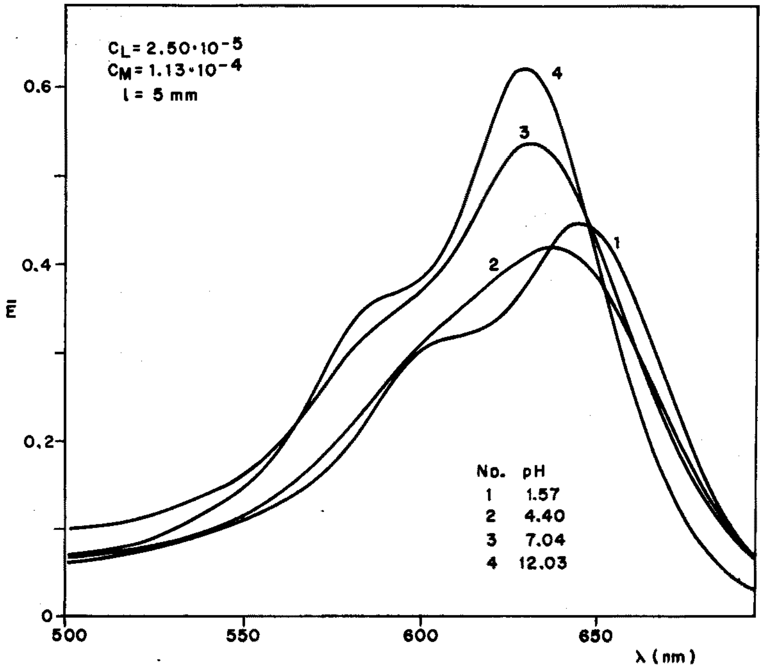

Fig. 3. Absorption of aqueous solns of arsenazo III–Pd(II) complex at different optimum pH values (palladium in excess).

In contrast to the red–crimson solutions of "common" arsenazo III, these treated solutions may be pink or deep blue in colour (depending on the extent of the transformation involved), and can be designated as arsenazo III isomeric "blue" solutions[26]. It is very interesting that these transformations are of an irreversible nature. The frequently observed lack of reproducibility in some important physicochemical properties of different arsenazo III[28,29] and palladiazo[26] samples obtained commercially or synthesized, seems to support the argument that the main troubles derive directly from the varying isomeric compositions of each particular "arsenazo" preparation. It seems reasonable that each isomer of the particular reagent will not necessarily react in the same way with palladium(II), hence the overall reaction picture can be very confusing, especially when "rare" metal:ligand stoicheiometries are obtained as often happens, especially with the palladiazo reagent. Since the preparation of well-defined "isomeric" reagent compositions has so far proved impossible, it is necessary to establish a more or less arbitrary average "reagent equivalence" by resorting to the use of isomerically unspecific titration techniques (elemental analysis, potentiometric acid–base titration, or ion-exchange determination of the average number of groups dissociated by the reagent in the pure acid form in aqueous solutions)[26]. The application of potentially specific isomeric titration techniques, such as the titration of the reagent with a given cation, would probably not lead to meaningful results, since they would be a function of the particular unknown isomeric composition of the reagent, variable fractional stoicheiometries being obtained for different preparations. Strangely, no author seems to have considered the "isomeric" question posed by this type of reagent before. The titration criterion proposed by NEMODRUK[30] based on the determination of the molar absorptivity values of arsenazo III preparations protonized in strong sulfuric acid media, is not entirely satisfactory, since the different "arsenazo" isomers do not protonize in the same way[31]. Thus, there is a distinct need to establish reference standards upon which to base unequivocal criteria for the determination of the analytical equivalence of bisdiazoarsono derivatives of chromotropic acid. The varying, irreproducible, unknown isomeric composition of the different reagents synthesized makes it impossible to consider the spectrophotometric characteristic constants determined, either for the pure reagents or for their metallic complexes, as definitely well-established values. Such data must rather be considered as average approximate values, which must be treated with great reserve.

The combined influence of all the above-mentioned factors was not fully appreciated in the earlier paper on the palladiazo–palladium(II) system[1]; it was erroneously stated that in the system considered ($\text{pH}=3.0\pm0.5$; absence of buffer), the formation of a unique M_2L_3 complex with a molar absorptivity of $5.7\cdot10^4$ (640 nm) occurred. Present knowledge makes it necessary to correct this assertion as follows: when excess of metal ion is present, ML and, possibly, M_3L_2 complexes are formed, whose maximum absorption wavelength is located at *ca.* 640 nm, but when excess of ligand is present, an M_2L_3 complex is formed which exhibits maximum absorption at *ca.* 665 nm with a molar absorptivity of *ca.* $3.7\cdot10^4$.

Spectrophotometric studies of some of the palladiazo–palladium(II) (Fig. 2) and arsenazo III–palladium(II) (Fig. 3) systems at pH values corresponding to the different maxima found for the absorbance *vs.* pH function (Fig. 1), confirm without any doubt that several complex species exist in both systems. Not only do the spectra differ in shape — quite substantially in some cases — but there are also important shifts (15–30 nm) of the wavelength of maximum absorbance at equilibrium in the different systems. The marked variations of the apparent maximum molar absorptivities again indicate the existence of complex species of varying stoicheiometry. The different kinetic features (attainment of constant values of the maximum absorbances) of the systems considered, indicate the role played by competitive buffer ligands in the complexation with palladium(II) and/or by the formation of mixed complexes and/or polynuclear species.

All these considerations apply to the kinetic features of the systems in the presence of large excesses of metal. There is no corresponding information for the systems in which the ligand is in excess, except for systems where only one complex species is formed. This latter simplified case occurs exceptionally for the arsenazo III–palladium(II) system only at pH 4.5, and its practical significance will be discussed elsewhere[32] in connection with the determination of the analytical equivalence of arsenazo III preparations.

Even with excess of ligand present, the nature of the buffer media and the pH value must have a great effect on the kinetics and stoicheiometry of the palladiazo–palladium(II) systems. It therefore seems unlikely that the extraction processes in

TABLE I

THE MAIN PHYSICOCHEMICAL PROPERTIES OF SOME PALLADIAZO–Pd(II) AND ARSENAZO III–Pd(II) SYSTEMS (ROOM TEMPERATURE)

$c_M > c_L$		*pH*	*$c_L > c_M$ $\lambda_{max.}$ (nm)*	*M:L ratios*		*Apparent formation constants*[f] *(μ = 0.15)*[g]
$\lambda_{max.}$ (nm)	*Time for equilibrium*			*Probable*	*Doubtful*	
Palladiazo–Pd(II)						
640	≦ 24 h	3.0[a]	665	ML, M_2L_3	M_4L, M_3L_2	$\log \gamma_{1.1}$ = 4.92(33–35) $\log \gamma_{2.3}$ = 27.0(36);26.8(37)
640	≦ 24 h	3.50[a]	670	ML, M_2L_3	M_4L, M_3L_2	$\log \gamma_{1.1}$ = 5.08(33–35) $\log \gamma_{2.3}$ = 24.6(36,37)
642.5 540	≦ 18 h	7.00[b]	670	ML, ML_2		$\log \gamma_{1.1}$ = 5.58(33–35);5.83(38); 6.1(41);5.68(36);5.85(40); 5.78(37) $\log \gamma_{1.2}$ = 11.6(41)
620	> 30 days	9.25[c]	665	ML, M_2L_3	ML_2	$\log \gamma_{1.1}$ = 5.8(41);5.85(40);5.77(37) $\log \gamma_{1.2}$ = 11.5(41)
Arsenazo III–Pd(II)						
645	~ 3 h	1.60[d]	630	ML, M_2L	M_4L, ML_2	$\log \gamma_{2.1}$ = 11.5(38)
637.5	~ 2 h	4.50[a]	637.5	M_2L		$\log \gamma_{2.1}$ = 11.8(38);11.9(41);11.9(37)
630	≦ 24 h	7.00[b]	635	M_3L_2, M_2L, ML	M_4L	$\log \gamma_{2.1}$ = 12.1(41);11.3(37) $\log \gamma_{1.1}$ = 6.0 (41)
630	≧ 21 days	10.9[e]	627.5	M_2L, ML, M_2L_3	M_3L, M_3L_2	$\log \gamma_{2.1}$ = 11.5(38);11.1(41);10.6 (37) $\log \gamma_{1.2}$ = 11.1(41)

[a] Biphthalate buffer; [b] phosphate buffer; [c] borate buffer; [d] HCl + KCl; [e] carbonate buffer.

[f] The numbers in parentheses refer to the literature method used to evaluate the particular constant value.

[g] The ionic strength was kept constant by the addition of sodium nitrate.

the different systems considered satisfy all the equilibrium requirements as was assumed initially in these investigations.

The main physicochemical properties established so far for the different systems investigated are summarized in Table I. With the exception of the palladiazo–palladium(II) system at pH 7, which shows a principal absorption maximum at 642.5 nm and a secondary one at 540 nm (coincident with the main absorption maximum of the free reagent), all the systems considered here show a unique absorption maximum in the visible region located in the 635 ± 15 nm wavelength interval (Figs. 2 and 3). In Table I are included the different M:L stoicheiometries which seem probable under the given conditions for each system; these ratios are inferred from the results of applying many spectrophotometric methods under conditions of significant excess of metal or excess of ligand.

Table I indicates that in both systems several complexes of M_4L, M_3L, M_2L, M_3L_2, ML, M_2L_3 and ML_2 types may co-exist under given conditions. The real composition of the different complex species will follow the general formulation:

$$[M_n(OH)_pH_qL_m]_x^{2n+q-(p+8m)}$$

wherein the possible existence of different acid–base isomers[42] and polymeric[43] "arsenazo"–palladium(II) complex species must be taken into account, as well as possible mixed complexes containing the buffer ligands. However, it is sufficient at this stage to consider the simplified picture provided by the metal:ligand ratios only.

There is little doubt about the occurrence of stepwise complex formation in some of these systems; this probability was indicated previously[1]. The stepwise formation is especially clear in the case of the arsenazo III–palladium(II) systems at pH 1.5, 7.0 and ≧10.8, as inferred by comparison of the results obtained by ASMUS' isosbestic point method[44] and BUDĚŠÍNSKÝ's differential isosbestic point method[45] in connection with JOB's isomolar continuous variations method[46]. Moreover, frequent inconsistencies in the location of the stoicheiometric (optimum) point of the systems have been detected from the use of the direct and inverse molar ratio[47], isomolar continuous variations[46] and proportional absorptivities[41] methods, for these systems. These inconsistencies most probably derive from the coexistence of several complexes present in considerable relative concentrations[48–52]. The inconsistencies caused particular problems in most of the palladiazo–palladium(II) systems investigated where the stepwise complex formation was less clear than in the corresponding arsenazo III–palladium(II) systems. The very frequently observed 1:1.225 (Pd(II):palladiazo) molar ratio (optimum point of the different absorbance functions), confirmed independently by different spectrophotometric methods, seems to indicate the coexistence of the ML, M_2L_3 and, possibly, ML_2 species present in appreciable concentrations in such systems. On the other hand, it is very difficult to predict the influence of the slow kinetic factors disclosed, on the overall stoicheiometric composition of the systems upon the attainment of the final equilibrium state, since the steady-state establishment may require months in some cases (excess ligand concentration conditions). The general inapplicability of the JOB–SCHWARZENBACH–BUDĚŠÍNSKÝ[38] treatment, which was systematically observed in attempts to evaluate the equilibrium constants of complex species exhibiting an apparent fractional stoicheiometry (*i.e.*, M_3L_2 and

M_2L_3-types) seems to favour the above statement concerning the coexistence of several complex species (with an "average" 1:1.225 metal:ligand stoicheiometry).

Although M_3L_2 and M_2L_3 complexes are somewhat infrequent, SANGAL[53] has also characterized M_2L_3 complexes in the nitroso-R-salt–palladium(II) system, which provides further evidence that palladium(II) tends to build this type of complex with certain reagents.

The extraction of the palladium(II) complexes of palladiazo and arsenazo III has been attempted by means of *n*-butanol with the following salts: cetyltrimethylammonium bromide (CTMA), cetyldimethylbenzylammonium chloride (CDBA) and diphenylguanidine chloride (GUAN).

Preliminary ion-exchange experiments carried out with both anion- and cation-exchange resins showed conclusively that in all the systems investigated, there exist only negatively-charged anionic complex species which are readily sorbed on a very thin layer of the anionic resin columns. No detectable sorption of the complexes could be observed on cationic resins.

EXPERIMENTAL

Instruments

A single-beam manual "Beckman" DU spectrophotometer, and a double-beam recording "Beckman" DK-2A spectrophotometer were used with matched 10-mm glass cells. A Universal Pye pH-meter was used for pH measurements.

Chemicals

Cetyltrimethylammonium bromide (Fluka), cetyldimethylbenzylammonium chloride (Koch–Light) and diphenylguanidine (Fluka) were used without further purification. Other reagents used were of reagent grade. Palladium chloride (Fluka) was used. Arsenazo III and palladiazo reagents were prepared and purified as described elsewhere[26] (about 95% purity).

Procedures

Solutions of the palladium(II) complexes of palladiazo and arsenazo III were prepared at pH values approaching those of maximum absorbance (Fig. 1) under both $c_M \gg c_L$ and $c_L > c_M$ conditions. The preparation and main properties of the twelve systems studied are summarized in Table II. The order of reagent addition was always: buffer, ligand, chloropalladite solution and water to dilute to 250 ml.

After a suitable time for establishment of equilibrium, 10 ml of each test solution was transferred to a 25-ml separating funnel followed by the addition of varying volumes (3–6 ml) of each extractant; 0.5% CTMA or CDBA solution in *n*-butanol was used. The extraction with GUAN was carried out by first adding to the test solution 1 ml of 10% diphenylguanidine chloride slightly acidified with hydrochloric acid[6], followed by the above varying volume of *n*-butanol. Since *n*-butanol dissolves appreciably in water (0.975 ml/10 ml of water)[43], no attempt was made to extract with 1-ml portions of *n*-butanol; extraction with 2-ml portions of *n*-butanol was unsuccessful because of persistent emulsion formation, and "salting out" electrolytes to enhance the extraction conditions were not tested because of the excessive complications of the systems.

TABLE II

EXPERIMENTAL CONDITIONS ESTABLISHED FOR THE DIFFERENT COMPLEX SOLUTIONS RELATED TO THE PALLADIAZO–Pd(II) AND ARSENAZO III–Pd(II) SYSTEMS SUBMITTED TO EXTRACTION

pH	*Buffer composition/250 ml*	$c_M \gg c_L$			$c_L > c_M$		
		$c_M \cdot 10^5$	$c_L \cdot 10^6$	*Ratio M:L*[a]	$c_M \cdot 10^5$	$c_L \cdot 10^5$	*Ratio M:L*[a]
Palladiazo system							
2.4	42 ml 0.1 *M* HCl 50 ml 0.25 *M* $KHC_8H_4O_4$	8.90	9.10	ML	2.22	4.55	M_2L_3
6.5	25 ml 0.5 *M* KH_2PH_4 25 ml 0.3 *M* NaOH	8.90	9.10	ML	2.22	4.55	ML_2
9.3	25 ml 0.20 *M* $Na_2B_4O_7 \cdot 10\ H_2O$	8.90	9.10	ML	2.22	4.55	M_2L_3
Arsenazo-III system							
4.5	50 ml 0.25 *M* $KHC_8H_4O_4$ 25 ml 0.1 *M* NaOH	8.90	10.4	M_2L	2.22	2.70	ML,M_2L
6.5	25 ml 0.5 *M* KH_2PO_4 25 ml 0.3 *M* NaOH	8.90	10.4	M_2L	2.22	2.70	ML,M_3L_2
12.0	25 ml 0.5 *M* $NaHCO_3$ 25 ml 0.4 *M* NaOH	8.90	10.4	M_2L	2.22	2.70	ML,M_2L_3

[a] Predominant complex species.

In all cases, the solutions were hand-shaken for 1 min and then the emulsions formed were left to separate for about 5 min. The phase separation usually proceeded very quickly and cleanly but in a few cases centrifugation proved to be necessary (15–30 min at 3,200 r.p.m.). The aqueous raffinates were then discarded and the organic extracts were transferred quantitatively to 10-ml volumetric flasks which were then filled to the mark with *n*-butanol. The different organic extracts thus prepared were measured against suitable blanks to establish the wavelength of maximum absorbance. Two types of blank solutions were prepared, depending on the particular nature of the systems involved:

(i) Test solutions under $c_M \gg c_L$ conditions. The organic extracts were measured against pure *n*-butanol since the absorbance of the free ligand was negligible under these conditions, while the aqueous test solutions were measured against distilled water.

(ii) Test solutions under $c_L > c_M$ conditions. Since the absorption caused by the excess of ligand in these cases may be considerable, the aqueous solutions and organic extracts were measured against suitable blanks prepared as follows. From the data in Table II, the excess ligand concentration was calculated for each system. The aqueous test solutions were measured against aqueous blanks containing the calculated free ligand concentration while the organic extracts were measured against the corresponding organic extracts of aqueous solutions containing the calculated excess ligand concentration, under identical extraction conditions. Although not absolutely rigorous, this procedure seemed the best practical approach to the different problems posed by blank solutions corresponding to the $c_L > c_M$ aqueous starting solutions and their extracts.

Conformity with Beer's law was checked for each of the complex systems investigated, both in aqueous and in butanolic solutions. The partition coefficients were then calculated directly from the absorbance data obtained, according to eqn. (1):

$$\alpha = \frac{[\mathrm{M}_n\mathrm{L}_m]_{\mathrm{org.}}}{[\mathrm{M}_n\mathrm{L}_m]_{\mathrm{aq.}} - [\mathrm{M}_n\mathrm{L}_m]_{\mathrm{org.}}} = \frac{E_{\mathrm{org.}}{}^{\lambda'}}{E_{\mathrm{aq.}}{}^{\lambda} - E_{\mathrm{org.}}{}^{\lambda'}} = \frac{E_{\mathrm{org.}}{}^{\lambda'}}{\Delta E} \qquad (1)$$

where

$[\mathrm{M}_n\mathrm{L}_m]_{\mathrm{org.}}$ = concentration of complex(es) in the organic extract,
$[\mathrm{M}_n\mathrm{L}_m]_{\mathrm{aq.}}$ = concentration of complex(es) in the initial aqueous test solution,
$E_{\mathrm{org.}}{}^{\lambda'}$ = absorbance (measured against organic blank) of the organic extract at its maximum absorbance wavelength (λ'),
$E_{\mathrm{aq.}}{}^{\lambda}$ = absorbance (measured against aqueous blank) of the aqueous test solution at its maximum absorbance wavelength (λ),
ΔE = absolute difference between the absorbances of the aqueous (before the extraction) and organic (after extraction) phases.

Since the final volumes of the aqueous starting solutions and of the organic extracts were always adjusted to 10 ml, the direct quotient of the absorbances measured (corrected for the blank) for both types of solutions makes it possible to calculate the partition coefficients as in eqn. (1) instead of dealing with quotients in terms of concentrations. This simplified treatment is sufficient to provide a fairly good idea of the analytical applicability of the extraction processes investigated.

Since the extraction processes under the conditions selected are accompanied by a net concentration effect of the complex compound(s) in the organic phase, it was considered of interest to evaluate the extent to which the palladium(II) complexes become concentrated in the organic layers under the different experimental conditions tested. This was done by means of the formula:

$$\phi \cong \frac{E_{\mathrm{red.org.}}{}^{\lambda'}}{E_{\mathrm{aq.}}{}^{\lambda}} = \frac{\dfrac{E_{\mathrm{org.}}{}^{\lambda'} \cdot 10}{V - 0.975}}{E_{\mathrm{aq.}}{}^{\lambda}} \qquad (2)$$

where

ϕ = concentration factor achieved through the extraction process,
$E_{\mathrm{red.org.}}{}^{\lambda'}$ = absorbance corresponding to the organic extract phase before its dilution to 10 ml measured at its maximum wavelength (λ'),
V = initial n-butanol volume used to carry out a particular extraction process,
$E_{\mathrm{aq.}}{}^{\lambda}$ = same meaning as in eqn. (1)

In eqn. (2) the factor $\cdot 10$ refers to the final volume of 10 ml to which the different organic extracts were diluted, while the factor 0.975 corresponds to the solubility of n-butanol in 10 ml of water[54]. Under the conditions selected it is evident from eqn. (2) that the maximum attainable value for ϕ amounts to 4.94 for the limiting case of 100% extraction of a given complex (or mixture of complexes) into the organic phase, *i.e.*, when $E_{\mathrm{org.}}{}^{\lambda'} = E_{\mathrm{aq.}}{}^{\lambda}$ and $V = 3$ ml (neglecting the spectrophotometric changes undergone by the complexes resulting from the extraction process).

The knowledge of the concentration factors in every case (ϕ_i) enables rapid calculation of the percentage of palladium extracted into the organic phase from any given complex aqueous solution by means of the relationship $\%\ \mathrm{Pd} = (\phi_i/4.94) \cdot 100$.

RESULTS AND DISCUSSION

The main spectrophotometric characteristics of the different systems investigated are summarized in Table III. These data indicate that in 4 of the 12 systems investigated no appreciable extraction of complexes could be achieved with any of the extractants used (with the exception of the palladiazo–palladium(II) system at pH 4.5 under $c_M \gg c_L$ conditions which was satisfactorily extracted only by GUAN). On the other hand, in only 3 of the 12 systems did persistent emulsion formation necessitate centrifugation to accomplish clear phase separation.

TABLE III

MAIN PROPERTIES OF THE AQUEOUS SOLUTIONS AND THEIR CORRESPONDING ORGANIC EXTRACTS IN THE PALLADIAZO–Pd(II) AND ARSENAZO III–Pd(II) COMPLEX SYSTEMS INVESTIGATED

$c_M \gg c_L$			*pH*	$c_L > c_M$		
Aq. phase $\lambda_{max.}$ *(nm)*	*Organic extract*			*Aq. phase* $\lambda_{max.}$ *(nm)*	*Organic extract*	
	Extractn. with	$\lambda_{max.}$ *(nm)*			*Extractn. with*	$\lambda_{max.}$ *(nm)*
Palladiazo						
640	CTMA	645	2.4		CTMA	[a]
640	CDBA	645	2.4		CDBA	[a]
640	GUAN	630[c]	2.4		GUAN	[a,c]
630	CTMA	635	6.5	550	CTMA	560[b]
630	CDBA	635	6.5	550	CDBA	566[b]
630	GUAN	630[c]	6.5	550	GUAN	566[b,c]
625	CTMA	630	9.3	540	CTMA	544[b]
625	CDBA	635	9.3	540	CDBA	550[b]
625	GUAN	640[c]	9.3	540	GUAN	550[b,c]
Arsenazo III						
625	CTMA	[a]	4.5		CTMA	[a]
625	CDBA	[a]	4.5		CDBA	[a]
625	GUAN	640[c]	4.5		GUAN	[a,c]
630	CTMA	635	6.5	630	CTMA	630[b]
630	CDBA	640	6.5	630	CDBA	630[b]
630	GUAN	645[c]	6.5	630	GUAN	630[b,c]
625	CTMA	630	12.0		CTMA	[a]
625	CDBA	635	12.0		CDBA	[a]
625	GUAN	645[c]	12.0		GUAN	[a,c]

[a] No extraction of the complex into the organic phase could be observed.

[b] The extraction process resulted in the formation of persistent emulsions (centrifuging proved necessary).

[c] Initial formation of a white bulky precipitate which dissolved on addition of *n*-butanol and shaking.

Table III shows apparent anomalies in the maximum wavelength values for the initial aqueous solutions (540–550 nm) and organic extracts (544–566 nm) of the palladiazo–palladium(II) systems at pH 6.3 and 9.3; with accurate blank compensation, these wavelengths should be located in the 630–665 -nm interval. The disagreement between the results obtained and the theoretical predictions probably derives from the presence of an excess of ligand in both the aqueous solutions and the organic extracts, since both free ligand and palladium(II) complexes are extracted similarly. Since the c_L/c_M ratios established for these solutions were rather low (*ca.* 2), the anomalies are probably caused by insufficient displacement of the equilibria established between the different complex species and the excess of free ligand; it thus becomes impossible to calculate accurately the total free ligand concentration which should be used in each particular blank solution so that the true absorbance of the palladium complexes present can be measured. The situation is particularly inconvenient in the case of palladiazo, since the apparent molar absorptivities of both the pure reagent and the palladium(II) complexes are of a similar order of magnitude in the 630-nm region, and the molar absorptivity of the free ligand is considerably higher at 540 nm than that of any of the palladiazo–palladium(II) complexes.

It is of interest that whenever the extraction was made with guanidine, the initial addition of this reagent caused the formation of a voluminous white precipitate which dissolved readily on addition of the appropriate volume of *n*-butanol. This phenomenon can be explained as the formation of an azo dye–guanidonium salt (neutralization of the sulfonic groups by guanidonium cation) which is insoluble in water but readily soluble in the alcoholic medium.

The absorbance measurements were always carried out as soon as possible after dilution of the extracts to 10 ml, since in some cases bluish precipitates were observed on standing, presumably because of the slight solubility of the extracted complexes in *n*-butanol. In other cases, no precipitation was observed on standing, but the colour of the organic extracts faded considerably so that eventually nearly colorless solutions were obtained, possibly because of ill-defined competitive side-reactions.

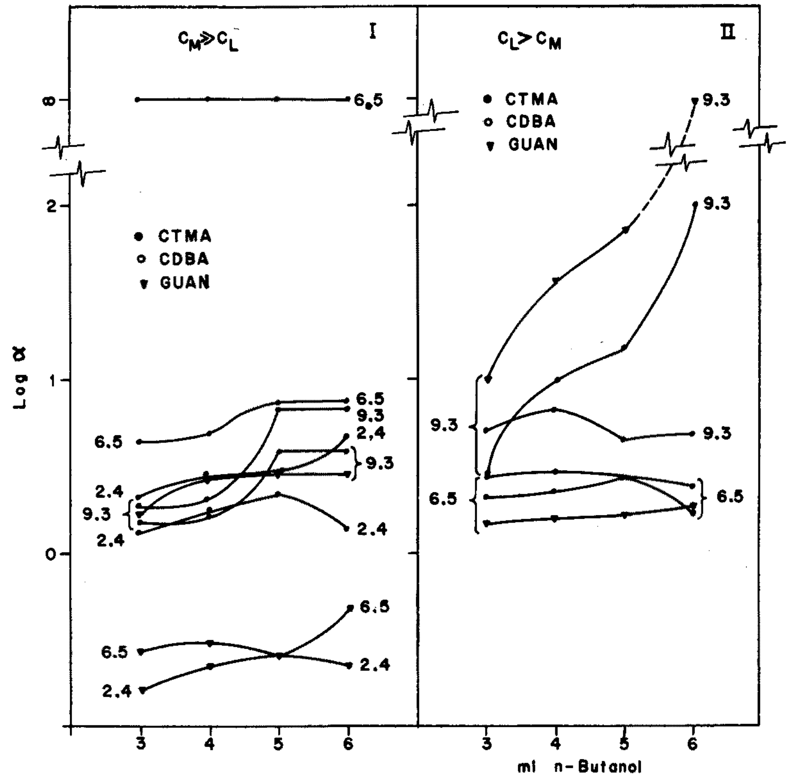

Fig. 4. Characteristics of extraction of palladiazo–Pd(II) complex solns. as a function of the particular extractant, pH of aqueous solns and volume of organic phase.

*Partition coefficients**

The results obtained are shown in Figs. 4 and 5; log α is plotted against the n-butanol volume calculated from eqn. (1). The following conclusions can be drawn.

Palladiazo–palladium(II) systems. Under $c_M \gg c_L$ conditions (Fig. 4, I), the extraction of complexes is practically quantitative at pH 6.5 with CTMA, and satisfactory with CDBA, but very low α-values are obtained with GUAN ($0.2 \leqq \alpha \leqq 0.5$). At pH 2.4 and 9.3, the extractions with CTMA and CDBA are very similar ($1.3 \leqq \alpha \leqq 6.7$) whereas systematically lower results are obtained with GUAN ($0.16 \leqq \alpha \leqq 0.26$ at pH 2.4 and $1.7 \leqq \alpha \leqq 3.0$ at pH 9.3).

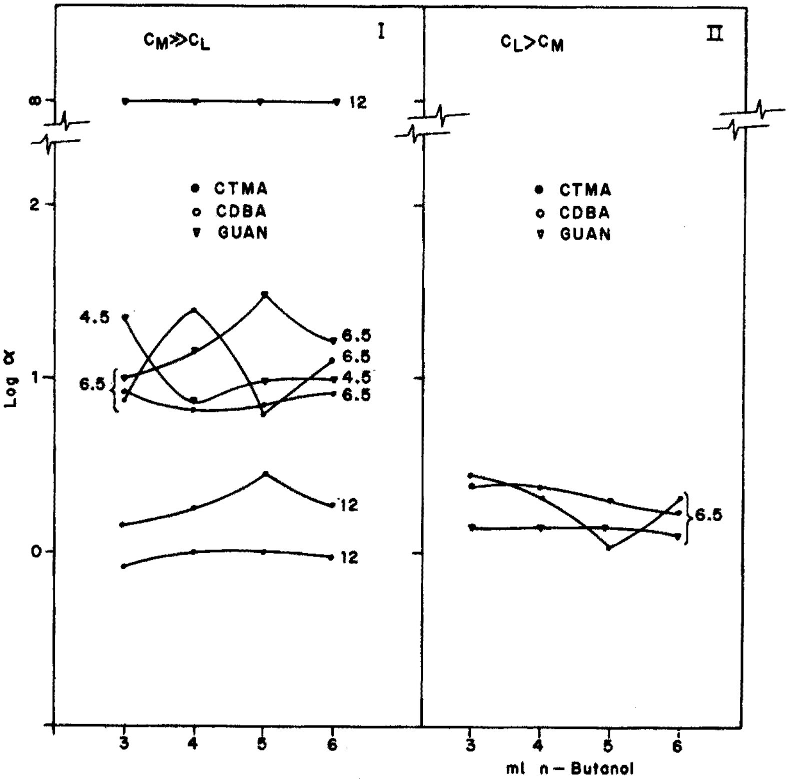

Fig. 5. Characteristics of extraction of arsenazo III–Pd(II) complex solns. as a function of the particular extractant, pH of the aqueous solns and volume of organic phase.

Under $c_L > c_M$ conditions (Fig. 4, II), there is no complex extraction at pH 2.4. The best results are obtained at pH 9.3, where the extraction efficiency is in the order, GUAN ≫ CDBA > CTMA. Rather low α-values are obtained at pH 6.5 ($1.6 \leqq \alpha \leqq 2.5$) where the 3 extractants exhibit similar behaviour.

Arsenazo III–palladium(II) systems. Under $c_M \gg c_L$ conditions (Fig. 5,I), complexes are readily extracted at pH 4.5 only by GUAN ($7 \leqq \alpha \leqq 22$). At pH 12, the

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* For α-values $\geqq$ 40 the term "quantitative extraction" is used and the results are presented graphically as log $\alpha = \infty$; the practical limitations of the spectrophotometric method used did not allow accurate calculation of the real values of the partition coefficients in such cases.

extraction of complexes is quantitative with GUAN, while CTMA and CDBA behave similarly yielding comparatively low results ($0.7 \leqq \alpha \leqq 3.0$). At pH 6.5 the extraction is satisfactory with all 3 extractants ($6 \leqq \alpha \leqq 30$); CTMA and CDBA exhibit similar extraction characteristics while GUAN gives rather better results.

Under $c_L > c_M$ conditions (Fig. 5, II), the complexes are extracted only at pH 6.5; the α-values obtained are rather low and similar with all 3 extractants ($1.1 \leqq \alpha \leqq 3.5$).

Concentration factors

The results obtained for the ϕ *vs.* *n*-butanol volume function are shown in Figs. 6 and 7, as calculated by eqn. (2). The following conclusions can be drawn.

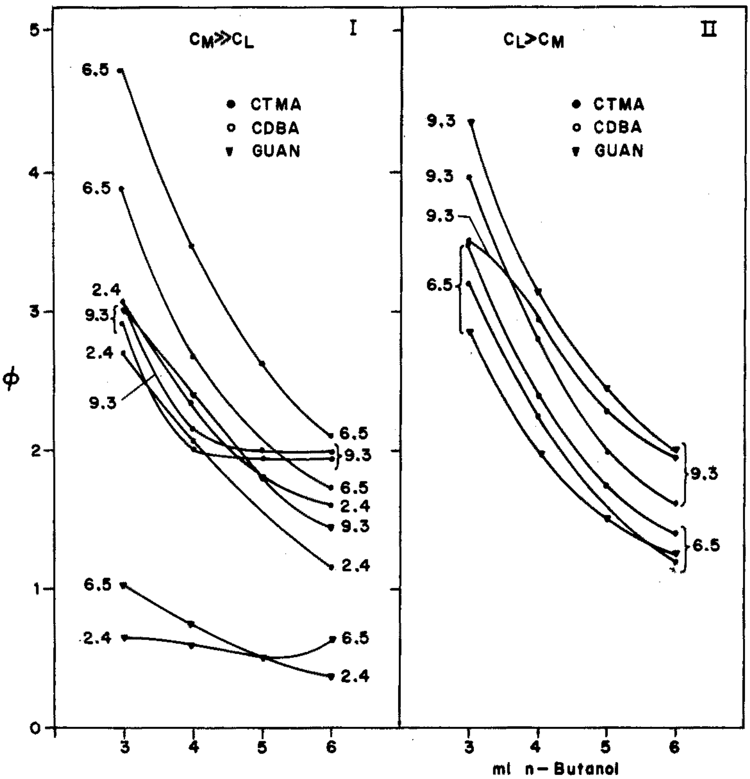

Fig. 6. Concentration factors obtained by extraction of palladiazo–Pd(II) complexes into the organic phase under different experimental conditions.

Palladiazo–palladium(II) systems. Under $c_M \gg c_L$ conditions (Fig. 6, I), the highest ϕ-values are obtained at pH 6.5 with CTMA and CDBA ($\phi_{\max.} \sim 4.7$) while very low results are obtained with GUAN ($\phi_{\max.} \sim 1$). Similar results are obtained with CTMA and CDBA at pH 2.4 ($\phi_{\max.} \sim 3$) while much lower ones are given by GUAN ($\phi_{\max.} \sim 0.7$). Similar results are also obtained with the 3 extractants at pH 9.3 ($\phi_{\max.} \sim 3$). It is interesting to note the striking differences showed by GUAN, compared with CTMA and CDBA, as a function of pH.

Under $c_L > c_M$ conditions (Fig. 6, II), there is no complex extraction at pH 2.4 with any of the extractants tested. In all cases, the ϕ-values obtained are higher at pH 9.3 than at pH 6.5. At pH 9.3 GUAN yields higher ϕ-values than CTMA and CDBA ($1.6 \leqq \alpha \leqq 4.0$) while at pH 6.5 the reverse occurs.

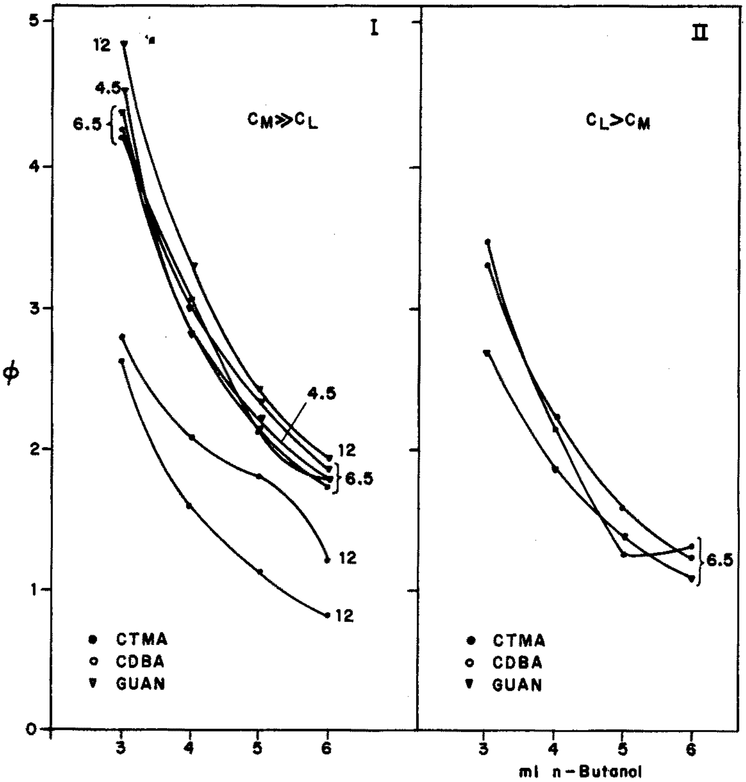

Fig. 7. Concentration factors obtained by extraction of arsenazo III–Pd(II) complexes into the organic phase under different experimental conditions.

Arsenazo III–palladium(II) systems. Under $c_M \gg c_L$ conditions (Fig. 7, I), GUAN is the only extractant that gives satisfactory results at pH 4.5 ($1.8 \leqq \phi \leqq 4.6$). At pH 6.5 all 3 extractants yield similar satisfactory results ($1.8 \leqq \phi \leqq 4.4$) while at pH 12, GUAN is superior ($1.8 \leqq \phi \leqq 4.8$) to the other two extractants ($1.0 \leqq \phi \leqq 2.7$).

Under $c_L > c_M$ conditions (Fig. 7, II), extraction of the complexes is only significant at pH 6.5; the results obtained with CTMA and CDBA are superior ($1.2 \leqq \phi \leqq 3.4$) to those obtained with GUAN ($1.1 \leqq \phi \leqq 2.7$).

Absorption spectra of the complexes in the aqueous and organic phases

Although correlation of the spectral properties in the visible region, of the complexes present in the initial aqueous solutions and the organic extracts, can be only qualitative, it may be of interest to comment briefly on the main spectral modifications caused by the extraction.

Palladiazo–palladium(II) systems. Figure 8 shows the spectra of 4 of the 6 systems investigated.

At pH 6.5 (Fig. 8, I) under $c_M \gg c_L$ conditions, the aqueous starting solution (no. 1) shows maximum absorbance at 635 nm whereas the CTMA (no. 2) and CDBA (no. 3) extracts show maximum absorbance at 650 nm; the spectrum of the GUAN extract (no. 4) possesses two wide absorption bands with maxima located at *ca.* 560 and and 635 nm. At pH 9.3 (Fig. 8, II) the results closely resemble those obtained at pH 6.5, the greatest differences again being furnished by the GUAN extract (no. 4). Thus, the extraction of the complexes by CTMA and CDBA is accompanied by a slight bathochromic shift of the wavelength of maximum absorbance compared to its location in aqueous solutions, but no other significant variations in the spectra occur. In contrast, the organic GUAN extracts exhibit much less accentuated bathochromic shifts but the shapes of their spectra differ sharply from those corresponding to the aqueous solutions; this fact seems to indicate an important chemical interaction between the extracted complexes and guanidine.

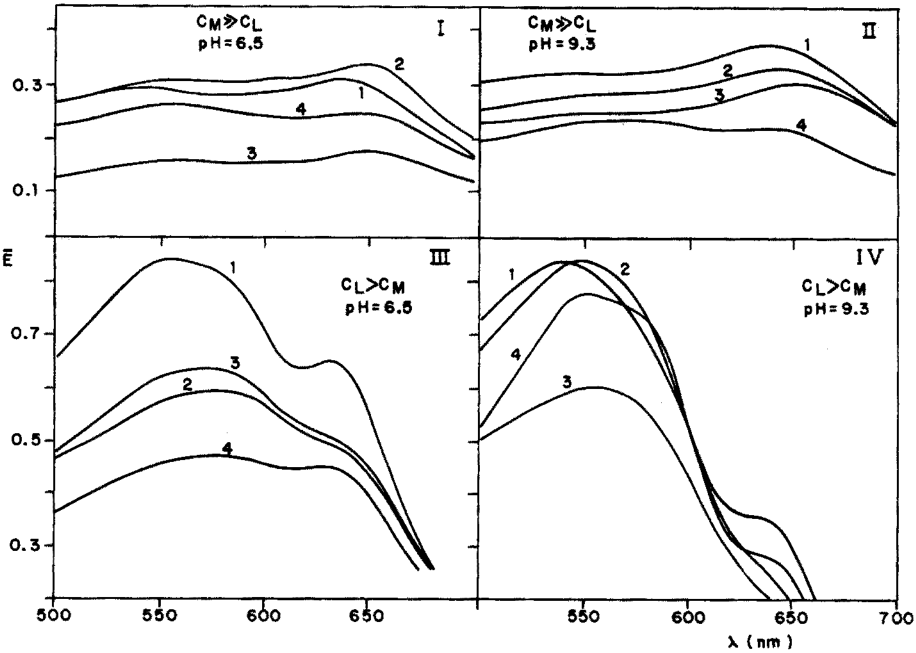

Fig. 8. Qualitative correlation of spectra shown by some of the starting palladiazo–Pd(II) complex aqueous solns and their corresponding organic extracts. (1) Aqueous starting soln; (2) CTMA organic extract; (3) CDBA organic extract; (4) GUAN organic extract.

Under $c_L > c_M$ conditions, the predominance of the main absorption band of palladiazo ($\lambda_{max.} = 540$ nm) is clearly observed in all cases (Figs. 8, III and IV, spectra 1–4); this indicates the presence of an excess of free ligand not compensated for by the particular blank solutions used, as discussed earlier. As indicated in the preceding paragraph, under $c_L > c_M$ conditions, the CTMA and CDBA extracts (Fig. 8, III and IV, spectra 2 and 3) behave similarly while those of GUAN (spectra 4) again show the greatest differences compared with aqueous solutions.

Arsenazo III–palladium(II) systems. The absorption spectra of the aqueous solutions and organic extracts of 4 of the 6 systems investigated are shown in Fig. 9.

At pH 4.5 under $c_M \gg c_L$ conditions (Fig. 9, I), extraction is possible only with GUAN (no. 4). Comparison of spectra 1 and 2 shows that the spectrum of the organic extract exhibits a considerable solvochromic–bathochromic shift ($\Delta\lambda = 22.5$ nm) as well as a new absorbance maximum at 607.5 nm in the spectral region where the aqueous solution shows a submerged band. At pH 6.5 (Fig. 9, III) and 12 (Fig. 9, II), the same remarks are again applicable for the GUAN extracts (*cf.* spectra 1 and spectra 4). At both these pH values, the CTMA (spectra 2) and CDBA (spectra 3) extracts show very similar variations which differ to a smaller extent from the spectral characteristics

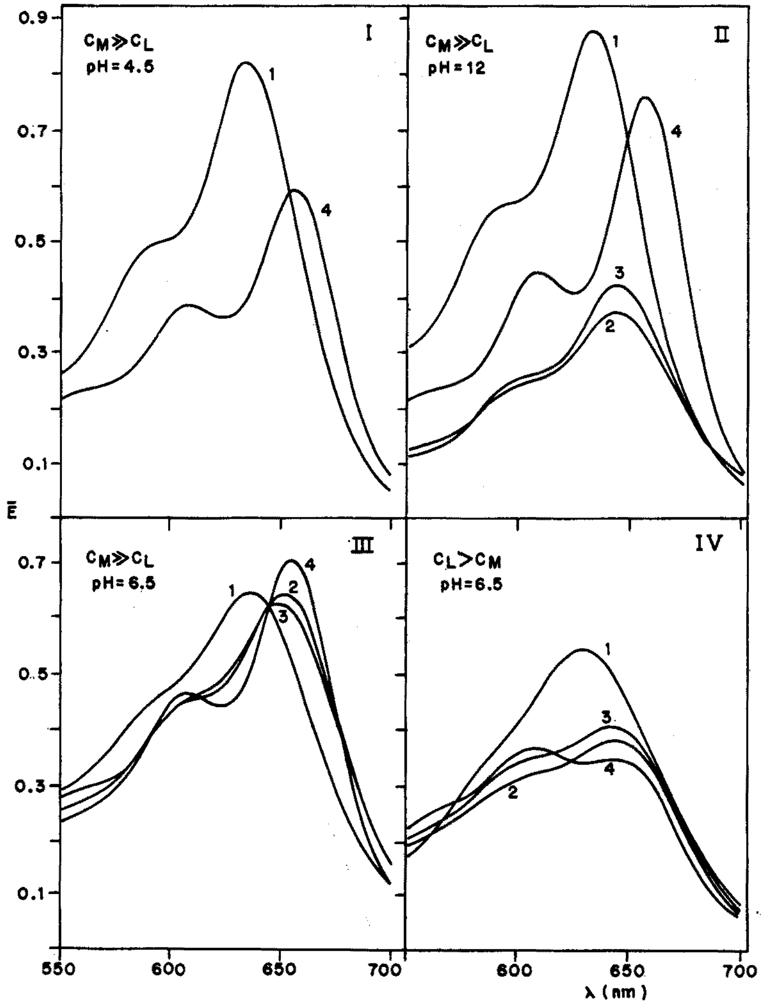

Fig. 9. Qualitative correlation of spectra shown by some of the starting arsenazo III–Pd(II) complex aqueous solns and their corresponding organic extracts. (1) Aqueous starting soln; (2) CTMA organic extract; (3) CDBA organic extract; (4) GUAN organic extract.

of the aqueous solutions (spectra 1) than the GUAN extracts. Important solvochromic–bathochromic shifts are observed ($\Delta\lambda \sim 17.5$ nm), but there is no resolution of a second absorbance maximum in the region of the submerged band of the aqueous solutions, such as occurs with GUAN extracts (λ_{max}' 607.5 nm).

At pH 6.5 under $c_L > c_M$ conditions (Fig. 9, IV), all 3 organic extracts show spectra which differ considerably from that of the aqueous complex solution (no. 1) but the solvochromic–bathochromic effects are less pronounced ($\Delta\lambda \simeq 12$–15 nm). The spectra of the CTMA (no. 2) and CDBA (no. 3) extracts are very similar, exhibiting a wide absorption band in the 575–650-nm region; the existence of a submerged band, absent in the aqueous solution (no. 1) is obvious, for spectrum 1 shows a symmetrical form. As in previous cases, the spectrum of the GUAN extract (no. 4) again departs very sharply from the others. The curious appearance of a new absorbance maximum at 610 nm in the GUAN extract in the region where the CTMA (no. 2) and CDBA (no. 3) spectra show the presence of a submerged band, which is not shown at all by the aqueous test solution (no. 1), is of interest; the hyperchromic effect is remarkable, for the molar absorptivity exceeds that of the normally principal maximum located at 650 nm. At pH 12 (spectra not included) very slightly colored spectra with weak absorbance maxima in the 680-nm region were obtained in all cases for the organic extracts. All these extracts showed accentuated fading of colour with time, which seems to indicate the possibility of the formation of mixed colorless arsenazo III–palladium(II) extractant cationic complex species.

SUMMARY

The extraction characteristics of the palladium(II) complexes of arsenazo III and palladiazo were investigated at different pH values under conditions of both metal and ligand excess. Partition coefficients and concentration factors were estimated spectrophotometrically as a function of pH, volume of the organic phase and nature of the auxiliary organic cations introduced. Depending on the extraction conditions, the different complexes were extracted to very varying extents despite their consistently anionic nature. A summary of physicochemical data of interest for the complex systems is given. The two quaternary ammonium salts used gave very similar extraction results which differed sharply from those obtained with guanidine. A qualitative correlation of the spectra of the initial aqueous test solutions and their different organic extracts for 12 different systems is discussed; there is a strong chemical interaction between the extracted complex compounds and the organic cations of the extractant, so that nearly colorless ternary complexes may result. The suitability of some of the systems tested, for the direct extraction-spectrophotometric determination of palladium(II), is mentioned.

RÉSUMÉ

On examine l'extraction des complexes du palladium(II) avec l'arsènazo III et le palladiazo, à divers pH avec métal ou ligand en excès. Les coefficients de partage et les facteurs de concentration sont estimés spectrophotométriquement en fonction du pH, du volume de la phase organique et la nature des cations organiques introduits. Les deux sels d'ammonium quaternaires utilisés donnent des résultats d'extraction très proches, différant beaucoup de ceux obtenus avec la guanidine. On examine également la relation entre les spectres des solutions initiales et leurs extraits organiques pour 12 systèmes différents. On signale quelques systèmes pouvant convenir au dosage spectrophotométrique direct du palladium(II), après extraction.

ZUSAMMENFASSUNG

Die Extraktion der Palladium(II)-Komplexe von Arsenazo III und Palladiazo wurden bei verschiedenen pH-Werten und beim Überschuss sowohl des Metalls als auch des Liganden untersucht. Die Verteilungskoeffizienten und die Konzentrationsfaktoren wurden spektralphotometrisch in Abhängigkeit vom pH-Wert, der Volumen der organischen Phase und der Natur der zur Unterstützung hinzugefügten organischen Kationen bestimmt. In Abhängigkeit von den Extraktionsbedingungen wurden die verschiedenen Komplexe in sehr unterschiedlichem Ausmass extrahiert trotz ihrer systematischen anionischen Natur. Die interessierenden physikalisch-chemischen Daten der Komplexsysteme werden in einer Zusammenfassung angegeben. Die verwendeten zwei quaternären Ammoniumsalze zeigen sehr ähnliche Extraktionsergebnisse, welche sich jedoch scharf von denen unterscheiden, welche mit Guanidin erhalten wurden. Eine qualitative Beziehung der Spektren von den wässrigen Testlösungen und ihre unterschiedlichen organischen Extrakte von 12 verschiedenen Systemen wird diskutiert. Es wurde eine starke chemische Wirkung zwischen den extrahierten Komplexen und den organischen Kationen des Extraktionsmittels festgestellt, so dass nahezu farblose ternäre Komplexe angenommen werden können. Die untersuchten Systeme eignen sich zur direkten spektralphotometrischen Bestimmung von Palladium(II).

REFERENCES

1 J. A. Pérez-Bustamante and F. Burriel-Martí, *Anal. Chim. Acta*, 37 (1967) 49, 62.
2 J. G. Sen Gupta, *Anal. Chem.*, 39 (1967) 18.
3 M. T. Sardiña, R. F. Cellini and T. Batuecas Rodríguez, *J. Inorg. Nucl. Chem.*, 24 (1962) 721.
4 L. M. Gindin, S. N. Ivanova, A. A. Mazurova and L. Ya. Mironova, *Zh. Neorgan. Khim.*, 10 (1965) 502.
5 B. L. Karger, A. B. Caragay and S. B. Lee, *Separ. Sci.*, 2 (1967) 39.
6 V. I. Kuznetsov and S. B. Savvin, *U.S.S.R. Patent 133,257*, Nov. 10, 1960; *Radiokhhimiya*, 6 (1960) 682; *Dokl. Akad. Nauk SSSR*, 140 (1961) 125.
7 V. I. Kuznetsov and Ni Chzhao-Ai, *Zh. Analit. Khim.*, 18 (1963) 915.
8 I. P. Alimarin, S. B. Savvin and Yu. M. Dedkov, *Zh. Analit. Khim.*, 19 (1964) 328.
9 S. B. Savvin, P. N. Romanov and Yu. G. Eremin, *Zh. Analit. Khim.*, 21 (1966) 1423.
10 S. B. Savvin, Yu. M. Dedkov and P. N. Romanov, *Zh. Analit. Khim.*, 22 (1967) 65.
11 V. N. Tolmachev, L. A. Kvichko and V. D. Konkin, *Zh. Analit. Khim.*, 22 (1967) 11.
12 V. N. Tolmachev, I. M. Gol'tsbert and V. D. Konkin, *Zh. Analit. Khim.*, 22 (1967) 950.
13 E. S. Pal'shin, B. F. Myasoedov and N. P. Palei, *Zh. Analit. Khim.*, 17 (1962) 471.
14 I. P. Alimarin and Khan'Si-i, *Zh. Analit. Khim.*, 18 (1963) 82
15 Yu. A. Zolotov and V. V. Bagreev, *Zh. Analit. Khim.*, 21 (1966) 649.
16 H. A. Droll, B. P. Block and W. C. Fernelius, *J. Phys. Chem.*, 61 (1957) 1000.
17 S. A. Shukarev, O. A. Lobaneva, M. A. Ivanova and M. A. Kononova, *Vestn. Leningr. Univ. Ser. Fiz. i Khim.*, 10 (1961) 2.
18 A. A. Biryukov and V. I. Shlenskaya, *Zh. Neorgan. Khim.*, 9 (1964) 813.
19 D. Dyrssen and K. Burger, *Acta Chem. Scand.*, 17 (1963) 1489; K. Burger, *Magy. Kem. Folyoirat*, 70 (1964) 179; *Acta Chim. Acad. Sci. Hung.*, 40 (1964) 261.
20 A. A. Grinberg, M. I. Gel'fman and N. V. Kiseleva, *Zh. Neorgan. Khim.*, 12 (1967) 1171.
21 V. I. Kazakova and B. V. Ptitsyn, *Zh. Neorgan. Khim.*, 12 (1967) 620.
22 R. Wyatt, *Chem. Weekblad*, 62 (1966) 310.

23 R. M. Izatt, D. Eatough and J. J. Christensen, *J. Chem. Soc.*, A (1967) 1301.
24 J. A. Pérez-Bustamante, to be published.
25 L. Bocanegra, *Doctoral Thesis*, to be published.
26 J. A. Pérez-Bustamante, *Doctoral Thesis*, Madrid, 1967.
27 W. R. Brode, *Recent Advances in the Chemistry of Colouring Matters, Chem. Soc., London, Spec. Publ.*, 4 (1956) 1–16.
28 S. Abbey, *Anal. Chim. Acta*, 30 (1964) 176.
29 P. Pištek, J. Rais and M. Kurš, *Z. Physik. Chem., Leipzig*, 232 (1966) 103.
30 A. A. Nemodruk, *Zh. Analit. Khim.*, 22 (1967) 629.
31 J. A. Pérez-Bustamante, F. Palomares Delgado and F. Burriel Martí, to be published.
32 J. A. Pérez-Bustamante and F. Burriel Martí, to be published.
33 J. Bjerrum, *Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd.*, 21 (1944) 1.
34 S. K. Banerji and A. K. Dey, *J. Indian Chem. Soc.*, 38 (1961) 121.
35 S. N. Sinha and A. K. Dey, *Chim. Anal. Paris*, 45 (1963) 224.
36 A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 72 (1950) 4488.
37 J. A. Pérez-Bustamante and F. Burriel-Martí, to be published.
38 B. Buděšínský, *Z. Anal. Chem.*, 195 (1963) 244.
39 P. Job, *Compt. Rend.*, 180 (1925) 928.
40 N. Tanaka and T. Takamura, *J. Inorg. Nucl. Chem.*, 9 (1959) 15.
41 B. Buděšínský, *Z. Anal. Chem.*, 209 (1965) 379.
42 V. Frei, *Z. Physik. Chem. Leipzig*, 234 (1967) 337.
43 B. Buděšínský, *Z. Anal. Chem.*, 202 (1964) 6.
44 E. Asmus, *Z. Anal. Chem.*, 193 (1963) 81.
45 B. Buděšínský, *Z. Anal. Chem.*, 202 (1964) 96.
46 P. Job, *Ann. Chim. Paris*, 9 (1928) 113.
47 J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, 16 (1944) 111.
48 F. Woldbye, *Acta Chem. Scand.*, 9 (1955) 229.
49 L. Sommer, *Folia Fac. Rer. Nat. Univ. Purkyně, Brno*, 5 (1964) 1.
50 L. Sommer, J. Kučerová, H. Procházková and M. Hniličková, *Publ. Fac. Sci. Univ. J. E. Purkyně, Brno*, 464 (1965) 249.
51 L. Sommer and M. Hniličková, *Bull. Soc. Chim. France*, (1959) 36.
52 T. V. Mal'kova, N. A. Fateeva and K. B. Yatsimirskii, *Zh. Neorgan. Khim.*, 12 (1967) 2905.
53 S. P. Sangal, *J. Prakt. Chem.*, 31 (1966) 68.
54 *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 35th Edn., 1953–54.

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DISUBSTITUTED METHANES AS FLUORIMETRIC REAGENTS

PART I. DIBENZOTHIAZOLYLMETHANE

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Several disubstituted methanes have been used as ligands in producing fluorescent metal chelates. The rare earth chelates of dibenzoylmethane and benzoylacetone exhibit line spectra of very high intensity, at liquid nitrogen[1,2] temperatures, that might prove useful as lasers. Variations in luminescent lifetimes of a number of dibenzoylmethane and benzoylacetone metal complexes have been suggested to be the result of ligand–metal interaction[3] or chelate composition[4]. Diquinolylmethane and its analogs have been intensively studied by SCHEIBE AND DALTROZZO[5]. These compounds vary markedly in the acidity of the methylene hydrogen and in their ability to form fluorescent metal chelate compounds. Since none of these disubstituted methanes has been used analytically, a program has been initiated to investigate the analytical potentialities of some disubstituted methanes containing different donor atoms in (or attached to) various aromatic systems.

Dibenzothiazolylmethane [$(C_7H_4NS)_2CH_2$, DBTM] forms chelates which fluoresce at room temperature and has been applied to the determination of zinc[6] and lithium[7]; only simple fluorimeters were available to us at that time and a detailed study of the fluorescence reaction was not possible. This paper reports the results of such a study; a greater sensitivity with purified reagents permits 2 p.p.b. of zinc to be determined.

EXPERIMENTAL

Apparatus

An Aminco-Bowman Spectrophotofluorimeter was used for recording fluorescence spectra and for intensity measurements at a particular wavelength. Absorption, infrared, and NMR spectra were done with Bausch and Lomb 505, Perkin Elmer 237B, and Varian A60 spectrometers, respectively.

Reagents

The reagent, prepared as described previously[6] and recrystallized from ethanol, showed appreciable fluorescence under the usual reaction conditions for zinc. Further recrystallizations from other organic solvents did not appreciably decrease the background fluorescence. A chloroform solution of the reagent was therefore extracted 3 times with a 0.1 *M* ethylenediaminetetraacetic acid solution (buffered at pH 10 with ammonia–ammonium chloride) and the reagent was recovered from the organic phase (after washing with distilled water) by vacuum evaporation. The background fluorescence of the DBTM, after recrystallization from ethanol, was one-half that of untreated reagent.

Trace metals were removed from 0.5 *M* potassium hydroxide by extraction with a carbon tetrachloride solution of dithizone. The resultant solution was red in color and this color was removed, after washing with carbon tetrachloride, by treatment with Amberlite IR-45 ion exchange resin; the resin was prewashed with 10–12 l of distilled water and 500 ml of 0.1 *M* potassium hydroxide before the treated solution was passed through the column. The effluent stock solution was standardized with potassium acid phthalate.

The absolute ethanol was distilled after drying over anhydrous calcium chloride. The alcohol showed no absorption beyond 210 nm in a 10-cm cell and only a slight fluorescence (4–5 divisions at 450 nm when excited at 410 nm) with the highest instrument sensitivity (meter multiplier, 0.001; sensitivity, 50).

The stock zinc solution was prepared from Analar zinc nitrate and was 0.01005 *M* (standardized with EDTA using eriochrome T indicator). More dilute solutions (10^{-4} and 10^{-5} *M*) were prepared daily from this standard.

Procedure

The procedure with the Turner Fluorimeter Model 110 was essentially as that previously recommended[6] (primary filter Corning #7–60, secondary filter #2A, range extension filter ND 1%). The excitation and emission wavelengths with the Aminco-Bowman Spectrophotofluorimeter were 410 nm and 450 nm respectively. For 10–50 p.p.b. of zinc, 1 ml of 0.3 *M* potassium hydroxide was present in a final 10-ml volume of 7:3 ethanol to water; an acetate buffer was used for higher zinc concentrations. However, for solutions containing less than 5 p.p.b., the amount of water had to be decreased from 30 to 20%, in the final solution, to obtain satisfactory results.

RESULTS

Different calibration curves were prepared for 5–25 p.p.b., 10–50 p.p.b. and 0.050–0.25 p.p.m. of zinc; straight lines passing through the origin were obtained. The standard deviation on analyzing eleven samples was 6.9, 4.7, and 3.2% for the three regions; the reproducibility for 2 p.p.b. of zinc was ±10%.

Figure 1 shows the excitation and emission spectra for the zinc complex. Corrections of spectral intensity for emission characteristics of the xenon lamp or for photomultiplier (R 136) response are unnecessary in the 400–500 nm region. Figure 2 shows the difference in spectral intensity obtained with specially purified reagents; the decrease in background intensity of reagent permits a tenfold increase in sensitivity with the Turner Fluorimeter.

The fluorescence intensity at 450 nm for $7 \cdot 10^{-5}$ *M* reagent in 7:3 ethanol to water solutions is 19 in 0.03 *N* sodium hydroxide, 13 in 0.03 *N* potassium hydroxide, and 2 in 0.03 *N* ammonia (MM, 0.01; S, 0.00). Such results suggest that the sodium ion chelates more strongly to the thiazole nitrogens to give a ring system and fluorescence; the sensitivity is, however, very much less than for zinc. The low background intensity when ammonia is used permits a higher instrument sensitivity and it is probable that less than one p.p.b. of zinc could be determined; relative intensities for 32 p.p.b. of zinc were 36 ± 1 in solutions $3 \cdot 10^{-6}$ to 10^{-4} *M* in ammonia at the relatively low sensitivity setting of MM, 0.1; S, 0.00 but quenching was quite pronounced after 5 min and further studies were not made.

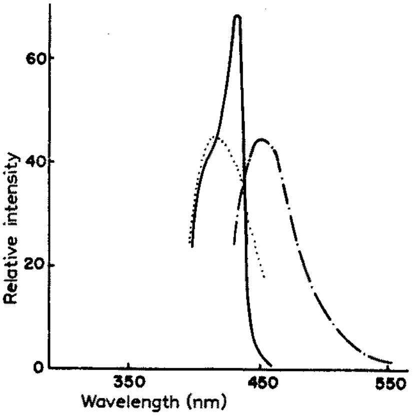


Fig. 1. Fluorescence spectra of Zn–DBTM ($5 \cdot 10^{-7}$ *M*). (——) uncorrected excitation spectrum (measured at 450 nm); (—•—) uncorrected emission spectrum (measured at 410 nm); (...) corrected excitation spectrum.

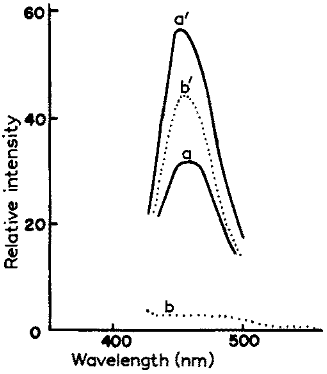
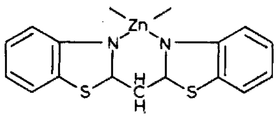


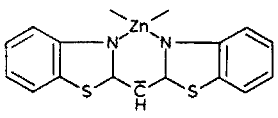
Fig. 2. Variation in emission intensity with purity. (a, a') reagent and zinc complex; (b, b') same spectra after purification.

Zinc–DBTM complexes were prepared by the addition of an equimolar amount of zinc nitrate to $2.5 \cdot 10^{-2}$ *M* reagent solutions. The compound precipitated from absolute ethanol was pale green whilst that from alkaline 7:3 ethanol–water solutions was yellow in color. The fluorescence spectra of the two compounds in ethanol were similar to those given in Fig. 1. The fluorescence intensity for 5 μg per ml of the species precipitated from neutral ethanol solution was higher initially (96) than that precipitated from alkaline solution (32) for the same meter multiplier and sensitivity settings (MM, 1.0; S, 0.00). However, in 7:3 ethanol–water solutions, the fluorescence of the neutral species was completely quenched whilst that obtained from alkaline solution decreased to 16; addition of alkali to the quenched solution raised the fluorescence from 0 to 21. In the compound obtained from neutral solution, zinc is chelated to the thiazole nitrogens without proton removal from the methylene bridge whilst a methylene proton has been removed in the complex precipitated from alkaline solution (NMR and IR confirmed). The greater sensitivity of the neutral species to water is undoubtedly due to the lower stability of the zinc chelate and destruction of the chelate ring system through competition of water molecules for nitrogen sites. Further confirmation is provided by the fluorescence behaviour of the reagent in acid solution; the intensity in 7:3 ethanol–water solution for $7 \cdot 10^{-5}$ *M* reagent was

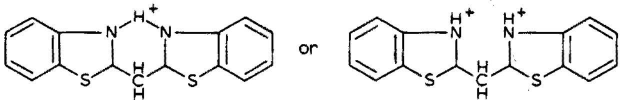
2 to 3 divisions at MM 0.01 and S 0.00 whilst a similar solution 0.03 N in hydrochloric acid gave an intensity of 23 at the same sensitivity settings. It is suggested that the fluorescent species are as follows:



(Zinc complex from neutral solution)



(Zinc complex from alkaline solution)



(Reagent in acid solution)

Nature of reaction

Figure 3 shows the absorption spectra, in ethanol, for benzothiazole and dibenzothiazolylmethane. The initial spectra are similar except for a broad band of very weak intensity ($\lambda_{max} \sim 355$ nm) in DBTM. The intensity of this band increases with time and the molecular extinction coefficient (ε) is approximately 12,000 after six days ($1.25 \cdot 10^{-5}$ M solution); the absorption spectrum was similar after two months and the ε value was 13,500. Since the acidity of the methylene bridge can lead to the formation of a tautomeric species, it was initially thought that the absorption data supported the concept of tautomer formation (despite the slow equilibrium rate) as described for diquinolylmethanes[5]. However, the paramagnetism observed for reagent in ethanol[6] and the separation of a canary-yellow compound,

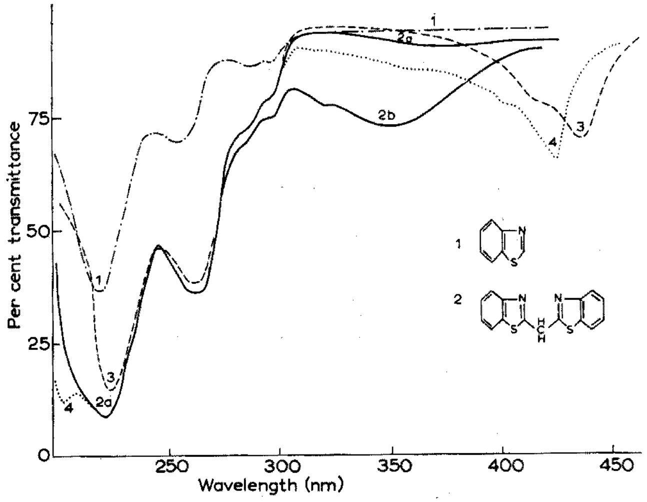
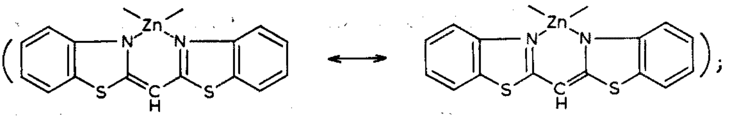


Fig. 3. Absorption spectra of DBTM ($2.5 \cdot 10^{-6}$ M in ethanol). (1) benzothiazole; (2a) DBTM immediately after dissolution; (2b) DBTM after equilibrium; (3) DBTM in 0.03 N NaOH; (4) DBTM in 0.03 N HCl.

from the two-month-old solution, with a melting point of 176–178° (melting point of DBTM is 96°) suggested that increased absorption was due to the presence of a new compound formed possibly through free radical oxidation or dimerization. An NMR spectrum of this compound showed no evidence of a CH or CH_2 group; the CH_2 evident in the infrared spectrum of reagent had disappeared in the yellow compound and a strong carbonyl peak appeared at 1660 cm^{-1}. It is probable that increased absorption at 355 nm is due to oxidation of reagent to form $(C_7H_4NS)_2C=O$ but further studies are contemplated for DBTM and related compounds.

In the presence of acid or base changes occur in the absorption spectrum of freshly prepared reagent solutions. In addition to minor changes in the 200–300 nm wavelength region, an absorption band, with λ_{max} at 423 nm for acid and 437 nm for base, appears in the visible region (Fig. 3). In 0.3 N acid the intensity at 423 nm decreases with time in 99:1 ethanol–water solutions, and is replaced by a broad band ($\varepsilon \sim 12000$) at 355 nm; the intensity in 7:3 ethanol–water solutions is initially less ($\varepsilon \sim 6000$) but the band remains unaltered on standing for several days. In 0.03 N base the molecular extinction coefficient at 437 nm is *ca.* 20,000 in 99:1 ethanol–water solutions but *ca.* 5,000 in 7:3 ethanol–water solutions; the absorption intensity decreases in both solutions on standing and the bands disappear entirely within 18 h. It is evident that initial changes in absorption spectra are due to protonation in acid and removal of the methylene proton in base; on standing new compounds are formed in both acid $[(C_7H_4NS)_2C=O]$ and base.

The absorption spectrum of the zinc complex was obtained from solutions containing 0.7 ml of 10^{-3} M DBTM, 1 ml of 0.3 N base, and 1 ml of 10^{-3} M zinc solution diluted to 10 ml with ethanol; the blank was the same except that 1 ml of water was added in place of the zinc solution. A shoulder at 395 nm and two peaks at 410 nm and 433 nm are observed but the intensity varies with the base present. Initial absorbances at 433 nm were 0.87 (NH_3), 1.35 (KOH) and 2 (NaOH); the intensity decreases to one-half the initial value within 3 h for the alkali metal base solutions, but increases in ammonia (A, 1.50) after 2 h. It is probable that the competing reaction of zinc with hydroxide ion to give hydroxo zinc complexes is responsible for the absorbance decrease in the alkali metal solutions. Figure 4 shows the absorption spectra obtained in different solvents containing 7 μg/ml of the zinc complex (pale green) obtained from ethanol. The spectra are similar to those obtained in ethanol but the absorption intensity increases with solvent basicity; addition of strong base, such as potassium hydroxide, further increases the intensity of absorption. The spectrum of the yellow zinc compound precipitated from alkaline ethanol, however, was unaltered in the three solvents and on addition of base. The absorption intensity reflects the extent of removal of proton from the methylene bridge and the formation of a stronger chromophore. As basicity increases a proton is more easily removed and there is increased formation of =CH species



the zinc compound precipitated from basic solution is, of course, already completely in the =CH form and is unaffected by basicity change.

NMR and IR spectra

The nuclear magnetic resonance spectrum of the reagent has an aromatic multiplet at 7.6 δ (integrated intensity, eight protons) and a single peak at 4.85 δ (intensity corresponding to two protons); there was no evidence of $=$CH proton. The pale green zinc complex precipitated from ethanol shows a similar aromatic multiplet and a single CH_2 peak. The yellow zinc complex obtained from alkaline ethanol has an aromatic multiplet centred on 7.2 δ and a single peak at 5.9 δ (one-eighth the intensity of the aromatic multiplet) confirming the presence of the $=$CH grouping. The NMR spectrum of the yellow compound, separated from reagent solutions in ethanol that had been standing for two months, shows that no CH_2 or CH hydrogens (other than aromatic) are present.

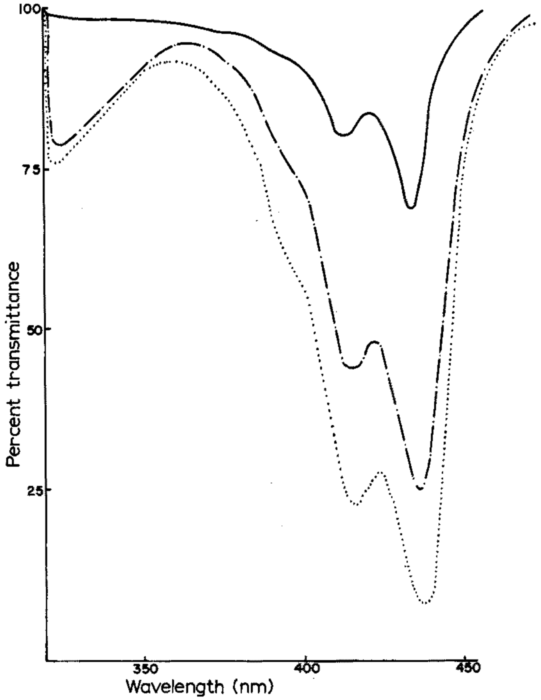


Fig. 4. Absorption spectra of Zn–DBTM in 7:3 ethanol–water, dimethylformamide, and ethylamine.

The infrared spectrum confirms that the DBTM existed in the CH_2 form. The peaks (2900–2950 cm^{-1}) for the CH_2 are absent, however, in the yellow compound separated from aged solution and a strong carbonyl peak at 1660 cm^{-1} is evident.

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SUMMARY

Disubstituted methanes, such as dibenzothiazolylmethane, react to form fluorescent species with metals through chelation to the thiazole nitrogens. A number of ions, such as hydrogen, sodium, potassium, form weakly fluorescent products but only zinc and lithium (with ionic radii of 0.72 and 0.71 Å respectively) form strongly fluorescent chelates at room temperature. Proton removal is not required for the formation of fluorescent species but stabler complexes, more resistant to the quenching action of water, are formed if a proton is removed from the methylene bridge. The reagent is slowly oxidized in ethanolic solutions, background intensity increases, and freshly prepared solutions are desirable for highest sensitivity. For zinc, the excitation and emission maxima are 410 nm and 450 nm respectively; 2 p.p.b. of zinc can be determined with a simple fluorimeter.

RÉSUMÉ

Des méthanes disubstitués, tels que dibenzothiazolylméthane, donnent des complexes métalliques fluorescents par chélation aux azotes thiazole. Les chélates de zinc et lithium sont fortement fluorescents à la température ordinaire. Un déplacement de proton n'est pas nécessaire pour la formation de particules fluorescentes, mais les complexes obtenus sont plus stables et plus résistants à l'action de l'eau si un proton est déplacé du pont méthylène. Le réactif s'oxyde lentement en solution alcoolique; il est recommandé d'utiliser des solutions fraîchement préparées pour avoir une meilleure sensibilité. Pour le zinc les maxima d'excitation et d'émission sont respectivement 410 nm et 450 nm, on peut doser 2 p.p.b. de zinc à l'aide d'un simple fluorimètre.

ZUSAMMENFASSUNG

Disubstituierte Methane, wie z.B. Dibenzothiazolylmethan, bilden mit Metallen durch Chelatbildung fluoreszierende Spezies. Eine Anzahl von Ionen, wie Wasserstoff, Natrium, Kalium, bilden schwachfluoreszierende Produkte, aber nur Zink und Lithium (mit einem Ionenradius von 0.72 bzw. 0.71 Å) bilden bei Raumtemperatur starkfluoreszierende Chelate. Die Entfernung des Protons ist zur Bildung der fluoreszierenden Spezies nicht erforderlich, jedoch werden stabilere Komplexe, die gegenüber Wasser beständiger sind, gebildet, wenn ein Proton aus der Methylen-Brücke entfernt wird. Als Folge der leichten Oxydierbarkeit des Reagenzes in äthanolischen Lösungen steigt die Intensität des Untergrundes an. Deshalb sind für hohe Empfindlichkeiten frisch hergestellte Lösungen wünschenswert. Für Zink liegen die Anregungs- und Emissionsmaxima bei 410 bzw. 450 nm. Mit einem einfachen Fluorimeter können 2 p.p.b. Zink bestimmt werden.

REFERENCES

1 G. A. Crosby, R. E. Whan and R. M. Ahire, *J. Chem. Phys.*, 34 (1961) 743.
2 R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, 8 (1962) 315.

3 H. Samuelson and A. Lempicki, *J. Chem. Phys.*, 39 (1963) 110.
4 N. Metlay, *J. Chem. Phys.*, 39 (1963) 491.
5 G. Scheibe and E. Daltrozzo, Diquinolylmethane and its analogs, in *Advances in Heterocyclic Chemistry*, Vol. 7, Academic Press, 1966.
6 R. Trenholm and D. E. Ryan, *Anal. Chim. Acta*, 32 (1965) 317.
7 A. E. Pitts and D. E. Ryan, *Anal. Chim. Acta*, 37 (1967) 460.

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CHEMICAL PROPERTIES OF THE BIS-(2,3,5,6-TETRAKIS(2'-PYRIDYL) PYRAZINE)-IRON(II) COMPLEX

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During the investigation of 2,3,5,6-tetrakis(2'-pyridyl)pyrazine, (TPP) as an organic analytical reagent for iron(II), it was found that the complex would undergo protonization in aqueous solution, accompanied by a bathochromic shift in absorption maximum[1]. The present paper describes the chemical properties of the ligand and complex. The acid–base properties of the ligand, the formation constant of the complex, and the behavior of the isolated complex in non-aqueous media are reported.

EXPERIMENTAL

Apparatus and reagents

Spectrophotometric measurements were made with a Beckman DB-G grating spectrophotometer, with 1.00-cm silica cells for all measurements. A Beckman Zeromatic II pH meter and a Corning Model 10 pH meter with saturated calomel and glass electrodes were used for the aqueous titrations. Non-aqueous determinations were carried out with a Beckman Zeromatic II pH meter and glass–calomel electrodes, a saturated solution of potassium chloride in methanol being used in the calomel electrode. Thermal decomposition data were obtained from a student-constructed thermobalance.

2,3,5,6-Tetrakis(2'-pyridyl)pyrazine. This was prepared by the method of GOODWIN AND LIONS[2]. α-Pyridoin (K and K Laboratories, 40 g, 0.2 mole) was heated with 180 g (0.42 mole) of ammonium acetate at 180° for 2 h. The solid reaction product obtained on cooling was recrystallized from a pyridine–ethanol mixture (m.p. 296°; 284° lit.)

A stock solution of the ligand was made by dissolving 0.2944 g of the ligand in concentrated hydrochloric acid and distilled water and diluting to 250 ml with distilled water.

Buffer solution. A 2 *M* acetic acid–2 *M* sodium acetate solution was prepared at a pH of 5.0.

Standard iron solution. This was prepared by dissolving 0.6250 g of reagent-grade iron wire (Merck) in concentrated hydrochloric acid and concentrated nitric acid, and diluting to 250 ml with distilled water.

Sodium hydroxide solutions. In the aqueous titrations a 0.4568 *M* solution was used; this was standardized against potassium biphthalate. The non-aqueous titrant prepared by diluting 5 ml of tetra-N-butylammonium hydroxide titrant (25% in methanol, Eastman Organic Chemicals) to 100 ml with nanograde benzene (Mallinckrodt). It was standardized against benzoic acid and found to be 0.0371 *N*.

Sodium tetraphenylboron (J. T. Baker & Co.) was used as a precipitating agent. The nitrobenzene used as solvent was analytical grade.

Investigation of the complex system

The hydrochloride salt of the ligand was prepared by bubbling hydrogen chloride into a solution of the ligand in glacial acetic acid. The salt was filtered, washed with acetone, and dried in a vacuum oven at 30° for 12 h.

In the presence of concentrated hydrochloric acid, 0.2489 g ($6.408 \cdot 10^{-4}$ mole) of the ligand was dissolved in distilled water. In a separate beaker, 0.0890 g ($3.201 \cdot 10^{-4}$ mole) of iron(II) sulfate was dissolved in distilled water. The two solutions were mixed and diluted to *ca.* 1 l. The pH of the solution was adjusted to 5 with sodium hydroxide. To this solution was added an excess of sodium tetraphenylboron in aqueous solution. The dark purple solid was filtered, washed with distilled water, and dried in a vacuum oven at 30–40° for 15 h. (Yield 0.3 g; m.p. 264–266°.)

The same procedure was followed in the isolation of the protonated complex; 0.5000 g ($12.87 \cdot 10^{-4}$ mole) of ligand and 0.1782 g ($6.409 \cdot 10^{-4}$ mole) of iron(II) sulfate were used, and the pH was adjusted to *ca.* 1 rather than 5 with concentrated hydrochloric acid. (Yield 1.7 g; m.p. 103–106°.)

The conformance of the complex in aqueous solution to Beer's law was determined over a concentration range of $8.95 \cdot 10^{-6}$–$5.37 \cdot 10^{-5} M$ iron(II) concentration. Solutions containing iron and an excess of TPP were prepared and buffered at pH 5. Each solution contained 5 ml of aqueous 10% hydroxylamine hydrochloride and 2 ml of acetate buffer. The absorbance values for these solutions were obtained at 575, 585, and 590 nm, with maximum absorbance at 575 nm.

The combining ratio of the ligand and the iron(II) ion was determined by the method of continuous variations[3] on a series of solutions prepared from $8.953 \cdot 10^{-4} M$ TPP and $8.953 \cdot 10^{-4} M$ iron(II) stock solutions. The solutions were combined in amounts to vary the mole ratio of iron from 0.1 to 1.0. Each solution contained in addition 5 ml of 10% hydroxylamine hydrochloride solution and 5 ml of acetate buffer.

The hydrochloride salt of the ligand in aqueous solution was titrated with sodium hydroxide. A dried sample of the salt weighing 0.0712 g was analyzed thermogravimetrically.

The tetraphenylboron salts of both protonated and non-protonated complexes were titrated with tetrabutylammonium hydroxide in non-aqueous systems, nitrobenzene serving as solvent for the salts.

DISCUSSION

The hydrochloride salt of TPP required 4 equivalents of base for each mole of salt. The equivalent weight calculated from potentiometric data on 3 samples of the salt were: 134.5, 133.5, and 132.7 (average: 133.6). The theoretical equivalent weight for the tetrachloride salt is 133.6. It is assumed, therefore, that the tetrahydrochloride salt has been formed. The data obtained from the thermal decomposition of the salt also support the theoretical formula, TPP·4HCl. Of the initial 0.0712 g of solid compound subjected to analysis, 0.0190 g was lost during the first period of weight loss, up to 300°. This loss represents 27.67% of the initial weight. The theoretical weight loss of 4 hydrochlorides is 27.30%. The remaining material was completely vaporized.

The complex was found to conform to Beer's law (Table I) over the concentration range studied. The solutions buffered at pH 5 excited a peak of maximum absorbance at a wavelength of 575 nm with a molar absorptivity of 19,210. Data were also recorded at 585 nm ($\varepsilon = 16{,}000$), and at 590 nm ($\varepsilon = 13{,}000$).

TABLE I

BEER'S LAW DATA

Complex concn.·10⁶ M	$A_{575\ nm}$	$A_{585\ nm}$	$A_{590\ nm}$
Non-protonated species			
8.95	0.203	0.170	0.136
17.9	0.377	0.311	0.253
26.8	0.549	0.451	0.365
35.8	0.728	0.601	0.487
44.7	0.892	0.749	0.615
Protonated species			
8.95	0.159	0.171	0.174
17.9	0.319	0.344	0.350
26.8	0.444	0.478	0.484
35.8	0.553	0.597	0.606
44.7	0.708	0.768	0.777

In the presence of strong acid (*ca.* 1.0 *M*) the complex underwent a bathochromic shift to a maximum absorbance at 590 nm, with a molar absorptivity of 16,700. At 575 nm the molar absorptivity of the protonated complex was 15,250, and 16,540 at a wavelength of 585 nm. Rapid fading of color was noted in the protonated complex in highly acidic solution. Because of this behavior, the complex was allowed to develop at a higher pH, and 5 ml of concentrated hydrochloric acid were added to each solution. Each solution was then diluted immediately to 50 ml and the spectrophotometric measurements obtained. There was no apparent decrease in the absorbance of the buffered solutions over a period of several days.

A third series of solutions was prepared from the same concentrations of ligand and iron(II) ion as the first two series. Varying amounts of concentrated hydrochloric acid were added to these solutions without completely protonating the complex. The peaks of maximum absorbance were noted to vary in wavelength, but remained within the range 575–590 nm. The spectrophotometric data and the pH of each solution were obtained simultaneously. The linear relationship of pH *vs* wavelength of maximum absorbance indicates that protonation does not occur as a stepwise process.

The stoichiometry of the iron(II) complex was determined by the method of continuous variations. The results show the existence in solution of one complex with a composition of one mole of iron(II) and two moles of TPP as previously reported[1].

The overall formation constant for the complex was obtained from the results of the continuous variations and Beer's law studies. The log K value obtained for the bis-(2,3,5,6-tetrakis(2′-pyridyl)pyrazine)–iron(II) complex was 8.5 ± 0.3.

The protonated and non-protonated complexes were isolated as the tetraphenylboron salts. Each of the two solids was decomposed by sodium fusion and a positive test for chloride was obtained on addition of 0.1 N silver nitrate in aqueous solution. As previously reported for boron-organic compounds, elemental analyses were not consistent and the samples were analyzed thermogravimetrically[4]. Pyrolysis curves obtained for both the protonated and non-protonated complex show that decomposition is not complete, even at 1200°.

The isolated salts of the protonated and non-protonated complex were titrated in nitrobenzene with tetra-N-butylammonium hydroxide. The protonated species exhibits three breaks requiring one, two, and one equivalents of base respectively. The non-protonated complex shows one break with a half neutralization potential equal to that of the third break of the protonated complex (Fig. 1). Therefore, the following mechanism is proposed for the ionization reaction.

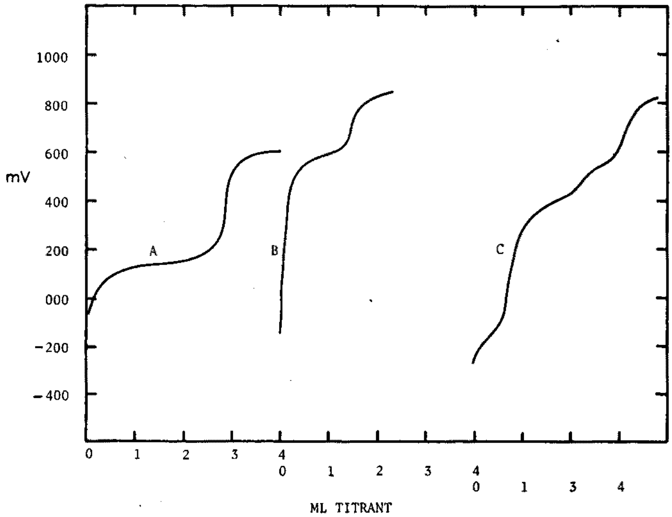

Fig. 1. Potentiometric titration with tetra-N-butylammonium hydroxide in nitrobenzene. (A) $Na\phi_4B$; (B) $Fe(TPP)_2Cl\phi_4B$; (C) $Fe(TPP)_2H_3Cl(\phi_4B)_4$.

Protonated

1st break $Fe(TPP)_2H_3Cl(\phi_4B)_4 + (C_4H_9)_4NOH \rightleftharpoons (C_4H_9)_4N\phi B +$

$H_2O + Fe(TPP)_2H_2Cl(\phi_4B)_3$

2nd break $Fe(TPP)_2H_2Cl(\phi_4B)_3 + 2(C_4H_9)_4NOH \rightleftharpoons 2(C_4H_9)_4N\phi_4B +$

$2H_2O + Fe(TPP)_2Cl\phi_4B$

3rd break $Fe(TPP)_2Cl\phi_4B + (C_4H_9)_4NOH \rightleftharpoons (C_4H_9)_4NCl + Fe(TPP)_2OH\phi_4B$

Non-protonated

$$Fe(TPP)_2Cl\phi_4B + (C_4H_9)_4NOH \rightleftharpoons (C_4H_9)_4NCl + Fe(TPP)_2OH\phi_4B$$

The data and proposed mechanism indicate that the complex can accept three protons. Equivalent weights calculated from the titrations are shown in Table II.

TABLE II

EQUIVALENT WEIGHTS OF COMPLEX SALTS

	Experimental	*Theoretical*
Protonated		
1st break	2167	2145
2nd break	733	716
3rd break	519	537
Non-protonated	1190	1192

The authors thank the Gustavus Research Fund and the Research Corporation for the financial support of this work.

SUMMARY

2,3,5,6-Tetrakis(2′-pyridyl)pyrazine forms an iron(II) complex containing 2 moles of ligand for each mole of iron. In aqueous solution, the wavelength of maximum absorbance shifts from 575 nm to 590 nm when the complex solution is treated with strong acid. Both the protonated and non-protonated forms of the complex obey Beer's law over the range $8.95 \cdot 10^{-6}$–$5.37 \cdot 10^{-5}$ *M*, the molar absorptivities of the protonated and non-protonated complexes being 16,700 and 19,210 respectively. The overall stability constant of the iron complex was found to be 8.5 ± 0.3. There are 3 protons per molecule in the protonated form.

RÉSUMÉ

La 2,3,5,6-tétrakis-(2′-pyridyl)-pyrazine donne un complexe avec le fer(II) contenant 2 moles de ligand pour chaque mole de fer. En solution aqueuse, la longueur d'onde de l'absorbance maximum passe de 575 nm à 590 nm lorsque le complexe est traité par un acide fort. La loi de Beer s'applique soit à la forme proton soit à la forme non-proton du complexe, de $8.95 \cdot 10^{-6}$ à $5.37 \cdot 10^{-5}$ *M*. Les absorptions molaires des complexes proton et non-proton sont respectivement 16,700 et 19,210. Dans la forme proton, il existe 3 protons par molécule.

ZUSAMMENFASSUNG

2,3,5,6-Tetrakis-(2′-pyridyl)-pyrazin bildet einen Eisen(II)-Komplex, der 2 Mole des Liganden auf 1 Mol Eisen enthält. In wässriger Lösung verschiebt sich die Wellenlänge der maximalen Absorption von 575 nach 590 nm, wenn starke Säure zugegeben wird. Sowohl die protonisierte als auch die nichtprotonisierte Form des

Komplexes gehorchen dem Beerschen Gesetz im Bereich von $8.95 \cdot 10^{-6}$–$5.37 \cdot 10^{-5}$ *M*. Die molaren Extinktionen des protonisierten und nichtprotonisierten Komplexes sind 16700 bzw. 19210. Die Bruttostabilitätskonstante des Eisenkomplexes beträgt 8.5 ± 0.3. Die protonisierte Form enthält 3 Protonen pro Molekül.

REFERENCES

1 R. T. Pflaum, C. J. Smith, Jr., E. B. Buchanan, Jr. and R. E. Jensen, *Anal. Chim. Acta*, 31 (1964) 341.
2 H. Goodwin and F. Lions, *J. Am. Chem. Soc.*, 81 (1959) 6415.
3 P. Job, *Ann. Chim. (Paris)*, 9 (1928) 113.
4 F. Pregl and H. Roth, *Quantitative Organische Mikroanalyse*, 7th Edn., Springer-Verlag, Wien, 1958, p. 36.

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THE REACTION BETWEEN MERCURY(II) AND ORGANIC COMPOUNDS

PART I. COMPLEXIMETRIC DETERMINATION OF MERCURY(II) WITH *o*-(2-THIAZOLYLAZO)CRESOL AS INDICATOR

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Several studies of *o*-(2-thiazolylazo)phenols as substitutes for pyridylazophenols for spectrophotometric or titrimetric methods have been reported during recent years. The titrimetric determination of mercury(II) with EDTA is predominantly based on replacement titrations or back-titrations. Several indicators[1-3] are known for the direct titration of mercury(II) ions with EDTA, but these are usually applicable only in acidic media. The only example involving direct titration in an alkaline medium requires an excess of ammoniacal buffer in order to prevent hydrolysis of mercury(II)[4,5].

In the present paper, *o*-(2-thiazolylazo)cresol, TAC, is suggested as a suitable metallochromic indicator for the direct titration of mercury(II) ions with EDTA in alkaline medium. The suitability of TAC as the indicator for this titration has been investigated theoretically by an indicator transition[6] calculated from the formation constant of the mercury(II)–TAC chelate, and the results obtained have been confirmed experimentally by photometric titrations.

TAC was expected to be reasonably selective for mercury(II) because it forms different colored metal chelates with only a small number of metal ions such as nickel(II)[7] and uranyl(II)[8].

EXPERIMENTAL

Reagents

TAC. The commercial material (Dojindo & Co., Ltd.) was twice recrystallized from hot ethanol; the crystals containing 99–100% of active dye. Aqueous dioxane solutions of TAC were used for the study of the composition of the chelate, whereas alcoholic solutions of TAC were used as the indicator.

Dioxane. Crude dioxane was purified as follows: sulfuric acid (10 ml) and water (100 ml) were added to the crude material (1 kg) and after 2 h, potassium iodide (10 g) was stirred into the mixture; tablets of potassium hydroxide were added until the mixture was separated into two layers. After filtration of the upper layer it was distilled twice.

Mercury(II) solution. Mercury(II) chloride (reagent grade) was purified by sublimation, and a 10^{-2} *M* stock solution slightly acidified with hydrochloric acid was prepared. This solution was standardised colorimetrically[9,10] or gravimetrically as mercury(II) sulfide.

pH control. The pH was adjusted with HCl–KCl, Na_2HPO_4–KH_2PO_4 and CH_3COOH–NaOH buffer systems; in all cases, the mixtures were 0.1 *M* and the ratios of the components were adjusted to give the required pH.

Ionic strength. For spectrophotometric studies an ionic strength of about 0.1 was maintained with sodium acetate.

All the reagents used were of analytical or special grade; they were used without further purification. Conductivity water was used for preparation of all the solutions.

Instruments

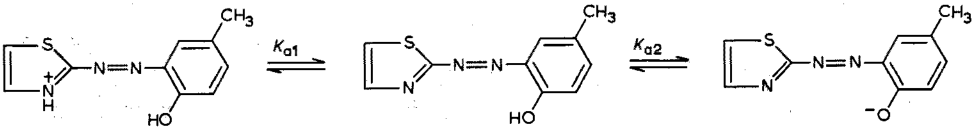
The absorption spectra and the absorbances were recorded with a Hitachi recording spectrophotometer (EPS-2 type) and Hitachi photoelectric spectrophotometer (EPU-2 type) with 10-mm silica cells respectively.

The pH was measured with a glass electrode (Hitachi-Horiba F-5 type).

RESULTS AND DISCUSSION

Acid dissociation constant of TAC in 10% (v/v) dioxane–water solution

TAC is a monobasic acid and its dissociation scheme is as follows:



The acid dissociation constants were obtained spectrophotometrically. If the acid dissociation constants are given by

$$K_{a1} = [HR][H^+]/[H_2R^+] \quad \text{and} \quad K_{a2} = [R^-][H^+]/[HR] \tag{1}$$

then for the second step only:

$$\log \{(A - \varepsilon_{HR}C_R)/(\varepsilon_R C_R - A)\} = pH + \log K_{a2} \tag{2}$$

where A is the total absorbance, C_R the analytical concentration of TAC and ε_x is the molar absorptivity of species x.

The molar absorptivity was calculated from the horizontal lines of pH–absorbance plots.

The absorption spectra of TAC scanned at various pH values are illustrated in Fig. 1. There is an isosbestic point at 474 nm and the absorption maxima appear at 535 nm. Above pH 8.25, TAC is red in color owing to the R^- species. The pK_{a2} value was obtained from the absorbance at 535 nm by means of eqn (2). An accurate pK_{a1} value was not obtained because the value occurs at a pH < 0. These values are in reasonable agreement with those obtained in 20% (v/v) dioxane–water solution[7].

Absorption spectra of the mercury(II)–TAC chelate in dioxane–water solution

The spectra of the mercury chelates were measured for the 10% (v/v) dioxane–water solution containing various concentrations of the components at different pH values. Figure 2 shows the absorption spectra of a mixture containing a 10-fold excess of mercury(II) compared to TAC. In the pH range 4.5–8.8, the spectra show an isosbestic point at 492 nm and absorption maxima at 602 nm. The deep blue complex with mercury(II) is obtained with only two other chelates, *viz.*, nickel(II)–TAC and uranyl(II)–TAC. Accordingly, TAC appears from these spectra, to be a suitable metallochromic indicator for the titration of mercury(II) ions.

Figure 3 shows the absorption spectra of a mixture containing a 10-fold excess

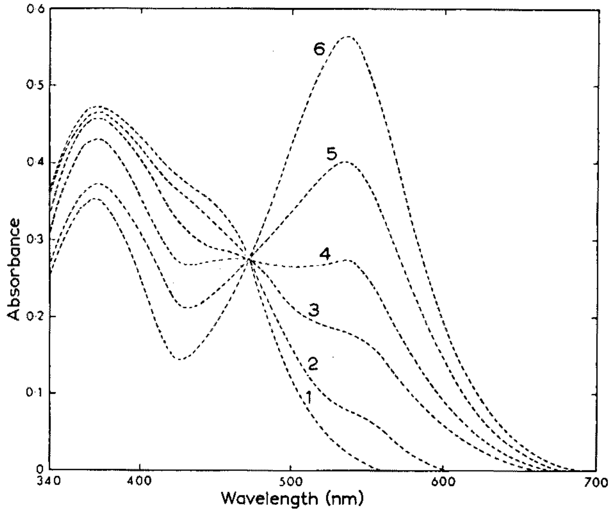


Fig. 1. Absorption spectra of TAC in 10% (v/v) dioxane–water at various pH values. Concn of TAC = $5 \cdot 10^{-5}$ *M*; pH: 1 = 7.05; 2 = 8.25; 3 = 8.56; 4 = 8.88; 5 = 9.12; 6 = 11.30.

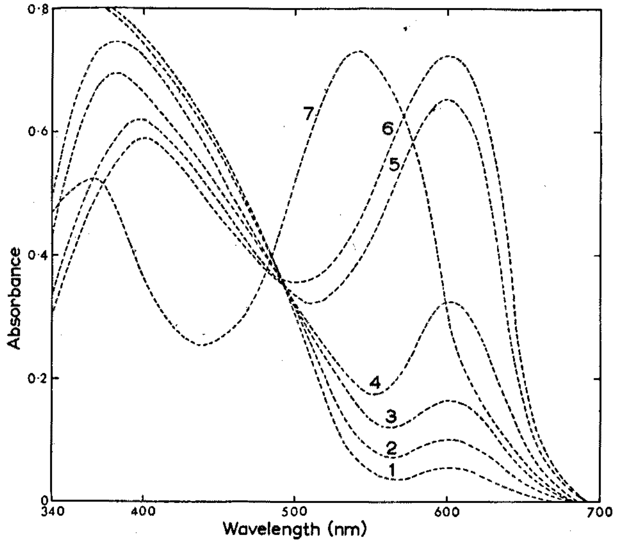


Fig. 2. Absorption spectra of mercury(II) and TAC mixture in 10% (v/v) dioxane–water at various pH values. Concn: TAC = $7 \cdot 10^{-5}$ *M*; Hg^{2+} = $7 \cdot 10^{-4}$ *M*. pH: 1 = 4.48; 2 = 4.99; 3 = 5.45; 4 = 6.02; 5 = 6.98; 6 = 8.79; 7 = 9.90.

of TAC compared to mercury(II). The spectra were scanned with a similar TAC solution as the reference because the mixture showed a strong absorption on account of the large concentration of TAC.

Composition of the chelate

Comparison of the spectra in Figs. 2 and 3 shows that within the appropriate pH range, the wavelength of maximum absorbance remained constant, but the intensities at the maxima differed greatly. The molar absorptivities in Fig. 3 were nearly twice those in Fig. 2. The formation of the 1:1 chelate, namely HgR^+, is probable in the case of excess of mercury(II) (Fig. 2) and the 1:2 chelate, HgR_2, in the case of excess of TAC (Fig. 3). Similar situations have been indicated by Schwarzenbach with respect to the zinc–erio T chelate[11], and by Nakagawa and Wada[7,12] with respect to analogous azo dyestuffs.

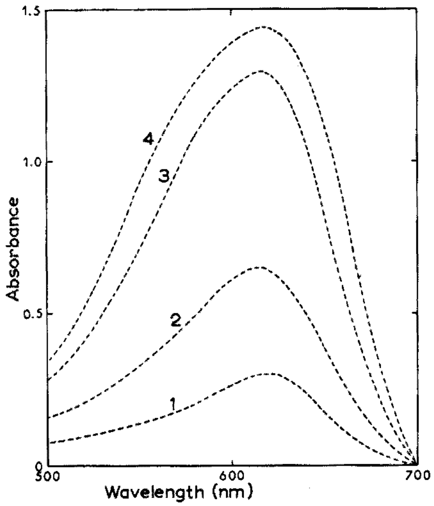


Fig. 3. Absorption spectra of mercury(II) and TAC mixture in 10% (v/v) dioxane–water at various pH values. Concn: TAC = $7 \cdot 10^{-4}$ *M*; Hg^{2+} = $7 \cdot 10^{-5}$ *M*. pH: 1 = 5.05; 2 = 5.30; 3 = 6.98; 4 = 8.79. Ref. = corresponding reagent blank.

Formation constants of the chelate

The successive and over-all formation constants are given as:

$$K_{HgR^+} = [HgR^+]/[Hg^{2+}][R^-] \tag{3}$$

$$K_{HgR_2} = [HgR_2]/[HgR^+][R^-] \tag{4}$$

$$K_{HgR^+} \cdot K_{HgR_2} = [HgR_2]/[Hg^{2+}][R^-]^2 \tag{5}$$

When a large excess of mercury(II) is present, the following reaction should occur at pH 7.5–8.4.

$$Hg^{2+} + HR \overset{K_1}{\rightleftarrows} HgR^+ + H^+ \tag{6}$$

Consequently, the equilibrium constant of eqn (6) is:

$$K_1 = [HgR^+][H^+]/[Hg^{2+}][HR] \tag{7}$$

The formation constant, K_{HgR^+}, is represented by the equilibrium constant, eqn. (7), and by the second acid dissociation constant of TAC, eqn (2), as:

$$K_{HgR^+} = K_1/K_{a2} \tag{8}$$

Substituting eqns (1) and (7) into eqn (8) and rearranging to logarithmic form:

$$\log K_{HgR^+} = \log \{[HgR^+]/[HR]\} + pHg + pK_{a2} - pH \tag{9}$$

Equation (9) indicates that the plot of log $[HgR^+]/[HR]$ against pH should give a straight line with a slope of unity; the formation constant can be calculated from the pH at which log $[HgR^+]/[HR]$ equals zero, the acid dissociation constant of TAC and the initial concentration of mercury(II) ions. Figure 4a shows the plot of log $[HgR^+]/[HR]$ *versus* pH. The pHg value was calculated on the assumption that it should be decreased by 10% from the initial concentration according to the 1:1 chelate formation, because of the initial ratio of $[Hg^{2+}]/[TAC] = 10$. As a result, the formation constant, log K_{HgR^+} obtained was 6.1_1.

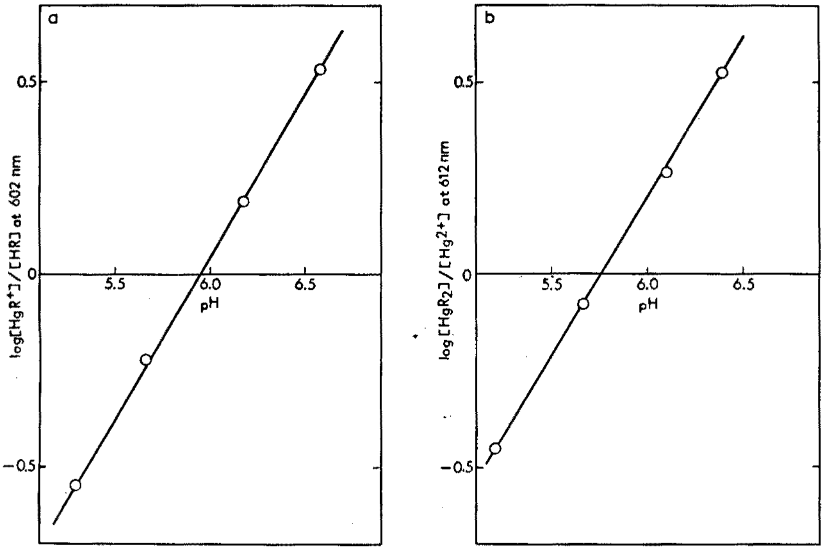


Fig. 4. (a) Plot of log$[HgR^+]/[HR]$ *vs* pH. (b) Plot of log$[HgR_2]/[Hg^{2+}]$ *vs* pH.

The second successive formation constant cannot be obtained directly, but can be calculated indirectly from the over-all formation constant. If the total concentration of TAC and the concentration of unbound mercury(II) are denoted as $[HR]_t$ and $[R]_f$ respectively, then:

$$[R]_f = [H_2R^+] + [HR] + [R^-] = [R^-]\alpha_{H(R)} \tag{10}$$

where $\alpha_{H(R)} = 1 + [H^+]/K_{a2} + [H^+]^2/K_{a1} \cdot K_{a2}$.

When the TAC concentration is much larger than that of mercury(II), $[HR]_t$ is almost equal to $[R]_f$, and $[H_2R^+]$ and $[R^-]$ are negligible compared with $[HR]$.

Accordingly, eqn (10) can be reduced to eqn (11):

$$[HR]_t=[R^-][H^+]/K_{a2} \qquad (11)$$

From eqns (5) and (11), the following equation can be derived:

$$\log\{[HgR_2]/[Hg^{2+}]\}=\log K_{HgR^+}\cdot K_{HgR_2}+2\log[HR]_t-2\,pK_{a2}+2\,pH \qquad (12)$$

Equation (12) indicates that the over-all formation constant can be calculated from the pH at which log $[HgR_2]/[Hg^{2+}]$ equals zero, the acid dissociation constant of TAC and an experimental value of $[HR]_t$. Figure 4b shows the plot of log $[HgR_2]/[Hg^{2+}]$ *versus* pH. Here, the $[HR]_t$ value was calculated by assuming that the initial concentration of the ligand is decreased by 20% owing to the 1:2 chelate formation because the initial mixture was composed of $[TAC]/[Hg^{2+}]=10$. The over-all formation constant, log $K_{HgR^+}\cdot K_{HgR_2}$, thus found was 12.2_2. Accordingly, the second successive formation constant, log K_{HgR_2}, was also 6.1_1. These values are listed in Table I together with the acid dissociation constant of the ligand.

TABLE I

ACID DISSOCIATION CONSTANT OF TAC AND FORMATION CONSTANT OF THE MERCURY(II)–TAC CHELATE

(10% (v/v) dioxane–water solution; room temp.)

Acid dissociation constant of TAC	*Chelate*			
	Composition	λ_{max} *(nm)*	ε_{max}	*Formation constant*
$pK_{a1} < 0.4$	1:1	602	$1.03\cdot10^4$	$\log K_{HgR^+} = 6.1_1$
$pK_{a2} = 8.31$	1:2	612	$2.10\cdot10^4$	$\log K_{HgR_2} = 6.1_1$

Applicability of TAC as metallochromic indicator of mercury(II)

In the case of the titration of mercury(II) with EDTA titrant in the presence of TAC as the indicator, the sharpness of the color change of the indicator in the vicinity of the equivalence point was studied theoretically by means of the formation constants obtained above. The range of varying pHg values for the indicator transition can be calculated by eqn (13) as proposed by TANAKA AND NAKAGAWA[6].

$$Hg^{2+}=\frac{1-\phi}{\phi}\cdot\frac{\alpha_{H(R)}}{K_{HgR^+}+2K_{HgR^+}\cdot K_{HgR_2}[HR]_t\cdot\phi/\alpha_{H(R)}} \qquad (13)$$

where $\phi=[R]_f/[HR]_t$.

The pHg values calculated according to eqn (13), *i.e.*, $\phi=0.1-0.9$, are illustrated in Fig. 5.

The change of $[Hg^{2+}]$ values during the titration with EDTA titrant is given as[6]:

$$C_Y/C_{Hg^{2+}}=[Hg^{2+}]\alpha_{Hg^{2+}}/C_{Hg^{2+}}+\alpha_{H(Y)}/K_{HgY}[Hg^{2+}] \qquad (14)$$

where C_Y = total concentration of EDTA,
$C_{Hg^{2+}}$ = total concentration of mercury(II) ions to be determined,
$\alpha_{Hg^{2+}}$ = side-reaction coefficient of mercury hydroxide formation,
$\alpha_{H(Y)}$ = side-reaction coefficient of EDTA with respect to protonation,
K_{HgY} = formation constant of the HgY^{2-} chelate*.

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* The value, $K_{HgY}=10^{21.8}$, was used for the calculation.

By means of eqn (14), the theoretical titration curves for $C_{Hg^{2+}}=5\cdot10^{-4}$ M, at pH 5–9 adjusted with phosphate buffer* were calculated and the results are also shown in Fig. 5. Figure 5 indicates that a sharp color change should occur near pH 8. At the other pH values, the color change starts before the equivalence point; at none of the pH values tested does the color change appear after the equivalence point.

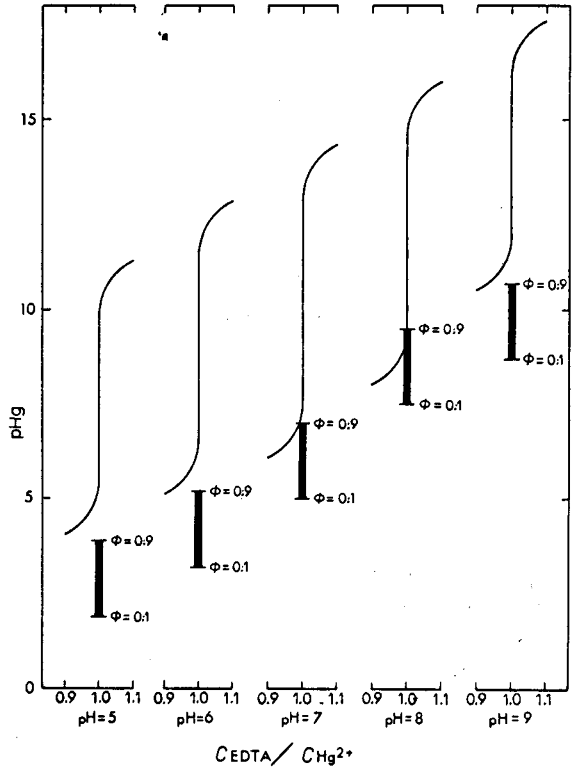

Fig. 5. Indicator transition (ϕ = 0.1–0.9) in the vicinity of equivalence point and theoretical titration curves of mercury(II) with EDTA. $C_{Hg^{2+}}=5\cdot10^{-4}$ M; TAC = $4\cdot10^{-5}$ M.

Photometric titration

The above theoretical considerations were confirmed by photometric titrations. The concentrations of mercury(II) and of TAC tested were maintained at the same values as those used above. An ethanolic solution of TAC was used. The concentration of EDTA used was 10^{-2} M. As can be seen in Fig. 6, in the pH range 7.0–8.3, sharp color changes, *i.e.*, from blue to yellow at pH 7.0–7.5 and from blue to red at pH 7.6–8.3, were observed at the equivalence point. The theoretical and experimental results agreed well, hence the values of the formation constants of the mercury(II)–TAC chelate obtained above appear to be sufficiently reliable.

Effect of diverse ions

Interference by foreign ions was studied, by checking the absorbances of the

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* The side-reaction coefficient, α_{Hg}, concerning to this buffer system may be negligible on this occasion.

solution after the titration with EDTA at 602 nm at several pH values in the range of 7.0–8.3.* It was shown that ammonium, cyanide, nickel(II), uranyl(II) and halide ions (except for a considerable amount of chloride ion) caused errors.

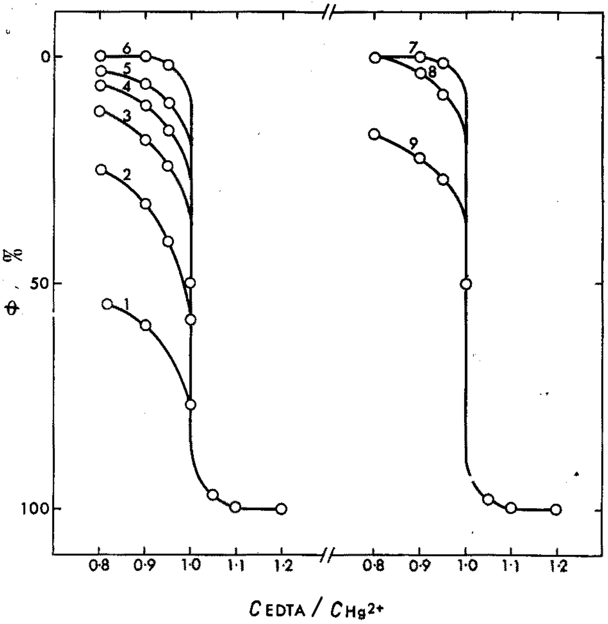

Fig. 6. Photometric titration curves. $C_{Hg^{2+}} = 5\cdot10^{-4}$ *M*; $4\cdot10^{-5}$ *M* TAC; 0.01 *M* EDTA; $Na_2HPO_4 + KH_2PO_4$ buffer soln. pH: 1 = 5.0; 2 = 6.0; 3 = 7.0; 4 = 7.8; 5 = 8.3; 6 = 8.6; 7 = 8.8; 8 = 9.0.

Conclusion

On the basis of the above results, the recommended procedure for the direct titration of mercury(II) ions with TAC as the indicator is as follows. Take about 100 ml of sample solution containing not more than 10^{-2} *M*** as mercury(II) ions at pH 7.0–8.3, adjusted with a suitable 0.1 *M* phosphate buffer system. Add several drops of alcoholic 10^{-2} *M* TAC solution and titrate with 10^{-2} *M* EDTA. The error was found to be within 0.1%.

The author wishes to express his thanks to Prof. D. YAMAMOTO of this University and Mr. K. TAMAOKU of the research laboratories of Dojindo & Co., Ltd. for their useful discussions.

SUMMARY

A direct EDTA titration method for mercury(II) ions with *o*-(2-thiazolylazo)-cresol (TAC) as the metallochromic indicator at pH 7–8.3 is described. Sharp color

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* The change from blue to yellow was also observed in the same pH range at concentrations of mercury higher than 10^{-2} *M*.

** At higher concentrations than 10^{-2} *M*, mercury(II) oxide was apt to form; an ammoniacal buffer may be suitable in this case.

changes from blue to yellow or red indicate the equivalence point. The indicator transition of TAC is discussed theoretically by using the formation constants of the mercury(II)–TAC chelate; the results obtained were confirmed experimentally by photometric titration.

RÉSUMÉ

On décrit une méthode de titrage directe à l'EDTA pour le dosage du mercure(II) en présence de *o*-(2-thiazolylazo)-cresol (TAC) comme indicateur métallochromique au pH 7–8.3. On observe un virage du bleu au jaune, ou rouge au point équivalent. On examine théoriquement les constantes de formation du chélate mercure(II)–TAC.

ZUSAMMENFASSUNG

Die direkte Titration mit ÄDTE von Quecksilber(II) unter Verwendung von *o*-(2-Thiazolylazo)-kresol (TAC) als Indikator beim pH 7–8.3 wird beschrieben. Scharfe Farbwechsel von blau nach gelb oder rot zeigen den Äquivalenzpunkt an. Der Übergang des Indikators vom TAC wird theoretisch diskutiert unter Verwendung der Bildungskonstanten des Quecksilber(II)–TAC-Chelats. Die erhaltenen Ergebnisse wurden experimentell durch die photometrische Titration bestätigt.

REFERENCES

1 H. FLASCHKA AND H. ABDINE, *Chemist-Analyst*, 45 (1956) 58.
2 J. KÖRBL AND R. PRIBIL, *Chemist-Analyst*, 45 (1956) 162.
3 R. PRIBIL, *Chem. Listy*, 51 (1957) 302.
4 N. IRITANI, T. TANAKA AND H. SAKAI, *Nippon Yakugaku Zasshi*, 76 (1956) 1068.
5 N. IRITANI, T. TANAKA AND H. SAKAI, *Nippon Yakugaku Zasshi*, 77 (1957) 106.
6 M. TANAKA AND G. NAKAGAWA, *Anal. Chim. Acta*, 32 (1965) 123.
7 G. NAKAGAWA AND H. WADA, *Nippon Kagaku Zasshi*, 85 (1964) 54.
8 A. KAWASE, *Bunseki Kagaku*, 11 (1962) 621.
9 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959, p. 621.
10 F. D. SNELL AND C. T. SNELL, *Colorimetric Method of Analysis*, Van Nostrand, Philadelphia, 1959, p. 63.
11 F. SCHWARZENBACH, *Komplexometrische Titration*, Ferdinand Enke Verlag, Stuttgart, 1955, p. 26.
12 G. NAKAGAWA AND H. WADA, *Nippon Kagaku Zasshi*, 83 (1962) 30.

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QUINOLINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE, A SELECTIVE AND SENSITIVE COPPER REAGENT*

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(Received August 1st, 1968)

Despite the number of excellent methods that have developed for the trace analysis of copper, there is a need for a simple and selective method that will permit the direct determination of less than 1 p.p.m. of copper. Neutron activation[1,2] and atomic absorption[3] techniques have been applied recently but good sensitivity is dependent upon preliminary concentration procedures. The chloramine T–phenol reaction, which is catalyzed by trace amounts of copper[4], is extremely sensitive, but more than 2 μg of iron and metals which form hydrous oxides or hydroxides (if present in sufficient quantities to precipitate) interfere. The ternary copper complex with phenanthroline and rose bengal[5] has been used to determine parts per billion of copper; selectivity is achieved through preliminary reaction and separation with neocuproine. The cuproines[6–10], because of their high selectivity, have been most useful for determining 1–10 p.p.m. of copper and have been used to confer selectivity, in other procedures, through extraction of copper–cuproine complexes. The present study was initiated to develop a sensitive and selective reagent that could be applied quickly and simply to the direct determination of copper.

The tridentate reagent, pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) has been used for the absorptiometric determination of palladium[11], cobalt[12], and nickel[12,13]; under controlled conditions the procedures developed were specific for the metal involved. Since PAQH gives a sensitive reaction with copper, attempts were made to apply this reagent to the selective determination of less than 1 p.p.m. of copper. In the initial experiments, however, the elimination of interferences did not look very promising and attention was therefore directed to similar compounds with extended π systems and different basicity. It was found that quinoline-2-aldehyde-2-quinolylhydrazone (QAQH) reacted with copper to give a red-colored species that was insoluble in water or water–ethanol mixtures; the complex was readily soluble in benzene. The red color of the complex contrasted with the yellow reagent color permitted very small amounts of copper to be detected visually; 0.01 μg of copper were detectable in the presence of 500 μg of a large number of metals (including nickel, iron, cobalt) in 50% water:acetone solutions. This paper reports the results of a detailed investigation of QAQH and the development of a general procedure for determining less than 1 p.p.m. of copper.

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* Abstracted from the M.Sc. thesis of G. G. SIMS.

EXPERIMENTAL

Apparatus and reagents

Bausch and Lomb Spectronic 505 and Unicam SP 500 spectrophotometers were used for recording absorption spectra and for measurements at a particular wavelength.

Copper standards were obtained by dilution of 0.01 *F* copper stock solutions prepared from primary standard copper wire.

Quinoline-2-aldehyde-2-quinolylhydrazone was quickly and easily prepared. Quinoline-2-aldehyde was dissolved in 5–10 ml of ethanol (containing a drop of glacial acetic acid) and an equimolar quantity of 2-hydrazinoquinoline (dissolved in a minimum amount of hot ethanol) was added. The resultant solution was refluxed for a few minutes and the reagent was separated, after cooling, by filtration. The reagent was recrystallized from acidified ethanol (m.p. 264°, yield 80%). Reagent solutions (0.02–0.05%) were freshly prepared in water containing 1 ml of concentrated hydrochloric acid per 100 ml of solution.

The phosphate buffer was a 0.2 *F* disodium hydrogen phosphate solution.

Solvent effects

The copper–QAQH species is insoluble in water and ethanol but dissolves in acetone. In 50% acetone:water solutions, the complex has a molecular extinction coefficient of $5.2 \cdot 10^4$; 500 μg of cobalt, nickel, cadmium and zinc cause less than 5% interference in the determination of 32.6 μg of copper but more than 0.1 g of sodium chloride, nitrate, or sulphate result in cloudy solutions and sample size is therefore limited. The complex is readily extracted from aqueous solutions by chloroform, isoamyl alcohol, and benzene; the molecular extinction coefficients are 4.2, 4.9 and $5.8 \cdot 10^4$, respectively.

Effect of pH

Figure 1 shows the effect of pH on the completeness of reaction; the aqueous solution contained 34.6 μg of copper and the final volume of the benzene extract was 50 ml (0.69 p.p.m. Cu). Essentially no color is formed or extracted below pH 5.3 whilst complete color formation is observed above pH 6.5; absorbances are constant at higher pH values and the same intensity is obtained for extracts from 3 *N* basic solutions.

The reactivities of cobalt, nickel, cadmium, and zinc decrease as the pH decreases. At pH 13, cadmium and zinc interfere strongly in the determination of copper but, at pH 7, these interferences are greatly reduced. A detailed study of different buffers at various acidities showed that solutions buffered at pH 6.9 to 7.4 with phosphate are most suitable for determining copper with minimal interference from other metals.

Reagent effect

The reagent solution decreases in reaction sensitivity after standing for 1–2 h (possibly owing to tautomeric or isomeric equilibria); absorbance readings at 540 nm (from recorded spectra for 34.6 μg of copper extracted into 50 ml of benzene) with reagent solutions that had stood for various time intervals, were 0.677 (immediate), 0.674 (1 h), 0.658 (2 h), 0.654 (3 h), and 0.650 (5 h).

The red copper–QAQH species is formed immediately and acceptable results are obtained for extractions carried out at once or after many hours of standing; absorbance readings for solutions similar to the above were 0.676 (immediate extraction) and 0.666 (extraction after 26 h). After extraction, however, the color is stable for only 1 h; absorbance readings were 0.670 (10 min), 0.668 (1 h), 0.659 (1.5 h), and 0.648 (4 h). For best sensitivity and reproducibility, the color should be developed with freshly prepared reagent solutions and, once extracted, absorbance readings should be made within 1 h.

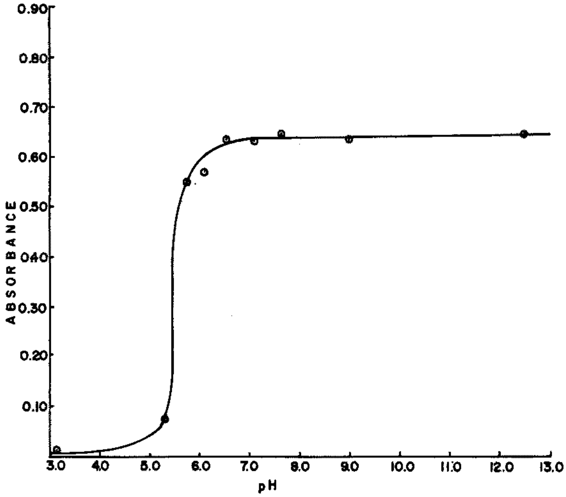

Fig. 1. Effect of pH.

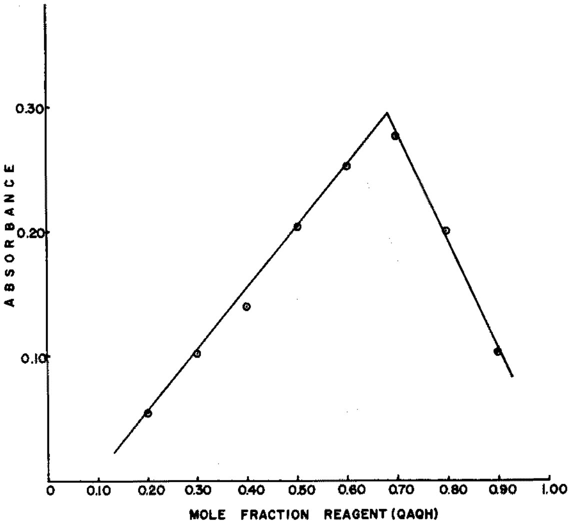

Fig. 2. Job's plot. $1.091 \cdot 10^{-4}$ F solutions of copper and QAQH were used.

Composition, spectra, and Beer's law

A Job's plot (Fig. 2) shows that the complex extracted from aqueous solutions, buffered at pH 6.9 to 7.4 with phosphate, is a 2:1 QAQH to copper species. The proposed structures are

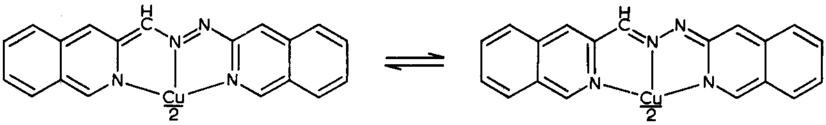

Figure 3 shows the absorption spectra for reagent and complex. The slight reagent absorption at the absorption maximum for the complex (540 nm) is advantageous since excess of reagent is not critical and a blank is necessary only as a check on the purity of chemicals used to adjust the reaction conditions.

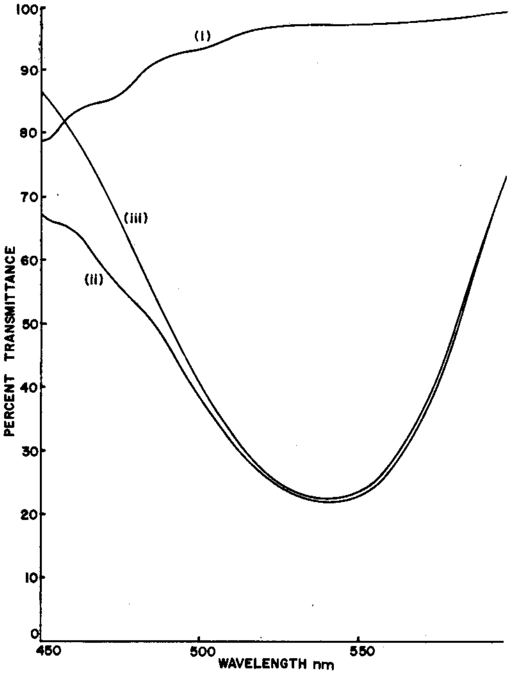

Fig. 3. Absorption spectra in benzene. (i) $8.38 \cdot 10^{-5}$ *F* QAQH *versus* benzene blank; (ii) $1.09 \cdot 10^{-5}$ *F* copper in the presence of $8.38 \cdot 10^{-5}$ *F* QAQH *versus* benzene blank; (iii) as (ii) *versus* $8.38 \cdot 10^{-5}$ *F* QAQH blank.

A Beer's law plot gives a straight line through the origin for 0.1–1 p.p.m. of copper; the molecular extinction coefficient is $5.8 \cdot 10^4$ l mole^{-1} cm^{-1}. The absorbance obtained in a 1-cm cell for 14 µg of copper, extracted from a 500-ml sample volume into 25 ml of benzene, was 0.589; the concentration of copper, based on the sample taken for analysis, is 28 p.p.b. and much smaller concentrations of copper can therefore be accurately determined.

Reactions of other metal ions

Zinc, cadmium, cobalt and nickel react readily with QAQH to form pink to red complexes. At high pH, 500 μg of these metals interfered strongly in the determination of copper but interferences were greatly reduced in a phosphate buffer (pH 7–8); 2.5 mg of cadmium and zinc gave no noticeable color reaction and the absorbance for 34.6 μg of copper (complex extracted into 50 ml of benzene) in the presence of 500 μg of cadmium was 0.626 in the phosphate buffer; a similar solution containing no cadmium had an absorbance of 0.630. However, more than 35 μg of cobalt and 70 μg of nickel gave absorbances that were high by more than 5% and masking agents (fluoride, citrate, ethylenediaminetetracetic acid, and thiourea) did not improve results. In the presence of fluoride 500 μg of aluminium, chromium, iron, niobium, thorium or tin, and 2.5 mg of beryllium, lead or uranium did not interfere in the determination of 34.6 μg of copper; low results, through either a bleaching effect or incomplete extraction, were obtained if fluoride was not present.

The initial volume of solution and order of reagent addition are also important factors which determine the magnitude of interference by metal ions. In a 10-ml initial volume, 500 μg of magnesium interferes but 10 mg does not interfere significantly in a 60-ml volume. Large amounts of strontium interfere to a lesser extent if QAQH is added to the sample before sodium fluoride whilst chromium shows lesser interference if fluoride is added before QAQH. In the compromise procedure developed, a 15-fold excess (500 μg) of most metal ions does not interfere in the determination of copper (34.6 μg).

Recommended procedure

Adjust the sample solution, containing 2–50 μg of copper to pH 4–5 and dilute to 50–70 ml with distilled water. Add 10 ml of 2.5% sodium fluoride, 5 ml of 0.05% QAQH and 10 ml of 0.2 *F* disodium hydrogen phosphate (pH between 6.9 and 7.4) and extract the solution with two 20-ml aliquots of benzene. Dilute the combined extracts to 50 ml with benzene and measure the absorbance at 540 nm within 1 h.

RESULTS

Typical results for copper, alone and in the presence of metals which can give

TABLE I

DETERMINATION OF COPPER WITH QAQH

Copper taken (μg)	*Copper found (μg)*	*Comments*
6.9	6.8 ± 0.1	3 determinations
20.7	20.7 ± 0.2	5 determinations
34.6	34.6 ± 0.3	10 determinations
34.6	34.8	500 μg Cd present
34.6	34.6	500 μg Zn present
34.6	34.4	500 μg Fe present
34.6	34.4	500 μg Hg present
34.6	33.0	500 μg Pd present
34.6	35.6	35 μg Co present
34.6	36.0	70 μg Ni present

colored complexes with QAQH, are shown in Table I. The results show that 500 μg of cadmium, zinc, iron, mercury, and palladium interfere by less than 5% in the determination of 34.6 μg of copper. Similar results were obtained in the presence of 500 μg of the following ions: Ag^+, Al^{3+}, As^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Ce^{4+}, Cr^{3+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Mo^{6+}, Nb^{5+}, Pb^{2+}, Sb^{3+}, Sn^{4+}, Sr^{2+}, Th^{4+}, U^{6+}, V^{5+}, W^{6+} and Zr^{4+}. Most of these ions are acceptable in much larger quantities but others are near their allowable limit. For example, 10 mg of magnesium and 2.5 mg of manganese do not interfere but acceptable results are not obtained if much more than 500 μg of tin or chromium are present. Mercury forms a yellow complex with QAQH which is insoluble in both water and benzene; the solid sometimes remains partially suspended in the benzene layer and the solution must be centrifuged before absorption measurements are made. Palladium, when present in quantities approaching 500 μg, also gives a cloudy extract which should be centrifuged. Equivalent amounts of cobalt and twice as much nickel can be tolerated in the determination of 34.6 μg of copper.

A special procedure can be applied if the amounts of cobalt and nickel exceed the limits permitted by the general procedure; the color is developed in acetone:water solution and the absorbance is measured at 505 nm. The sample pH is adjusted to 4–5, 25 ml of acetone, 5 ml of 0.04% QAQH and 5 ml of a phosphate buffer (10:1 of 0.2 *F* dibasic: 0.2 *F* monobasic sodium phosphate) are added, and the solution is diluted to 50 ml with distilled water. With this procedure, results within 5% of the true value are obtained for 34.6 μg of copper in the presence of 500 μg of cobalt and nickel. However, since more than 0.1 g of sodium chloride, nitrate or sulphate give a "salting-out" effect, sample size is limited; a large scale interference study was not done but the acetone:water medium appears to have merit if cobalt and nickel are present in 15- to 20-fold excess of copper.

No interference results from the presence of 1 g of sodium chloride, nitrate, perchlorate, or sulphate in the extraction procedure. Cyanide and ethylenediaminetetraacetic acid, however, are serious interferences and must be absent.

CONCLUSIONS

Pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) and quinoline-2-aldehyde-2-quinolylhydrazone (QAQH) permit the sensitive and selective determination of a few transition metals. Their reaction products differ in color and stability. Although the stability of the copper–PAQH complex is greater than that of the copper–QAQH species (copper–PAQH is not appreciably affected by EDTA), the corresponding lesser stability of other metal–QAQH complexes permits a highly selective procedure for copper to be developed.

The favorable distribution coefficient between water and benzene for the QAQH–copper complex permits very small amounts of copper to be recovered from large sample volumes and to be directly analyzed; preliminary investigations suggest, for example, that copper can be quickly and accurately determined in sea waters (2–4 p.p.b.). Copper can be determined with QAQH in a wide range of materials with limitations only on the amount of cobalt and nickel present (equivalent cobalt and twice as much nickel are permissible in the general procedure); 15- to 20-fold excesses of these metals are permissible if the red copper–QAQH complex is formed in 50% acetone:water solutions.

NOTE

Attention is drawn to a recent paper on quinoline-2-aldehyde-2-quinolylhydrazone (QAQH) by RICHARD E. JENSEN, NORMAN C. BERGMAN AND RICHARD J. HELVIG, *Anal. Chem.*, 40 (1968) 624; this work was not available to the authors when the present article was written.

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

SUMMARY

Quinoline-2-aldehyde-2-quinolylhydrazone (QAQH) allows a simple and rapid direct determination of less than 1 p.p.m. of copper. The red 2:1 QAQH to copper complex has a molecular extinction coefficient in benzene of $5.8 \cdot 10^4$ at the absorption maximum of 540 nm. Most metals (up to 500 μg) do not interfere in the determination of 35 μg of copper. Equivalent amounts of cobalt and twice as much nickel can be present; 15- to 20-fold excesses of these metals are allowable in acetone:water solutions and 0.01 μg of copper is detectable in this medium. Very small amounts of copper (1 p.p.b.) can be recovered from large sample volumes and determined directly.

RÉSUMÉ

La quinoléine-2-aldéhyde-2-quinolylhydrazone (QAQH) permet une détermination directe, simple et rapide de moins d'1 p.p.m. de cuivre. Le complexe rouge de cuivre [2:1 QAQH/Cu] a un coefficient d'extinction moléculaire dans le benzène de $5.8 \cdot 10^4$ au maximum d'absorption (540 nm). La plupart des métaux (jusqu'à 500 μg) n'interfèrent pas pour la détermination de 35 μg de cuivre. Des quantités équivalentes de cobalt et des quantités doubles de nickel peuvent être présentes sans gêner. Il est possible d'avoir des excès de 15 à 20 fois de ces métaux dans des solutions acétone/eau et on peut détecter 0.01 μg de cuivre dans ce milieu. Il est possible de récupérer de très petites quantités de cuivre (1 p.p.b.) à partir d'échantillons plus volumineux et de déterminer directement la teneur en métal.

ZUSAMMENFASSUNG

Chinoline-2-aldehyd-2-chinolylhydrazon (QAQH) ermöglicht eine einfache und schnelle Bestimmung von weniger als 1 p.p.m. Kupfer. Der rote Komplex mit einem Molverhältnis von 2:1 von QAQH zu Kupfer besitzt einen molaren Extinktionskoeffizienten in Benzol von $5.8 \cdot 10^4$ bei einem Absorptionsmaximum von 540 nm. Die meisten Metalle (bis zu 500 μg) stören nicht bei der Bestimmung von 35 μg Kupfer. Gleiche Mengen Kobalt und doppelt so viel Nickel können anwesend sein; ein 15 bis 20-facher Überschuss dieser Metalle ist zulässig, wenn Aceton-Wasser-Lösungen verwendet werden. Es sind dann 0.01 μg Kupfer noch nachweisbar. Aus sehr grossen Probenvolumina können bis hinab zu 1 p.p.b. Kupfer gewonnen und direkt bestimmt werden.

REFERENCES

1 M. Krivanek, F. Kukula and J. Slunecko, *Talanta*, 12 (1965) 721.
2 F. Adams and J. Hoste, *Talanta*, 12 (1965) 221.
3 H. Khalifa, G. Svehla and L. Erdey, *Talanta*, 12 (1965) 703.
4 Y. Kakita, M. Namiki and H. Goto, *Talanta*, 12 (1966) 1561.
5 B. W. Bailey, R. M. Dagnall and T. S. West, *Talanta*, 13 (1966) 753.
6 G. F. Smith and D. H. Wilkins, *Anal. Chem.*, 25 (1953) 510.
7 G. F. Smith and W. H. McCurdy, Jr., *Anal. Chem.*, 24 (1952) 371.
8 D. H. Wilkins and G. F. Smith, *Anal. Chim. Acta*, 9 (1953) 538.
9 J. Hoste, *Anal. Chim. Acta*, 4 (1950) 23.
10 J. Hoste, J. Eeckhout and J. Gillis, *Anal. Chim. Acta*, 9 (1953) 263.
11 M. L. Heit and D. E. Ryan, *Anal. Chim. Acta*, 34 (1966) 407.
12 S. P. Singhal and D. E. Ryan, *Anal. Chim. Acta*, 37 (1967) 91.
13 B. K. Afghan and D. E. Ryan, *Anal. Chim. Acta*, 41 (1968) 167.

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THE GRAVIMETRIC DETERMINATION OF RHENIUM AS AMINE PERRHENATES

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Few methods are available for the determination of rhenium[1,2]. Titrimetric methods based on oxidation–reduction reactions are unsatisfactory owing to the difficulties of establishing well-defined lower valency states of rhenium, and most gravimetric methods yield variable results unless great precautions are taken to minimize the solubility of the precipitates involved. The most widely used procedures for the determination of macro amounts of rhenium are those based on the precipitation of tetraphenylarsonium perrhenate[3,4] or nitron perrhenate[5]. No solubility data have been published for these compounds, but the originators of the methods stress the importance of volume and temperature control, and it has been stated[5] that less than 5 mg of rhenium cannot be determined with nitron.

Recent work on the development of precipitants for the nitrate ion based on di-(1-naphthylmethyl)amine has shown that N-(*p*-chlorobenzyl)-1-naphthylmethylamine is superior to nitron, being a more sensitive, though only slightly more selective, precipitant[6]. Other derivatives of N-benzyl-1-naphthylmethylamine also proved to be sensitive precipitants for nitrate[6,7]. At the same time it was shown that these amines gave precipitates with, among other ions, perchlorate, permanganate and perrhenate ions, although only qualitative assessments of these precipitation reactions were made. Since these compounds are more accessible synthetically than nitron, and have considerable advantages of stability over that reagent, it was considered worthwhile to study their properties as precipitants for the perrhenate ion. The compounds studied were those which had previously been found most sensitive for nitrate, *i.e.* N-benzyl-1-naphthylmethylamine, N-(*p*-chlorobenzyl)-1-naphthylmethylamine and di-(1-naphthylmethyl)amine.

Sensitivity tests and solubilities

The suitability of the reagents for the precipitation of perrhenate was first assessed by simple sensitivity tests. These were done by mixing 1 ml of a saturated solution of the amine salt with 2 ml of solutions containing varying amounts of perrhenate; after five days of intermittent shaking at the required temperature, the mixtures were inspected for precipitate formation. The results (Table I) indicated di-(1-naphthylmethyl)amine to be as sensitive as nitron, whereas the other reagents were less sensitive.

These indications were confirmed by the solubilities of the amine perrhenates (Table I). The solubilities were determined by heating the amine perrhenate with distilled water to 60°, shaking, and leaving for 4 days at the required temperature.

TABLE I

SENSITIVITY OF THE REAGENTS FOR PERRHENATE AND SOLUBILITY DATA

Amine	*Sensitivity (mg/l)*[a]		*Solubility of salts (g/l)*					
	21°	*0°*	*ReO_4^-*		*SO_4^{2-}*		*HCl*	
			21°	*0°*	*21°*	*0°*	*21°*	*0°*
N-Benzyl-1-naphthylmethylamine	0.07	0.06	1.75	—	—	—	38.4[b]	—
N-(*p*-Chlorobenzyl)-1-naphthylmethylamine	0.07	0.04	0.58	0.37	7.2	5.7	4.0[b]	—
Di-(1-naphthylmethyl)-amine	—	0.02	—	0.18	1.7[b]	0.95	0.46[b]	—
Nitron	—	0.02	—	0.17[c]	—	—	—	—

[a] See text.
[b] Refs 6 and 7.
[c] 0.18 g/l[5].

After filtration, aliquots were evaporated to dryness on a boiling water bath, and the residues were weighed; alternatively, the solutions were titrated potentiometrically with standard alkali.

The solubilities of the amine perrhenates in water alone do not, of course, allow a true estimate of their suitability for gravimetric purposes, because no account is taken of a common ion effect. The solubility of the reagent salt itself is of importance because it is the controlling factor for the possible excess of reagent. It can be seen from Table I that both the sulphate and hydrochloride salts of N-(*p*-chlorobenzyl)-1-naphthylamine are considerably more soluble than the corresponding salts of di-(1-naphthylmethyl)amine, hence both these amines were also examined for quantitative work. *N*-Benzyl-1-naphthylmethylamine was rapidly eliminated from consideration, because of the comparatively high solubility of its perrhenate.

Quantitative precipitation of perrhenate

*N-(*p*-Chlorobenzyl)-1-naphthylamine.* The first tests were made with N-(*p*-chlorobenzyl)-1-naphthylmethylamine hydrochloride as the reagent. The results were unsatisfactory, because the solubility of the amine perrhenate made quantitative precipitation at room temperature impossible, whereas the rapid decrease in solubility of the amine hydrochloride with decreasing temperature caused coprecipitation when a sufficient excess of reagent was present at lower temperatures. Only 5 ml of 1% reagent solution (an excess of *ca.* 300%) could be tolerated for the precipitation of 10 mg of perrhenate (*ca.* 7.5 mg of rhenium) without coprecipitation. Even under the optimal carefully controlled conditions, results were low (Table II).

Accordingly, the more soluble amine sulphate was studied. The solubility of this salt was found to be considerably greater than that of the analogous hydrochloride (Table I), hence almost twice the amount of reagent could be added before coprecipitation occurred. The results obtained with this reagent were essentially equivalent to those obtained with nitron (Table II), similar precautions with respect to volume and temperature control being taken, but any deviation from the optimal conditions caused unreliable results. Some further tests were made with this amine as its acetate salt, which is very soluble in 1:1 acetic acid, but the results were unreliable, because a fairly high concentration of acetic acid was necessary to prevent hydrolysis of the reagent on dilution.

TABLE II

QUANTITATIVE COMPARISON OF THE AMINE REAGENTS FOR PERRHENATE

Precipitant	*Perrhenate taken (mg)*	*Perrhenate found (mg)*	*Av. error (mg)*
N-(*p*-Chlorobenzyl)-1-naphthylmethylamine hydrochloride	10	9.83 (14)[a]	0.15
N-(*p*-Chlorobenzyl)-1-naphthylmethylamine sulphate	10	9.97 (6)	0.04
Di-(1-naphthylmethyl)amine sulphate	10	10.02 (17)	0.08
	5	4.94 (3)	0.06
	2	1.98 (3)	0.06
	1	1.00 (3)	—
Nitron acetate	10	9.98 (10)	0.05

[a] Average value, the number of determinations being indicated in brackets.

Di-(1-naphthylmethyl)amine. The perrhenate of this amine has a solubility in water equal to that of the nitron salt (Table I). However, the solubility of the amine sulphate precludes the addition of a large excess of reagent without coprecipitation, hence volume and temperature control during the procedure remains essential. Nevertheless, this amine perrhenate was much less affected by washing with ice-cold water than the perrhenate of the *p*-chlorobenzyl analogue, and a moderate degree of latitude in the general precipitation and washing techniques was permissible. The use of 10 ml of wash water decreased the weight of the precipitate by only 0.5%. The results obtained with this amine are shown in Table II. The di-(1-naphthylmethyl)-amine sulphate reagent is undoubtedly the best of those tested in the present work. Its performance as a perrhenate precipitant is at least as good as that of nitron, and it is considerably simpler to prepare; moreover, the control of conditions need not be so strict as with nitron.

Precipitation of pertechnetate

The similarity of the reactions of the pertechnetate ion, TcO_4^-, to those of perrhenate prompted an examination of N-(*p*-chlorobenzyl)-1-naphthylmethylamine and di-(1-naphthylmethyl)amine as precipitants for this ion. It was found, however, that when the procedure for the determination of the solubilities of the amine perrhenates was followed, the solubilities of the corresponding pertechnetates were 0.88 and 0.46 g per litre respectively, at 0°. These compare with the literature value of 0.36 g per litre for nitron pertechnetate. Thus, although there is little to choose between nitron and di-(1-naphthylmethyl)amine in this connection, the arguments presented for the use of the latter as precipitant for perrhenic acid can also be applied to its use for technetium(VI). Unfortunately. insufficient technetium(VI) was available to test this precipitant quantitatively.

Precipitation of hexachlororhenate(IV)

Hexachlororhenate(IV) is known to form sparingly soluble salts with large aromatic cations[1,2] and N,N'-tetramethyl-*o*-tolidine has been reported as a suitable reagent[9]. It was shown in the present work that copious precipitation occurred with all the 1-naphthylmethylamine derivatives tested; nitron, and even quinoline, gave appreciable precipitation.

The N-(*p*-chlorobenzyl)-1-naphthylmethylamine hexachlororhenate(IV) proved to be unsatisfactory for gravimetric purposes, because of its low melting point (89°), unless precipitation and drying were done at room temperature. The N-benzyl-1-naphthylmethylamine salt was preferable, because of its higher melting point (110°) which allowed precipitation at 50° and drying at 105°.

However, such methods[10] have only very limited value in the absence of reliable, simple means of producing hexachlororhenate(IV) quantitatively from other forms of rhenium, although the greatly improved conversion factor obtainable with the divalent anion would clearly be beneficial.

Various reducing agents have been employed for the conversion of perrhenate to hexachlororhenate(IV)[2], but the course of reaction is complex. In the present work, iodide, and tin(II) chloride were tested, but in both cases, the amount of halide ion required for acidification during the conversion was incompatible with the later use of the amine reagents. No apparent reduction occurred with sulphur dioxide or ascorbic acid. Thus no simple mode of reduction appears to be available.

It should be noted that the use of these reagents for hexachlororhenate(IV) is based simply on their function as large organic cations and is unrelated in principle to their use as precipitants for monovalent species such as nitrate, perchlorate and perrhenate.

EXPERIMENTAL

*Preparation of N-(*p*-chlorobenzyl)-1-naphthylmethylamine sulphate*

The most convenient route to this salt was as follows. The hydrochloride was prepared as described previously[6] and after treatment of the solution with warm aqueous sodium hydroxide solution (2 *N*) until alkaline, the liberated amine was extracted with ether. The ethereal layer was separated and concentrated sulphuric acid was added dropwise until complete precipitation of the amine sulphate was obtained. The precipitate was then filtered off and recrystallised from 2 *M* sulphuric acid.

The reagent was used as a 2% (w/v) solution in water containing 1 ml of 0.5 *M* sulphuric acid to prevent hydrolysis. The solution was heated to 80° and filtered just before use. Fresh reagent solution was used because prolonged heating caused hydrolysis.

Preparation of di-(1-naphthylmethyl)amine sulphate

Di-(1-naphthylmethyl)amine was prepared by the method of RUPE AND BECHERER[11] with certain modifications[7]. The product of hydrogenation, an oily solid, was taken up in *ca.* 4 *M* sulphuric acid and the solution was boiled several times with charcoal until it was colourless. The conversion of the oily solid to the sulphate gave about a 50% yield.

The reagent was used as a 2.5% (w/v) solution in water containing 1 ml of 2 *M* sulphuric acid. The reagent solution was heated and filtered before use as described for the *p*-chlorobenzyl salt.

Procedure.

Add hot reagent solution to the 5–10 ml sample of perrhenate solution containing 1–10 mg of perrhenate as the ammonium salt at *ca.* 80°. In the case of the *p*-chlorobenzyl salt, use 4.5 ml of reagent solution for each 10 ml of sample solution; with the dinaphthyl salt, use 4 ml of reagent solution for each 10 ml of sample solution. Cool the solution in ice for 2 h. Filter on a No. 3 sintered glass crucible, transferring the precipitate with some of the filtrate. Wash with three 2-ml portions of ice-cold water. (When the *p*-chlorobenzyl salt is used, wash first 2 ml of ice-cold saturated amine perrhenate solution, and then with 2 ml of ice-cold water.) Drain thoroughly and dry at 110° to constant weight.

The formulae of the respective amine perrhenates are $C_{18}H_{17}ClNReO_4$ and $C_{22}H_{20}NReO_4$.

We are grateful to Professor R. BELCHER for his support of this work.

SUMMARY

Various substituted 1-naphthylmethylamines have been studied as precipitants for the perrhenate ion. The perrhenate of the N-benzyl derivative is too soluble for analytical purposes, but both N-(*p*-chlorobenzyl)-1-naphthylmethylamine and di-(1-naphthylmethyl)amine can be used, the latter being preferable, because of the greater permissible variation of conditions. This reagent is approximately equivalent to nitron in sensitivity and selectivity but has the advantage of being more easily prepared. *N*-Benzyl-1-naphthylmethylamine is a suitable precipitant for hexachlororhenate(IV), but there is no simple quantitative means of converting perrhenate to this ion, hence advantage cannot be taken of the improved conversion factor for rhenium. The pertechnetate ion also yields sparingly soluble salts with these amines.

RÉSUMÉ

Diverses 1-naphtylméthylamines sont examinées comme réactif de précipitation des perrhénates. Le perrhénate du dérivé N-benzyl est trop soluble pour être utilisé en analyse. Par contre, la N-(*p*-chlorobenzyl)-1-naphtylméthylamine et la di-(1-naphtylméthyl)amine peuvent être utilisées; c'est cette dernière qui convient le mieux. Ce réactif correspond à peu près au nitron, comme sensibilité et sélectivité; mais il présente l'avantage de se préparer plus facilement. La N-benzyl-1-naphtylméthylamine permet de précipiter l'hexachlororhénate(IV), mais il n'existe pas de moyens quantitatifs simples pour transformer le perrhénate en cet ion. Le pertechnétate donne également des sels peu solubles avec ces amines.

ZUSAMMENFASSUNG

Zahlreiche substituierte 1-Naphthylmethylamine wurden auf ihre Eignung als Fällungsmittel für das Perrhenat-Ion untersucht. Das Perrhenat des N-Benzylderivats besitzt für analytische Zwecke eine zu grosse Löslichkeit, aber sowohl N-(*p*-Chlorobenzyl)-1-naphthylmethylamin als auch Di-(1-Naphthylmethyl)amin können verwendet werden, wobei das letztere vorzuziehen ist, weil es eine grössere

Variation der Versuchsbedingungen zulässt. Dieses Reagenz ist in seiner Empfindlichkeit und Selektivität dem Nitron nahezu gleichwertig; jedoch ist es leichter herzustellen. N-Benzyl-1-Naphthylmethylamin ist ebenso als Fällungsmittel für Hexachlororhenat(IV) geeignet. Das Pertechnetat-Ion bildet ebenfalls wenig lösliche Salze mit diesen Verbindungen.

REFERENCES

1 See, *e.g.*, I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part II, Vol. 7, Interscience, J. Wiley & Son, New York, 1961.
2 R. D. PEACOCK, *The Chemistry of Technetium and Rhenium*, Elsevier Publishing Co., Amsterdam, 1966.
3 H. H. WILLARD AND G. M. SMITH, *Ind. Eng. Chem., Anal. Ed.* 11 (1939) 305.
4 H. H. WILLARD AND G. M. SMITH, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 186.
5 W. GEILMANN AND A. VOIGT, *Z. Anorg. Allgem. Chem.*, 193 (1930) 311.
6 R. C. HUTTON, S. A. SALAM AND W. I. STEPHEN, *J. Chem. Soc.*, A, (1966) 1573.
7 R. C. HUTTON AND W. I. STEPHEN, *J. Chem. Soc.*, A, (1967) 1426.
8 G. W. PARKER AND W. J. MARTIN, *ORNL Report*, 1950, p. 870.
9 W. GEILMANN AND L. C. HURD, *Z. Anorg. Allgem. Chem.*, 203 (1933) 336.
10 For details, see M. H. B. MORTON, *M.Sc. Thesis*, University of Birmingham, 1967.
11 H. RUPE AND F. BECHERER, *Helv. Chim. Acta*, 6 (1923) 880.

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AN INVESTIGATION OF BARIUM OXALATE BY COMBINED DERIVATOGRAPHIC AND THERMO-GAS ANALYSIS

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The thermal decomposition of barium oxalate has been studied by several authors[1-4]; the investigations were generally carried out in the presence of air. In air, barium oxalate hemihydrate proved to decompose in two steps as is also indicated by the derivatogram shown in Fig. 1. The first step of the thermogravimetric curve (denoted as step A in the subsequent discussion) corresponds to the removal of crystal water while the second step (B) corresponds to the decomposition process of barium oxalate to yield barium carbonate. The barium carbonate so produced proved to be of constant weight up to 920°.

It is, however, less well known that when the same experiment is conducted under exclusion of air, *e.g.* in a nitrogen atmosphere, the thermal decomposition

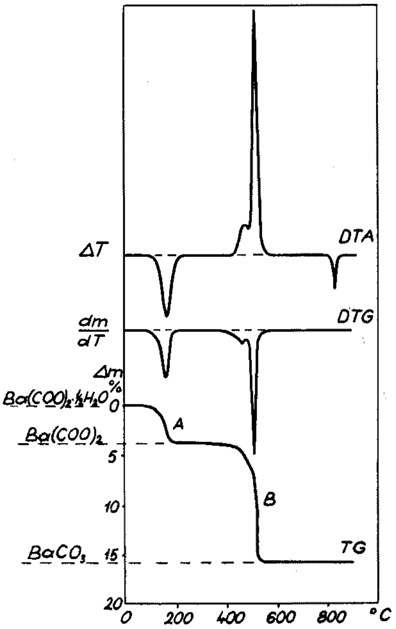


Fig. 1. Derivatogram of $Ba(COO)_2 \cdot \frac{1}{2}H_2O$, investigated in air.

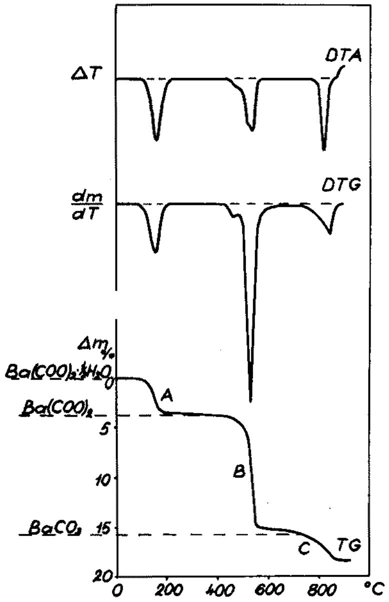


Fig. 2. Derivatogram of $Ba(COO)_2 \cdot \frac{1}{2}H_2O$, investigated in nitrogen.

proceeds in a different way (Fig. 2). The first step (A) of the thermogravimetric curve is the same as that found when the experiment is conducted in air. However, the second step (B) shows a different course, and a third step (C) also appears at a temperature between 580 and 920°. Step A is smaller while the combined sum of steps B+C is higher than the weight change corresponding to the splitting off of one mole of carbon monoxide.

Since the thermal decomposition of barium oxalate in nitrogen could not be elucidated by derivatographic measurements alone[5], it was necessary to complement them with other measurements. Combined derivatographic and thermo-gas-titrimetric experiments[6,7] were therefore carried out. When this method was applied, it proved possible to establish the quantity of the gaseous decomposition products (CO, CO_2) developed against temperature, with the same single sample, in parallel with the derivatographic measurements.

EXPERIMENTAL

Barium oxalate hemihydrate was separated by means of a solution of ammonium oxalate, from a boiling acetic acid solution of barium(II) which contained ammonium chloride.

The measurements were carried out with a MOM (Magyar Optikai Müvek, Budapest) type derivatograph. The inner space of the derivatograph was modified as described previously[6,7]. This made possible the quantitative collection of the gaseous decomposition products in the space surrounding the sample, as well as their continuous removal from this space by a steady suction of gases. The removed gas was allowed to pass through an absorbent solution in which the decomposition products transported could be continuously titrated by means of an appropriate titrant and indicator. In the present case, for example, the carbon dioxide developed was absorbed by an absorbent solution which contained barium chloride, and was titrated in the presence of phenolphthalein with a 0.1 *M* sodium hydroxide solution.

The direct determination of carbon monoxide was impossible. In order to be able to follow the course of its formation, oxygen was introduced into the gas current, before the insertion of the absorber, and a U-tube packed with Hopcalite catalyst and maintained at 100° was inserted into the gas flow. In the presence of oxygen, carbon monoxide was oxidized on the catalyst to carbon dioxide, and the carbon dioxide formed could then be continuously titrated as described above.

In general, purified nitrogen, and in some experiments argon, served as the inert gas. During the measurements, it was possible to mix the inert gas, on attaining a previously chosen temperature, with carbon dioxide or oxygen, and thus, to conduct the measurement in a way that the sample was surrounded by a gas containing carbon dioxide or oxygen.

The inert gas was introduced into the apparatus at a rate of 20 l/h, and was removed at a rate of 6 l/h, when it was passed through the absorbent solution.

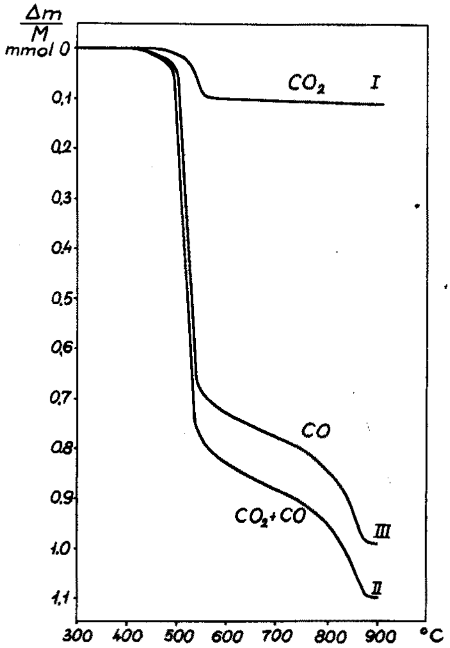
The heating rate during the measurements was 5°/min. In these investigations, the platinum sample-supporting crucible of the derivatograph was used. However, in order to study the possible effects of the structural material and of the shape of the sample holder, the experiment was repeated with a quartz sample holder and also with a quartz sample holder equipped with a small plate[6,7].

Each time a 1-mmole sample was weighed with an accuracy of ±5 mg. The results of investigations were referred to exactly 1 mmole of substance, and plotted after evaluation.

RESULTS

In the presence of air, the decomposition of $Ba(COO)_2 \cdot \frac{1}{2}H_2O$ took place, as shown in Fig. 1 and as has been previously discussed, with liberation of 0.50 mmole of water and 1.00 mmole of carbon monoxide. As is proved by the exothermic peak of the DTA curve, carbon monoxide is oxidized to carbon dioxide by atmospheric oxygen.

In a nitrogen atmosphere (Fig. 2) a weight decrease identical with the above-mentioned loss is caused by the splitting off of the water of crystallization. In order to elucidate the decomposition processes corresponding to the steps B and C, the process of development of carbon dioxide (curve I in Fig. 3) was investigated parallel to the derivatographic measurement. In subsequent experiments, oxygen was mixed with the gases removed from the apparatus by suction, the gas mixture was allowed to pass through the Hopcalite catalyst, and the combined sum of the carbon dioxide evolved in the decomposition process and of carbon dioxide formed by the oxidation of carbon monoxide (curve II) was determined by titration. Curve III is, in turn,



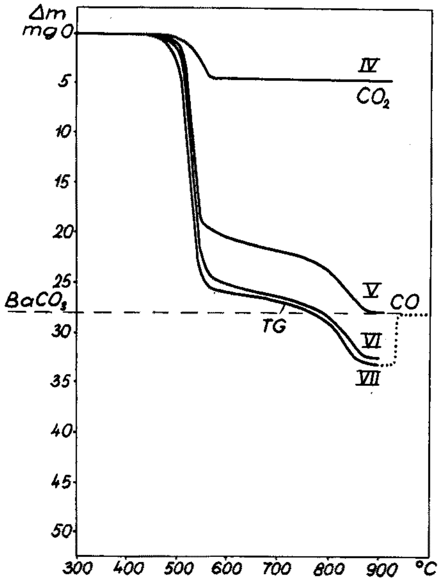


Fig. 3. (I) Amount of CO_2 measured by titration; (II) combined amount of CO_2 and CO_2 formed from CO, measured by titration; (III) differential curve of II and I.

Fig. 4. (IV) Amount of CO_2 measured by titration; (V) amount of CO calculated on the basis of curve III; (VI) summation curve of IV and V; (VII) weight changes of $Ba(COO)_2$, calculated on the basis of the TG curve of Fig. 2.

the differential curve of curves II and I by means of which the formation of carbon dioxide equivalent to the liberated carbon monoxide can be followed.

The curves IV and V of Fig. 4 indicate the amount of the components in milligrams and represent the process of formation of carbon dioxide and carbon monoxide; these curves were calculated on the basis of the data of curves I and III. The sum of curves IV and V is shown by curve VI, while curve VII records the weight changes measured in the temperature range 300–900°; these amounted, according to the Figure, to 33.2 mg. The combined amount of carbon monoxide and carbon monoxide calculated from the titration results was 32.5 mg (curve VI), which, considering the rather complicated experimental technique, may be considered in reasonably good agreement.

The curves of Fig. 4 show that carbon dioxide is formed only at temperatures below 600°, and that above that temperature only carbon monoxide is liberated. The amount of carbon dioxide (Fig. 3) in this experiment averaged 0.11 mmole, while that of carbon monoxide averaged 0.99 mmole, totalling 1.10 mmoles. Consequently, about 0.1 mmole of barium oxide should also have been developed during the decomposition process. If, however, at a temperature over 900°, carbon dioxide was mixed with the inert gas introduced around the sample, a rapid weight increase was recorded by the thermobalance (section of curve VII indicated by interrupted line in Fig. 4) and the weight of the sample attained the weight corresponding to a decomposition stage to barium carbonate. The weight increase, calculated from the carbon dioxide uptake, averaged 0.1 mmole, *i.e.* just the amount which can be bound by the presumed amount of barium oxide.

In the next experiment, the temperature was raised only to 600°, and carbon dioxide was introduced to the sample at this constant temperature; no weight change was observed. Thus, despite the fact that during the decomposition of oxalate, carbon dioxide was formed only below 600°, barium oxide was developed solely at temperatures over 600°. The observation that at 600° the weight of the substance remains unchanged on introduction of carbon dioxide, indicates also that this particular behaviour of barium oxalate cannot be explained by the transitory formation of less stable decomposition products; for these would be decomposed by carbon dioxide, with development of barium carbonate.

At 900° when about 20% of oxygen was mixed with the nitrogen allowed to pass over the sample, no changes were perceptible either in the derivatographic curves or in the titration results. However, when oxygen was mixed with nitrogen at 600°, a rapid weight decrease was observed with an exothermic effect, and the weight of the sample attained the weight corresponding to a residue of barium carbonate. At the same time, besides the already developed 0.1 mmole of carbon dioxide (Fig. 3), the rapid development of a further 0.1 mmole of carbon dioxide was found by the titration of the absorbent solution.

DISCUSSION

For the interpretation of the observed phenomena, only one explanation seems probable and is in complete accordance with the experimental results. Thus, in the course of the first step of the decomposition process of barium oxalate, *i.e.* during the formation of the step B in Fig. 2, the reaction

$$Ba(COO)_2 = BaCO_3 + CO \quad (1)$$

takes place. Part of the carbon monoxide formed undergoes further conversion in which, according to the reaction

$$2\,CO = CO_2 + C \quad (2)$$

about 0.1 mole of carbon dioxide is formed and 0.1 mole of carbon is liberated. This latter forms a residue in the sample and so decreases the size of the weight change in section B of the thermogravimetric curve.

The liberated carbon reacts with barium carbonate, owing to the rise of temperature, at steadily increasing rates. This process can be described by the equation:

$$BaCO_3 + C = BaO + 2\,CO \quad (3)$$

The liberated 0.1 mmole of carbon is capable of decomposing an identical amount of barium carbonate. Meanwhile, 0.2 mmole of carbon monoxide leaves the sample. This latter process explains the formation of step C in Fig. 2.

The reaction between barium carbonate and carbon is not unknown in inorganic chemistry, though according to the literature, this reduction takes place at a temperature higher than that observed in the present work. In the present experiments, apparently, the extremely fine dispersion of carbon is responsible for the shift to lower temperature.

In the presence of atmospheric oxygen (Fig. 1), the carbon monoxide formed in the first step of the decomposition process (eqn. (1)), is then oxidized to carbon dioxide. If some carbon were formed according to eqn. (2), it would be similarly oxidized below 600°, so that above this temperature, the residue of decomposition would contain exclusively barium carbonate.

It may be assumed that in the course of the decomposition process in the presence of oxygen, traces of barium peroxide are also formed which may facilitate the oxidation of any carbon which may be liberated. This is supported by the observation that any carbon already liberated is very quickly oxidized when oxygen is introduced to the sample heated in nitrogen to 600°. The same process takes a slow prolonged course when other alkaline earth metal oxalates are being decomposed.

According to the Bouduard equilibrium, at about 500° a much greater portion of carbon monoxide should be decomposed to carbon dioxide and carbon than the amount found by the present measurements. The likely explanation of this smaller conversion is that under the given experimental conditions the rate of decomposition of carbon monoxide is too low for even an approximate formation of the gas concentration conditions corresponding to the Bouduard equilibrium.

Changes in the experimental conditions did not affect the decomposition described above. When the platinum sample holder was replaced by a quartz crucible, or when the measurements were repeated with a sample holder equipped with a small plate, or when nitrogen was replaced by argon, or when the heating rate was decreased from 5 to 2.5°/min, the amounts of carbon dioxide and carbon monoxide produced remained constant within the accuracy of the measurements.

The above results not only explain fully the process of thermal decomposition of barium oxalate, but also provide an excellent demonstration that the combined derivatographic and thermo-gas analytical method is suitable for the investigation of thermal decomposition processes where carbon dioxide and carbon monoxide are simultaneously formed.

SUMMARY

The thermal decomposition of barium oxalate was investigated in a nitrogen atmosphere, by a combined derivatographic and thermo-gas analytical method. In contrast to studies conducted in air, a portion of the carbon monoxide formed in the nitrogen atmosphere during the decomposition of oxalate, undergoes further decomposition to yield carbon dioxide and carbon. At higher temperatures, the liberated carbon reacts with barium carbonate, and carbon monoxide and barium oxide are formed.

RÉSUMÉ

On examine la décomposition thermique de l'oxalate de baryum en atmosphère azote, à l'aide d'une technique combinée dérivatographique et thermo-gaz analytique. Contrairement aux études effectuées dans l'air, une partie de l'oxyde de carbone formé dans une atmosphère azote au cours de la décomposition de l'oxalate se transforme pour donner anhydride carbonique et carbone. A des températures plus élevées, le carbone libéré réagit avec le carbonate de baryum; il se forme oxyde de carbone et oxyde de baryum.

ZUSAMMENFASSUNG

Die thermische Zersetzung von Bariumoxalat in Stickstoffatmosphäre wurde untersucht mit einer kombinierten derivatographischen und thermogasanalytischen Methode. Im Gegensatz zu Untersuchungen, die in Luft ausgeführt wurden, bildet sich ein Anteil Kohlenmonoxid bei der Zersetzung des Oxalates, das dann weiterhin in Kohlendioxid und Kohlenstoff zerfällt. Bei höheren Temperaturen reagiert der freie Kohlenstoff mit dem Bariumcarbonat und Kohlenmonoxid und Bariumoxid werden gebildet.

REFERENCES

1 L. Erdey and F. Paulik, *Acta Chim. Acad. Sci. Hung.*, 7 (1955) 27.
2 L. Erdey and F. Paulik, *Magy. Tud. Akad. Kem. Tud. Oszt. Kozlemen.*, 5 (1955) 461.
3 B. V. Strizhkov, A. V. Lapitskii and L. G. Vlasov, *Zh. Neorgan. Khim.*, 7 (1962) 2352.
4 L. Walter-Levy and J. Laniepce, *Compt. Rend.*, 261 (1965) 3789.
5 F. Paulik, J. Paulik and L. Erdey, *Z. Anal. Chem.*, 160 (1958) 241; *Talanta*, 13 (1966) 1405.
6 J. Paulik, *Proc. Anal. Chem. Conf., Budapest, 1966*, Vol. III, p. 339.
7 J. Paulik, F. Paulik and L. Erdey, *Mikrochim. Acta*, (1966) 886; *Anal. Chim. Acta*, 34 (1966) 419; *Hung. Sci. Instr.*, No. 9 (1967) 7.

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SEPARATION AND PURIFICATION OF BERYLLIUM BY THE FRACTIONAL SUBLIMATION OF BERYLLIUM ACETYLACETONATE

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Studies[1–10] carried out in this laboratory in recent years have clearly shown that many metals can be isolated and purified by the fractional sublimation of their β-diketone chelates. The fractionation technique devised is simple, requires little time, and has proven surprisingly effective.

The purpose of the work reported in this paper is to demonstrate that the fractional sublimation technique is suitable for the isolation and purification of beryllium in the form of a β-diketone chelate when beryllium is present initially with a number of potentially contaminating metals. Beryllium is a relatively rare metal that occurs in nature principally as beryl, a double silicate of aluminum, but is also associated with yttrium, cerium and zirconium in the minerals gadolinite, muromontite, and cyrtolite and is alloyed in metallurgy principally with copper.

Of all the chelating ligands studied, acetylacetone offered the greatest promise for the purification of beryllium because the greatest separation factors were attainable with metal acetylacetonates. Table I lists the sublimation recrystallization temperature zones for a number of the more common metal acetylacetonates. These data clearly indicate that beryllium should be recoverable in a highly purified form as the acetylacetonate by fractional sublimation because its recrystallization temperature zone is far removed from those of all the other common metals with the exception of zinc. One certainly should anticipate that zinc is a potential contaminant in any fractional sublimation recovery of the beryllium acetylacetonate.

BERG AND HARTLAGE[7] demonstrated that synthetic mixtures of magnesium, aluminum and beryllium acetylacetonates could be quantitatively resolved by fractional sublimation and the aluminum and beryllium fractions recovered quantitatively. They showed also that when mixtures of magnesium, aluminum and beryllium salts were treated with acetylacetone, chelates could be collected, washed, dried and fractionally sublimed to yield aluminum and beryllium in pure fractions but the recoveries were not quantitative. The recovery yields were not quantitative because of an incomplete formation of the chelates and not because of an incomplete sublimation of the chelates placed in the sublimator. The formation of the chelates was very pH-dependent and the magnesium acetylacetonate formed only to a slight extent under the conditions required for the formation of the aluminum and beryllium acetylacetonates and consequently no magnesium sublimate was observed. Thus, ionic mixtures of magnesium, aluminum and beryllium were resolved by fractional sublimation (although magnesium was lost by default) but not recovered quantitatively. In the same paper[7] it was shown that synthetic mixtures of the acetylacetonates

TABLE I

SUBLIMATION RECRYSTALLIZATION TEMPERATURE ZONES FOR VARIOUS METAL ACETYLACETONATES[8,10]

Metal	*Temperature zone (°)*	*Metal*	*Temperature zone (°)*
Be(II)	31–15	Sc(III)	77–52
Mg(II)	141–120	Y(III)	nv
Ca(II)	203–167	Ce(III)	nv
Sr(II)	nv[a]	Zr(IV)	102–77
Ba(II)	nv	Th(IV)	116–78; 134–82
		U(IV)	129–92
		UO_2(II)	146–114
Al(III)	81–60		
Ga(III)	92–70	V(III)	111–94
In(III)	85–66	Cr(III)	106–80
		Mn(II)	90–70
		Cu(II)	102–82
Fe(III)	85–66		
Co(II)	88–67	Zn(II)	38–31
Ni(II)	111–88	Cd(II)	137–117
Pd(II)	94–74	Hg(II)	75–55
Pt(II)	102–80		
Rh(III)	118–96	Lanthanides	nv

[a] nv = non-volatile.

of nickel, iron and beryllium could be resolved with the quantitative recovery of the beryllium.

The present study was undertaken to demonstrate the more general applicability of the fractional sublimation technique for the isolation and purification of beryllium and to establish some limits on the degree of purification attainable.

EXPERIMENTAL

Reagents

Acetylacetone (2,4-pentanedione; Matheson, Coleman and Bell) was used without further purification. All other reagents used were of reagent grade.

Apparatus

A schematic diagram of, and specifications and operating procedures for, the fractional sublimator used in this work were reported earlier[7]. Briefly, the apparatus consists of a 1-m (11-mm o.d.) pyrex tube with a continuous temperature gradient maintained along its length and evacuated to 1 mm of mercury pressure with a carrier gas (air) flowing from the high-temperature to the low-temperature end of the sublimator.

The sample which had been chelated with acetylacetone was placed in a small glass boat and inserted into the high-temperature end of the sublimator and carrier gas passed over the sample for 2 h at 1 mm pressure. The chelates present in the sample recrystallized on the walls of the pyrex tube in discrete and reproducible temperature zones. The individual chelate fractions were recovered by cutting the pyrex tube into appropriate lengths to match the chelate crystal zones. The sublimate was recovered by mechanically scraping the solid from the tube and/or by dissolving the sublimate in acetone and evaporating off the solvent.

The spectroscopic purity of the recovered fractions was established with a Perkin-Elmer (model 303) atomic absorption spectrometer with an air–acetylene flame. A single-element hollow-cathode lamp was used as the source of radiation.

Preparation of pure metal chelates

Exact procedures for the preparation of the various metal chelates studied have been described previously[2,3,6,9]. The following general procedure was found suitable in most instances.

An excess of a 5% solution of the metal nitrate (sulfate in the case of beryllium) buffered with sodium acetate was added to an alcoholic solution of the ligand. If the chelate did not precipitate quickly, the solution was evaporated on a steam bath until precipitation occurred. The precipitate was collected by filtration, washed and air-dried. In most cases the crude material was recrystallized from ethanol or ethanol and water. In cases where the chelates would not dissolve in ethanol, benzene and petroleum ether were used.

Standard procedure for sample treatment

Dissolved samples containing beryllium(II) were made 0.5 M with ammonium thiocyanate, the pH was adjusted to about 7 with sodium acetate and an alcoholic solution of acetylacetone was added to precipitate the acetylacetonate. The precipitate was filtered, washed, dried and transferred to the sublimation apparatus. The sample of chelate was fractionally sublimed for 2 h at 170° at 1 mm mercury pressure with air as a carrier gas. The sublimate zone was recovered mechanically or by dissolving in an appropriate solvent such as acetone.

RESULTS AND DISCUSSION

In most of the fractional sublimation studies which involved the metal acetylacetonates it has been observed that the sublimate zones are well defined. Generally the high-temperature end of the zone is sharply defined whereas the low-temperature end may be somewhat diffuse. One may conclude, therefore, from the sublimation recrystallization temperature zones of the common metal acetylacetonates reported in Table I, that beryllium can be separated from all the common metals (except zinc) by the fractional sublimation of the beryllium acetylacetonate. Earlier studies[6–10] showed that the recrystallization zone data were a reliable guide for predicting separation. Consequently, there is no reason to doubt the significance of the data when applied to the isolation of beryllium. To further confirm this idea, binary mixtures of weighed quantities of the acetylacetonates of beryllium and one other metal (Mg, Al, Cu, Mn or Zn) were fractionally sublimed. The data are presented in Table II. The beryllium was recovered quantitatively from each binary mixture. All visual checks of the sublimate zones made before individual fractions were recovered from the sublimator indicated that zinc was the only metal that contaminated the beryllium fraction. This was confirmed by digesting each of the beryllium fractions in a nitric acid solution which was evaporated nearly to dryness and diluted to 10.0 ml with distilled water. The aqueous solution was then fed into the air–

acetylene flame of the atomic absorption spectrometer and checked for the presence of the potentially interfering metal with the appropriate hollow-cathode source. Only zinc was detected as a contaminant in the beryllium fractions. The concentration of zinc found in the dissolved beryllium fraction was 0.5 p.p.m. which corresponds to 5 μg of zinc in the 5.3 mg of beryllium acetylacetonate recovered or a 0.1% contamination. Because the limits of detection by atomic absorption measurements are 0.02, 1.9, 0.15, 0.02 and 0.04 p.p.m. for Mg, Al, Cu, Mn and Zn respectively, one must conclude that the beryllium fractions were contaminated by *less* than 0.2 μg Mg, 19 μg Al, 1.5 μg Cu and 1.0 μg Mn. There is nothing, however, to suggest that the level of contamination by these elements even approaches this limiting value.

TABLE II

RECOVERY DATA FOR THE FRACTIONAL SUBLIMATION OF BERYLLIUM ACETYLACETONATE IN MIXTURE WITH OTHER METALS

Mixture	*mg Be taken*	*mg Be found*	*mg second metal taken*	*% Be recovered*
Be–Al	4.7	4.69	4.2	100
Be–Mg	5.8	5.8	4.6	100
Be–Cu	4.9	4.91	4.3	100
Be–Mn	4.5	4.48	3.6	100
Be–Zn	5.3	5.31	6.1	100

Various attempts were made to improve the separation of Be–Zn mixtures by altering system parameters such as sample size, relative amounts of metals taken, and the maximum temperature of the sublimation, but to no avail; all beryllium fractions were found to be contaminated by zinc.

Inasmuch as it was not possible completely to resolve the mixture of beryllium and zinc acetylacetonates by fractional sublimation, it was recognized that a successful purification of beryllium would depend upon the selective formation of the beryllium acetylacetonate in the presence of zinc. Solutions containing beryllium and zinc salts were buffered to about pH 7 with sodium acetate and added to an alcoholic solution of acetylacetone. The precipitate, mixed acetylacetonates, was filtered, washed, dried and fractionally sublimed. In every instance the recovered beryllium fraction was contaminated with zinc to about the same extent reported for the separation of the synthetic mixtures of the Be–Zn acetylacetonates.

Next, various masking agents were introduced to the salt mixture before mixing with acetylacetone, in order to find an agent that would mask the zinc, but permit the formation of the beryllium acetylacetonate. It was found that a 3-fold excess (compared to the zinc) of EDTA (ethylene diaminetetraacetic acid) was effective in sequestering the zinc but not the beryllium. To check the effectiveness of EDTA as a masking agent for zinc, a mixture of salts was prepared as a synthetic sample for study. The salt mixture contained 1.3108 g of manganese(II) acetate, 1.3720 g of aluminum(III) acetate, 2.85 g of magnesium(II) acetate, 2.2108 g of copper(II) acetate, 1.009 g of zinc(II) acetate, and 2.0990 g of beryllium(II) sulfate. The mixture was dissolved in water and diluted to 250 ml. Excess of EDTA was added to the solution, and then sodium acetate was added to adjust the pH to about 7. After this solution had been mixed with an alcoholic solution of acetylacetone, the acetylacetonate was filtered, washed, dried and fractionally sublimed. The recovered beryllium sublimate was checked by atomic absorption spectrometry for the presence of each potential contaminant. Only zinc was detected as a contaminant and its concentration was so low as to be detected but not determined. On the basis of the known detection limit for zinc with the atomic absorption spectrometer it was established that the beryllium sublimate contained no more than 0.4 μg of zinc.

Thiocyanate appeared to be a better masking agent for zinc. Two samples were prepared for study which possessed approximately a 1:1 and 1:10 Be:Zn ratio respectively. For the 1:1 Be:Zn mixture, 0.7965 g of beryllium(II) sulfate was mixed with 0.7700 g of zinc(II) nitrate. For the 1:10 Be:Zn mixture, 1.1475 g of beryllium(II) sulfate were mixed with 12.1257 g of zinc(II) nitrate. The mixtures were dissolved in water and made 0.5 *M* with ammonium thiocyanate and the pH was adjusted to near 7 with sodium acetate. An alcoholic solution of acetylacetone was added to precipitate the beryllium acetylacetonate, which was filtered, washed, dried and weighed; 0.6322 and 0.7202 g of precipitate were obtained for the two samples respectively. Weighed portions of each precipitate, 6.3 mg and 5.6 mg, respectively, were sublimed and recovered by dissolving in 3.0 ml of acetone. The acetone solutions were checked directly for zinc by atomic absorption spectrometry but no zinc was detectable in the beryllium fractions; from the limit of detection by standard atomic absorption techniques, one must conclude that the beryllium acetylacetonate sublimate contains less than 0.002% zinc. Similar results were obtained for the purification of beryllium when mixtures containing Al, Cu, Mg, Mn, Zn and Be in roughly equal molar quantities were treated in the same fashion.

There is unfortunately one serious shortcoming to this procedure. Although all the beryllium acetylacetonate which is formed can be quantitatively recovered from the sublimate, it has not been possible to devise a procedure that yields a quantitative precipitation of the beryllium acetylacetonate. The average yield of the beryllium acetylacetonate was only 62% but this was recoverable after a single sublimation in high purity. The fractional sublimation of beryllium acetylacetonate which has been formed in the presence of ammonium thiocyanate to mask zinc appears to be an excellent method to purify beryllium if quantitative yields are not required. The authors believe, however, that by recovering the freshly formed beryllium acetylacetonate by solvent extraction the overall recovery yields can be increased to nearly 100 per cent.

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SUMMARY

Solutions containing beryllium(II) in admixture with most common metals can be treated with acetylacetone to form the beryllium and various other acetylacetonates which precipitate. The precipitate is filtered, washed, dried and fractionally sublimed in a special sublimator. After sublimation with air as a carrier gas the beryllium acetylacetonate fraction is recoverable in high purity. Zinc is the only detectable contaminant by atomic absorption spectrometry but can be eliminated by masking with ammonium thiocyanate before the formation of the metal acetylacetonates. Beryllium fractions were checked for purity by atomic absorption spectrometry and

found to contain less than 0.002% Zn after a single sublimation. The method appears to offer an excellent method of purification for beryllium if quantitative recoveries are not required.

RÉSUMÉ

On peut traiter avec l'acétylacétone des solutions contenant du béryllium(II) mélangé à plusieurs métaux communs de façon à former l'acétylacétonate de béryllium et d'autres acétylacétonates divers qui précipitent. Le précipité est filtré, lavé, séché et subit une sublimation fractionnée dans un sublimateur spécial. Après sublimation, la fraction de l'acétylacétonate de béryllium est récupérée avec un haut degré de pureté en utilisant l'air comme gaz porteur. Le zinc est le seul contaminant lors de la détection par spectrophotométrie d'absorption atomique, mais on peut l'éliminer en masquant avec du thiocyanate d'ammonium avant la formation des acétylacétonates de métaux. La pureté des fractions de béryllium est contrôlée par spectrophotométrie d'absorption atomique; on trouve moins de 0.002% de zinc après une seule sublimation. La méthode apparaît comme excellente pour la purification du béryllium si des récupérations quantitatives ne représentent pas le but recherché.

ZUSAMMENFASSUNG

Aus Lösungen die Beryllium(II) zusammen mit den meisten üblichen Metallen enthalten, kann das Beryllium zusammen mit zahlreichen anderen Metallen als Acetylacetonat gefällt werden. Der Niederschlag wird filtriert, gewaschen und getrocknet und in einer Spezialapparatur fraktioniert/sublimiert. Nach der Sublimation mit Luft als Trägergas wird die Fraktion des Beryllium-Acetylacetonats in hoher Reinheit zurückgewonnen. Als einzige Verunreinigung wird Zink mit der Atomabsorption nachgewiesen, jedoch kann es durch Maskierung mit Ammoniumthiocyanat vor der Bildung der Metallacetylacetonate eliminiert werden. Das Verfahren scheint eine ausgezeichnete Methode zur Reinigung von Beryllium zu sein, wenn quantitative Rückgewinnungen nicht erforderlich sind.

REFERENCES

1 J. T. Truemper, *A Study of the Volatile Characteristics of Various Metal β-Diketone Chelate Compounds*, Ph.D. Dissertation, Louisiana State University, Baton Rouge, La, 1959.
2 E. W. Berg and J. T. Truemper, *J. Phys. Chem.*, 64 (1960) 487.
3 E. W. Berg and J. T. Truemper, *Anal. Chim. Acta*, 32 (1965) 245.
4 H. W. Dowling, *A Study of the Volatile Characteristics of Some Co(III) and Fe(II) β-Diketone Chelate Compounds*, M.S. Thesis, Louisiana State University, Baton Rouge, La, 1960.
5 E. W. Berg and H. W. Dowling, *J. Chem. Eng. Data*, 6 (1961) 556.
6 F. R. Hartlage, Jr., *Sublimation Separation Studies of Various Metal β-Diketone Chelate Compounds*, Ph.D. Dissertation, Louisiana State University, Baton Rouge, La, 1964.
7 E. W. Berg and F. R. Hartlage, Jr., *Anal. Chim. Acta*, 33 (1965) 173.
8 E. W. Berg and F. R. Hartlage, Jr., *Anal. Chim. Acta*, 34 (1966) 46.
9 J. J. Chiang A., *A Study on the Volatility of the β-Diketone Chelates of Group III B Elements*, Ph.D. Dissertation, Louisiana State University, Baton Rouge, La, 1967.
10 E. W. Berg and J. J. Chiang A., *Anal. Chim. Acta*, 40 (1968) 101.

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ETUDE DE L'EVOLUTION THERMIQUE DU BROMATE DE BARYUM

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Le bromate de baryum est un sel suffisamment peu soluble pour être préparé aisément par double décomposition entre un sel de baryum et un bromate alcalin. Il cristallise avec une molécule d'eau environ. Son étude structurale par infrarouge[1] est compatible avec un ion BrO_3^- pyramidal (symétrie C_{3v}).

ν_1	ν_3	ν_2	ν_4
815 cm^{-1}(m)	780–790 cm^{-1}(TF)	435 cm^{-1}(F)	360–390 cm^{-1}(F)

(m = moyenne; TF = très forte; F = forte).

Certains dédoublements des maximums caractéristiques sont vraisemblablement dus au fait que la symétrie de site est inférieure à celle de l'ion libre. L'eau de cristallisation se manifeste par deux bandes de vibration de valence à 3450 et 3510 cm^{-1} et une bande de déformation à 1595 cm^{-1}.

La courbe de thermolyse de ce bromate (prise d'essai 150 à 250 mg) effectuée à l'air à l'aide de thermobalances ADAMEL en *chauffage dynamique* (150°/h) montre que la déshydratation est totale vers 160–180°. Le sel anhydre formé reste stable jusque vers 300°. Il se décompose alors avec perte d'oxygène. La transformation en bromure est totale vers 400°. En utilisant un thermoanalyseur Mettler beaucoup plus sensible, on observe que le palier AB correspondant au sel anhydre (Fig. 1) est légèrement incliné, traduisant une perte de poids de 0.5% environ.

Les températures correspondant aux divers accidents de la courbe de thermolyse varient d'un instrument à l'autre. Ces écarts sont surtout dus aux diverses positions du thermocouple par rapport au creuset. C'est avec le thermoanalyseur Mettler que la température mesurée représente le mieux la température vraie de l'échantillon.

Thermobalance	*Prise d'essai (mg)*	*Températures (°)*			
		t_A	t_B	t_C	t_D
ADAMEL (1)	200–250	180	320	355	390
ADAMEL (2)	150	160	300	315	360
Mettler	100	160	290	310	360

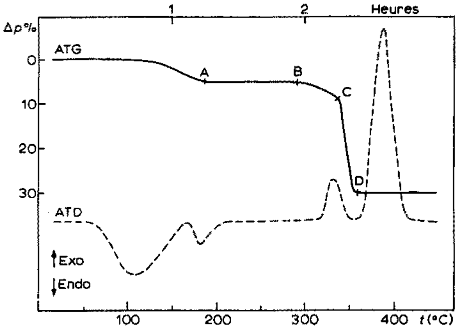
La courbe d'analyse thermique différentielle du bromate de baryum hydraté est présentée également sur la Fig. 1 (appareils utilisés: thermoanalyseur Mettler ou microanalyseur Bureau de Liaison).

ÉTUDE DE LA DÉSHYDRATATION DU BROMATE DE BARYUM

Les spectres d'absorption infrarouge (spectrophotomètre Beckman IR-12, poudre entre lames en CsBr, ou pastilles de KBr) de divers prélèvements effectués entre 180° et 290° (points A et B de la courbe d'A.T.G.) présentent des caractéristiques différentes de celles du bromate de départ (Fig. 2).

ν_1	ν_3	ν_2	ν_4
845 cm^{-1}(F)	790 cm^{-1}(TF)	440–430 cm^{-1}(F)	390–380–360 cm^{-1}(m)

Deux faits nouveaux sont à relever: l'apparition d'une bande intense à 845 cm^{-1} et le dédoublement de la bande de 440 cm^{-1}. Si le produit est laissé à l'air, il se réhydrate et son spectre se modifie peu à peu (les cuves précédentes étaient confectionnées à l'abri de l'humidité). Au bout de quelques heures, il est identique à celui du bromate à une molécule d'eau, mis à part le dédoublement de ν_3 qui est alors très faible.



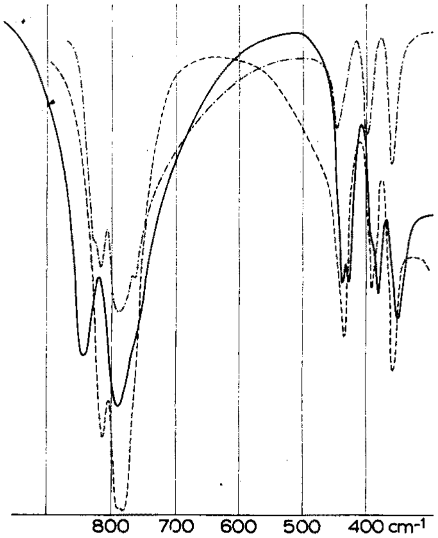


Fig. 1. Courbes de thermolyse (A.T.G.) et d'analyse thermique différentielle (A.T.D.) du bromate de baryum hydraté.

Fig. 2. Spectres d'absorption infrarouge du bromate de baryum hydraté, du bromate anhydre I et du bromate anhydre II. (——) bromate II; (—.—) bromate I; (— — —) bromate à 1 H_2O.

La présence de la bande forte à 845 cm^{-1} peut suggérer qu'il se forme du perbromate à partir du bromate au cours du chauffage, dans une réaction sans changement de poids, du type:

$$4\ BrO_3^- \rightarrow 3\ BrO_4^- + Br^-$$

par analogie avec la formation de perchlorate à partir de chlorate[2]. Cette transformation ne serait que partielle, car le spectre infrarouge montre toujours les bandes de bromate. La formation de perbromate impliquant celle de bromure, nous avons recherché celui-ci dans les différents résidus de chauffe entre 180° et 290°. L'analyse à la touche permet de déceler la présence de bromure, mais en quantité si faible qu'elle s'interprète plus vraisemblablement par une décomposition partielle du bromate avec perte d'oxygène (inférieure à 0.5%). D'après la réaction précédente, la proportion de perbromate formé serait également très faible et ne pourrait donc pas donner lieu à la forte absorption observée à 845 cm^{-1}. L'hypothèse de formation de perbromate semble donc peu probable. La recherche des perbromates s'est d'ailleurs toujours soldée par un échec[3]. URCH[4] a tenté d'expliquer cet insuccès en étudiant théoriquement la liaison X–O dans différents anions XO_n^{p-}. Il montre que la liaison π entre les orbitales $2\,p$ de l'oxygène et $4\,d$ du brome est très peu importante: d'où la non-existence des perbromates.

Nous rejetons donc l'hypothèse de formation de perbromate. Il faut plutôt envisager l'existence de *bromate anhydre*, dont le spectre d'absorption infrarouge présente des déplacements des bandes caractéristiques par rapport à celles du bromate hydraté. Il est fréquent que la déshydratation entraîne une modification du réseau cristallin avec des changements de symétrie décelables sur le spectre infrarouge.

Nous avons ensuite déshydraté le bromate de baryum par des *chauffages isothermes*. Le maintien à 105, 110 ou 120° pendant quelques heures conduit à un composé répondant à la formule $Ba(BrO_3)_2$. Son spectre infrarouge est cependant différent de celui du bromate anhydre précédent (appelé bromate II) (pas de bande à 845 cm^{-1}, pas de dédoublement de celle de 440 cm^{-1}). Ce bromate (que nous appellerons bromate I) se transforme en bromate II quand on élève la température. Le Tableau I résume les résultats obtenus (en cm^{-1}) pour le bromate hydraté, le bromate I et le bromate II (TF = très forte, F = forte, m = moyenne).

Les spectres de poudres (rais Kα du cobalt) du bromate hydraté et des bromates I et II sont différents (Fig. 3). Il est à noter cependant la grande similitude entre

TABLEAU I

SPECTRES INFRAROUGES DES BROMATES

	ν_1	ν_3	ν_2	ν_4
Bromate à 1 H_2O	815 (m)	780–790 (TF)	435 (F)	360–390 (F)
Bromate I	815 (m)	790 (TF)	450 (F)	400–360 (F)
Bromate II	845 (F)	790 (TF)	440–430 (F)	390–380–360 (m)

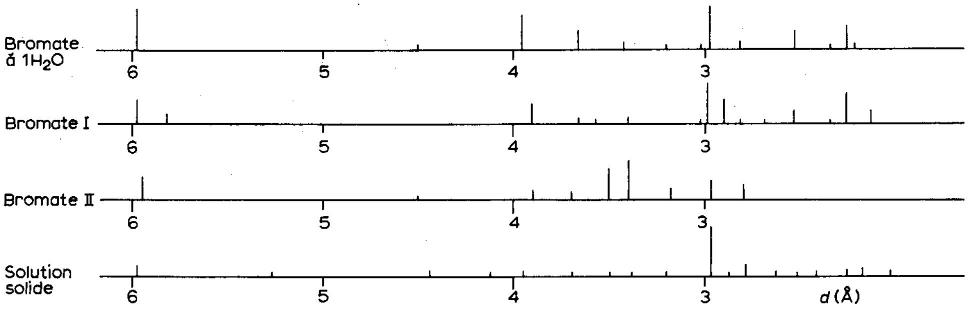


Fig. 3. Spectres X du bromate hydraté, des bromates anhydres I et II et de la solution solide formée au cours de la décomposition thermique du bromate de baryum.

les spectres d'absorption infrarouge et les spectres X du bromate à 1 H_2O et du bromate I.

On peut mettre aussi en évidence les bromates I et II par analyse thermique différentielle. On observe un premier pic endothermique s'amorcant vers 60° (Fig. 1), et correspondant au départ de la molécule d'eau, suivi d'un second pic endothermique moins intense débutant vers 160°. On peut séparer ces deux pics endothermiques en ralentissant le chauffage aux environs de 100°, jusqu'à disparition totale de l'eau de cristallisation. Le produit prélevé entre les deux pics est identique au bromate I. La courbe d'A.T.D. du bromate I présente le pic endothermique vers 160°; mais celle du bromate II ne le présente pas. On peut donc attribuer ce deuxième pic à la transformation du bromate I en bromate II. Le spectre infrarouge du produit prélevé après ce pic présente d'ailleurs bien les caractéristiques du bromate II.

L'étude de la déshydratation du bromate de baryum permet donc de mettre en évidence deux types de bromate anhydre, caractérisés par des spectres d'absorption infrarouge et des spectres X différents.

ÉVOLUTION THERMIQUE DU BROMATE II (AVEC FORMATION D'UNE SOLUTION SOLIDE)

Considérons de nouveau la courbe de thermolyse du bromate de baryum (Fig. 1). En chauffage dynamique, on observe une perte de poids s'effectuant lentement entre B et C, puis rapidement jusqu'en D, qui marque le début du palier du bromure de baryum. Cette décomposition en deux temps est décelable également sur la courbe d'analyse thermique différentielle (deux pics exothermiques débutant à 320° (assez fort) et à 360° (très fort)).

Détermination de l'ordre de la réaction

Nous avons utilisé la méthode de HOROWITZ[5] pour déterminer l'ordre de la réaction de décomposition, et éventuellement l'énergie d'activation E^*. Dans cette méthode, on étudie les variations de log log $(w_0-w_f)/(w-w_f)$ en fonction de $\theta=T-T_s$, avec les significations suivantes:

w_0 = poids initial
w_f = poids final
w = poids au temps t
T = température au temps t
T_s = température correspondant à la valeur w, telle que $(w-w_f)/(w_0-w_f)=1/e$.

Dans le cas d'une réaction du premier ordre, log log $(w_0-w_f)/(w-w_f)$ est une fonction linéaire de θ. La pente de la droite vaut $E^*/R\,T_s^2$.

Pendant la première partie de la décomposition (portion BC de la courbe d'A.T.G.), on obtient une droite, à laquelle correspond pour E^* une valeur de 47.5 kcal/mole. Nos résultats sont à rapprocher de ceux de BANCROFT ET GESSER[3], qui trouvent 52 kcal/mole. Dans la portion CD, les points s'alignent de nouveau, avec une pente différente. La valeur de E^* est alors égale à 182 kcal/mole.

Identification des phases au cours de la perte d'oxygène (portion BD de la courbe d'A.T.G.)

Chauffage dynamique. Le spectre d'absorption infrarouge d'un prélèvement effectué entre B et C est presque identique à celui du bromate II. On voit apparaître cependant deux épaulements vers 800 cm^{-1} et vers 410 cm^{-1} (non présents dans le spectre du bromate II). A partir de C, les caractéristiques du spectre du bromate II s'affaiblissent; on relève les maximums suivants (en cm^{-1}): 845 (m), 800 (m et fine), 780 (TF), 440 (F), 410 (m), 385 (F), 360 (f). La bande de 845 cm^{-1} disparaît très vite après exposition du produit à l'air: elle est remplacée par une bande faible vers 820 cm^{-1} (ν_1 du bromate hydraté), mais la bande fine et nette de 800 cm^{-1} subsiste toujours. Il est à noter que le spectre d'un produit prélevé entre C et D, différent des spectres des bromates I et II, présente aussi les caractéristiques d'un spectre de BrO_3^- (Fig. 4).

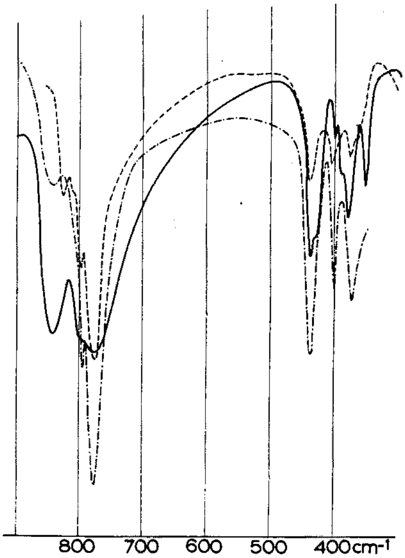


Fig. 4. Spectres d'absorption infrarouge de divers prélèvements entre B et D (avant et après lavage à l'éthanol). (——) prélèvement entre B et C; (—.—) prélèvement entre C et D; (— —) idem, après lavage EtOH.

Le spectre infrarouge du produit prélevé entre C et D et laissé à l'air est pratiquement identique à celui du *bromite de baryum* étudié par TANGUY *et al.*[6]. Par dégradation thermique ménagée du bromate de baryum (maintien à 270° pendant une dizaine d'heures au minimum, sous pression d'oxygène d'un bar), ces auteurs mettent en évidence, par diffractométrie X et par spectrométrie infrarouge, l'apparition d'une nouvelle phase qu'ils identifient à du bromite de baryum. Ce dernier se formerait par réaction du bromure libéré sur le bromate restant. Nous avons vérifié par des maintiens en thermostat que l'on obtenait également le même produit (même spectre infrarouge, même spectre X).

Dans tous les prélèvements entre B et D, on décèle par analyse à la touche des quantités importantes de bromure de baryum, que nous avons essayé d'éliminer par des lavages répétés à l'éthanol anhydre en atmosphère sèche. On constate qu'une partie seulement du bromure théoriquement formé s'élimine sous l'action de l'alcool. Si le prélèvement est fait aux alentours du point C, les lavages n'enlèvent que peu (ou pas) de bromure. Après lavages jusqu'à l'obtention d'un poids constant, on a mesuré le pouvoir oxydant en milieu acide des produits restants. Les dosages iodométriques doivent permettre de distinguer $Ba(BrO_2)_2$ *pur* de $Ba(BrO_3)_2$ *pur*: une mole de bromite libère 2 moles d'iode, alors qu'une mole de bromate en libère 3. Si l'on a affaire à un mélange bromate–bromure, le pourcentage de brome actif diminue, et, pour le mélange particulier 72.6–27.4% bromate–bromure, tout se passe comme si l'on avait du bromite pur. Les produits recueillis vers le point C présentent des teneurs en brome actif variant de 28.1 à 34.7% (compté en bromate) ou de 42.1 à 52.1% (compté en bromite). TANGUY *et al.* trouvent un pourcentage de 44.6 (compté en bromite), très voisin du pourcentage théorique 44.2 correspondant au bromite pur. Nos résultats s'en écartent plus. Ils varient d'un essai à l'autre et manifestent également une certaine hétérogénéité.

Si, après lavages à l'éthanol jusqu'à poids constant, on opère des lavages au méthanol, dans lequel le bromure est beaucoup plus soluble, on peut éliminer tout ce dernier. On obtient alors un résidu de bromate, caractérisé par sa teneur en brome actif, son spectre infrarouge, son spectre X et sa courbe d'A.T.D.

Les seules mesures de pouvoir oxydant en milieu acide ne peuvent pas nous permettre d'affirmer si l'on a affaire à du bromite ou à du bromate (l'un ou l'autre avec des quantités variables de bromure qu'on ne peut éliminer par l'éthanol). Considérons donc de nouveau le spectre infrarouge de ce produit. Supposons que ce soit du bromite de baryum (ion BrO_2^- de symétrie C_{2v}). La comparaison avec les spectres d'absorption infrarouge de l'ion ClO_2^- [7] et IO_2^- [8] permet de supposer que la vibration de valence symétrique ν_1 de l'ion BrO_2^- sera située entre 700 et 625 cm^{-1}. L'expérience le vérifie, car EVANS[9] attribue à cette vibration la forte bande polarisée qu'il observe à 700 cm^{-1} dans les spectres Raman de divers bromites, ainsi que dans leurs spectres d'absorption infrarouge. Cette valeur de 700 cm^{-1} est compatible avec la constante de force k(Br–O) de 4.2 mdynes/Å, qui se place de manière satisfaisante dans les deux séries indiquées ci-dessous:

	k (mdynes/Å)		*k (mdynes/Å)*		*k (mdynes/Å)*
ClO_3^-	5.7	ClO_2^-	4.35	ClO^-	3.3
BrO_3^-	5.2	BrO_2^-	*4.2*	BrO^-	3.0

D'après ce tableau, et avant toute attribution, on doit s'attendre à trouver la constante k de BrO_2^- inférieure à celle de ClO_2^-. Or TANGUY *et al.*, attribuant la bande de 775 cm^{-1} à la vibration ν_1, trouvent pour k la valeur très élevée de 4.87 mdynes/Å, qui ne permet pas à l'ion BrO_2^- de prendre place dans la série BrO_n^- comparée à la série ClO_n^-. Le fait que toutes les bandes du spectre infrarouge du produit en question se trouvent dans les régions caractéristiques de l'ion BrO_3^-, et qu'aucune bande ne soit décelable à 700 cm^{-1}, n'est pas en faveur de la présence de bromite.

Par ailleurs les bromites, à l'encontre des bromates, présentent un pouvoir oxydant sur l'anhydride arsénieux en milieu alcalin. Or tous les essais ont conduit à un pouvoir nul à pH 8 et à pH 10.

La formation de bromite nous semble donc peu probable. Comme on obtient des teneurs en brome actif variables, et un spectre infrarouge qui ressemble à celui d'un bromate, on peut penser plutôt à la formation d'une solution solide de bromure dans le bromate, une partie du bromure formé au cours de la décomposition du bromate étant retenue dans le réseau du bromate, et ne pouvant être éliminée par lavages à l'éthanol.

Cette hypothèse semble confirmée par les études par diffractométrie X. Les différences entre les spectres X du bromate hydraté, des bromates I et II et de la solution solide ne résident pas dans la *position* des raies mais dans leurs *intensités relatives*. Ainsi, les raies de 2.97 et 5.96 Å, très intenses dans les spectres du bromate hydraté et du bromate I, deviennent peu importantes dans le spectre du bromate II, qui est surtout caractérisé par le doublet intense 3.40–3.46 Å. Quant à la solution solide, son spectre X présente essentiellement une raie à 2.97 Å ($I/I_0 = 100$) (pour toutes ses autres raies, I/I_0 est inférieur à 20). Quand on passe du bromate à 1 H_2O à la solution solide bromate–bromure, on voit donc certaines raies intenses s'affaiblir. Lorsque le réseau du bromate s'appauvrit progressivement en atomes d'oxygène, il retient inclus du bromure de baryum formé *in situ*. Ce bromure, dont la teneur peut atteindre 29.7% du poids de la solution, ne peut être chassé par lavages à l'éthanol, et ne peut être décelé que si l'on détruit la solution solide (par exemple par mise en solution dans l'eau). La présence de bromure dans le réseau du bromate entraîne une modification du spectre infrarouge du bromate, ce qui est conforme aux résultats obtenus généralement avec les solutions solides.

La courbe d'A.T.D. de la solution solide (lavée à l'éthanol) est différente de celle du bromate hydraté. Elle présente un pic exothermique débutant vers 240°, d'intensité variable. La décomposition a lieu à une température inférieure à celle du bromate seul: elle se traduit par un seul pic exothermique débutant à 325°. Par ailleurs la courbe de thermolyse ne montre pas de discontinuité au cours de la décompo-

TABLEAU II

CHAUFFAGES ISOTHERMES

Température (°) (échantillon au contact du thermocouple)	*Durée thermostat (h)*	*Atmosphère (1 bar)*	*Phases identifiées par IR, RX, A.T.D.*	*Perte de poids (%)*
220	Jusqu'à 140 h	Air	Bromate II	0
240	15	Air	Bromate II	0.2
	63	Air	Bromate II + solution solide	1.5
	81	Air	Bromate II + solution solide	2.4
245	21	Air	Bromate II + solution solide	5
250	20	Oxygène	Bromate II + solution solide	8
	18	Azote	Bromate II + solution solide	8
255	20	Air	Bromate II + solution solide + carbonate	10.5
260	20	Oxygène	Bromate II + solution solide	22
	20	Azote	Bromate II + solution solide	22
270	21	Air	Bromate II + solution solide + carbonate	22
280	15	Air	Carbonate + bromure	29

sition. La solution solide se montre un peu moins stable sous l'action de la chaleur que le bromate de départ.

Si, après avoir porté la solution solide vers 290–300° (avant le pic de décomposition), on la laisse refroidir puis la chauffe de nouveau jusqu'à décomposition, on n'observe pas de pic exothermique débutant à 240°. Ce pic pourrait correspondre à une organisation de la solution solide.

Chauffage isotherme. Nous avons également étudié les produits formés par maintiens en thermostat du bromate de baryum à différentes températures. Mise à part la possibilité de formation de carbonate, les chauffages isothermes conduisent à des résidus analogues à ceux obtenus en chauffage dynamique. L'ensemble des résultats est consigné dans le Tableau II. La perte de poids théorique pour atteindre la solution solide est de 7.7%.

Il ressort de ces essais que si le bromate anhydre II est très stable à 220°, il n'en est plus de même à 240°. En perdant très lentement de l'oxygène, il se transforme peu à peu en solution solide.

ÉTUDE DE LA RÉACTION POSSIBLE DANS LES MÉLANGES BROMATE–BROMURE (2/1) PORTÉS À DIFFÉRENTES TEMPÉRATURES

La solution solide qui se manifeste vers 320° quand on chauffe le bromate de baryum présente à peu près la composition du mélange de deux molécules de bromate et d'une molécule de bromure. C'est pourquoi nous avons cherché si ces deux composés mélangés anhydres dans le même rapport pouvaient se combiner à plus basse température par un chauffage approprié.

Mélanges bromate–bromure (2/1) chauffés jusqu'à la décomposition. De tels mélanges fournissent une courbe d'A.T.D. très semblable à celle des constituants pris séparément. Il ne semble pas se manifester de combinaison au cours de ce chauffage avant la décomposition du bromate.

Mélanges bromate–bromure (2/1) chauffés jusqu'à 320°. Comme dans le cas du bromate chauffé seul, le résidu de tels mélanges chauffés à 320° est identique (après lavage à l'éthanol) à la solution solide étudiée plus haut (même teneur en brome actif, même spectre infrarouge, même courbe d'A.T.D.).

Mélanges bromate–bromure (2/1) gardés en thermostats à 280°, 240° et 220°. Les résultats sont analogues à ceux obtenus avec le bromate seul.

RÉSUMÉ

L'analyse chimique, l'analyse thermogravimétrique (A.T.G.), l'analyse thermique différentielle (A.T.D.), la spectrophotométrie d'absorption infrarouge et la diffractométrie X, ont permis de mettre en évidence l'existence de deux formes cristallines du bromate de baryum anhydre, et la formation d'une solution solide au cours de sa décomposition thermique.

SUMMARY

Chemical, thermogravimetric, differential thermal, infrared spectroscopic and X-ray diffractometric analyses have been used to provide evidence for the existence of two crystalline forms of anhydrous barium bromate; a solid solution is formed during the thermal decomposition.

ZUSAMMENFASSUNG

Um die Existenz von 2 kristallinen Formen des wasserfreien Bariumbromats zu bestätigen, wurden chemische, thermogravimetrische, differentialthermische, infrarotspektroskopische und Röntgenstruktur-Analysen durchgeführt. Bei der thermischen Zersetzung wird eine feste Lösung gebildet.

BIBLIOGRAPHIE

1 C. Rocchiccioli, *Compt. Rend.*, 249 (1959) 236; *Ann. Chim. Paris*, 5 (1960) 999.
2 M. M. Markowitz, P. A. Boryta et H. Stewart, Jr., *J. Phys. Chem.*, 28 (1964) 2286.
3 G. M. Bancroft et H. D. Gesser, *J. Inorg. & Nucl. Chem.*, 27 (1965) 1545.
4 D. S. Urch, *J. Inorg. & Nucl. Chem.*, 25 (1963) 771.
5 H. H. Horowitz et G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
6 B. Tanguy, B. Frit, G. Turrell et P. Hagenmuller, *Compt. Rend.*, 264 série C (1967) 301.
7 J. P. Mathieu, *Compt. Rend.*, 234 (1952) 2272.
8 M. Harmelin et C. Duval, *Compt. Rend.*, 260 (1965) 2461.
9 J. C. Evans et G. Y. S. Lo, *Inorg. Chem.*, 6 (1967) 1483.

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STUDIES IN THE TETRAARYLBORATES

PART III. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE AND SODIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

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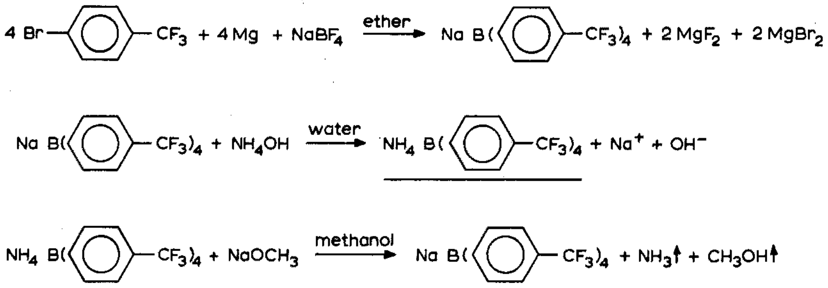
In a continuation of the study of substituent effects on reagent stability and selectivity, two new tetraaryl–boron compounds, sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate, have been prepared via a new experimental *in situ* procedure. Both compounds are more resistant to decomposition in acid media than sodium tetrakis(*p*-chlorophenyl) borate and sodium tetrakis(*p*-fluorophenyl) borate[1,2]. It is felt that electron density in the vicinity of the carbon to boron bonds has been adjusted so that susceptibility to electrophilic attack is reduced. This favorable property is derived from the inductive effect of the highly electronegative fluorine atom in the *m*-position and the strongly deactivating trifluoromethyl group in the *p*-position for the tetrakis(*m*-fluorophenyl) borate and tetrakis(*p*-trifluoromethylphenyl) borate anions, respectively.

EXPERIMENTAL

*Synthesis of sodium tetrakis(*p*-trifluoromethylphenyl) borate*

Sodium tetrakis(*p*-trifluoromethylphenyl) borate is synthesized by the following sequence of reactions:



Distill 400 ml of ether previously dried over sodium into a 500-ml 3-necked flask equipped with a stirrer, water-cooled condenser, thermometer and a dropping funnel. Transfer 100 ml of the freshly distilled ether to the dropping funnel, dissolve 45.0 g (0.2 mole) of *p*-bromobenzotrifluoride and arrange for dropwise addition to the flask. Add 4.9 g (0.2 mole) of dry magnesium turnings and 5.5 g (0.05 mole) of dry sodium fluoroborate to the 500-ml 3-necked reaction flask. Sweep the assembly with dry nitrogen. Add approximately 10 ml of the *p*-bromobenzotrifluoride solution to the flask while rapidly stirring the solution. The reaction generally starts within 20 min. When the reaction starts, immediately cool the reaction flask to 16° and maintain this temperature while the remaining 90 ml of solution is added dropwise over a 3-h period. After completing the addition, stir the reaction mixture for an additional 30 min while the temperature is allowed to rise to 25°.

Immediately pour the contents of the reaction flask onto 300 ml of crushed ice made slightly alkaline with dilute sodium hydroxide solution. Add *ca.* 1 g of sodium carbonate, and stir. A white precipitate of inorganic material forms in the aqueous layer. Separate the ether layer with a separatory funnel. Saturate the aqueous layer with sodium chloride and extract the aqueous phase 3 times with 50-ml portions of ether. Add these to the previously separated ether layer. Add 300 ml of slightly basic distilled water to the ether portion. Evaporate the ether while rapidly stirring the mixture and heating to 45°. Filter the ether-free aqueous solution through a "Celite" analytical filter aid mat and Buchner funnel arrangement. Transfer the filtrate to a 1-l beaker and dilute to 900 ml with distilled water. Heat the solution to 35° and slowly add dropwise a 2.5% ammonium hydroxide solution. Filter the ammonium tetrakis(*p*-trifluoromethylphenyl) borate and air-dry. Recrystallize the white ammonium salt twice from a methanol–water solution, filter and dry under vacuum over phosphorus pentoxide at 80°.

(Analysis: m.p. 185–6°; found, C 55.53%, H 3.50%, N 2.29%; calculated, C 55.25%, H 3.32%, N 2.30%.)

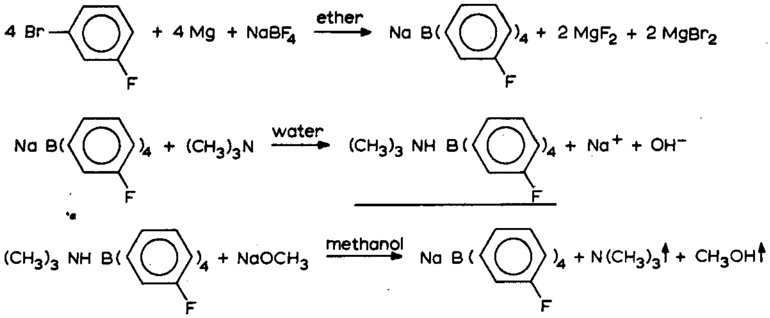
To prepare the pure sodium salt, dissolve 10 g (0.017 mole) of the ammonium salt in 150 ml of anhydrous methanol contained in a 250-ml 3-necked flask equipped with a stirrer, air-cooled condenser and a dropping funnel. Heat the solution to vigorous methanol reflux. Dissolve 1.8 g (0.033 mole) of sodium methylate in 75 ml of anhydrous methanol and add dropwise to the reaction flask. Ammonia gas escapes through the air condenser while the solution is vigorously refluxed for 4 h. Remove the air condenser and evaporate most of the methanol. Remove the remainder under vacuum at 70°. Dissolve the solid sodium salt in 100 ml of anhydrous ether and pass through a basic alumina adsorption column. The ether eluate, which amounts to about 400 ml, is removed using a rotary vacuum evaporator or air evaporation. Any remaining ether is removed under vacuum at 80°. The crystals of the white sodium salt start to appear when most of the ether has been removed. The salt crystallizes as the monohydrate, but the water of hydration can be removed by drying under vacuum and over phosphorus pentoxide at 80°. Yield 17.9 g.

(Analysis: found, C 53.06%, H 2.88%; calculated, C 53.19%, H 2.88%.)

*Synthesis of sodium tetrakis(*m*-fluorophenyl) borate*

Sodium tetrakis(*m*-fluorophenyl) borate is synthesized by the following sequence of reactions:

The procedure for the preparation of sodium tetrakis(*m*-fluorophenyl) borate



is similar to that described for the synthesis of sodium tetrakis(*p*-trifluoromethylphenyl) borate. The reaction assembly is identical. An ether solution of 35 g (0.2 mole) of *m*-fluorobromobenzene is added dropwise to a 500-ml 3-necked flask containing an ether mixture consisting of 4.9 g (0.2 mole) of dry magnesium turnings and 5.5 g (0.05 mole) of sodium fluoroborate. During the addition of the *m*-fluorobromobenzene solution, the temperature of the reaction flask is held at 30°. Extract the aqueous layer, as previously indicated, with ether. Evaporate the ether and dissolve the salt in 300 ml of water made slightly basic. Filter and precipitate the trimethylamine tetrakis(*m*-fluorophenyl) borate salt by dropwise addition of a 2.5% aqueous trimethylamine solution to the diluted tetrakis(*m*-fluorophenyl) borate anion solution. Filter the trimethylamine tetrakis(*m*-fluorophenyl) borate and dry under vacuum at 80°. Recrystallize the white amine salt twice from a methanol–water solution, filter and dry under vacuum and over phosphorus pentoxide at 80°. Yield 15.0 g.

(Analysis: m.p. 150–1°; found, C 71.78%, H 5.82%, N 3.12%; calculated, C 71.85%, H 5.82%, N 3.10%.)

To prepare the pure sodium salt, add dropwise a solution of 2.4 g (0.044 mole) of sodium methylate in 75 ml of anhydrous methanol to the previously described flask assembly containing 10 g (0.022 mole) of trimethylamine tetrakis(*m*-fluorophenyl) borate in 150 ml of anhydrous methanol at vigorous reflux. After addition of the sodium methylate solution, remove the air condenser to speed evaporation of the trimethylamine. Heat the reaction solution until there is no further liberation of trimethylamine. Remove the remaining methanol under vacuum at 70°. Dissolve the solid sodium salt in anhydrous ether and pass through a basic alumina adsorption column. The ether eluate is removed as before using a rotary vacuum evaporator or air evaporation. Any remaining ether or water is removed by drying under vacuum over phosphorus pentoxide at 80°. Yield 13.7 g.

(Analysis: found, C 69.43%, H 3.88%, F 18.00%; calculated, C 69.59%, H 3.90%, F 18.35%.)

*Reagent properties of the tetrakis(*p*-trifluoromethylphenyl) borate anion*

Qualitative testing was done with a 1% solution of the sodium salt. Approximately 1 ml of the reagent was added to 1 ml of a 0.1 *M* solution of the ion to be tested. The following ions gave heavy precipitates: potassium, ammonium, silver and thallium(I). However, the silver and thallium(I) ions appeared to be slightly reduced. The following ions tested gave slight precipitates: rubidium and cesium.

No precipitates were obtained with copper, nickel, cobalt, calcium, barium or magnesium.

The reagent was tested for its ability to precipitate compounds containing a basic nitrogen atom which had been protonated and quaternary ammonium compounds. These compounds were dissolved in distilled water and precipitated with a 1% solution of the reagent. A few of the precipitates were filtered, recrystallized, dried and analyzed for nitrogen, and melting points were taken on a melting point block. The results are summarized in Table I. Quinidine, cinchonine, quinine and 1-phenylethylamine also gave heavy precipitates.

TABLE I

SOME BASIC NITROGEN COMPOUNDS FORMING SALTS WITH TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE ANION

Material tested	*M.p. (°)*	*% Nitrogen*	
		Found	*Calc.*
Tetrabutylammonium iodide	145–6	1.70	1.68
N-Butylamine	107–9	2.38	2.10
Benzidine	188–191 (not sharp)	2.27 (di-substituted salt)	2.05
Ethylamine	121–3	2.17	2.20
N-Ethylaniline	113–4	1.94	1.96
β-Alanine	>300	2.20	2.06
Ammonium hydroxide	185–6	2.29	2.30

The reagent was tested for its ability to precipitate potassium ion by mixing 2 ml of a 0.03 *M* reagent solution with 2 ml of the test solution. For a comparison, sodium tetraphenylborate, sodium tetrakis(*p*-fluorophenyl) borate, sodium tetrakis(*p*-chlorophenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate were used in a similar series of tests. The results are summarized in Table II.

*Sodium tetrakis(*p*-trifluoromethylphenyl) borate as a reagent for potassium*

The procedure described by GLOSS[3] in the determination of potassium with sodium tetraphenylborate was selected but slightly modified for the study of the precipitation of potassium with sodium tetrakis(*p*-trifluoromethylphenyl) borate.

TABLE II

COMPARATIVE SENSITIVITIES OF SOME TETRAARYLBORATES AS PRECIPITANTS FOR POTASSIUM

K taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4\text{p-}F)_4$	$NaB(C_6H_4\text{p-}Cl)_4$	$NaB(C_6H_4\text{m-}F)_4$	$NaB(C_6H_4\text{p-}CF_3)_4$
2.0	Heavy, immed.	None	Heavy, immed.	Heavy, immed.	Heavy, immed.
0.2	Heavy, immed.	None	Heavy, immed.	Slight, slow	Heavy, immed.
0.1	Medium, immed.	None	Medium, immed.	None	Heavy, immed.
0.05	Medium, immed.	None	Medium, slow	None	Heavy, immed.
0.02	Slight, immed.	None	Slight, slow	None	Medium, slow
0.01	Slight, immed.	—	Trace, slow	None	Medium, slow
0.005	Trace, slow	—	None	—	Slight, slow
0.002	None	—	None	—	Trace, slow

The preparation of the reagent for the quantitative study was performed as described by GLOSS, except that the aqueous reagent solution was filtered through a basic alumina adsorption column before use. A 2% solution of the reagent in water, pH 8, was used. The sample containing the potassium ion was adjusted to 50 ml and heated to 70°. The reagent which usually amounted to 30 ml was added dropwise from a buret. The sample was allowed to stand at room temperature for 1 h immersed in an ice bath for 1 h, transferred to a tared fine sintered-glass filter crucible and washed with three 5-ml portions of ice water. The crucible was dried at 110° for 1 h, cooled in a desiccator and weighed, and the recovery of potassium was calculated from the theoretical gravimetric factor 0.06203. The results are shown in Table III.

TABLE III

RECOVERY OF POTASSIUM FROM PURE POTASSIUM SOLUTIONS

K taken (mg)	*K found (mg)*	*% Recovery*	*K taken (mg)*	*K found (mg)*	*% Recovery*
20.38	20.30	99.6	4.98	4.80	96.4
20.38	20.28	99.5	4.98	4.87	97.8
12.46	12.29	98.6	4.98	4.92	98.8
12.46	12.31	98.8	4.98	4.91	98.6
12.46	12.49	100.2	4.98	4.89	98.2
12.46	12.40	99.5		$\sigma = \pm 0.05$	
12.46	12.34	99.0			
12.46	12.31	98.8			
	$\sigma = \pm 0.08$[a]				

[a] σ = standard deviation.

TABLE IV

SOLUBILITY OF POTASSIUM TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE

pH	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
3.3	25	68	0.163
6.3	25	68	0.168
10.2	25	68	0.176
7.0	0	48	0.145

The solubility of the pure potassium salt was determined at 25° and at 0°. At 25° the solubility is unaffected by pH in the range 3.3 to 10.2. The solubilities, which were computed from flame photometric data on the potassium ion in solution, were taken after 68 h (Table IV). Since this salt possesses good stability at various pH values, relatively long equilibration times were employed. Solubility values obtained immediately following precipitation were essentially the same as shown in Table IV.

*Reagent properties of the tetrakis(*m*-fluorophenyl) borate anion*

A 1% solution of the sodium salt was used for qualitative testing. About 2 ml of the reagent was added to 2 ml of a 0.1 *M* solution of the ion to be tested. Heavy precipitates were given with cesium, silver and thallium(I) ions. However, reduction seemed to be occurring in the silver and thallous solutions during the precipitation.

The rubidium ion gave a medium precipitate while potassium and ammonium ions gave slight precipitates. No precipitates were obtained with copper, nickel, cobalt, barium, calcium and magnesium.

Some quaternary ammonium compounds and other compounds containing a basic nitrogen atom were precipitated with the tetrakis(*m*-fluorophenyl) borate anion. The protonated nitrogen-compound was dissolved in water and precipitated with a 1% solution of the reagent. Some of the precipitates were filtered, recrystallized, dried and analyzed for nitrogen, and melting points were obtained on a melting point block. The results are shown in Table V. In addition, N-butylamine, benzidine, N-ethylaniline, quinidine and quinine gave heavy precipitates.

TABLE V

SOME BASIC NITROGEN COMPOUNDS FORMING SALTS WITH TETRAKIS(*m*-FLUOROPHENYL) BORATE ANION

Material tested	*M.p. (°)*	*% Nitrogen*	
		Found	*Calc.*
Trimethylamine	150–1	3.12	3.10
Tetrabutylammonium iodide	176–7	2.13	2.21
Brucine	141–2	3.64	3.55
Ethylamine	124–5	3.18	3.20
1-Phenylethylamine	122–3	2.86	2.73

A sensitivity test was performed on the reagent for its ability to precipitate cesium ion by mixing 2 ml of a 0.03 *M* reagent solution with 2 ml of the test solution. To make a comparison, a similar series of tests were done with sodium tetraphenylborate, sodium tetrakis(*p*-fluorophenyl) borate, sodium tetrakis(*p*-chlorophenyl) borate and sodium tetrakis(*p*-trifluoromethylphenyl) borate (Table VI).

*Sodium tetrakis(*m*-fluorophenyl) borate as a reagent for cesium*

The gravimetric studies on the sodium tetrakis(*m*-fluorophenyl) borate were performed by the procedure described above for sodium tetrakis(*p*-trifluoromethylphenyl) borate. The recovery of cesium was calculated from the theoretical gravimetric factor 0.2536 (Table VII).

TABLE VI

COMPARATIVE SENSITIVITIES OF SOME TETRAARYLBORATES AS PRECIPITANTS FOR CESIUM

Cs taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4p\text{-}F)_4$	$NaB(C_6H_4p\text{-}Cl)_4$	$NaB(C_6H_4m\text{-}F)_4$	$NaB(C_6H_4p\text{-}CF_3)_4$
2.0	Heavy, immed.	Heavy, immed.	Heavy, immed.	Heavy, immed.	Medium, immed.
0.2	Heavy, immed.	Medium, immed.	Heavy, immed.	Heavy, immed.	Slight, immed.
0.1	—	Slight, slow	—	Heavy, immed.	Trace, immed.
0.05	—	Trace, slow	—	Medium, immed.	Trace, immed.
0.02	Light, immed.	None	Slight, immed.	Slight, immed.	Trace, immed.
0.01	Slight, immed.	None	Slight, immed.	Trace, immed.	None
0.005	Trace, immed.	None	Slight, immed.	Trace, immed.	None
0.002	None	None	None	None	None

The solubility of the pure cesium salt was determined at 25° and 0°. At 25° the solubility is essentially unaffected by pH in the range 3.5 to 10.0. The solubilities were calculated from flame photometric data and are listed in Table VIII.

Additional solubility values were determined for potassium tetrakis(*m*-fluorophenyl) borate and rubidium tetrakis(*m*-fluorophenyl) borate salts (Table IX).

TABLE VII

RECOVERY OF CESIUM FROM PURE CESIUM SOLUTIONS

Cs taken (mg)	*Cs found (mg)*	*% Recovery*	*Cs taken (mg)*	*Cs found (mg)*	*% Recovery*
70.52	70.50	100.0	23.51	23.48	99.9
70.52	69.79	99.0	23.51	23.38	99.4
			23.51	23.28	99.0
47.02	46.99	99.9		$\sigma = \pm 0.09$	
47.02	46.94	99.8			
47.02	46.92	99.8	9.40	9.26	98.5
47.02	46.97	99.9	9.40	9.23	98.2
47.02	46.99	99.9	9.40	9.36	99.6
	$\sigma = \pm 0.03$		9.40	9.33	99.3
			9.40	9.43	100.3
23.51	23.33	99.2	9.40	9.46	100.6
23.51	23.26	98.9		$\sigma = \pm 0.09$	
23.51	23.46	99.8			

TABLE VIII

SOLUBILITY OF CESIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

pH	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
3.5	25	68	0.057
6.5	25	68	0.061
10.0	25	68	0.079
7.0	0	48	0.047

TABLE IX

SOLUBILITY VALUES OF POTASSIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE AND RUBIDIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

Salt	*pH*	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
$\mathrm{RbB(C_6H_4}m\text{-}\mathrm{F)_4}$	6.4	25	68	0.169
$\mathrm{KB(C_6H_4}m\text{-}\mathrm{F)_4}$	3.5	25	68	0.540
	6.7	25	42	0.607
	10.4	25	42	0.660

DISCUSSION

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate have been synthesized by a new *in situ* procedure. Ammonium ion and trimethylamine have been used in purification steps of these salts by forming precipitates with the tetrakis(*p*-trifluoromethylphenyl) borate and tetrakis(*m*-

fluorophenyl) borate anions, respectively. Extension of this procedure should be possible by employing amines selective for certain tetraarylborate compounds.

The data in Tables III and VII indicate that potassium and cesium can be gravimetrically determined with tetrakis(*p*-trifluoromethylphenyl) borate and tetrakis(*m*-fluorophenyl) borate anions, respectively. Neither anion is a specific reagent for the above cations. Both precipitates separate as white crystalline compounds with desirable analytical properties. They are easily filterable and attain constant weight rapidly at 110°. A prolonged heating of 16 h caused no further weight loss or sign of decomposition with either salt.

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate should be excellent reagents for use in quantitative analysis where interference from coprecipitation is absent. Aqueous solutions of these soluble salts are stable and very active at pH 8 when tested over a 6-month period.

In addition, these tetraarylborate anions form insoluble salts with various protonated amine, alkaloid and amino acid compounds. This should allow qualitative or quantitative analyses to be performed with these salts.

The authors wish to express their appreciation to the National Science Foundation for partial support of this work under grant #GP6857, and to acknowledge the contribution of Miss DENISE MADIGAN in the initial attempts to prepare the *m*-fluoro compound.

SUMMARY

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate were synthesized by a new *in situ* method. Both salts formed precipitates with potassium, rubidium and cesium ions, quaternary ammonium and protonated basic nitrogen compounds. Potassium tetrakis(*p*-trifluoromethylphenyl) borate was more insoluble than potassium tetraphenylborate while cesium tetrakis-(*m*-fluorophenyl) borate was less soluble than cesium tetrakis(*p*-fluorophenyl) borate. The salts formed with nitrogen-containing compounds offer possibilities for qualitative and quantitative analyses.

RÉSUMÉ

On décrit un nouveau procédé pour la synthèse de tétrakis(*p*-trifluométhylphényl)borate de sodium et de tétrakis(*m*-fluophényl)borate de sodium. Ces deux sels donnent des précipités avec les ions potassium, rubidium et césium, l'ammonium quaternaire, et les composés azotés protoniques basiques. Le tétrakis(*p*-trifluométhylphényl)borate de potassium est moins soluble que le tétraphénylborate de potassium, tandis que tétrakis(*m*-fluophényl)borate de césium est moins soluble que le tétrakis-(*p*-fluophényl)borate de césium. Les sels formés avec des composés azotés permettent des analyses qualitatives et quantitatives.

ZUSAMMENFASSUNG

Natriumtetrakis(*p*-trifluoromethylphenyl)borat und Natriumtetrakis(*m*-

fluorophenyl)borat wurden mit einer neuen *in situ*-Methode synthetisiert. Beide Salze bilden Niederschläge mit Kalium-, Rubidium- und Cäsium-Ionen, quaternären Ammonium- und protonisierten basischen Stickstoffverbindungen. Kaliumtetrakis-(*p*-trifluoromethylphenyl)borat war unlöslicher als Kaliumtetraphenylborat, während Cäsiumtetrakis(*m*-fluorophenyl)borat weniger löslich als Cäsiumtetrakis-(*p*-fluorophenyl)borat war. Die Salze, welche mit stickstoffhaltigen Verbindungen gebildet werden, bieten Möglichkeiten für die qualitative und quantitative Analyse.

REFERENCES

1 F. P. Cassaretto, J. J. McLafferty and C. E. Moore, *Anal. Chim. Acta*, 32 (1965) 376.
2 C. E. Moore, F. P. Cassaretto, H. Posvic and J. J. McLafferty, *Anal. Chim. Acta*, 35 (1966) 1.
3 G. H. Gloss, *Chemist-Analyst*, 42 (1953) 50.

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PRECIPITATION OF LEAD AS LEAD MOLYBDATE FROM HOMOGENEOUS SOLUTION

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The gravimetric determination of lead or molybdenum by precipitation as lead molybdate is unpopular, largely because of filtration difficulties that arise from the colloidal nature of the precipitate if it is formed in neutral solution. In addition, the precipitate suffers from contamination by molybdic oxide, especially if it is formed in acidic solution and/or in the presence of a large excess of molybdate. Except for these difficulties, it is an excellent method for lead, since the substance has a high molecular weight, is less soluble than lead sulfate or chromate, is not reduced when heated in the presence of filter paper, and undergoes no change upon ignition. CHATARD[1] was possibly the first to use the method for the determination of molybdenum. Since then, numerous investigators[2-6] have reported gravimetric lead molybdate methods for the determination of both lead and molybdenum. These methods generally involve precipitation from slightly acidic solution containing a relatively large concentration of inert salt—sodium or ammonium acetate or chloride—which aids digestion and renders the precipitate granular and more easily filterable. The precipitate is washed with dilute ammonium nitrate solution, filtered, and ignited to constant weight. The precipitate attains constant weight at 500–600°, but does not decompose even if heated to 980° [7]. A large excess of molybdate should be avoided in the determination of lead because contamination of the precipitate by molybdic oxide increases in proportion to the excess of reagent. To insure against high results the precipitate may be dissolved in mineral acid and reprecipitated[3].

There is some disagreement[8-12] concerning the extent to which elements like copper and cadmium interfere in the lead molybdate precipitation. It appears that the method is applicable to the determination of lead in the absence of the alkaline earths, which form insoluble molybdates, and in the absence of chromates, arsenates, and phosphates, which form insoluble lead compounds. It serves to separate lead from zinc, nickel, cobalt, and manganese.

Interferences in the determination of molybdenum by this method include vanadium(V) and tungsten(VI), which form insoluble lead salts, and arsenic, antimony, chromium(III), and phosphate. The latter four elements can be removed, together with aluminum, by precipitation from ammoniacal solution with excess iron(III) chloride. Large concentrations of chloride and sulfate must be avoided since their lead salts are insoluble. Silicic acid, tin, titanium, and metal salts which hydrolyze easily, also interfere. Manganese, copper, cobalt, nickel, zinc, mercury, calcium,

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strontium, barium, magnesium, alkali metals, and uranium reportedly do not interfere when present as their nitrates, chlorides, or acetates.

NEWCOMB AND MARKHAM[13] recently reported the only method to date for the precipitation of lead molybdate from homogeneous solution (PFHS). It is applicable only to the determination of molybdenum, and is based on the release of lead ion from a lead–EDTA reagent solution by chromium(III), also present in the solution, which slowly displaces lead from the chelate.

The objective of the present work was to develop a simple method for the gravimetric determination of lead as lead molybdate by PFHS. A precipitate formed in this manner should be more easily filterable and less subject to coprecipitation errors than a precipitate formed by the conventional gravimetric method. The high solubility of lead molybdate in strong acid solution suggested the possibility of PFHS by adding an excess of molybdate reagent to an acidic lead solution and slowly raising the pH by the well established urea hydrolysis procedure[14].

EXPERIMENTAL

Apparatus and reagents

Standard lead solutions. Spectrographically pure lead rod was weighed, dissolved in nitric or perchloric acid, and diluted to known volume in a volumetric flask.

Motybdate solution. 4.00 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in water and diluted to 200 ml. The salt was assayed for MoO_3 as described in the 1960 A.C.S. publication[15] on reagent chemicals, and was found to contain 81.5% MoO_3. Thus, 1.00 ml of this solution was equivalent to 23.5 mg Pb.

Baird 3-meter-grating spectrograph. Used with electrodes UCP No. 1988 and 1964.

Procedures

Two satisfactory procedures were developed for the determination of lead by precipitation as lead molybdate. Both procedures take advantage of the relatively long (3–5 min) induction period for the formation of the precipitate in strong acid solution. The difference between them lies in the method used to adjust the final pH to make the precipitation quantitative. In the first procedure, the pH is adjusted by the well established urea hydrolysis method, whereas in the second procedure it is adjusted by dropwise addition of ammonia.

Procedure A. Place the sample solution containing 0.05–0.5 g of lead in a 400-ml beaker and dilute to 150 ml with water. Add 2–5 ml of 1:1 nitric acid or an equivalent amount of perchloric acid, followed by a 5% excess of 2% molybdate reagent and 5 g of urea. Heat to just below the boiling point for 30–40 min. Add methyl orange indicator and continue heating until the solution becomes alkaline. This takes 1–2 h depending on the excess of acid present initially. Cool the solution to 55° and filter through a medium porosity porcelain crucible or Whatman #40 or 42 filter paper. Wash the precipitate with hot 2% ammonium nitrate solution followed by methanol. Ignite to constant weight at 725°.

Procedure B. Follow procedure A, omitting the addition of urea. Heat until the bulk of the precipitate has formed; 15–20 min is required. Add methyl orange indicator and 1:1 ammonia dropwise, with stirring, until the solution is alkaline.

Reheat for an additional 15 min to digest the newly formed precipitate. Cool to 55°, filter, wash, ignite and weigh as described above.

RESULTS AND DISCUSSION

Tables I and II summarize the results obtained by the two procedures described above. Similar results were obtained when an equivalent amount of perchloric acid was substituted for nitric acid, and also when samples of reagent-grade lead nitrate were assayed by these procedures.

TABLE I

PRECIPITATION OF $PbMoO_4$ BY PROCEDURE A

Pb present (g)	*% Recovery at different ignition conditions*				
	130° 1 h	*550°*		*725°*	
		1 h	*4 h*	*1 h*	*2 h*
0.0503	101.47	100.91	100.46	99.78	99.78
0.1508	101.52	100.80	100.66	100.20	100.20
0.2514	101.67	101.11	100.95	100.52	100.36
0.2514	101.63	101.03	100.88	100.44	100.36
0.5028	101.11	100.50	100.45	100.04	99.84

TABLE II

PRECIPITATION OF $PbMoO_4$ BY PROCEDURE B

Pb present (g)	*% Recovery at different ignition conditions*		
	130° 24 h	*550° 2 h*	*725° 2 h*
0.0505	—	—	98.78
0.1513	—	—	100.00
0.2522	—	—	100.28
0.2522	101.78	101.34	100.51
0.5045	101.50	101.13	100.57

Both of the procedures outlined above yielded granular precipitates which were easily filtered, either through medium porosity porcelain crucibles or through filter paper (Whatman #40 or 42). On the other hand, a precipitate formed by neutralizing the solution with 1:1 ammonia immediately after adding the molybdate reagent, although granular in appearance after digestion, rapidly clogged the filter crucible making filtration virtually impossible.

In preliminary experiments, 1–2 ml of 1:1 nitric acid added to 150 ml of solution containing 0.25 g of lead (final pH *ca.* 1.0) was sufficient to prevent immediate precipitation when the 5% excess of molybdate reagent was added. After standing momentarily, the clear solution developed a pale yellow color, and after standing for 3–5 min it became cloudy as lead molybdate began to precipitate. The solution, without urea, was heated to just below the boiling point for 30–40 min, after which no further precipitation was apparent and the precipitate was granular and well digested. Without adjustment of the pH of the supernatant solution, the precipitate was filtered, washed, and ignited to constant weight. Recoveries on several lead samples treated in this manner ranged from 94 to 99%, indicating that, even at pH 1.0, more than 90% of the lead was precipitated as lead molybdate. Recoveries were quantitative in subsequent experiments following the two recommended procedures in which the pH of the solution was adjusted before filtration to pH 3.0 or higher, either by urea hydrolysis or by dropwise addition of ammonia.

Contamination by molybdic oxide.

The recoveries listed in Tables I and II are higher than 100%, especially at the lower ignition temperatures, as might be expected since it is known that coprecipitation of molybdic oxide is a major source of error in the gravimetric lead molybdate method. To determine the extent of this contamination, aliquots of standard lead solution were analyzed by the two recommended procedures except that the excess of molybdate reagent was varied from 5 to 100%. Results shown in Table III indicate that the coprecipitation error increased with increase in excess of molybdate. This is in agreement with a literature statement[3] that contamination of lead molybdate by molybdic oxide is roughly proportional to the excess of reagent.

TABLE III

EFFECT OF EXCESS OF MOLYBDATE

Pb present (g)	*Excess molybdate reagent present*	*% Recovery at different ignition conditions*			
		130° 2 h	*550° 2 h*	*725°*	
				2 h	*4 h*
Procedure A					
0.1508	5	101.52	100.66	100.20	—
0.1508	25	102.12	101.19	100.44	100.53
0.1508	50	103.18	102.25	100.99	101.06
0.1508	100	103.38	102.39	101.33	101.26
Procedure B					
0.2522	5	—	—	100.28	—
0.2522	25	102.97	102.37	101.37	—
0.2522	50	103.54	102.88	101.69	—
0.2522	100	104.56	103.69	102.50	—

A reagent blank containing 2 ml of 1:1 nitric acid, 11 ml of 2% molybdate reagent, and 5 g of urea in 150 ml of water was heated for 45 min. About 5 mg of white solid separated, indicating that molybdic oxide precipitates from a molybdate solution of that acidity whether or not a precipitate of lead molybdate is present or being formed. The contamination of the precipitate may, therefore, be the combined result of coprecipitation and simultaneous precipitation.

The data in Tables I and II indicate that recoveries were best at an ignition temperature of 725°. Higher than theoretical recoveries were obtained at the two lower ignition temperatures. The weight loss between 130° and 550° can be attributed to loss of residual water and conversion of coprecipitated ammonium molybdate to molybdic oxide since ammonium molybdate is converted quantitatively to molybdic oxide at 550°. The weight loss between 550° and 725° can be attributed to partial volatilization of molybdic oxide. Analytical procedures for molybdenum, in which the final weighing form is MoO_3, stress that the ignition should be done at 550° since the oxide becomes increasingly volatile above 600°.

Contamination by copper and cadmium.

The interference of copper and cadmium was investigated to resolve uncertainties in the literature regarding the effect of these two ions, and to evaluate the effectiveness of the two recommended procedures for the determination of lead. Varying amounts of copper and cadmium were added to aliquots of standard lead solution and lead was precipitated by procedure B. The unignited precipitates were analyzed spectrographically for copper and cadmium; calibration standards were prepared by blending known amounts of cadmium oxide or copper oxide with pure lead molybdate. The results are shown in Table IV.

TABLE IV

COPRECIPITATION OF COPPER AND CADMIUM WITH $PbMoO_4$[a]

wt Cu : wt Pb	*p.p.m. Cu in ppt.*	*wt Cd : wt Pb*	*p.p.m. Cd in ppt.*
1:10	67	1:10	250
1:5	120	1:5	1000
1:1	80	1:1	3000
5:1	250	5:1	5000
10:1	v. high, ppt. green	10:1	6500

[a] A 14 CFH flow of 30% oxygen in argon was used to minimize self-absorption of the Cd line — 3274 Å. Cu line — 3261 Å. Exposure 20 sec for Cd, 30 sec for Cu, with a d.c. arc of 13–14 A.

The interference of copper is negligible up to a Cu:Pb ratio of 5:1, which is in agreement with reports in the literature[5,6]. However, at a Cu:Pb ratio of 10:1, serious contamination by copper is evident even from the appearance of the precipitate. The interference is not due to coprecipitation but to insolubility of a copper salt. Contamination by cadmium obviously is more serious, even at low Cd:Pb ratios. This is not surprising in view of the reported solubility product of $6.05 \cdot 10^{-8}$ for cadmium molybdate[16].

Solubility of lead molybdate.

No value for the solubility product of lead molybdate could be found in the literature. Accordingly, the solubility of lead molybdate in water was determined by analyzing a saturated solution (24°) of a freshly prepared, washed lead molybdate precipitate for lead by carbon tetrachloride extraction of the lead–dithizone complex[17]. The data yielded a value of $2.9 \cdot 10^{-14}$ for the solubility product of lead molybdate. The accuracy of this value is questionable in view of the possible excess of molybdate in the precipitate and the relatively small absorbance of the sample extract.

Rate of precipitation

In the two procedures described above there is a 3–5 min induction period before any precipitate appears. Thereafter, the precipitation is still relatively slow, requiring 15–20 min before the bulk (>90%) of the precipitate has formed. The rate of precipitation probably is controlled by the rate at which the polymolybdate species ($Mo_7O_{24}^{6-}$ and/or $Mo_8O_{24}^{4-}$), known to exist in strongly acidic solutions[18], depolymerize to yield simple molybdate ions (MoO_4^{2-}). BAKER[19] carried out radioactive molybdenum exchange studies on heteropolymolybdates and reported that, at 29.5° and in the pH range 2.5–4.5, all molybdenum exchanges were complete in less than 0.5 min, and that the rate of exchange increased with increasing pH. It seems likely that such species would be less labile at lower pH. AVESTON *et al.*[20] in discussing the nature of isopolymolybdates, indicate that at high acidities "chemical processes become slow". Recently STREULI AND ROGERS[21], using gel permeation chromatography, were able to separate two different species, presumably MoO_4^{2-} and either $Mo_7O_{24}^{6-}$ or a mixture of $Mo_7O_{24}^{6-}$ and $Mo_8O_{24}^{4-}$, from molybdate solutions in 0.1 *M* or 2.0 *M* sulfuric acid. A separation of this sort is further evidence that equilibrium between polymolybdate species and simple molybdate ion is established only very slowly in strongly acidic solutions.

CONCLUSIONS

The simple new method described for the gravimetric determination of lead by PFHS uses the well-established urea hydrolysis procedure. The faster alternative method is "semi-homogeneous" in the sense that all but a small fraction of the precipitate is formed from homogeneous solution, the remainder being formed by dropwise addition of ammonia.

In the absence of more extensive, careful studies of cation and anion coprecipitation, it is impossible to compare foreign ion contamination of the precipitates obtained by the two recommended procedures and by the conventional gravimetric technique.

Contamination of the precipitate by molybdic oxide is still a serious problem, even when the precipitate is formed from acidic homogeneous solution, and it is important to keep the excess of molybdate reagent small to minimize this error. When a 5% excess of molybdate is used and the ignition is carried out at 725°, the error does not generally exceed 0.5%. Again, accurate comparison data are unavailable for the conventional procedure, and it is quite possible that the error is somewhat larger by the two recommended procedures since molybdic oxide precipitates more readily from highly acidic solutions. Nevertheless, many gravimetric procedures require a compromise between form and purity of the precipitate, and if an error of 0.5% does constitute a small sacrifice in purity, it is justified by the improved form (filterability) of the precipitate. The precipitate obtained by either of the two recommended procedures is granular and easy to filter, whereas that obtained by conventional techniques frequently is finely divided and difficult to filter, even after digestion, depending on the pH of the solution from which the precipitate is formed.

The application of these procedures to the determination of molybdenum has not been investigated.

Finally, although the first procedure represents a true PFHS procedure, it is more time-consuming than the second procedure which yields comparable results despite its "non-homogeneous" finish.

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SUMMARY

Lead molybdate can be precipitated in a granular form from a homogeneous solution by taking advantage of the long induction period for the formation of the precipitate in strong acid solution. The rate of precipitation is probably controlled by the rate at which the polymolybdate species depolymerize to yield simple molybdate ions. Although the bulk ($>90\%$) of the precipitate forms at pH *ca.* 1.0, quantitative recovery requires final adjustment of the pH of the digested solution, either homogeneously (urea hydrolysis) or heterogeneously (dropwise addition of ammonia), to pH 3.0. Contamination by molybdic oxide occurs but both methods yield reliable results if the excess of molybdate is limited to 5% and the precipitate is ignited to 725°. Contamination by copper and cadmium was also studied.

RÉSUMÉ

On peut précipiter le molybdate de plomb sous forme de granules en solution homogène par une longue période d'induction de formation du précipité en milieu acide fort. La vitesse de précipitation est probablement contrôlée par la vitesse à laquelle les particules de polymolybdate se dépolymérisent pour former des ions molybdates simples. Bien que le précipité ($>90\%$) se forme à un pH de 1.0 environ, il est nécessaire, pour avoir un rendement quantitatif, d'ajuster le pH à 3, soit de manière homogène par hydrolyse de l'urée, soit hétérogène, par addition d'ammoniaque. Il peut se produire une contamination en oxyde molybdique, mais les deux méthodes fournissent des résultats satisfaisants si l'excès de molybdate ne dépasse pas 5% et si le précipité est calciné à 725°. On examine également l'influence du cuivre et du cadmium.

ZUSAMMENFASSUNG

Bleimolybdat kann aus homogener Lösung in granulierter Form gefällt werden, wenn man die Vorteile einer langen Induktionsperiode für die Bildung des Niederschlages in stark saurer Lösung berücksichtigt. Die Fällungsgeschwindigkeit wird wahrscheinlich durch die Geschwindigkeit, mit der die Polymolybdat-Spezies zu einfachen Molybdationen depolymerisieren, bestimmt. Obgleich mehr als 90% des Niederschlages bei einem pH-Wert von etwa 1.0 gebildet wird, erfordert eine quantitative Fällung eine endgültige Einstellung des pH-Wertes der erhitzten Lösung auf 3.0; und zwar entweder homogen durch Harnstoffhydrolyse oder heterogen durch tropfenweise Zugabe von Ammoniak. Es treten Verunreinigungen durch Molybdänoxid auf, aber beide Methoden liefern verlässliche Ergebnisse, wenn der Überschuss des Molybdats nicht mehr als 5% beträgt und der Niederschlag bei 725° geglüht wird. Verunreinigungen durch Kupfer und Cadmium wurden ebenfalls untersucht.

REFERENCES

1 T. M. Chatard, *Am. J. Sci.*, 1 (1871) 416.
2 H. B. Weiser, *J. Phys. Chem.*, 20 (1916) 640.
3 F. Ibbotson and L. Aitchinson, *The Analysis of Non-Ferrous Alloys*, Longmans, Green Co., New York, 1915, p. 54.
4 F. Van Dyke Cruser and E. H. Miller, *J. Am. Chem. Soc.*, 26 (1904) 676.
5 B.I.S.R.A. Methods of Analysis Committee, *J. Iron Steel Inst. (London)*, 193 (1959) 350.
6 W. Brüggemann, *Chemiker Ztg.*, 57 (1933) 863.
7 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 1953, p. 33.
8 T. W. Gilbert, Jr., in I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 6, Interscience, New York, 1964, p. 113.
9 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Edn., Wiley, New York, 1961, p. 482.
10 J. W. Price and R. A. Chalmers, in C. L. Wilson and D. A. Wilson, *Comprehensive Analytical Chemistry*, Vol. 1C, Elsevier, New York, 1962, pp. 188, 589, 592.
11 L. Erdey, *Gravimetric Analysis*, Part II, Pergamon Press, New York, 1962, p. 532.
12 W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd Edn., Wiley, New York, 1953, pp. 229, 311.
13 G. Newcomb and J. J. Markham, *Anal. Chim. Acta*, 35 (1966) 261.
14 L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution*, Wiley, New York, 1959, p. 7.
15 Committee on Analytical Reagents, *Reagent Chemicals, American Chemical Society Specifications 1960*, Am. Chem. Soc., Washington, D.C., 1960, p. 60.
16 W. F. Linke (editor), in Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, 4th Edn., Vol. 1, D. van Nostrand, New York, 1958, p. 742.
17 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1958, p. 563.
18 F. A. Cotton and C. Wilkinson, *Advanced Inorganic Chemistry*, 2nd Edn., Interscience, New York, 1966, pp. 937–40.
19 L. C. W. Baker, in S. Kirschner, *Advances in the Chemistry of the Coordination Compounds*, MacMillan, New York, 1961, p. 607.
20 J. Aveston, E. W. Anacker and J. S. Johnson, *Inorg. Chem.*, 3 (1964) 735.
21 C. A. Streuli and L. B. Rogers, *Anal. Chem.*, 40 (1968) 653.

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COLLECTION OF TRACES OF SILVER ON PREFORMED *p*-DIMETHYLAMINOBENZYLIDENERHODANINE PRECIPITATES

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Numerous organic gathering precipitates or collectors have been proposed to carry down traces of various metal ions in aqueous solution[1,2]. In conventional methods, an organic reagent solution is added to a sample solution to give small amounts of precipitates of the organic reagent itself or its metal complex (in the presence of a carrier metal element) *in situ*. In the present work, preformed voluminous *p*-dimethylaminobenzylidenerhodanine (PDR) precipitates with large effective surface areas are used to collect microgram or submicrogram quantities of silver in dilute nitric acid solutions. Since the proposed method can be used even at an acidity of 0.5 *N*, where the conventional coprecipitation method is not applicable, it is successfully applied as a preliminary separation step to the photometric determination of a few p.p.m. of silver in high-purity bismuth metal.

EXPERIMENTAL

Apparatus

γ-Activities were measured with a Kobe Industries Corp. well-type NaI (Tl) scintillation counter. A Hirama model V photoelectric filter photometer with matched 5-cm micro cells was used for photometry.

Reagents

PDR solution (5 mg of PDR per ml). Dissolve PDR in a 10:1 (v/v) mixture of ethanol and 10 *N* sodium hydroxide. Use this solution within about 5 h.

Silver-110m solutions (0.02–500 µg of silver per ml). Add silver-110m (Radiochemical Centre, Amersham; silver nitrate in 0.1 *N* nitric acid; specific activity, 0.37 mCi/ml) and silver nitrate to 0.1 *N* nitric acid.

All the reagents used were of reagent grade. Water purified by distillation and ion exchange was used throughout the work.

Procedure

Place 0.04–0.8 ml of PDR solution in a beaker of suitable capacity, and add 5–10 ml of 0.1 *N* nitric acid over a 30-sec period of swirling to give *ca.* 0.2–4 mg of voluminous PDR precipitate. Add a sample solution (50–2000 ml, 0.01–0.5 *N* acidity) containing 0.05–50 µg of silver to the beaker, and stir with a magnetic stirrer (150 to 300 r.p.m.) for 5–10 min. Filter off the precipitate on a sintered-glass disk (No. 4, 2 cm diam.) at a flow rate of 50–100 ml per min, wash 5 times with 3 ml of 0.1 *N* nitric acid, and discard the filtrate and washings. Dissolve the precipitate in 10 ml of concentrated nitric acid, wash the disk with 3 ml of 0.1 *N* nitric acid, and combine these solutions.

Tracer experiments

The recoveries of silver were determined by γ-activity measurement, with coefficients of variation of 1–3%.

RESULTS AND DISCUSSION

Effect of collecting time and aging of precipitates on silver recovery

The effect of collecting time (contact time of PDR precipitates with sample solutions) on silver recovery is shown in Fig. 1. A 5-min agitation is sufficient to

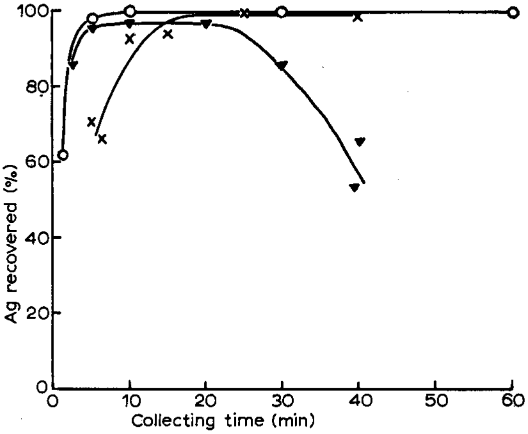

Fig. 1. Effect of collecting time on silver recovery. Solution volume, 100 ml. Silver present, 0.05 μg. PDR used, 0.2 mg. (○) With agitation, 0.2 *N* HNO_3. (×) Without agitation, 0.2 *N* HNO_3. (▼) With agitation, 0.5 *N* HNO_3.

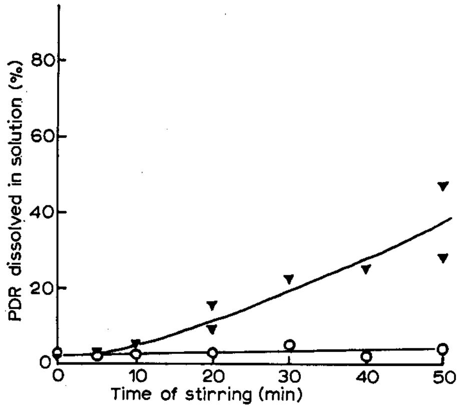

Fig. 2. Dissolution of PDR precipitates. Solution volume, 100 ml. PDR used, 0.2 mg. (○) 0.2 *N* HNO_3. (▼) 0.5 *N* HNO_3.

collect 0.05 µg of silver in more than 98% yields from 100 ml of 0.2 *N* nitric acid with 0.2 mg of PDR. Without agitation, however, at least 20 min is required to attain the same recovery. In 0.5 *N* nitric acid solution, the silver recovery is about 95% over the range 5–20 min, and then decreases with the time of agitation. To investigate the dissolution of PDR precipitates during the collection step, the solution was filtered through a sintered-glass disk, the filtrate made alkaline with sodium hydroxide, and then its absorbance at 532 nm was measured. The results illustrated in Fig. 2 correspond with those in Fig. 1.

Aging 1 mg of PDR precipitates for up to 71 h at room temperatures before their contact with sample solutions has little effect on silver recovery. No change in the appearance of the precipitates upon aging was observed under an optical microscope (90×).

Required quantity of PDR

Experiments were carried out to find the required quantity of PDR for collecting 0.05–50 µg of silver from 50–100 ml of 0.2 *N* nitric acid with a 10-min agitation. The results shown in Table I indicate that 0.2–1 mg of PDR assures recoveries of more than 98%. It is interesting to note that nanogram amounts of silver in up to 2000 ml of solutions can be almost completely collected on a few mg of PDR precipitates with the same period of agitation.

TABLE I

COLLECTION OF SILVER ON PDR PRECIPITATES FROM 0.2 *N* NITRIC ACID

(10-min agitation)

Solution volume (ml)	*Ag present (µg)*	*PDR used (mg)*	*Ag recovered (%)*
50	0.2	0.2	100, 99
	4	0.05	66
		0.1	96
		0.2	98
		0.5	98
		1.0	100, 99
	50	1.0	97
100	0.05	0.05	62
		0.15	95
		0.2	99, 98
		0.25	98
		1.0	99
	4	1.0	100
500	0.05	1.0	100
2000	0.02	1.0	60
		4.0	97

Effect of acidity on silver recovery

The effect of the acidity of the sample solution on silver recovery was studied and compared with that in the conventional coprecipitation method[3–5], in which 0.4–4.0 ml of ethanolic 0.05% (w/v) PDR solution was added to a sample solution to give PDR precipitates *in situ*. As shown in Table II, the proposed method is applicable to 0.01–0.5 *N* acidity, whereas the conventional one can be used only in the range of 0.01 to 0.1 *N*.

TABLE II

EFFECT OF ACIDITY ON SILVER RECOVERY

(Solution volume, 50 ml. Silver present, 4 μg)

HNO$_3$ acidity (N)	*PDR used (mg)*	*Collecting time[a] (min)*	*Ag recovered (%)*	
			Proposed method	*Conventional coprecipitation method*
0.01	1.0	10	100	100
0.1	0.2	10	100	99
	1.0	10	100	100
0.2	0.2	10	100	0
	0.2	360[b]	99	39
	0.2	300[c]	100	43
	1.0	360[b]	—	77
	1.0	300[c]	—	68
0.5	0.2	10	96	0
	1.0	10	97	2
	1.0	360[b]	96	53
1.0	1.0	5	87	0
	2.0	5	93	0
3.0	1.0	5	0	0

[a] Stirred continuously unless otherwise stated.
[b] Stirred for a few min at intervals of 30 min (~70°).
[c] Stirred for a few min at intervals of 30 min (~20°).

Separation from matrix elements

Table III shows that p.p.m. amounts of silver in bismuth or copper matrices can be separated in greater than 97% yields at an acidity of about 0.5 *N* by the proposed method. The concentration factors of silver with respect to bismuth or copper were determined by EDTA titration, and found to be *ca.* $2 \cdot 10^3$ to $1 \cdot 10^4$.

TABLE III

SEPARATION OF SILVER FROM MATRIX ELEMENTS IN NITRATE SOLUTIONS

(PDR used, 0.5 mg. 10-min agitation)

Solution volume (ml)	*Present*			*Acidity (N)*	*Ag recovered (%)*
	Bi (g)	*Cu (g)*	*Ag (μg)*		
50	1.0	—	4	0.4	99
100	2.0	—	8	0.4	97
50	—	5.0	1.5	0.5	99

DETERMINATION OF SILVER IN HIGH-PURITY BISMUTH

The proposed method was applied to the photometric determination of silver in high-purity bismuth metal. A large amount of bismuth interferes with the photometric PDR method[6]. Also, the conventional PDR coprecipitation method cannot be used because of hydrolysis of bismuth at lower acidities (less than about 0.1 *N*). The recommended procedure is as follows.

Procedure

Transfer a weighed sample (2.00 g) to a 50-ml conical flask, add 12 ml of 6.5 N nitric acid, and heat to dissolve. Cool the solution, and dilute to 100 ml in a volumetric flask with 0.1 N nitric acid. Take a 25-ml aliquot into a 100-ml beaker, dilute to 50–100 ml with water, and separate silver as described under *Procedure*, using 0.2 ml of PDR solution. Add 1 ml each of concentrated sulfuric acid and 10% ammonium persulfate solution to the resulting solution. Evaporate the solution just to dryness on a water bath, cool to room temperature, add 3 ml of buffer solution (8 g of ammonium acetate in 100 ml of 33% (v/v) acetic acid) to dissolve the residue, and then add 2 ml of 0.01% acetic acid solution of PDR. Measure the absorbance of the solution in a 5-cm micro cell at 575 nm against water. Determine the silver concentration by reference to a calibration curve prepared with standard silver nitrate solutions.

With regard to the photometry, the calibration curve is linear up to at least 10 μg of silver, and the error is about 0.2 μg in this range. No interference results from the presence of 1 mg of copper, 500 μg of bismuth, 100 μg of iron, and 50 μg of lead. Table IV shows the silver content of a sample of commercial high-purity bismuth metal determined by the proposed method. The blank value through the entire procedure was 0.0 μg of silver. The error is less than 10%, and the time required for a determination is about 2 h.

The proposed method may also be applied to the separation of traces of gold, mercury, and palladium.

TABLE IV

DETERMINATION OF SILVER IN HIGH-PURITY BISMUTH

Sample taken (g)	*Ag found (μg)*	*Ag in Bi (p.p.m.)*
0.50	2.2	4.4
0.50	2.3	4.6
0.50[a]	4.3	4.6
0.50[a]	4.1	4.2
		av. 4.5

[a] 2.0 μg of silver was added immediately after dissolution of the sample.

SUMMARY

Microgram or nanogram quantities of silver ion can be collected on 0.2–4 mg of preformed voluminous *p*-dimethylaminobenzylidenerhodanine precipitates from 50–2000 ml of 0.01–0.5 N nitric acid solution within 10 min. This separation method is successfully applied to the photometric determination of a few p.p.m. of silver in high-purity bismuth metal.

RÉSUMÉ

Des micro- ou nanoquantités d'argent peuvent être recueillies sur 0.2–4 mg de précipité volumineux préalablement formé de *p*-diméthylaminobenzylidènerhodanine, dans 50–2000 ml de solution acide nitrique 0.01–0.5 N en 10 minutes.

Cette séparation a pu être appliquée avec succès au dosage photométrique de quelques p.p.m. d'argent dans du bismuth métal, très pur.

ZUSAMMENFASSUNG

Mikro- oder Nanogramme von Silberionen können innerhalb von 10 Minuten auf 0.2–4 mg voluminösen *p*-Dimethylaminobenzylidenrhodanin aus 50–2000 ml 0.01–0.5 *N* salpetersaurer Lösung gesammelt werden. Diese Trennungsmethode wird erfolgreich bei der photometrischen Bestimmung von wenigen p.p.m. Silber in hochreinem Wismut-Metall angewandt.

REFERENCES

1 T. S. West, *Anal. Chim. Acta*, 25 (1961) 405.
2 A. Mizuike, in G. H. Morrison, *Trace Analysis: Physical Methods*, Interscience, New York, 1965, p. 131.
3 S. Hirano, A. Mizuike and Y. Ujihira, *Japan Analyst*, 12 (1963) 160.
4 Y. Ujihira, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, 84 (1963) 642.
5 Y. Ujihira, *Ph.D. Thesis*, The University of Tokyo, 1964.
6 D. Ishii and T. Takeuchi, *Japan Analyst*, 11 (1962) 174.

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PRECISE INTEGRATION OF VOLTAGE (CURRENT)–TIME FUNCTIONS WITH A FIXED FIELD D.C. MOTOR-COUNTER

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The rotational speed of a fixed field (permanent magnet) d.c. motor is very nearly directly proportional to the voltage applied to the armature. Such a motor driving a revolution counter serves very conveniently to integrate voltage–time functions, and thus to obtain the time integral of any quantity which can be transduced to a voltage. Integrating units of this type, with maximum input voltages ranging from 1.5 V to 24 V, and with either digital or scalar counters, are manufactured by Ether Ltd. (formerly Electro Methods Ltd.), Stevenage, Herts, England, and are available in the U.S.A. from Acromag Inc., 30765 Wixom Road, Wixom, Mich. 48096.

These integrators are particularly useful as coulometers to integrate the current–time function in coulometric analyses. The current to be integrated is passed through a resistor, and the *iR* drop across this resistor is applied to the motor terminals. When used to integrate an approximately constant current in coulometric titrations, and provided that the shunt resistor is selected so that the input voltage is at least half the permissible maximal value, the integration error is as small as ±0.1%[1–5].

Although these instruments are constructed extraordinarily skillfully to have a very small inertia, nonetheless the counting rate does decay as the current decreases, because a small fraction of the energizing voltage (current) is dissipated in operating the motor against the rotational inertia of its armature and the frictional resistance of the mechanical counter. Consequently, when employed in coulometric analysis at controlled potential, in which the current decreases over a range of 100:1 or more,

TABLE I

CALIBRATION DATA WITHOUT COMPENSATION
(24-V Electro Methods integrator with 200-ohm shunt resistance)

i (*mA*)	t (*sec*)	N (*counts*)	iR (*V*)	$\frac{dN}{iRdt}$ (*counts/sec/V*)	β	$\left(\frac{dN}{iRdt}+\frac{\beta}{iR}\right)$
112.29	200.03	521.7	22.458	0.11615	—	0.1162
67.51	300.05	469.9	13.501	0.11601	0.0019	0.1163
31.415	400.00	290.7	6.283	0.11567	0.0030	0.1163
10.637	800.00	194.4	2.1274	0.11422	0.0041	0.1161
5.402	1000.0	121.6	1.0804	0.1126	0.0039	0.1163
1.073	3200.0	64.6	0.2147	0.0940	0.0048	0.1126
				Av. (last four)	0.0040	

the cumulative negative integration error can amount to many percent[5]. This decay of the counting rate is demonstrated in Table I.

These data were obtained with a 24-V model of the Electro Methods integrator (scaler revolution counter) with a 200-ohm ($\pm 0.05\%$) shunt resistance. Constant current ($\pm 0.01\%$) was supplied by the amperostat previously described[5,6]. Time was measured (± 0.01 sec) by a Standard Electric Time Co. Model S-10 electric stopclock driven by a frequency-regulated power supply (American Time Products, Inc., Type 2005). The values of iR in the fourth column are nominal; *i.e.*, they have not been corrected for the small fraction of the current (0.04 mA) which branches through the motor. With the 200-ohm shunt resistance this iR loss is 0.008 V.

As pointed out in a previous study[5] the decay of the counting rate (counts/sec/V) is approximately inversely proportional to the nominal input voltage iR; that is

$$\frac{\mathrm{d}N}{iR\mathrm{d}t} \simeq k - \frac{\beta}{iR} \tag{1}$$

where N is number of counts, i is current (A), R is the shunt resistance, k is the counting rate at maximal input voltage, and β is a pseudo-constant. In agreement with data previously observed with a different digital model of the Electro Methods integrator[5], β is only a pseudo-constant, increasing from 0.0019 to 0.0048 counts/sec/V when iR decreases from about 0.5 to 0.01 of the maximal input voltage. When the average value of β (0.0040 counts/sec) is employed at iR values below 6.3 V the values of k shown in the last column of Table I are obtained. These values of k vary by $\pm 0.1\%$ down to an iR value of 1 V, and by -3% when iR is 0.01 of its maximal value.

Corresponding to eqn (1), the total quantity of electricity Q (coulombs) is

$$Q \simeq \frac{N}{kR} + \frac{\beta t}{kR} \tag{2}$$

where N is the total number of counts that accumulate in t sec. Even though the correction term $\beta t/kR$ is only an approximation, its application does decrease the cumulative integration error from the order of several percent to only a few tenths of a percent, even when the current decreases by a factor of 100, provided that R is selected to produce nearly the maximal input voltage with the initial current.

The correction term in eqn (2) is a significant improvement over no correction at all, but complete elimination of the decay of the counting rate is the obvious ultimate desirability. As shown in Fig. 1, this can be achieved quite simply by the two resistors R-2 and R-3 and the small mercury battery or dry cell in the input circuit of the integrator. The combination of R-2, R-3, and the battery introduces a small constant voltage, which adds to the voltage drop across the shunt resistor R-1, and counteracts decay of the counting rate with decreasing current. It is desirable that R-2 be small compared to the apparent resistance of the integrator and R-1. For the 24-V Electro Methods integrator a value of 20 ohms was satisfactory. When R-1 was 200 ohms the optimum value of R-3 was 667 ohms, and the compensating voltage produced across R-2 was 0.038 V.

Table II shows calibration data obtained with this compensation circuit. The counting rates over a 200-fold range of input currents with and without compensation are compared in Fig. 2. With compensation the counting rate is constant at 0.11615 ± 5 ($\pm 0.04\%$) counts/sec/V down to about 5% of the maximum permissible input voltage. Even with an input voltage only 1/200 of the maximum, the error is only −0.8%, in contrast to more than −40% without compensation.

Because of the background current, the final minimal current during a controlled potential electrolysis seldom is smaller than 1/200 of the initial current. Under this usual condition, and with the compensation circuit of Fig. 1, the cumulative error of the Electro Methods integrator will be of the order of only −0.1%. Ordinarily the uncertainty in the correction for the background current will be greater than this.

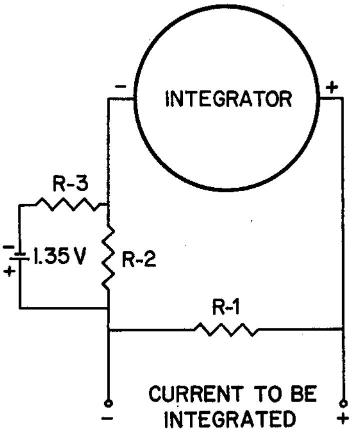

Fig. 1. Compensation circuit.

TABLE II

CALIBRATION DATA WITH COMPENSATION

(24-V Electro Methods integrator with R-2 = 20, R-3 = 667, and R-1 = 200 ohms (Fig. 1))

i (mA)	t (sec)	N (counts)	iR (V)	$\frac{dN}{iRdt}$ (counts/sec/V)
102.03	500.05	1185.0	20.406	0.11614
74.99	500.00	871.0	14.998	0.11615
66.46	500.00	772.2	13.292	0.11619
56.25	500.00	653.8	11.250	0.11632
30.013	1000.0	697.5	6.003	0.11620
14.686	1000.0	341.0	2.9372	0.11610
7.815	1000.0	181.4	1.5630	0.11606
2.555	2000.0	118.0	0.5110	0.1155
1.289	3000.0	89.1	0.2578	0.1152
0.664	3000.0	46.0	0.1328	0.1154

The optimum value of the compensating voltage across R-2 is quite critical and it depends on the magnitude of the shunt resistance R-1. It was found empirically that the optimum compensating voltage for the particular integrator studied is very nearly equal to $i_m R + 0.030$ V, where i_m is the current through the motor itself and R is R-1. This relation is a useful guide in the selection of the values of R-2 and R-3. For the integrator studied the motor current was $4.0 \cdot 10^{-5}$ A, for input voltages in the critical range below about 6 V. In close agreement with the foregoing relation the observed optimum values of the compensating voltage were 0.038 and 0.068 V with values of R-1 of 200 and 1000 ohms.

The motor current traverses R-1 in a direction opposite to the total current, so the actual voltage drop across R-1 is less than iR by $i_m R$ (0.008 V when R-1 was 200 ohms but 0.040 V when R-1 was 1000 ohms). The additional constant 0.030 V appears to be the product of the motor current and resistance of the armature. The nominal armature resistance stated by the manufacturer is 700 ohms, which yields 0.028 V when multiplied by the observed motor current.

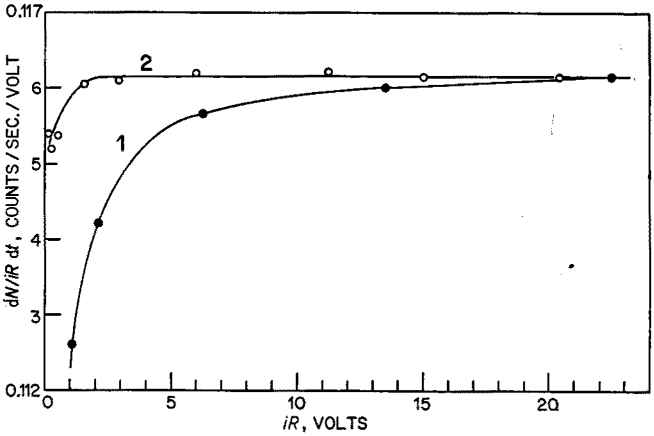

Fig. 2. Comparison of uncompensated (1) and compensated (2) counting rates as function of nominal input voltage.

Evidently, the compensation voltage is optimum when it just counteracts the sum of the iR loss in R-1 and the electrical and mechanical losses in the motor-counter unit itself. In applications, other than controlled potential coulometric analysis, when the energizing signal is a pure, current-independent voltage the optimum compensating voltage presumably will be solely the product of the motor current and its armature resistance. This should be true, for instance, when the instrument is employed to integrate the output of a voltage amplifier of low output resistance.

The response time of the instrument is stated by the manufacturer to be only 0.012 sec, and it is applicable to the integration of quite rapidly fluctuating current or voltage. However, it was observed that when used to integrate voltage, and when the signal was interrupted to leave an open circuit through the motor, the instrument required about 1 sec, to coast to a stop. This is easily corrected by keeping a shunt resistance across the input terminals (1500 ohms was satisfactory for the particular instrument studied) to maintain a closed circuit when the voltage signal is interrupted, so that the self-damping induced by the interaction of the fixed magnetic field with that produced by the moving armature stops the motor instantaneously.

The cost of the instrument (about $150) is much less than that of other integrating devices of comparable capability, and its service life is long. The particular unit used in this study has been in intermittent use for over ten years with no noticeable change in its characteristics.

SUMMARY

Because of electrical and mechanical losses, the counting rate of a fixed field d.c. motor-counter integrator becomes less than linear with decreasing input voltage. This decay of the counting rate can be counteracted very simply by introducing a small, constant compensation voltage into the input circuit. When properly compensated, the integrator manufactured by Ether Ltd. (formerly Electro Methods Ltd.) is capable of measuring the time integral of current or voltage over a 20 to 1 range with an error of only ±0.04%, and over a 200 to 1 range with an error of only about −0.1%.

RÉSUMÉ

A cause des pertes électriques et mécaniques, la vitesse de dénombrement d'un intégrateur, muni d'un moteur dénombreur, fonctionnant dans un domaine fixé de "d.c.", devient moins linéaire quand le potentiel d'entrée diminue. Cette perte de vitesse de dénombrement peut être contrebalancée très simplement en introduisant une petite compensation de potentiel constante dans le circuit d'entrée. Quand l'intégrateur, construit par Ether Ltd. (c'est-à-dire Electro Methods Ltd.), est compensé convenablement, il est capable de mesurer au cours du temps l'intégrale du courant ou du voltage au-dessus d'un domaine de 20 à 1, avec une erreur de ±0.04% seulement, et au-dessus de 200 à 1, avec une erreur d'environ ±0.1% seulement.

ZUSAMMENFASSUNG

Wegen der elektrischen und mechanischen Verluste wird die Zählrate eines Motorzählintegrators für ein festes Feld nicht mehr linear bei abnemender Eingangsspannung. Diesem Abfall der Zählrate kann man sehr einfach durch Einführung einer kleinen konstanten Kompensationsspannung in den Eingangskreis entgegenwirken. Bei guter Kompensation ist die integrale Zeitmessung des Stroms oder der Spannung über einen Bereich von 200:1 mit einem Fehler von etwa 0.1% möglich.

REFERENCES

1 B. M. WHEATLEY, *Brit. J. Radiol.*, 26 (1953) 382.
2 N. BETT, W. NOCK AND G. MORRIS, *Analyst*, 79 (1954) 607.
3 J. S. PARSONS, W. SEAMAN AND R. M. AMICK, *Anal. Chem.*, 27 (1955) 1754.
4 N. H. FURMAN AND A. J. FENTON, JR., *Anal. Chem.*, 29 (1957) 1213.
5 J. J. LINGANE, *Anal. Chim. Acta*, 18 (1958) 349; *Electroanalytical Chemistry*, 2nd Edn., Interscience, New York, 1958, p. 346.
6 J. J. LINGANE, *Anal. Chem.*, 26 (1954) 1021.

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POLAROGRAPHY OF SULFUR DIOXIDE (SULFITE) IN AQUEOUS HYDROFLUORIC ACID*

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It is possible by use of the proper reagents to convert many of the various sulfur compounds (both organic and inorganic) that occur in gases, liquids, and solids to sulfur dioxide or sulfite. Thus, methods to detect and measure sulfur dioxide are important. The areas of application are numerous and varied. They include studies of air pollution, determination of preservatives in foods, analysis of process liquors, and even such fundamental studies as the reduction of alkaline-earth sulfates by hydrogen.

The determination of sulfur dioxide in hydrofluoric acid media is of special interest in view of the increasing significance of anhydrous hydrogen fluoride as a solvent and a medium for chemical reactions[1] and because sulfur dioxide is a recognized impurity in hydrogen fluoride[2–5]. A number of articles describe the polarographic determination of sulfur dioxide[6–23]. Among these are descriptions of analyzers for the continuous automatic polarographic determination of sulfur dioxide in gases and liquids[11,14,15]. In none of these works was aqueous hydrofluoric acid the supporting medium.

The observation of a polarographic wave for sulfite in aqueous hydrofluoric acid was reported earlier[24]. The further study of this wave is described here. Polarography in aqueous hydrofluoric acid as a supporting medium is indicated to be a satisfactory direct way to determine sulfur dioxide.

EXPERIMENTAL

Instrumentation and apparatus

Polarographs. The polarographs were the ORNL models Q-1673 and Q-1988ES. The latter was used in both its two- and three-electrode function.

Electrodes. The *controlled* electrodes were dropping-mercury electrodes (D.M.E.). Both Sargent 3- to 5-sec glass capillaries and horizontal-orifice Teflon D.M.E.'s (47 and 78 μ-diam.-orifice Teflon segments) were used[24]. Initially, a glass capillary was used for work in the dilute hydrofluoric acid solutions. It was protected from the solution by a sheath of Tygon tubing and a coating of beeswax on part of its face away from the orifice.

The *reference* electrode was either an S.C.E., connected to the test solution by way of a sodium fluoride–agar salt bridge, or a mercury pool. When the Q-1988ES

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* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

polarograph was used as a three-electrode instrument, the *counter* electrode was a length of spectrographic graphite.

Polarographic cell. The polarographic cell and associated inlet and outlet tubes were made of HF-resistant materials.

Reagents

Hydrofluoric acid solutions. To eliminate the possibility of reducible metallic contaminants being present in the hydrofluoric acid used and to obtain a hydrofluoric acid solution of relatively high concentration, *ca.* 75 wt % hydrofluoric acid in water was prepared by gas-phase transfer from a cylinder of reagent-grade hydrogen fluoride. A quantity of triple-distilled water was placed in a polyethylene bottle that had been used previously to contain analyzed-reagent grade 49.2% hydrofluoric acid. The hydrogen fluoride gas was conducted from the pressure cylinder into the bottle through Tygon tubing arched in a way such that any condensate (*e.g* , H_2O–HF azeotrope) would fall back towards the cylinder and not be transferred to the bottle. Any non-gaseous materials would therefore have to be transferred by entrainment. The hydrofluoric acid solution was stored in the container in which it was prepared.

Test solutions of aqueous hydrofluoric acid were prepared by dilution from either the *ca.* 75 wt% hydrofluoric acid or Baker's analyzed-reagent grade 49.2% hydrofluoric acid.

Sulfurous acid. The sulfurous acid was ACS reagent-grade 6.8% aqueous solution.

Fluorosulfuric acid. Fluorosulfuric acid (*ca.* 98% HSO_3F; General Chemical Co.) was used.

All other reagents used in the work were ACS reagent grade.

Procedures

The polarographic cell was flushed with nitrogen or argon just before the addition of the sulfite to prevent loss of sulfite by volatilization and oxidation. Otherwise, the usual polarographic procedures were followed.

RESULTS AND DISCUSSION

The wave for sulfur dioxide (sulfite) in aqueous hydrofluoric acid

The polarographic wave for sulfite in 0.1 *M* hydrofluoric acid, together with polarograms of triple-distilled water and 0.1 *M* hydrofluoric acid, are presented in Fig. 1. The polarograms of Fig. 2 show the reduction wave for sulfite in aqueous hydrofluoric acid under conditions slightly different from those for Fig. 1. In each case the shape of the wave is excellent, the residual- and limiting-current regions being essentially parallel. With either sodium sulfite or sulfurous acid as the source of sulfite, the relation between C and i_d is linear over the range of C studied (0–$4.5 \cdot 10^{-5}$ M).

For the purpose of comparison and to demonstrate the reliability of the results for the aqueous hydrofluoric acid media, polarograms were recorded for sulfite in supporting media containing 0.1 *M* hydrochloric acid or 0.1 *M* nitric acid; these polarograms are given in Figs. 3 and 4, respectively. The mechanism of the polarographic reduction of sulfurous acid (sulfur dioxide) in 0.1–1 *N* solutions of strong

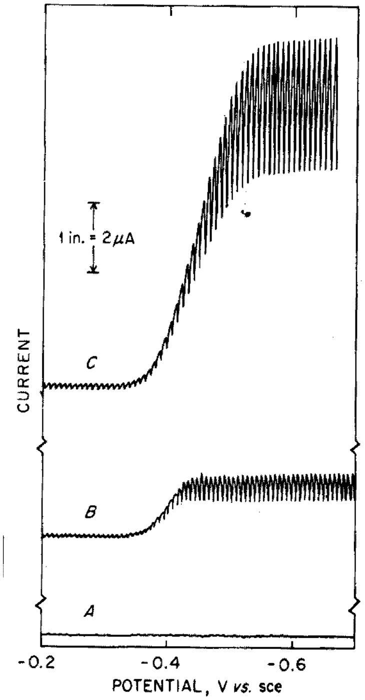


Fig. 1. Polarographic wave for sulfite in 0.1 *M* HF. Test solutions: (*A*) triple-distilled water; (*B*) 0.1 *M* HF (prepared from *ca.* 75 wt % HF); (*C*) 0.1 *M* HF–0.015% H_2SO_3. Polarograph, ORNL Q-1673. D.M.E., Sargent 2- to 5-sec (see text). Reference electrode, S.C.E. Salt bridge, sat. NaF soln.

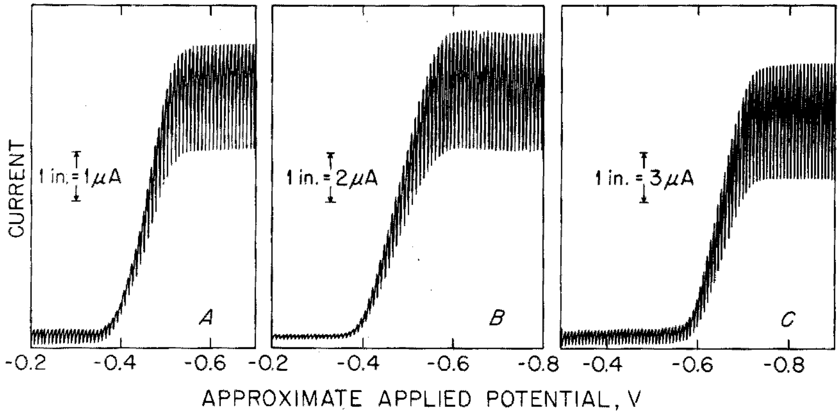
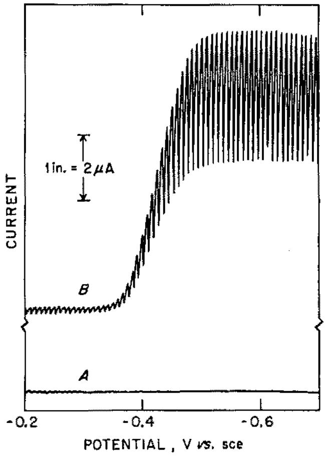


Fig. 2. Polarographic wave for sulfite in aqueous hydrofluoric acid under various conditions.

	Polarograms		
	A	*B*	*C*
Test solution	0.1 *M* HF–0.1 m*M* Na_2SO_3	0.25 *M* HF–1 m*M* Na_2SO_3	0.1 *M* HF–>2 m*M* Na_2SO_3
Polarograph	ORNL Q-1673	ORNL Q-1988ES	ORNL Q-1988ES
D.M.E.	Sargent 2- to 5- sec (see text)	63-μ-diam. Teflon	47-μ-diam. Teflon
Reference electrode	S.C.E.	S.C.E.	Mercury pool
Salt bridge	Sat. NaF soln	NaF–agar	———

mineral acids (not hydrofluoric) is discussed by KOLTHOFF AND MILLER[8], particularly with respect to an earlier discussion by GOSMAN[7]. By chronopotentiometry, controlled-potential coulometry, and cyclic voltammetry, JACOBSEN AND SAWYER[22] also have studied the electroreduction of sulfur dioxide. The results presented herein for the sulfite waves in the aqueous solutions of hydrofluoric, hydrochloric, and nitric acids are similar to each other and indicate that the redox behavior of sulfite is essentially the same in the three acids. These results are in general agreement with the data reported by KOLTHOFF AND MILLER for sulfite in *ca.* 0.1 N nitric acid. The polarographic wave is of essentially the same shape; the $E_{\frac{1}{2}}$ is about the same in 0.1 N hydrofluoric acid as in 0.1 N nitric acid.



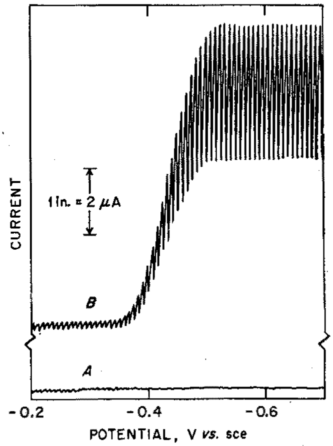


Fig. 3. Polarographic wave for sulfite in 0.1 M HCl. Test solutions: (A) 0.1 M HCl; (B) 0.1 M HCl–0.015% H_2SO_3. Other conditions: see Fig. 1.

Fig. 4. Polarographic wave for sulfite in 0.1 M HNO_3. Test solutions: (A) 0.1 M HNO_3; (B) 0.1 M HNO_3–0.015% H_2SO_3. Other conditions: see Fig. 1.

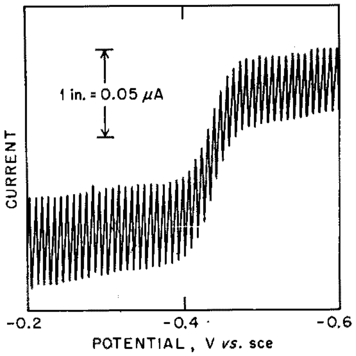


Fig. 5. Polarogram that shows the presence of sulfite in fluorosulfuric acid. Test solution, *ca.* 2.5% HSO_3F in triple-distilled water. Other conditions, see Fig. 1.

Sulfur dioxide as an impurity in hydrogen fluoride gas and in aqueous hydrofluoric acid

The polarograms of aqueous solutions of the *ca.* 75 wt % hydrofluoric acid prepared by gas-phase transfer from hydrogen fluoride and of commercial reagent 49% hydrogen fluoride show that sulfur dioxide is present as an impurity in both the gas and the reagent; polarogram *B* of Fig. 1 is typical. These results indicate that polarography of an aqueous solution of a particular hydrofluoric acid sample in question is a simple and direct means to detect and measure the sulfur dioxide contaminant. It is surely advisable to remove the traces of sulfur dioxide from hydrogen fluoride gas[3] and from aqueous hydrofluoric acid that are put to certain uses, for example, in fluorination processes where sulfur dioxide can possibly cause embrittlement and corrosion, and in polarography when the sulfite wave may interfere with the polarographic wave of another substance. Electrolytic-grade reagent aqueous hydrofluoric acid is recommended for polarographic work, because the sulfite wave has not been detected in polarograms of it.

Sulfur dioxide as an impurity in fluorosulfuric acid (HSO_3F)

The possibility was explored that fluorosulfuric acid might be the impurity in aqueous hydrofluoric acid that caused the wave which was later identified as the sulfite wave. The analysis of dilute aqueous solutions of *ca.* 98% fluorosulfuric acid showed, instead, that sulfite is a trace impurity in fluorosulfuric acid; the polarogram of Fig. 5 is evidence. This observation is of interest, because fluorosulfuric acid is a superacid that is becoming increasingly important as a solvent[25].

SUMMARY

A well-formed polarographic wave exists for sulfur dioxide (sulfite) in aqueous hydrofluoric acid at a half-wave potential ($E_{\frac{1}{2}}$) of about −0.4 V *vs.* S.C.E. The characteristics of the wave are similar to those of the wave for sulfite in aqueous solutions of hydrochloric acid and of nitric acid. The relation of sulfite concentration (*C*) to diffusion current (i_d) is linear, and the wave is reproducible. Polarography in aqueous hydrofluoric acid media is indicated to be a suitable method for the detection and direct determination of sulfur dioxide. Possible significant applications of the method are to determine contaminative sulfur dioxide in hydrogen fluoride gas, in reagent-grade hydrofluoric acid and fluorosulfuric acid, and in the atmosphere.

RÉSUMÉ

Une onde polarographique bien déterminée existe pour l'anhydride sulfureux (sulfite) dissous dans une solution aqueuse de l'acide fluorhydrique au potentiel demi-onde ($E_{\frac{1}{2}}$) d'environ −0.4 V, relatif à une electrode de calomel saturé (S.C.E.). Les caractéristiques de l'onde sont assimilables à celles de l'onde du sulfite dissous dans des solutions de l'acide nitrique ou chlorhydrique. La relation entre la concentration de sulfite (*C*) et le courant de diffusion (i_d) est linéaire, et l'onde est reproductible. La polarographie dans des milieux aqueux de l'acide fluorhydrique paraît comme méthode convenable pour la détection et la directe détermination quantitative de l'anhydride sulfureux. Des applications significatives possibles de la méthode sont la détermination de l'anhydride sulfureux présent comme impureté dans le fluorure de hydrogène gazeux, dans le réactif acide-fluorhydrique, et dans l'atmosphère.

ZUSAMMENFASSUNG

Das in einer wässrigen Flusssäurelösung gelöste Schwefeldioxyd zeigt eine ausgeprägte polarographische Welle bei einem Halbwellenpotential ($E_{\frac{1}{2}}$) von etwa -0.4 V gegen eine gesättigte Kalomelelektrode. Die Charakteristiken dieser Welle sind ähnlich wie die einer Welle von in wässrigen Salzsäure- bzw. Salpetersäurelösungen gelöste Sulfit. Das Verhältnis von Sulfitkonzentration (C) zu Diffusionsstrom (i_d) ist linear, und die Welle reproduzierbar. Polarographie in wässrigen Flusssäuremitteln scheint eine, zum Nachweis und zur direkten quantitativen Messung des Schwefeldioxyds geeignete Methode zu sein. Wichtige Anwendungsgebiete der Methode sind die Bestimmung von Schwefeldioxyd als Verunreinigung in gasförmigem Flusswasserstoff, in reagierender Flusssäure, und in der Luft.

REFERENCES

1 M. Kilpatrick and J. G. Jones, in J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents. Vol. II. Acidic and Basic Solvents*, Chap. 2, Academic Press, New York, 1967.
2 P. J. Elving, C. A. Horton and H. H. Willard, in J. H. Simons, *Fluorine Chemistry*, Vol. II, Chap. 3, Academic Press, New York, 1954, esp. p. 170.
3 V. Weinmayr (to the E. I. du Pont de Nemours & Co., Inc.), *U. S. Patent 2, 777, 754*, Jan. 15, 1957; *Chem. Abstr.*, 51 (1957) P6960*f*.
4 G. V. Rabovskii, T. N. Egorova and O. P. Kasatkina, *Zavodsk. Lab.*, 25(1) (1959) 36; *Chem. Abstr.*, 53 (1959) 11098*e*.
5 *A Manual of Methods for the Analysis of Anhydrous Hydrogen Fluoride*, United Kingdom At. Energy Authority Production Group Rept. PG 292 (S) (1962) Method 2.
6 V. Stefan, *Chem. Prumysl*, 12(12) (1962) 652.
7 B. Gosman, *Collection Czech. Chem. Commun.*, 2 (1930) 185.
8 I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 63 (1941) 2818.
9 O. Ya. Batmanova, *Gigiena i Sanit.*, No. 12 (1951) 17; *Chem. Abstr.*, 46 (1952) 3456*i*.
10 A. Foffani and G. Dall'Aglio, *Ric. Sci.*, 22 (Suppl. A) (1952) 107.
11 L. D. Wilson and R. J. Smith, *Anal. Chem.*, 25 (1953) 334.
12 J. Heyrovský, *Anal. Chim. Acta*, 8 (1953) 283.
13 J. Roubal, J. Zdrazil and F. Picha, *Cesk. Epidemiol. Mikrobiol. Imunol.*, 3 (1954) 188; *Chem. Abstr.*, 48 (1954) 13537*f*.
14 J. V. A. Novak, *Chem. Anal. (Warsaw)*, 1 (1956) 123; *Chem. Abstr.*, 51 (1957) 4766*i*.
15 J. Gottfried, *Chem. Prumysl*, 6 (1956) 143; *Chem. Abstr.*, 50 (1956) 16461*g*.
16 E. Zvinca-Selegean, L. Cariadi and N. Racoveanu, *Rev. Chim. (Bucharest)*, 9 (1958) 39; *Chem. Abstr.*, 53 (1959) 3991*c*.
17 M. Brezina and P. Zuman, *Polarography in Medicine, Biochemistry and Pharmacy*, Interscience, New York, 1958, p. 118.
18 D. T. Sawyer, R. S. George and R. C. Rhodes, *Anal. Chem.*, 31 (1959) 2.
19 C. F. Timberlake, *Analyst*, 84 (1959) 570.
20 H. G. Dassler and E. Ewert, *Z. Anal. Chem.*, 206 (1964) 380.
21 J. V. A. Novak, *Collection Czech. Chem. Commun.*, 30 (1965) 2703.
22 E. Jacobsen and D. T. Sawyer, *J. Electroanal. Chem. Interfacial Electrochem.*, 15 (1967) 181.
23 A. G. Voloshin, *Soviet Electrochem.*, 3 (7) (1967) 719; *Elektrokhim.*, 3(7) (1967) 813.
24 H. P. Raaen, *Anal. Chem.*, 34 (1962) 1714.
25 R. J. Gillespie, *Accounts Chem. Res.*, 1 (1968) 202.

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OSCILLOPOLAROGRAPHIC DETERMINATION OF INDIUM, LEAD AND CADMIUM IN A SUPPORTING ELECTROLYTE CONTAINING CUPFERRON

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The oscillopolarographic activity of several cations in supporting electrolytes containing cupferron, has already been described[1]. The incision of the cations on the $dE/dt = f(E)$ curve may be attributed to the reduction of either the cation or the anion of the corresponding chelates. In solutions buffered between pH 1 and 5, chelates such as those of gallium(III) and indium(III) are reduced to the metal whereas those of thorium(IV) and uranium(IV) are reduced to phenylhydrazine at more negative potentials.

The behaviour of uranium(VI or IV) and thorium(IV) in these supporting electrolytes has been used for their oscillopolarographic determination[1].

In the present paper, a method for the detection and determination of cadmium(II), lead(II) and indium(III) in a supporting electrolyte containing cupferron is described. The supporting electrolyte also contains sodium thiosulphate and a phosphate buffer solution of pH 7. Under these conditions the characteristic incisions of cupferron in the $dE/dt = f(E)$ curve have no effect and few other ions interfere. Cadmium(II), lead(II) and indium(III) form incisions which allow them to be detected and determined at *ca.* $2 \cdot 10^{-2}$ *M* concentrations. The incisions are produced by reduction of the cation, and the high sensitivity obtained can be ascribed to the adsorption of the chelates on the mercury surface.

Because of its specificity and sensitivity, the determination of indium(III) by this method has advantages over other oscillopolarographic methods described for this metal[2-5].

EXPERIMENTAL

Instrumentation and chemicals

A polaroscope Model P 576 (Křižik, Prague) was used. The supporting electrolyte contained 0.1 *M* sodium dihydrogen phosphate–disodium hydrogen phosphate buffer pH 7, 10^{-2} *M* sodium thiosulphate and 10^{-2} *M* cupferron. In the electrolytic cell a dropping mercury electrode was used as cathode with a mercury pool anode.

The cupferron used was of p.a. quality (Carlo-Erba, AnalaR, Union Chimie Belge, and Mathieson, Coleman and Bell). The results were the same for each source of supply and reproducible results were obtained with solutions stored for up to 15 days protected from light.

Standard solutions

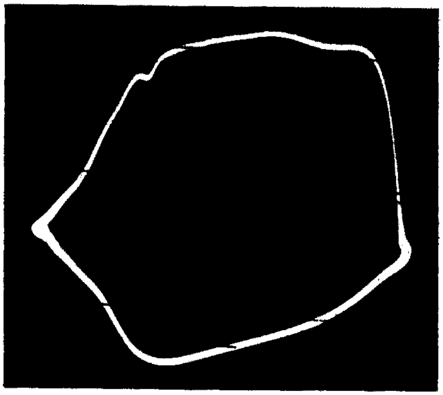
A 10^{-2} *M* indium(III) solution was prepared from indium metal (p.a., Union Chimie Belge); 57.4 mg of the metal were dissolved in 2 ml of 6 *M* nitric acid and the solution was diluted to 50 ml with water.

A 10^{-2} *M* lead(II) solution and a 10^{-2} *M* cadmium(II) solution were prepared from lead nitrate (p.a., Merck) and $3\,CdSO_4 \cdot 8H_2O$ (p.a., May and Baker) respectively.

All solutions were prepared in twice-distilled water.

RESULTS AND DISCUSSION

The oscillopolarogram of the supporting electrolyte is shown in Fig. 1. The most positive potential region is limited by the potential corresponding to the thiosulphate incision (reduction of tetrathionate), whereas the extreme right of the oscillopolarogram is determined by the potential corresponding to the characteristic cupferron incision. The portion of the curve where other incisions are developed (both on the negative and positive sides) are eliminated by the presence of an excess of cupferron.



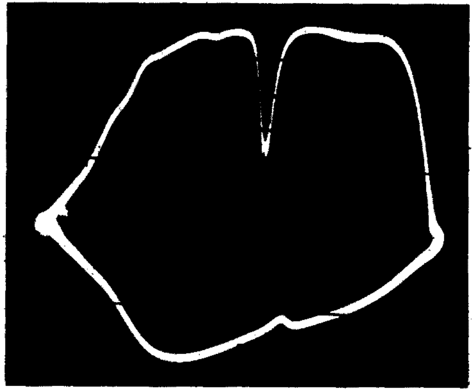


Fig. 1. Oscillopolarogram of supporting electrolyte.

Fig. 2. Supporting electrolyte with $2 \cdot 10^{-5}$ *M* indium(III).

TABLE I

OSCILLOPOLAROGRAPHIC ACTIVITY OF VARIOUS CATIONS

(a = anodic incision; c = cathodic incision; id = ill-defined)

Ion	*Q*	*Sensitivity (M)*	*Ion*	*Q*	*Sensitivity (M)*
Tl(I)	0.40 a,c	$1 \cdot 10^{-5}$	Fe(III)	0.76 c, id	$2 \cdot 10^{-5}$
Pb(II)	0.40 a,c	$2 \cdot 10^{-6}$	Ga(III)	0.30 c	$3 \cdot 10^{-4}$
Mn(II)	0.68 c,id	$2 \cdot 10^{-6}$		0.86 c	$3 \cdot 10^{-4}$
Co(II)	0.80 c, id		In(III)	0.52 a, c	$2 \cdot 10^{-6}$
	0.36 c, id	$1 \cdot 10^{-4}$	Sb(III)	0.44 c	$3 \cdot 10^{-5}$
Ni(II)	0.66 c, id	$1 \cdot 10^{-5}$	Bi(III)	0.20 c	$2 \cdot 10^{-4}$
Cu(II)	0.28 c	$5 \cdot 10^{-5}$	Th(IV)	0.68 c, id	$4 \cdot 10^{-6}$
Zn(II)	0.85 c	$3 \cdot 10^{-6}$	Ti(IV)	0.70 c, id	$1 \cdot 10^{-5}$
	0.70 a	$6 \cdot 10^{-6}$	V(V)	0.60 c, id	$1 \cdot 10^{-5}$
Cd(II)	0.45 a, c	$2 \cdot 10^{-6}$	Cr(VI)	0.86 c, id	$2 \cdot 10^{-6}$
Sn(II)	0.56 c	1.10^{-5}			
Cr(III)	0.90 c, id	$1 \cdot 10^{-5}$			

The oscillopolarogram shows a small incision (Q: 0.30) which must correspond to the reduction of mercury(II) sulphate, since sulphur, sulphides and carbon disulphide behave in exactly the same way in phosphate buffer solution[6]. Mercury(II) sulphate is produced at the surface of the mercury drop by disproportionation of thiosulphate.

The oscillopolarographic activities of various cations in this supporting electrolyte are shown in Table I. The position of the incision on the $dE/dt = f(E)$ curve is given in terms of Q values and the sensitivity of each incision in terms of molarity. No incisions were found with aluminium(III), arsenic(III, V), lanthanum(III), zirconium(IV), tin(IV) or tungsten(VI), and only very ill-defined incisions with molybdenum(VI) or uranium(VI).

Besides the reversible incision of indium(III) ($Q = 0.52$; $E = -0.92$ V *vs.* S.C.E.), the most sensitive incisions are those of lead(II) ($Q = 0.40$; $E = -0.75$ V *vs.* S.C.E.) and cadmium(II) ($Q = 0.45$; $E = -0.83$ V *vs.* S.C.E.) which are also reversible (Figs. 2 and 3). The other cationic incisions are both ill-defined and relatively insensitive.

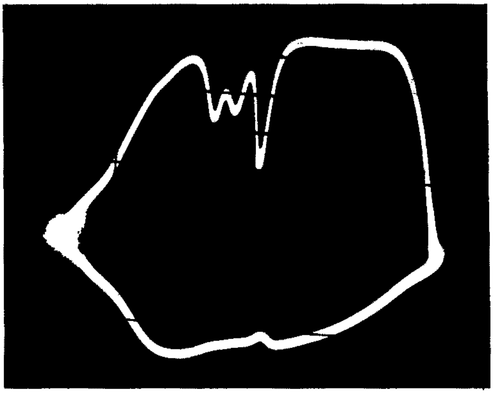


Fig. 3. Supporting electrolyte with $2 \cdot 10^{-5}$ *M* indium(III), $1.4 \cdot 10^{-5}$ *M* lead(II) and $2.5 \cdot 10^{-5}$ *M* cadmium(II).

The incisions of indium(III), lead(II) and cadmium(II) must correspond to the reduction of the chelates, whereas their high sensitivities show that there is an adsorption on the surface of the mercury drop. This interpretation is based on the following observations.

(*a*) Lead(II) and indium(III) do not give incisions in the supporting electrolyte in the absence of cupferron, whereas cadmium(II) gives only an insensitive incision.

(*b*) The chelates of lead(II), cadmium(II) and indium(III) prepared separately give the same indentation in the supporting electrolyte.

(*c*) Lead(II), cadmium(II) and indium(III) give polarographic waves in supporting electrolytes containing cupferron (sodium chloride, ammonium chloride). The $E_{\frac{1}{2}}$ value of the indium(III) wave is approximately 200 mV more negative than the normal wave in sodium chloride, whereas the $E_{\frac{1}{2}}$ values of the cadmium(II) and lead(II) waves are only slightly affected when cupferron is added to the supporting electrolyte. The heights of the three waves decrease in the presence of cupferron.

Detection and determination of indium

With the supporting electrolyte described above, the limit of detection is $2 \cdot 10^{-6}$ *M* and $2 \cdot 10^{-6}$–$5 \cdot 10^{-5}$ *M* indium(III) can be determined. These results were obtained by reference to a calibration curve (Fig. 4) drawn by plotting *h* values *vs.* concentration (*h* represents the distance between the extreme of the incision and the half line of the curve).

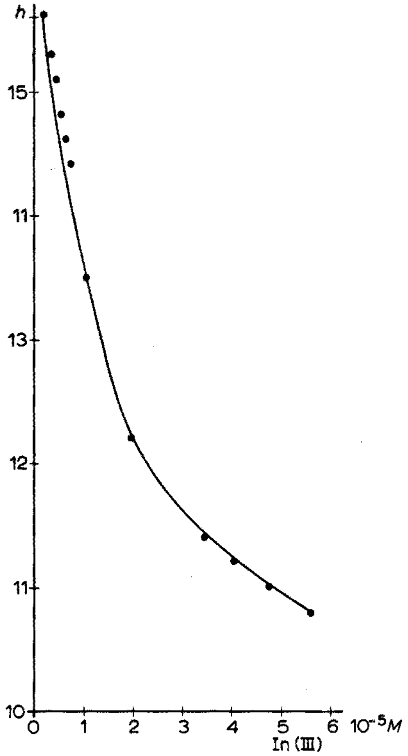


Fig. 4. Calibration curve for indium(III).

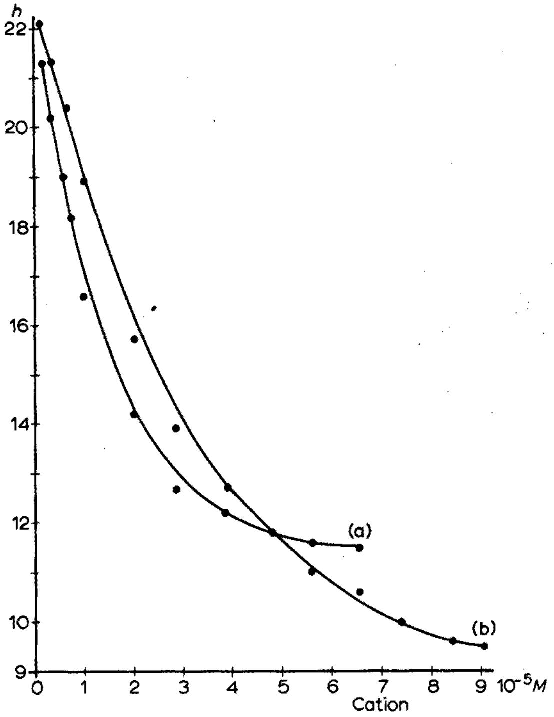


Fig. 5. Calibration curves. (a) Lead(II); (b) cadmium(II).

Cadmium(II), lead(II), tin(II) and antimony(III) give incisions close to that of indium(III). The cadmium(II) incision, which is nearest to that of indium(III) may be eliminated with potassium hexacyanoferrate(II). In a 0.1 *M* hexacyanoferrate(II) solution, the incision corresponding to 10^{-2} *M* cadmium(II) was eliminated without effect on the indium(III) incision. Lead(II) does not interfere even if its concentration is 30-fold that of indium(III). The incisions of tin(II) and antimony(III) are not sensitive; *ca.* 10^{-3} *M* concentrations of these cations do not interfere if they are previously oxidized to their higher valency states with hydrogen peroxide in acidic media.

Some ions decrease the sensitivity of the indium(III) incision. The limiting ratios for a maximum error of 5% are shown in Table II; these ratios were obtained without the addition of hexacyanoferrate(II) to the supporting electrolyte and without oxidation of tin(II) and antimony(III).

Many anions such as perchlorate, chloride, bromide, nitrate, sulphate, thiocyanate, hexacyanoferrate, formate, acetate, oxalate, tartrate, citrate, do not interfere in the detection and determination of indium, even at 0.1 *M* concentrations.

TABLE II

EFFECT OF DIVERSE IONS

(Limiting ratios for a maximum error of 5 %)

Ion	*$1.6 \cdot 10^{-5}$ M In(III)*	*10^{-5} M Pb(II)*	*10^{-5} M Cd(II)*
	Ion/In(III)	*Ion/Pb(II)*	*Ion/Cd(II)*
Tl(I)	370	1	5
Pb(II)	30	—	0.5
Mn(II)	200	400	100
Co(II)	110	50	50
Ni(II)	20	35	35
Cu(II)	40	100	100
Zn(II)	35	30	20
Cd(II)	10	2	—
Sn(II)	7	5	5
Cr(III)	30	100	100
Fe(III)	40	20	40
Al(III)	1000	1000	1000
Ga(III)	10	5	10
In(III)	—	2	2
As(III)	60	100	100
Sb(III)	6	4	2
Bi(III)	20	30	40
La(III)	32	4	4
Th(IV)	6	10	5
Ti(IV)	30	5	20
Zr(IV)	30	20	50
Sn(IV)	100	100	100
V(V)	1	3	3
As(V)	60	80	100
Mo(VI)	1	5	3
U(VI)	2	4	3
W(VI)	600	700	500
Cr(VI)	10	10	8

Detection and determination of lead(II)

The supporting electrolyte proposed also permits lead to be detected from $2 \cdot 10^{-6}$ *M* and determined in the range $2 \cdot 10^{-6}$–$5 \cdot 10^{-5}$ *M* (Fig. 5a). There are four incisions close to that of lead(II). Thallium(I) gives a reversible incision at the same potential as that of lead(II), but does not interfere at concentrations lower than 10^{-5} *M* in the electrolytic cell. The interferences of cadmium(II) and indium(III) may be completely eliminated with EDTA solution; cadmium(II) can also be masked with hexacyanoferrate(II) as in the determination of indium. Tin(II) and antimony(III) do not interfere in the detection of lead if they are previously oxidized with peroxide as described above.

As happens in other oscillopolarographic determinations, the presence of other ions decreases the sensitivity of the determination. Of all the ions examined, apart from those mentioned above, the greatest interferences were found with lanthanum(III), vanadium(V) and uranium(VI). The limiting ratios determined in the same way as in the case of indium, are shown in Table II.

There is no interference from the anions listed above for the determination of indium, even in 0.1 M concentrations.

Detection and determination of cadmium(II)

With the above-mentioned supporting electrolyte, the limit of detection for cadmium is $2\cdot10^{-6}\,M$, and $2\cdot10^{-6}$–$5\cdot10^{-5}\,M$ cadmium can be determined (Fig. 5b). Lead(II) and indium(III) must be absent. The interferences of tin(II) and antimony(III) can be eliminated as described above. Other interferences are lanthanum(III), vanadium(V), molybdenum(VI) and uranium(VI) (see Table II). The anions listed above do not interfere.

SUMMARY

In a supporting electrolyte containing phosphate buffer pH 7, $10^{-2}\,M$ sodium thiosulphate and $10^{-2}\,M$ cupferron, lead(II), cadmium(II) and indium(III) give reversible, sensitive and well-defined incisions in the $dE/dt=f(E)$ curves ($Q=0.40$, 0.45, and 0.52 respectively). The limit of detection is $2\cdot10^{-6}\,M$ in each case and $2\cdot10^{-6}$–$5\cdot10^{-5}\,M$ of each cation may be determined. There are few serious interferences.

RÉSUMÉ

Dans une solution électrolytique composée d'une tampon de phosphate 0.1 M, pH 7, thiosulfate de sodium $10^{-2}\,M$ et cupferron $10^{-2}\,M$, Pb(II), Cd(II) et In (III) donnent des incisions réversibles, très sensitives et bien développées sur la courbe $dE/dt=f(E)$ ($Q=0.40$, 0.45 et 0.52 respectivement). On peut doser de $2\cdot10^{-6}$ jusqu'à $5\cdot10^{-5}\,M$ de tous les trois. Il y a peu d'éléments qui gênent sérieusement.

ZUSAMMENFASSUNG

Bei der oscillopolarographischen Bestimmung von Blei(II), Cadmium(II) und Indium(III) ergeben sich reversible, empfindliche und gut definierte Schnitte in den $dE/dt=f(E)$-Kurven ($Q=0.40$, 0.45 und 0.52), wenn der Elektrolyt Phosphatpuffer vom pH 7, $10^{-2}\,M$ Natriumthiosulfat und $10^{-2}\,M$ Cupferron enthält. Die Nachweisgrenze beträgt in allen Fällen $1\cdot10^{-6}\,M$. Und $2\cdot10^{-6}$ bis $5\cdot10^{-5}\,M$ eines jeden Kations können bestimmt werden. Es gibt nur wenige ernsthafte Störungen.

REFERENCES

1 G. Donoso, M. A. Santa Ana and I. Chadwick, *Anal. Chim. Acta*, 42 (1968) 109.
2 J. Heyrovský and J. Forejt, *Oscilografická Polarografie*, State Publishing House of Technical Literature, Prague, 1953.
3 L. Treindl, *Chem. Listy*, 50 (1965) 534.
4 J. Matysik, *Chem. Zvesti*, 18, 5/6 (1964) 407.
5 S. Pao Chuan, J. Dolezal and J. Zýka, *Collection Czech. Chem. Commun.*, 30 (6) (1965) 1785.
6 R. Kalvoda, *Chem. Listy*, 49 (1955) 759.

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SEPARATION OF DICARBOXYLIC AND TRICARBOXYLIC ACIDS BY ANION-EXCHANGE CHROMATOGRAPHY IN MAGNESIUM ACETATE

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In the separation of organic acids by chromatography on anion-exchange resins, advantage can be taken of the complex formation between metal ions present in the eluant and the species to be separated. Copper acetate[1], zinc acetate[2] and magnesium acetate[3] have been employed in previous work. The use of acetate as the anion is advantageous since the eluate can be analyzed automatically by chromic acid oxidation. Of the metal ions studied to date, magnesium offers certain advantages[3] and a systematic study of the application of magnesium acetate for separating mixtures of various organic acids containing two or three carboxyl groups was therefore of interest.

EXPERIMENTAL

The equipment for the chromatographic separation was the same as that described previously[4]. The column, 3.2 × 1350 mm, was filled with Dowex 1-X8, 17–20 μm, and the temperature was kept at 70°.

The eluants were prepared from magnesium acetate with acetic acid added to obtain the desired pH. The eluant concentrations refer to the molarity with respect to magnesium.

Unless otherwise mentioned, the acids to be separated were applied to the column as their sodium salts. When the starting material was a lactone or contained lactones these were saponified carefully before application. The samples were purchased from various commercial sources and contained no appreciable amounts of impurities except for meso-tartaric acid which contained tartaric acid. This acid was purified by anion-exchange chromatography.

The automatic analysis of the eluate was carried out in the monitor described previously[4]. Only the chromic acid channel was employed. Separate tests showed that the following species were not recorded: succinic, methylsuccinic, glutaric and 3,3-dimethylglutaric acids. If these acids are to be determined, other analytical methods must be employed, *e.g.* evaporation of the eluate after removal of the magnesium ions by a cation exchanger.

RESULTS AND DISCUSSION

The volume distribution coefficients, D_v, were calculated[5] from the peak

TABLE I

VOLUME DISTRIBUTION COEFFICIENTS (D_v) AT 70° IN MAGNESIUM ACETATE AT VARYING pH AND CONCENTRATION

Acid	*pH 7.0*			*pH 3.9*
	0.2 M	*0.3 M*	*0.5 M*	*0.2 M*
Oxalic	2.07	0.83	0.32	1.76
Malonic	3.51	1.52	0.61	7.65
Adipic		8.65		4.44
Pimelic		12.1		5.86
Suberic		19.8		
Methylmalonic	6.06	2.62	0.84	11.5
Tartronic	4.36	1.59		4.11
Malic	6.31	2.63	0.85	4.95
L(+)Tartaric	16.2	6.33	2.08	9.76
meso-Tartaric	5.71	2.33		4.37
Dihydroxytartaric	4.30	1.67		4.13
β-Hydroxy-β-methylglutaric	10.6	3.90	1.50	4.91
Glucaric	9.75	3.84		5.49
Galactaric	10.5	4.13		5.77
Fumaric	54.0	25.3	9.48	31.9
Maleic	15.7	6.90	2.92	31.8
Citraconic	13.4	6.00	2.66	32.9
Itaconic	22.6	9.63	3.54	11.3
Muconic			13.8	
Mesoxalic			9.56	
Oxalacetic	8.18	5.81	3.99	5.85
α-Ketoglutaric	56.6	27.0	9.61	22.2
Citric	5.17	2.46		9.0
Isocitric	13.3	4.07		
Isocitric lactone	26.6	11.2		
cis-Aconitic	39.2	11.6	3.09	
trans-Aconitic			8.05	

TABLE II

VOLUME DISTRIBUTION COEFFICIENTS (D_v) AT 70° IN SODIUM ACETATE, pH 7.0

Acid	*0.4 M*	*0.8 M*	*1.0 M*
Oxalic	32.0	6.25	
Malonic	20.7	4.49	
Malic	20.5	4.48	
L(+)Tartaric	25.6	4.88	
Fumaric			7.72
Maleic			4.50
α-Ketoglutaric			7.36

elution volumes recorded in runs with single acids and check runs with suitable mixtures. In consecutive runs the deviations were less than 0.5%, but over a period of several months a decrease in all D_v values was observed which can be ascribed to a loss in exchange capacity (about 1% per month). The positions of the acids relative to each other were unchanged, however. The results obtained in experiments at pH 7.0 and 3.9 are listed in Table I.

For purposes of comparison the D_v values of some of the acids were determined in sodium acetate at pH 7.0. The results given in Table II show that oxalic, malonic, malic and tartaric acids are eluted much later in 0.4 *M* sodium acetate than in 0.2 *M* magnesium acetate. Likewise, malic acid is eluted later in 1 *M* sodium acetate than in 0.5 *M* magnesium acetate. Evidently, the formation of non-sorbable complexes or complex ions with a lower affinity for the resin than that of the non-complexed anions has a predominant influence upon the elution of these acids in magnesium acetate. In sodium acetate malonic and malic acids exhibit identical elution behavior whereas in magnesium acetate they are well separated. Fumaric and α-ketoglutaric acids are eluted earlier in 1 *M* sodium acetate than in 0.5 *M* magnesium acetate which shows that with some species held very strongly in magnesium acetate solution the complex formation with magnesium is less important than the complex formation between the magnesium and acetate ions. If only ions of this type are involved in the mixture to be analyzed, the application of magnesium acetate does not offer any advantages over sodium acetate.

At the lower pH level the complex formation with magnesium ions is still of great importance for some acids, *e.g.* oxalic acid, but less important for others[3].

Theoretically, the D_v value in magnesium acetate can be calculated from the values recorded in sodium acetate provided that the relevant stability constants are known. In the experiments at pH 7 the presence of protonated species can be disregarded with the stronger acids. According to CANNAN AND KIBRICK[6] the formation of binary compounds suffices to give a fairly satisfactory description of the complex formation with acetic, oxalic, malic and tartaric acids. Calculations made according to the principles previously outlined[5,7] showed that the deviations between the observed and calculated values were large and that only predictions of a qualitative kind could be made based upon published data.

The approximate correlation: $D_v = \text{const.} \cdot 1/[\text{Ac}^-]^2 \cdot 1/(1+\beta[\text{Mg}^{2+}])$ could be used, however, for a rough calculation of the D_v values in 0.2 *M* and 0.5 *M* magnesium acetate from the value determined in 0.3 *M* solution. The concentrations of magnesium and acetate ions were calculated from CANNAN AND KIBRICK's data and the stability constant, β, of the magnesium complex with the diprotic acid was obtained from the same work.

In agreement with theory, the D_v values of all species decrease rapidly with an increased concentration of magnesium acetate. With most acids the order of elution is independent of the eluant concentration. With some species, however, a reversal occurred confirming the supposition that the effect of the complex formation differs from one type of acid to another.

When no complex formation is involved monovalent anions are, as a rule, held less strongly than divalent anions. A lowering of the pH, therefore, can be predicted to result in lowered D_v values of those acids which exhibit negligible complex formation in neutral magnesium acetate. This is confirmed by the results obtained with fumaric and α-ketoglutaric acids (Table I).

An effect in the opposite direction is that protonization gives rise to increased attraction forces with the resin matrix. This effect is expected to be most important with the more non-polar species and above all with the unsaturated acids. The influence of this factor upon the D_v value can be assumed to increase with decreased acid strength. It is likely that the high D_v values obtained with maleic and methylmaleic (citraconic) acids at pH 3.9 can be ascribed to attraction forces of this type.

With most acids which give strong complexes at pH 7, the D_v values decrease when the pH is lowered, but from the results given in Table I, it is seen that with some species the opposite holds true. Available data do not permit reliable calculations of the influence of the pH on the distribution coefficients. From a practical point of view the fact that changes in the pH value exert effects in opposite directions with different acids is of great importance for the identification of unknown species based upon their D_v values and also for the resolution of complex mixtures of acids.

The application of magnesium acetate at pH 7 in practical analytical work is illustrated by the chromatogram reproduced in Fig. 1. Two of the added acids, malonic and dihydroxytartaric, exhibited only slightly different distribution coefficients, and as expected their elution curves overlapped seriously. The other acids were well separated. As can be seen from Table I, at pH 3.9 the distribution coefficients of malonic and dihydroxytartaric acids differed markedly and at this pH an excellent separation was achieved.

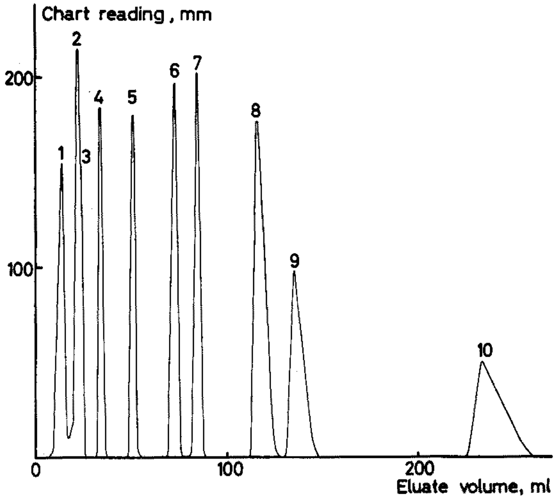

Fig. 1. Separation of 5 mg oxalic (1), 1.5 mg malonic (2), 1.0 mg dihydroxytartaric (3), 0.5 mg malic (4), 0.5 mg galactaric (5), 0.8 mg citraconic (6), 0.5 mg maleic (7), 1.0 mg itaconic (8), 1.0 mg *cis*-aconitic (9), and 2.0 mg suberic acid (10). Eluant: 0.3 M magnesium acetate, pH 7.0, flow rate: 4.5 ml cm^{-2} min^{-1}.

As usual most species which appeared early in the eluate gave rise to sharp elution curves. An exception was citric acid (not included in the run represented in Fig. 1) which appeared in a broad unsymmetrical band with a distorted leading edge. Likewise the leading edge of the first band (oxalic acid) was less sharp than that recorded with bands 3 and 4. The species which were strongly held by the resin gave broad, tailing elution curves.

Since solutes which appeared after oxalic and citric acids gave sharp and symmetrical curves the broadening of the bands corresponding to these two acids cannot be ascribed to unfavorable flow pattern effects. No appreciable improvement in the shape of the oxalic and citric acid bands was achieved by decreasing the flow rate to about one third of that employed in the run represented in Fig. 1. This indicates that the broadening cannot be attributed to a slow establishment of equilibria. The most probable explanation of the asymmetry, therefore, is that the sorption isotherms are non-linear.

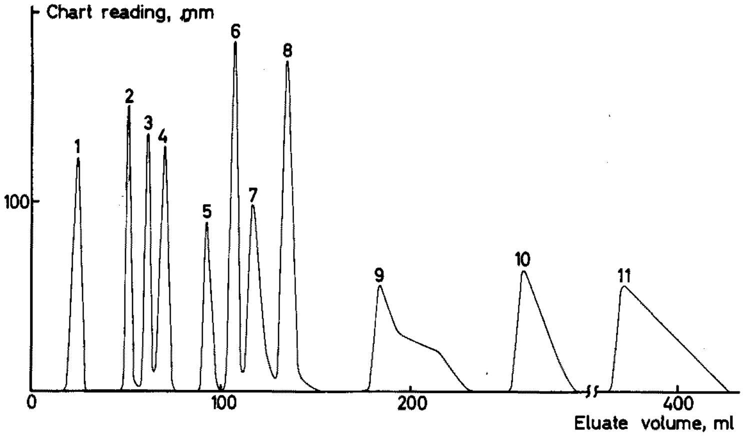

Fig. 2. Separation of 5.0 mg oxalic (1), 1.0 mg tartronic (2), 0.5 mg malic (3), 0.5 mg galactaric (4), 1.5 mg malonic (5), 1.6 mg citric (6), 1.0 mg L(+)tartaric (7), 1.0 mg itaconic (8), 2.0 mg isocitric lactone (9), 2.0 mg α-ketoglutaric (10), and 2.0 mg fumaric acid (11). Eluant: 0.2 *M* magnesium acetate, pH 3.9, flow rate: 4.2 ml cm^{-2} min^{-1}.

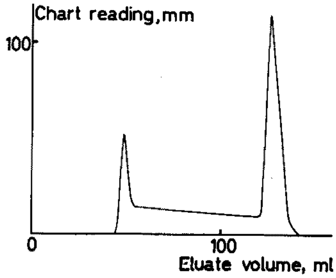

Fig. 3. Elution of 2.5 mg isocitric lactone with 0.3 *M* magnesium acetate at pH 7. Flow rate: 4.8 ml cm^{-2} min^{-1}.

Figure 2 illustrates the separation of eleven different acids at pH 3.9. The shape of the band corresponding to citric acid was more favorable at this pH although the acid appeared later in this medium. Again, oxalic acid exhibited an unsymmetrical band, and as usual the species which appeared very late on the chromatogram exhibited broad and tailing elution curves. Sharper bands were obtained at increasing concentrations of magnesium acetate, and in analyses of not too complicated mixtures the separation can be speeded up and the quantitative determinations simplified by the application of gradient elution.

In the run referred to in Fig. 2 a monolactone of a tribasic acid (isocitric lactone) was included. It was added as its disodium salt. As is seen from the figure this compound gave rise to a distorted broad band (denoted by 9) the shape of which indicated the presence of more than one compound. The behavior of the unsaponified lactone during the chromatographic run can be ascribed to a partial decomposition of the lactone during its passage down the column.

The behavior of isocitric lactone upon elution with magnesium acetate at pH 7 is shown in Fig. 3. In this run the commercial lactone was dissolved in water and applied to the column without previous addition of sodium hydroxide. It is seen that two elution peaks were recorded and that a considerable amount of material appeared in the eluate between the two peaks. The minor peak which appeared first had a position corresponding to that recorded with the trisodium salt of isocitric acid, whereas the second peak was found to contain the lactone. The fact that organic material was distributed between the peaks is explained by a saponification of the lactone during the elution.

These results demonstrate that it is extremely important that the lactones are completely saponified before mixtures containing lactones are analyzed.

The recorded chromatograms were evaluated quantitatively by the method suggested by MOORE, SPACKMAN AND STEIN[8]. In duplicate runs the maximum deviation from the mean was 2% provided that conditions were chosen which resulted in a complete separation of the added acids.

The financial support of the Swedish Council for Applied Research is gratefully acknowledged.

SUMMARY

An automatic method is described for the determination of acids containing two or three carboxyl groups. The acids are separated on an anion-exchange resin with magnesium acetate as the eluant and are determined colorimetrically by chromic acid oxidation.

RÉSUMÉ

Une méthode automatique est décrite pour la détermination d'acides contenant 2 ou 3 groupes carboxyles. Les acides sont séparés sur une résine échangeuse d'anions au moyen de l'acétate de magnésium comme éluant et sont déterminés colorimétriquement par dosage à l'acide chromique.

ZUSAMMENFASSUNG

Es wird eine automatischen Methode zur Bestimmung von Säuren, die 2 oder 3 Carboxylgruppen enthalten, beschrieben. Die Säuren werden an einem Anionenaustauscherharz durch Elution mit Magnesiumacetat getrennt und anschliessend kolorimetrisch durch Chromsäureoxydation bestimmt.

REFERENCES

1 B. JOHNARD AND O. SAMUELSON, *Svensk Kem. Tidskr.*, 73 (1961) 586.
2 T. ISAKSSON, U.-B. LARSSON AND O. SAMUELSON, *Acta Chem. Scand.*, 20 (1966) 1965.
3 K. S. LEE AND O. SAMUELSON, *Anal. Chim. Acta*, 37 (1967) 359.

4 S. Johnson and O. Samuelson, *Anal. Chim. Acta*, 36 (1966) 1.
5 O. Samuelson, *Ion Exchange Separations in Analytical Chemistry*, Almqvist and Wiksell, Stockholm; Wiley, New York, 1963.
6 R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, 60 (1938) 2314.
7 O. Samuelson, *Svensk Kem. Tidskr.*, 76 (1964) 635.
8 S. Moore, D. H. Spackman and W. H. Stein, *Anal. Chem.*, 30 (1958) 1190.

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SHORT COMMUNICATIONS

The density of nitric acid solutions of uranium and uranium–aluminium alloys

The solution obtained after dissolution in nitric acid of uranium fuel in the chemical reprocessing of irradiated reactor fuel of low enrichment is *ca.* 1.0–1.5 *M* in uranyl nitrate and 2.5–3.5 *M* in nitric acid. Uranium fuel of high enrichment, made of aluminium–uranium alloy, yields a solution which is either 1–2 *M* in basic aluminium nitrate and 1–2.5 *M* in hydroxyl, or 1–2 *M* in aluminium nitrate and 0.5–1.5 *M* in nitric acid. The uranium content of these solutions is up to 4 g/l or 0.02 *M*. Mercury(II) nitrate up to 1 g/l or 0.005 *M* is added as catalyst during the dissolution.

The content of nuclear materials in the dissolved fuel is established by measurement, in the plant, of the liquid height in the batch tank, the density of the solution at temperatures up to 65°, and the amount of material per unit of the solution at laboratory temperature. The density of different samples from the batch is also determined at laboratory temperature to check the homogeneity of the solution. For quality control of the measurements, it is essential to have an independent check on the measured values. To achieve this aim, empirical equations for the density and its temperature dependence as a function of the concentrations of the constituents of the mentioned solutions have been established. These relationships are also of interest for process control of the fuel dissolution and the extraction process following the dissolution.

Experimental

Three experiments were designed so that the statistical evaluation of the results could be simplified. Two or three concentration levels of the constituents were

TABLE I

CONCENTRATIONS OF THE EXPERIMENTAL SOLUTIONS

Uranium–acid solutions		*Basic aluminium solutions*			*Aluminium–acid solutions*	
U (M)	*H^+ (M)*	*Al (M)*	*OH (M)*	*U (g/l)*	*Al (M)*	*H^+ (M)*
1.46	3.66	1.00	1.05	2.00	0.94	0.41
1.46	3.14	1.00	1.05	4.00	1.88	0.41[a]
1.46	2.62	1.00	2.05	2.00	0.94	1.42[a]
1.25	3.66	1.00	2.05	4.00	1.88	1.42
1.25	3.14	2.00	1.6	2.00	0.94	0.41[a,b]
1.25	2.62	2.00	1.6	4.00	1.88	0.41[b]
1.04	3.66	2.00	2.6	2.00	0.94	1.42[b]
1.04	3.14	2.00	2.6	4.00	1.88	1.42[a,b]
1.04	2.62					

[a] Plus 0.92 g Hg/l.
[b] Plus 4.00 g U/l.

TABLE II

EQUATIONS FOR c, d_{20} AND d_{25} AS A FUNCTION OF THE MOLAR CONCENTRATIONS

Solutions	Equations	Estimated st. dev.	
		Exp. coeff. or density (%)	*Coeff. of the eqn*
Uranium–acid	$c = 3.41 \cdot 10^{-4} + 0.56 \cdot 10^{-4}\,\mathrm{H} + 1.05 \cdot 10^{-4}\,\mathrm{U}$	1	$0.04 \cdot 10^{-4}$
	$d_{20} = 1.0185 + 0.0294\,\mathrm{H} + 0.3086\,\mathrm{U}$	0.1	0.0004
	$d_{25} = 1.0171 + 0.0289\,\mathrm{H} + 0.3081\,\mathrm{U}$	0.1	0.0004
Basic aluminium	$c = 4.44 \cdot 10^{-4} - 0.36 \cdot 10^{-4}\,\mathrm{OH} + 2.95 \cdot 10^{-4}\,\mathrm{U} + 0.58 \cdot 10^{-4}\,\mathrm{Al}$	1	$0.04 \cdot 10^{-4}$
	$d_{20} = 0.9975 - 0.0383\,\mathrm{OH} + 0.4434\,\mathrm{U} + 0.1580\,\mathrm{Al}$	0.1	0.0004
	$d_{25} = 0.9951 - 0.0380\,\mathrm{OH} + 0.4403\,\mathrm{U} + 0.1573\,\mathrm{Al}$	0.1	0.0004
Aluminium acid	$c = 4.64.10^{-4} + 0.31 \cdot 10^{-4}\,\mathrm{H} - 3.17 \cdot 10^{-4}\,\mathrm{U} + 0.12 \cdot 10^{-4}\,\mathrm{Al} + 31.70 \cdot 10^{-4}\,\mathrm{Hg}$	4	$0.07 \cdot 10^{-4}$
	$d_{20} = 1.0064 + 0.0305\,\mathrm{H} + 0.3897\,\mathrm{U} + 0.1536\,\mathrm{Al} + 0.2726\,\mathrm{Hg}$	0.1	0.0004
	$d_{25} = 1.0042 + 0.0303\,\mathrm{H} + 0.3882\,\mathrm{U} + 0.1531\,\mathrm{Al} + 0.2455\,\mathrm{Hg}$	0.1	0.0004
BURGER *et al.*[6]	$d_{25} = 1.0012 + 0.0310\,\mathrm{H} + 0.3177\,\mathrm{U} + 0.1553\,\mathrm{Al} - 0.0310\,\mathrm{OH}$	0.0032	
	$d_t = 1.0125\,d_{25} + 0.000145\,t - 0.0005\,d_{25}t - 0.0036$		
TID-12100[7]	s.g. $55°/40° = 1.0012 + 0.0310\,\mathrm{H} + 0.3131\,\mathrm{U} + 0.1553\,\mathrm{Al} + 0.2407\,\mathrm{Hg}$		

selected. Solutions with concentrations equal to particular combinations of these levels, were prepared from concentrated standard solutions of uranyl nitrate, mercury(II) nitrate, nitric acid, aluminium nitrate and basic aluminium nitrate. The concentrations at 20° of the 8 or 9 combinations are listed in Table I. The error in the concentrations is less than 0.2%. The uranium concentration was standardized gravimetrically[1] and the mercury content by EDTA titration[2]; the acidity, the aluminium and the hydroxyl concentration were determined by a potentiometric titration with sodium hydroxide compared with a solution prepared by dissolution of known amounts of aluminium metal in sodium hydroxide[3].

Volumetric flasks (25 ml, calibrated at 20°) were filled with the different solutions and were placed in a thermostatted bath. The water bath was then held consecutively at 6 temperatures 15.0, 25.0, 35.0, 45.0, 55.0 and 65.0°; at each temperature the liquid meniscus was adjusted to the mark and the density of the solutions was determined from the weight of the solution. The volumes of the volumetric flasks were corrected for thermal expansion of the glass[4]. The experiments were repeated to obtain an estimate of the experimental error, which should include the errors in level and temperature adjustment and temperature equilibration. The relative standard deviation of a single density measurement, estimated from the duplicate values, was 0.15%. This error is acceptable for the purpose of this investigation. The average of the duplicates was used for analysis.

Results and discussion

The temperature dependence of a density can be expressed by the equation:

$$d_t = d_0/(1+ct) \quad \text{or} \quad 1/d_t = 1/d_0 + t\cdot c/d_0$$

in which c is the cubic expansion coefficient.

The series of 6 reciprocal densities, measured on each experimental solution, can thus be represented by an expression of the form: $Y_i = a + bX_i$. Regression analysis[5] of these results yields for each solution a value for the coefficients a and b. The value of d_0 and c for each solution can be found by calculating the reciprocal value of a and the ratio of b and a respectively.

Regression analysis of the coefficients c, which have the dimension degree^{-1}, and the concentrations at 20° expressed in moles/l as variables, gave the linear relationships collected in Table II.

The densities at 20° and 25° of each solution can be calculated from the corresponding d_0 and c values. The linear relationships between the densities, expressed in g/ml, and the concentrations can be found in a similar way (Table II). The relationships for d_{25} are obtained from our measurements after conversion of the concentrations at 20° to 25°, by means of an average cubic expansion coefficient.

A density at $t°$ can thus be calculated by introducing the relevant values of d_{20} and c in the equation: $d_t = d_{20}/\{1+c(t-20)\}$. The error in a density can then be estimated on the basis of the differences between calculated and measured values.

These residuals show a random distribution over the range of concentrations and temperatures investigated and can be explained by the measurement error. This shows the adequacy of the representation of a density by a function which is only linear in the concentration of the constituents. The larger differences in the calculated and measured values of the expansion coefficients must be explained by the stronger interaction of the constituents. The estimated standard deviations of a calculated expansion coefficient or a density and of the coefficients of the equations are summarized in Table II.

BURGER *et al.*[6] derived equations for the calculation of densities and their temperature dependence. An equation for the specific gravity at 55° compared to water at 40° is mentioned in an USAEC report[7] (Table II). The uranium–acid solutions used by BURGER *et al.* contained only up to 0.6 M in acid. In the range investigated in this work, BURGER's formula gives densities at 25° which are 0.004 too high and densities at temperatures above 25° that are still higher. The basic aluminium solutions prepared by BURGER *et al.* had a hydroxyl concentration of only 0.2 M. The density of solutions used in this investigation calculated by BURGER's formula is about 0.013 too high. The formulae for calculating densities of aluminium–acid solutions give results which are in good agreement.

LANE *et al.*[8] published a formula for temperature correction of densities of uranium–acid solutions at temperatures lower than 100°:

$$d_t = d_{100} + a(100 - t)$$

The value of a can be read from a graph as a function of the weight percentage of water present in the solution. It can be shown that the coefficient a is approximately identical with the product cd_{20}. Comparison of a and cd_{20} indicates that the first is 10–20% higher than our cd_{20} values.

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1 G. CHARLOT AND D. BÉZIER, *Quantitative Inorganic Analysis*, Methuen, London, 1957, p. 620.
2 *Komplexometrische Bestimmungsmethoden mit Titriplex*, 3 Aufl., E. Merck A.G., Darmstadt, 1962, p. 46.
3 H. H. PH. MOEKEN AND W. A. H. VAN NESTE, *Anal. Chim. Acta*, 39 (1964) 267.
4 *Handbook of Chemistry and Physics*, The Chemical Rubber Co, Cleveland, 1964, p. F3.
5 O. L. DAVIES, *Design and Analysis of Industrial Experiments*, Oliver and Boyd, London, 1963, p. 346, 330 and 519.
6 L. L. BURGER, I. M. REHN, H. R. SCHMIDT AND C. M. SLANSKY, *USAEC report HW-11276*, 1949, quoted in *Progress in Nuclear Energy*, Series III, Vol. 2, Pergamon Press, New York, 1958, p. 535.
7 *Nuclear Materials Control in Irradiated Fuel Reprocessing*, USAEC report TID-12100, 1961, p. 64.
8 J. A. LANE *et al.*, *USAEC report CL-697*, 1945, quoted in *Reactor Handbook. Vol. II. Reprocessing*, Interscience Publishers, New York, 1961, p. 118.

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Sorption of protonated complex anionic species of the palladiazo reagent on cation-exchange resins in concentrated neutral saline media

"Palladiazo" is a structural isomer of the arsenazo III reagent which exhibits very convenient sensitivity and selectivity in its reaction with palladium(II)[1]. As discussed in detail elsewhere[2], palladiazo behaves as a decaprotic organic acid which liberates its ten protons in a stepwise and reversible way within the acidity limits comprised between 10 *M* perchloric acid and 13 *M* sodium hydroxide.

When the sorption of the reagent on ion exchangers was attempted, strikingly varying behaviour was observed, depending on the particular media chosen[2]. In this communication, only the case of aqueous palladiazo solutions of pH approaching neutrality is considered. In the pH interval 6–7, palladiazo is mainly present in aqueous solutions in the form of the $[H_4L]^{4-}$ and $[H_5L]^{3-}$ protonic complexes [2] which may be expected to be strongly sorbed on anionic exchangers. This was confirmed experimentally for aqueous media of low to moderate ionic strength, the reagent being fixed very firmly on thin anion-exchange resin layers. However, when the sorption experiments were repeated in 9–12 *M* sodium perchlorate media (pH 6.5 ± 0.5), the behaviour was quite different. In media of moderate ionic strength, palladiazo was adsorbed quantitatively on Dowex 21K anion exchanger but there was no sorption at all on Dowex 50W cation-exchange resin in parallel experiments. However, in 9–12 *M* sodium perchlorate media, the reagent was sorbed on Dowex 21K to a considerable extent (not quantitatively) and sorption proceeded quickly and quantitatively on the Dowex 50W resin.

The elution of palladiazo fixed under these conditions of high ionic strength was subsequently attempted by changing suddenly the salinity of the interstitial liquid by washing with distilled water. In the case of the cationic column, this procedure resulted in the immediate and quantitative desorption of the sorbed palladiazo layer which could be eluted very quickly, the resin layer being restored to its initial state. Elution of the cationic resin by washing the column with 5–6 *M* sodium perchlorate, was unsuccessful.

A completely opposite behaviour was observed when attempts were made to elute the reagent from the anionic column. Washing with water caused no noticeable desorption, as expected from the above observations, but desorption was very considerable (though not quantitative) when the resin was washed with 5–6 *M* sodium perchlorate solutions.

These observations clearly indicate the influence of the ionic strength of the medium on the sorption sign of the palladiazo species on ion-exchange resins, although the nature of these remarkable sorption inversion phenomena remains to be explained conclusively. At present, it is uncertain if these sorption inversions derive from interaction of the neutral concentrated saline media with the resin network (swelling effects, electrolyte penetration, ion-pair formation, competitive sorption phenomena, etc.), or if they are related to interaction of the media with the anionic palladiazo species (complex or aggregate formation, solvation or dehydration effects, activity effects, formation of ion-pairs or slightly dissociated palladiazo–sodium salts, etc.).

Similar ion-exchange phenomena have been reported by KRAUS *et al.*[3], in the case of some negatively charged inorganic complexes whose sorption on cation-exchange resins has been shown to proceed quantitatively in very concentrated neutral saline media while the cationic species present percolate through without noticeable sorption. In media of low ionic strength, KRAUS *et al.* found entirely opposite behaviour. Despite the well-established empirical facts, which indicate useful practical analytical applications, no theoretical explanation of these curious phenomena can be provided. Inadequate theoretical knowledge of the physicochemical aspects involved in concentrated electrolyte solutions, and the additional complexity of the behaviour of ion-exchange resins in concentrated saline media, appear to make a proper explanation almost impossible.

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1 J. A. PÉREZ-BUSTAMANTE AND F. BURRIEL-MARTÍ, *Anal. Chim. Acta*, 37 (1967) 49.
2 J. A. PÉREZ-BUSTAMANTE, *Doctoral Thesis*, Madrid, 1967.
3 K. A. KRAUS, D. C. MICHELSON AND F. NELSON, *J. Am. Chem. Soc.*, 81 (1959) 3204.

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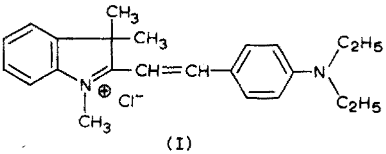
Anal. Chim. Acta, 44 (1969) 229–230

The spectrophotometric determination of dicyanoaurate(I) with astraviolet 3 R

It has recently been shown that malachite green is suitable for the photometric determination of potassium dicyanoaurate(I) without the destruction of the complex ion[1]. Further work has shown that 1-methyl-2-(*p*-diethylaminostyrene)-3,3'-dimethylindole chloride (Astraviolet 3 R, I) provides a superior method.



(I)

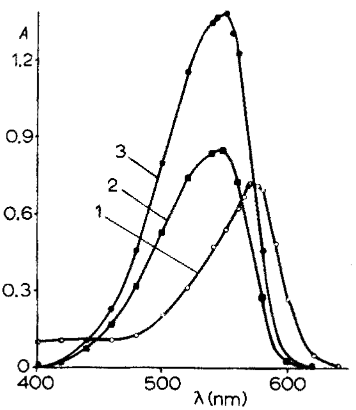
Reagents and equipment

Potassium dicyanoaurate(I) ($K[Au(CN)_2]$) was prepared from $HAuCl_4$ (p.a., Fluka) and potassium cyanide (p.a., U.C.B.). The aqueous 0.05% (w/v) dyestuff solution was prepared from Astraviolet 3 R extra (Bayer, Leverkusen). All the other reagents were of analytical reagent grade.

A Lange Kolorimeter (with a green VG9 filter) and a Jobin-Ivon spectrophotometer were used. The pH was measured with a Clamann and Grahnert MV-11 pH meter with glass electrode.

Procedure

To 25-ml volumetric flasks add dicyanoaurate(I) solution (4–27 μg Au) and 5.0 ml of reagent solution and dilute to volume with distilled water. Transfer the solution to a separatory funnel, add 10 ml of benzene and shake strongly. Measure the absorbance of the benzene phase in 1-cm cells at 570 nm against a pure benzene blank.



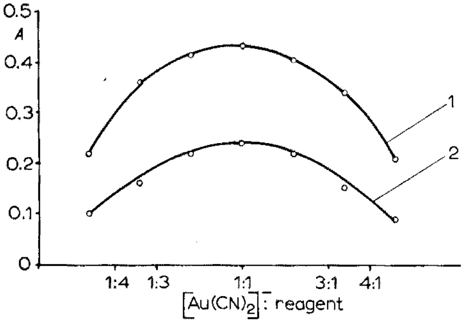


Fig. 1. Absorbance spectra: (1) Complex in benzene; (2) complex in water; (3) dyestuff in water.

Fig. 2. Job curves obtained with $2.0 \cdot 10^{-4}$ *M* solutions: (1) Values recorded with the filter VG9; (2) values recorded with the filter BG7.

Results and discussion

Optimal conditions. The complex formed between the dyestuff cation and cyanoaurate(I) can be readily extracted with benzene, bromobenzene, chloroform, isoamyl alcohol and methyl ethyl ketone; it is less readily extracted by ethyl ether, petroleum ether or carbon tetrachloride. Benzene is the best extraction solvent, since the reagent itself is extracted by the other efficient extractants for the complex.

The absorbance spectrum for the complex shows an absorbance maximum at 570 nm (Fig. 1), hence a green filter is suitable for measurements. There is no variation in the absorbance over the pH range 2.4–11.1, but in more strongly acidic or basic solutions, the dyestuff is bleached. An amount of 2 ml of 0.05% (w/v) reagent solution is sufficient for the determination of 13.2 μg of gold. When 5.0 ml of 0.05% (w/v) reagent solution is used, Beer's law is obeyed over the range 4.0–27.0 μg of gold, *i.e.* 0.16–1.08 μg Au/ml. A solution prepared from *ca.* 30 μg of gold gives an absorbance reading of *ca.* 0.400.

The reproducibility of the method was checked by 20 separate runs at the 10- and 20-μg levels; the standard deviation was found to be 0.02 μg.

Interferences. Many other complex cyanides are extracted along with the gold complex, including the dicyano complex of silver(I), the tetracyano complexes of zinc, cadmium, mercury and lead, and the hexacyano complexes of iron (II) and platinum. However, the gold complex can readily be extracted previously with isoamyl alcohol from mixtures containing the other complex cyanides[2,3]; the species extracted is $HAu(CN)_2$ at pH <1 and two extractions with volumes of isoamyl alcohol in a 1:10 ratio to the volume of the aqueous solution give complete extraction. The interference of cyanide itself in the general procedure increases as the pH increases (Table I).

TABLE I

THE INTERFERENCE OF CYANIDE

pH	11.1	9.6	8.2	7.0	6.2	5.0
Amount tolerated (mg)	0.9	1.5	4.5	12.0	39.0	100.0

TABLE II

CALCULATION OF THE INSTABILITY CONSTANT

	A	A_0	α	K	pK
Filter VG9	0.53	0.72	0.30	$3.9 \cdot 10^{-6}$	5.41
Filter BG7	0.34	0.49	0.26	$5.2 \cdot 10^{-6}$	5.28
		Average value		$4.5 \cdot 10^{-6}$	5.35

Stoichiometry of the reaction. The combining ratio was shown experimentally by JOB's method[4] (Fig. 2) to be 1:1. The complex is ionic in character (*cf.* Fig. 1, curves 2 and 3) and has the formula $C_{23}H_{29}N_2[Au(CN)_2]$.

The instability constant was established by a modification of the tangent method[5] (Table II). The average value obtained was $K = 4.5 \cdot 10^{-6}$ (pK=5.35).

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1 V. ARMEANU, L. M. BALOIU AND M. DAMIAN, *Rev. Roumaine Chim.*, in press.
2 D. E. ZVIAGHINTEV AND C. I. ZAHAROV-NARTISOV, *Zh. Prikl. Khim.*, 33 (1960) 55.
3 R. RIPAN, M. MARCU AND V. CORDIS, *Rev. Chim. (Bucharest)*, 15 (1964) 684.
4 P. JOB, *Ann. Chim. (Paris)*, 9 (1928) 113.
5 A. K. MAJUMDAR AND C. P. SAVARIAR, *Anal. Chim. Acta*, 21 (1959) 47.

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Study of hydroxy acids by nuclear magnetic resonance

It has been found that the type of a hydroxy acid (α or β or higher) can be established by the downfield chemical shift of the nuclear magnetic resonance absorption peak of the proton in the α-position to the hydroxy group in the trichloroacetylisocyanate derivatives of the acids.

Experimental

A Varian A-60A NMR spectrometer was used.

Deuterated chloroform was used as a solvent with tetramethylsilane as the internal standard ($\delta = 0$ p.p.m.). Trichloroacetylisocyanate (Eastman 9737) was used for derivative formation.

Results and discussion

Trichloroacetylisocyanate derivatives. GOODLETT[1] has discussed the study of alcohols by esterification which produces downfield shifts of NMR peaks that are caused by protons in the α-position to hydroxy groups. The magnitude of the shift, the multiplicity of the shifted peaks, and the relative areas of the shifted peaks are useful in structure elucidation of alcohols. When trichloroacetylisocyanate was used, GOODLETT found that downfield shifts of about 0.5 – 0.9 p.p.m. resulted for protons in the α-position to primary hydroxy groups and shifts of about 1.0–1.5 p.p.m. resulted for protons in the α-position to secondary hydroxy groups.

The main innovation in our studies is the application of isocyanate derivative formation to hydroxy acids. A change will occur in the NMR spectrum in the chemical shift of the proton in the α-position to the hydroxyl group in a hydroxy acid upon reaction with trichloroacetylisocyanate.

Table I shows the hydroxy acids studied, which include only secondary alcoholic groups. It was found that the changes in chemical shifts downfield for the proton in the α-position to the hydroxy group were 1.15–1.36 p.p.m. for β-hydroxy acids or higher, *i.e.*, γ, δ, etc., and 0.87–0.95 p.p.m. for α-hydroxy acids. The latter result is slightly lower than the range which GOODLETT reported for secondary

TABLE I

HYDROXY ACIDS STUDIED

Hydroxy acid	*Chemical shift (δ) for α protons (Trichloroacetylisocyanate addition)*		*$\Delta\delta$ (p.p.m.)*
	Before	*After*	
α-Hydroxyisocaproic	4.30	5.25	−0.95
α-Hydroxycaproic	4.32	5.19	−0.87
α-Hydroxy-β-methylvaleric	4.27	5.19	−0.92
DL-α-Hydroxyisovaleric	4.15	5.05	−0.90
α-Hydroxyvaleric	4.30	5.19	−0.89
9 or 10-Hydroxystearic	3.61	4.95	−1.34
12-Hydroxystearic	3.61	4.95	−1.34
β-Hydroxy-*n*-butyric	4.25	5.40	−1.15
β-Hydroxyisocaproic	3.87	5.23	−1.36

alcohols, namely, 1.0–1.5 p.p.m. The difference in ranges of the $\Delta\,\delta$ values for the α- and β-hydroxy acids is probably due to the proximity of the acid carbonyl group to the proton in the α-position to the hydroxy group. Clearly, these peak shifts allow the type of hydroxy acid to be determined.

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1 V. W. GOODLETT, *Anal. Chem.*, 37 (1965) 431.

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The use of 5,7-dibromo-8-hydroxyquinoline for the concentration of certain trace elements from sea water

The growing interest in marine geochemistry is accentuating the demand for analytical methods which will permit several trace elements to be determined simultaneously in sea water. Since the concentrations of such elements are very low ($< 5\ \mu$g/l) it is necessary to concentrate them before analysis. The difficulty of storing, unchanged, the large numbers of 3–5 l water samples collected during oceanographic cruises makes it advisable to carry out this preconcentration stage on board ship. For this purpose, techniques involving co-crystallization have much to recommend them. In these methods, which were first used for sea water by WEISS *et al.*[1-4], a solution of a water-insoluble organic complexing reagent in a water-miscible solvent is added to the sample at a suitable pH value. As the complexing reagent crystallizes, it carries down the insoluble complexes which it forms with trace elements. After filtration, the precipitate must normally be mineralized before determination of the trace elements.

Several biologically important trace elements are not concentrated efficiently by the co-crystallizing agents used by WEISS *et al.* Since 8-hydroxyquinoline and its derivatives are known to form insoluble complexes with a wide range of elements the possibility of using them for co-crystallization of trace metals was investigated. The parent compound and its methyl derivatives are too soluble in water to be used for this purpose. However, its 5,7-dibromo derivative has a low solubility and is known to form insoluble complexes with most of the metals which form complexes with 8-hydroxyquinoline itself. This short communication describes how this reagent can be used for the co-crystallization of several trace elements from sea water.

Co-crystallization of trace metals with 5,7-dibromo-8-hydroxyquinoline

Preliminary tests showed that the following procedure not only brings about efficient co-precipitation but also produces a highly crystalline precipitate which is easy to filter. The sample is heated to *ca.* 80° on a hotplate. A saturated solution of 5,7-dibromo-8-hydroxyquinoline in acetone (10 ml/l of sea water) is added slowly while stirring vigorously by means of a magnetic impeller. The sample is boiled for 5–10 min to remove most of the acetone and then allowed to stand overnight at room temperature. On the following day the solution is filtered through a 2-cm Whatman glass-fibre filter (GF/B) under suction.

Radiochemical methods were used to determine the optimum pH values for the co-crystallization of the elements listed in Table I. Except for manganese, the best recovery was found at pH 4.5–8.0; at pH values lower than 4 the recoveries fell rapidly. The optimum recovery for manganese occurred between pH 5.5–6.5. Failure to boil off the acetone after adding the co-crystallizing reagent was found to lead to variable recoveries.

Table I shows the results of co-crystallization experiments carried out at pH 8.0 as described above on both distilled water and sea water. It will be seen that copper, zinc, iron, cobalt and chromium can be recovered quantitatively from both media. Although the recovery of manganese from distilled water was almost quantitative, its recovery from sea water was less efficient but quite consistent. Co-crystallization thus provides a simple and convenient means for the preconcentration of these elements in sea water analysis.

TABLE I

PERCENTAGE RECOVERIES OF VARIOUS METALS AFTER CO-CRYSTALLIZATION WITH 5,7-DIBROMO-8-HYDROXYQUINOLINE AT pH 8

Ion	Cu^{2+}	Zn^{2+}	Fe^{3+}	Co^{2+}	Mn^{2+}	Pb^{2+}	Ag^{+}	Ce^{3+}	Cr^{3+}
Concentration (μg/l)	5	5	5	0.025	5	5	0.1	5	0.5
% Recovery from pure water	100	100	99	99	95	—	60	8	100
% Recovery from sea water	100	100	98	99	85	42	60	7	100

Atomic absorption techniques provide the simplest means of completing the analysis. The precipitate carrying the trace elements should be dissolved in 5 ml of concentrated nitric acid and diluted to 10 ml with water before spraying into the burner of the atomic absorption spectrophotometer. Since the presence of the organic reagent enhances the absorption produced by the trace elements it is essential to standardize the instrument with standard solutions made up in 50% nitric acid containing an appropriate amount of 5,7-dibromo-8-hydroxyquinoline.

The analysis may also be completed by spectrophotometry. In this instance the precipitate must first be decomposed by prolonged digestion and evaporation with nitric acid. The trace elements are absorbed from a solution in 7 ml of 12 *N* hydrochloric acid on to a 8 × 0.5 cm column of the chloride form of the anion exchanger DeAcidite FF. A modification of the procedure of Kraus and Moore[5] is used for their separation. Elution with 15 ml of 12 *N* hydrochloric acid serves to remove manganese. Copper and cobalt are eluted together with 40 ml of 6 *N* hydrochloric acid. Iron and zinc are removed from the column by means of 40 ml of 0.5 *N* hydrochloric acid and 45 ml of distilled water respectively. The separated elements are determined photometrically in the eluates after evaporation of the hydrochloric acid by means of established procedures with the following reagents: formaldoxime[6] (manganese); neocuproine[7] (copper); nitroso-R-salt[8] (cobalt); bathophenanthroline sulphonic acid[9] (iron); dithizone[8] (zinc).

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1 H. V. WEISS AND M. G. LAI, *Anal. Chem.*, 32 (1960) 475.
2 H. V. WEISS AND M. G. LAI, *Anal. Chim. Acta*, 28 (1963) 242.
3 H. V. WEISS AND J. A. REED, *J. Marine Res.*, 18 (1960) 185.
4 M. G. LAI AND H. V. WEISS, *Anal. Chem.*, 34 (1962) 1012.
5 K. A. KRAUS AND G. E. MOORE, *J. Am. Chem. Soc.*, 75 (1953) 1460.
6 E. G. BRADFIELD, *Analyst*, 8 (1957) 254.
7 P. D. JONES AND E. J. NEWMAN, *Analyst*, 87 (1962) 637.
8 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959.
9 J. P. RILEY AND H. WILLIAMS, *Mikrochim. Acta*, (1959) 804.

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A simple one-step method for the determination of α-hydroxyamino nitrogen

Methods for the determination of α-hydroxyamino compounds usually involve several more or less laborious steps which very often decrease the sensitivity of the assay by increasing the quantity of sample required for a single analysis. For instance, ammonia determination after periodate oxidation, which is the most specific reaction in this case, is applicable only by employing steam distillation[1,2], aeration methods[3] or Conway's diffusion method[4], since direct Nesslerization is impossible in the presence of the aldehydic products of periodate oxidation. On the other hand, formaldehyde assay after periodate oxidation, which might be a useful measure of the α-hydroxyamino nitrogen content of hydrolyzates of pure lipid fractions, total lipid extracts, or other natural products, requires removal of glycerol and/or sugar chromatographically[1,2] before periodate oxidation.

This analysis can be substantially simplified by the following technique.

Experimental

Modified Nessler Reagent. Mix 200 g of mercury(II) iodide and 150 g of potassium iodide in 1 l of preboiled distilled water. Mix 1 part of the supernate of this mixture with 3 parts of 2.5 *M* sodium hydroxide.

Procedure. The α-aminohydroxy compounds in a hydrolyzate (either in presence or in absence of glycerol and sugars) are oxidized with periodate by conventional methods, and the excess of periodate is destroyed with 10% sodium bisulfite [5].Then add 1 ml of Nessler reagent directly to 3 ml of the periodate-oxidation mixture (0.1–1.0 μmoles NH_4^+) in a centrifuge tube, and leave for 20 min at room temperature. Then add 1 ml of 2.5 *N* acetic acid to the turbid solutions, mix well and centrifuge at 3,000 r.p.m. for 5 min. Carefully withdraw a portion (3–4 ml) of the almost colorless supernate, transfer to a test tube and add 1 ml of Nessler reagent. Measure the optical density of this solution at 400 nm after 15 min against a reagent blank. Ammonium sulfate standards can be used for the determination of α-hydroxyamino nitrogen by this method.

Results and discussion

Duplicate experiments were carried out with artificial mixtures of ammonium sulfate and glycol, and the results were compared with control tests on identical concentrations of ammonium sulfate without glycol which were run through the entire procedure except for the centrifugation step. The results (Table I) indicated that the ammonium ions of the turbid mixtures remain quantitatively in the supernates after acidification and centrifugation. This property ensures reproducibility of the results and has the great advantage of permitting the use of ammonium standards.

When the present method of analysis was applied to known concentrations of ethanolamine and serine (Table I), a quantitative yield of ammonia by periodate oxidation was confirmed, in agreement with ARTOM's earlier data[1].

A modified Nessler reagent, more concentrated with respect to the HgI_2–KI complex than conventional ones, was used, although this is not a requirement of the present method. The reason for this modification, which is of wider interest, is as follows: a short-term investigation of the reasons for the well-known tendency of

TABLE I

RECOVERY OF NITROGEN IN PRESENCE OF ALDEHYDE

(All samples (2 ml of aqueous solutions) were oxidized with 0.5 ml of 0.1 M $NaIO_4$ in 2 M H_2SO_4, for 10 min in the dark. Excess of periodate was destroyed[5] with 0.5 ml of 10% $NaHSO_3$, and nitrogen was assayed as described in the text.)

Sample[a]	*OD_{420}*	*Nitrogen determined (μg)*	*Average recovery (%)*
Ammonium sulfate (14 μg N)	0.640		
	0.630[b]		
	0.635[b]		
Ammonium sulfate (14 μg N) in 1 μM glycol	0.620	13.50	
	0.635	14.00	98.5
	0.640	14.10	
Ammonium sulfate (7 μg N) in 5 μM glycol	0.315	6.95	
	0.320	7.05	100.0
	0.320	7.05	
Ethanolamine (18 μg N)	0.820	18.10	
	0.810	17.90	100.1
	0.830	18.30	
Ethanolamine (9 μg N) in 2 μM glycerol	0.415	9.15	
	0.415	9.15	100.1
	0.410	9.00	
Serine (16 μg N)	0.720	15.90	
	0.730	16.10	99.0
	0.710	15.65	
Serine (8 μg N) in 2 μM glycerol	0.360	7.95	
	0.370	8.15	99.0
	0.350	7.70	

[a] Total amount of nitrogen per tube and concentrations of glycol or glycerol in the medium (when present) are given.
[b] Centrifugation step omitted.

Nesslerized samples to become turbid indicated that the development of turbidity depends greatly on the ratio of the final concentration of the HgI_2–KI complex to that of sodium hydroxide, being minimal at higher values of this ratio. The reproducibility of the results is also greatly affected by the final value of this ratio, since a gradual shift of the absorption maximum towards higher wavelengths occurs as the ratio decreases. Unless the conditions of a colorimetric method for ammonia assay are selected so that the ratio of HgI_2–KI to sodium hydroxide falls well outside a critical range of maximum variability, a linear concentration curve cannot be obtained, and an increased standard error of duplicate samples can be expected.

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1 C. Artom, *J. Biol. Chem.*, 157 (1945) 585.
2 J. C. Dittmer, J. L. Feminella and D. J. Hanahan, *J. Biol. Chem.*, 233 (1958) 862.
3 D. D. Van Slyke, A. Hiller and D. A. MacFadyen, *J. Biol. Chem.*, 141 (1941) 681.
4 W. N. M. Ramsay and C. P. Stewart, *Biochem. J.*, 35 (1941) 39.
5 D. J. Hanahan and J. N. Olley, *J. Biol. Chem.*, 231 (1958) 813.

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The indirect determination of sulfur dioxide by atomic absorption spectrometry after precipitation of lead sulfate

A systematic study of spectrophotometric and atomic absorption spectrometric methods for the determination of nonmetals is in progress in our laboratory. Although a number of colorimetric methods have been used, only one atomic absorption spectrometric method involving the determination of sulfur in biological material by measuring the barium in a barium sulfate precipitate has been noted[1]. This paper reports the results of an investigation on the feasibility of determining sulfur dioxide by an indirect atomic absorption spectrometric method in which the lead(II) remaining in the supernate, after removal of lead sulfate by centrifugation, is measured by atomic absorption spectrometry. A preliminary conversion of the sulfur dioxide to sulfate by hydrogen peroxide is necessary.

Because of the toxicity, corrosiveness and extensive use of sulfur dioxide, there exists a need for a rapid, sensitive, and highly selective method for the 0.1–25 p.p.m. concentration range. The Reich method based on measuring the volume of gaseous phase required to titrate a specific volume of a standard iodine solution with starch as the indicator has been used extensively in determining the sulfur dioxide content of gases[2]. The enhancement of the electrical conductance of a solution of hydrogen peroxide upon absorption of sulfur dioxide to produce sulfuric acid has been used to develop an automatic apparatus for monitoring small concentrations of sulfur dioxide[3]. A polarographic method[4] has been modified by using a sodium tetrachloromercurate(II) solution as an absorbant[5] and hydrazine hydrate to precipitate the excess of absorbant before polarographic measurement[6]. Another method is based on the reduction of sulfur dioxide to hydrogen sulfide with platinum and then forming the molybdenum blue color by means of the reducing capacity of the hydrogen sulfide[7]. Several colorimetric methods have been based on forming a dye when sulfurous acid reacts with formaldehyde and fuchsin[8]. Pararosaniline[5,9,10] or *p*-aminoazobenzene[11] have been recommended as alternative reagents for the fuchsin. The indirect colorimetric method requiring conversion to the sulfate and measurement of the chloranilate liberated following addition of solid barium chloranilate to precipitate barium sulfate has been proposed[12–14]. The inherent simplicity and speed of the atomic absorption spectrometric method suggested the desirability of investigating the possibility of precipitating lead sulfate and measuring the excess lead by atomic absorption spectrometry. Lead has been determined extensively by the atomic absorption method[15,17].

Reagents

Standard lead(II) solution (ca. 0.01 M). Dissolve approximately 4.6 g of reagent grade lead perchlorate in distilled water and dilute to 1 l. Standardize this solution with 0.01 *M* EDTA as titrant and 1-(2-pyridylazo)2-naphthol as indicator[18]. After standardization, prepare a dilute reagent solution of lead(II) by diluting a 100-ml aliquot to exactly 1 l. Each ml of dilute reagent was found to contain 0.2044 mg of lead.

Standard sulfur dioxide solution (1.00 mg of SO_2/ml). Dissolve 0.1670 g of reagent-grade sodium bisulfite in distilled water and dilute to 100 ml. Prepare this solution each day.

Chemicals used for diverse ion studies were reagent grade.

Apparatus

Atomic absorption spectrometric measurements were made using a Beckman Model 1301 atomic absorption accessory, a Beckman Model DB prism spectrophotometer equipped with a Beckman potentiometric recorder, and a Techtron burner. A neon-filled, multi-element hollow-cathode tube was used. An acetylene–air flame and a slit width of 0.20 mm were used.

General procedure

Transfer 25 ml of sample solution containing 0.01–1 mg of sulfur dioxide per ml to a 100-ml volumetric flask. Add 3 drops of 3% hydrogen peroxide and mix solution thoroughly. Add 30 ml of dilute lead(II) perchlorate reagent (0.204 mg/ml). Add 25 ml of absolute ethanol, dilute to the mark with distilled water, and allow to stand for 5 min. Transfer the contents of the flask to a centrifuge tube and centrifuge for 15 min. Use the 283.3-nm resonance line for lead (a hollow-cathode current of 14 mA was used) and adjust the burner fuel restricter to obtain a reducing flame (a support gas pressure of 18 lbs and an acetylene pressure of 6 lbs were used). Aspirate a standard lead solution (30 p.p.m. of lead(II)) until monochromator and burner are adjusted to give maximum absorbance. Aspirate standard and unknown solutions using the %T setting of recorder. Prepare a calibration graph of absorbance *vs.* p.p.m. of sulfur dioxide.

Results

Solubility of lead sulfate. Although lead sulfate is slightly soluble in water, it is very insoluble in ethanol[19]. The effect of ethanol concentration on the solubility of lead sulfate when atomic absorption spectrometry was used to determine the lead(II) remaining in solution, was studied. It was found that the minimum solubility corresponded to the use of 20–50% by volume ethanol. Therefore, 25 ml of absolute ethanol is recommended per 100 ml of final supernate. The alcohol should be added after the addition of the lead(II) perchlorate reagent.

Time required for centrifugation. Samples containing lower concentrations of sulfate required longer times for centrifugation. However, 15 min was ample time for most samples.

Sulfur dioxide concentration. A linear Beer's law plot was obtained for the 2–20 p.p.m. of sulfur dioxide concentration range. It is likely this range could be extended if higher concentration of lead(II) perchlorate reagent were used.

Diverse ions. The effect of 15 diverse ions was studied with 5 p.p.m. of sulfur dioxide present. Errors of less than ±5% were considered negligible. Five hundred p.p.m. of chloride, nitrite, nitrate, perchlorate, sodium, potassium, ammonium, calcium and magnesium did not interfere. The permissible amounts of interfering ions were acetate, 250 p.p.m.; EDTA, 20 p.p.m.; barium, 10 p.p.m.; and aluminum, 10 p.p.m. Iron(III) and phosphate should be absent.

Precision. An estimate of the precision of this indirect atomic absorption spectrometric method for sulfur dioxide was obtained from the results of 8 samples, each containing 5 p.p.m. of sulfur dioxide. A mean absorbance value of 0.252 and a standard deviation of 0.009 absorbance unit, or a relative standard deviation of 3.6% were obtained.

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1 D. A. ROE, P. S. MILLER AND L. LUTWAK, *Anal. Biochem.*, 15 (1966) 313.
2 G. DRAGT AND K. W. GREENAN, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 883.
3 M. D. THOMAS, *Ind. Eng. Chem., Anal. Ed.*, 4 (1932) 253.
4 I. M. KOLTHOFF AND C. S. MILLER, *J. Am. Chem. Soc.*, 63 (1941) 2818.
5 P. W. WEST AND G. C. GAEKE, *Anal. Chem.*, 28 (1956) 1816.
6 L. L. CIACCIO AND T. COTSIS, *Anal. Chem.*, 39 (1967) 260.
7 H. STRATMANN, *Mikrochim. Acta*, 8 (1956) 1031.
8 A. STEIGMANN, *J. Ind. Chem. Soc.*, 61 (1942) 18.
9 S. ATKIN, *Anal. Chem.*, 22 (1950) 947.
10 F. P. SCARINGELLI, B. E. SALTZMAN AND S. A. FREY, *Anal. Chem.*, 39 (1967) 1709.
11 S. J. KNISELY AND L. J. THROOP, *Anal. Chem.*, 38 (1966) 1270.
12 R. J. BERTOLACINI AND J. E. BARNEY, *Anal. Chem.*, 29 (1957) 281; 30 (1958) 202.
13 R. M. CARLSON, R. A. ROSELL AND W. VALLEJOS, *Anal. Chem.*, 39 (1967) 688.
14 H. N. S. SCHAFER, *Anal. Chem.*, 39 (1967) 1719.
15 R. M. DAGNALL AND T. S. WEST, *Talanta*, 11 (1964) 1553.
16 C. L. CHAKRABARTI, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 34 (1966) 269.
17 J. W. ROBINSON, *Atomic Absorption Spectroscopy*, Marcel Dekker, Inc., New York, 1966, p. 131.
18 H. FLASCHKA AND H. ABDINE, *Chemist-Analyst*, 45 (1956) 58.
19 T. W. GILBERT, in I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part II, Vol. 6, Interscience, New York, 1964, p. 111.

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The reaction between mercury (II) and organic compounds. Part II. Determination of mercury(II) with *o*-(2-thiazolylazo)-4-methoxyphenol as spectrophotometric reagent and metallochromic indicator

o-(2-Thiazolylazo)-4-methoxyphenol, TAM, has been shown to be a sensitive reagent for mercury(II) ions, and has been used as indicator in titrations of mercury(II) with EDTA by CHROMÝ AND SOMMER[1]. In the present paper, it is shown that TAM is also suitable for the spectrophotometric determination of mercury(II) because of high solubility of the mercury(II)–TAM chelate in an organic solvent. The titrimetric method has been restudied, and the sensitivities of the two methods are compared.

Experimental

Reagents and equipment. TAM (Dojindo & Co., Ltd.) was recrystallized from hot ethanol. Alcoholic solutions of TAM were used as the indicator and aqueous dioxane solutions of TAM were used for the study of the composition and of the formation constant of the chelate.

Commercial dioxane was purified as described previously[2]. The mercury(II) solution, buffer solutions and other chemicals were the same as those described previously[2]. An ionic strength of 0.1 was maintained with potassium nitrate for spectrophotometric studies. Twice-distilled water was used for preparation of all the solutions.

The equipment used was described previously[2].

Standard procedure for the spectrophotometric determination. Mix 1 ml of aqueous 10^{-3} *M* mercury(II) and 20 ml of buffer solution (Na_2HPO_4–KH_2PO_4) of pH 8.40 in a 100-ml separatory funnel, and dilute to 50 ml with water. Add 10 ml of 10^{-4} *M* TAM solution in chloroform and shake for about 100 sec. Allow the layers to settle, transfer the chloroform layer containing the chelate to a 10-mm cell and measure the absorbance at 638 nm, with chloroform itself or a reagent blank as reference.

Standard procedure for the titrimetric determination. Adjust about 100 ml of $\not> 10^{-2}$ *M* mercury(II) solution to pH 6.3–7.5 with Na_2HPO_4–KH_2PO_4 buffer. Add several drops of alcoholic 10^{-2} *M* TAM solution and titrate with 10^{-2} *M* EDTA.

Spectrophotometric determination

Absorption spectra of the chelate in the chloroform layer. The absorption spectra for the chloroform layer obtained by the standard procedure at various pH values are shown in Fig. 1; there is an isosbestic point at 539 nm and the absorption maxima occur at 638 nm above pH 5.5. Maximum extractability was obtained at pH 8.40; above pH 8.5, hydrolysis occurred.

Organic solvent, shaking time and color stability. Chloroform, benzene, carbon tetrachloride, methyl isobutyl ketone (MIBK) and isoamyl alcohol were examined for the extraction. Nonpolar solvents such as benzene and carbon tetrachloride, gave poor extraction. Although the chelate was extracted into MIBK and isoamyl alcohol, these were less suitable because MIBK formed emulsions and isoamyl alcohol was too soluble. Chloroform was therefore preferred.

The shaking time in the extraction was varied from 10 to 120 sec. Complete extraction was obtained by shaking for 90 sec. The color of the extracts was stable even after 10 h.

Range and reproducibility. When the standard procedure was used, Beer's law was followed over the range $7 \cdot 10^{-5}$–$1 \cdot 10^{-5}$ M mercury(II) in the diluted aqueous solution. The molar absorptivity was found to be $1.75 \cdot 10^{4}$. The standard deviation in absorbance calculated from 10 repeated measurements with chloroform as reference, was 0.006.

Effect of diverse ions. Table I shows the effect of various ions added to the mercury(II) solution and taken through the standard procedure. A moderate amount of chloride did not interfere, but all the other anions tested interfered. Copper(II),

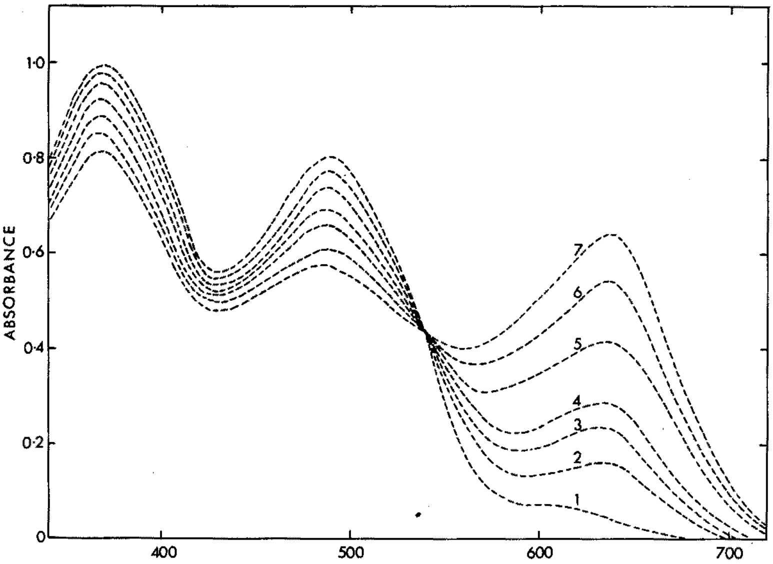

Fig. 1. Absorption spectra for the chelate extracted into chloroform at various pH values. 1 = reagent blank; pH: 2 = 5.66; 3 = 6.14; 4 = 6.37; 5 = 6.75; 6 = 7.57; 7 = 8.40.

TABLE I

EFFECTS OF DIVERSE IONS

(1 ml of 10^{-3} M mercury(II) taken)

Ion	*Added amounts as ions (mg)*	*Absorbance at 638 nm*	*Ion*	*Added amounts as ions (mg)*	*Absorbance at 638 nm*
None	—	0.64	S^{2-}	0.4	0.59
Cl^-	4.0	0.64	Cu^{2+}[a]	0.1	0.62
Br^-	0.5	0.60	Ni^{2+}[a]	0.1	0.71
I^-	0.5	0.59	Co^{2+}[b]	0.1	0.75
CN^-	1.0	0.55	Zn^{2+}[a]	0.1	0.72
SCN^-	1.0	0.60			

[a] Added as sulfate.
[b] Added as nitrate.

nickel(II), cobalt(II) and zinc(II) caused high results owing to the formation of colored chelates.

Titrimetric determination

The titration of mercury(II) with EDTA in the presence of TAM as indicator[1] was re-examined from the point of view of sensitivity. Several drops of alcoholic 10^{-2} *M* TAM solution were added to 100 ml of $5 \cdot 10^{-4}$ *M* mercury(II) solution at pH values from 4.0 to 9.5 adjusted with buffer solutions, and the solutions were titrated with 10^{-2} *M* EDTA (aqueous soln). The sharpness of the color change near the end-point was checked by measuring the absorbances at 625 nm. Figure 2 shows the indicator transition curves[3], $C_{EDTA}/C_{Hg^{2+}}$ *versus* ϕ. The value of ϕ is defined as $[R]_f/C_{TAM}$, where $[R]_f$ is the total concentration of unbound TAM and C_{TAM} is the total concentration of TAM taken. The sharpest color changes were observed in the pH range 6.5–7.5, *i.e.*, blue to orange or reddish brown. At the other pH values, the color changed before the equivalence point. Accordingly, titrations at pH 6, as reported by CHROMÝ AND SOMMER[1], will show the color change before the equivalence point. The error of the titration was found to be within 0.1%.

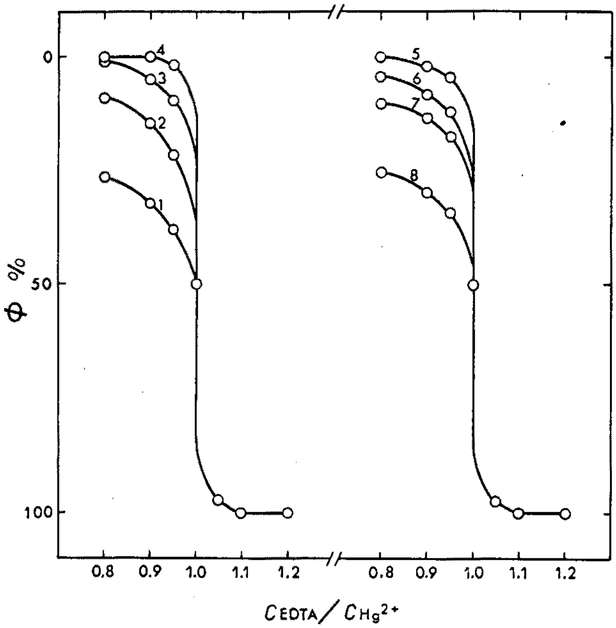

Fig. 2. Photometric titration curves. $C_{Hg^{2+}} = 5 \cdot 10^{-4}$ *M*; $4 \cdot 10^{-5}$ *M* TAM added as indicator; 0.01 *M* EDTA; $Na_2HPO_4 + KH_2PO_4$ buffer soln. pH: 1 = 4.0; 2 = 5.0; 3 = 5.5; 4 = 5.8; 5 = 6.1; 6 = 6.5–7.0; 7 = 7.2–7.5; 8 = 7.8; 9 = 8.3.

Composition and formation constant of the mercury(II)–TAM chelate

Acid dissociation constant of TAM in 30% (v/v) dioxane–water solution. TAM is a monobasic acid and also acts as a base in a strong acidic medium. The acid dissociation constants, as defined previously, obtained from the absorption spectra of TAM in 30% (v/v) dioxane–water at various pH values were $pK_{a1} < 0.3$ and $pK_{a2} = 7.90$. Accurate values of pK_{a1} were not obtainable.

Absorption spectra and composition of the Hg(II)–TAM chelate in aqueous dioxane. The spectra of the chelates formed from TAM and a 10-fold excess of mercury(II) were measured for the 30% (v/v) dioxane–water solution at different pH values. When chloroform was used as reference, the spectra were similar to those shown in Fig. 1, except that there was considerably less absorbance below 500 nm and there was a bathochromic shift of the maximum absorbance wavelength between pH 7.1 and 9.5. From pH 4.9 to 7.1, there was an isosbestic point at 530 nm; the maximal absorbance at 630 nm increased with pH in this range.

When an excess of TAM was used with a reagent blank as reference, the increase in the absorbance maxima at 630 nm with increase in pH was confirmed for the pH range 5–7. Essentially, the results were similar to those obtained with *o*-(2-thiazolylazo)cresol[2]. As in the case of the cresol analogue, a 1:1 chelate is formed when mercury(II) is in excess, whereas a 1:2 mercury(II)–ligand chelate may be formed when excess of TAM is present.

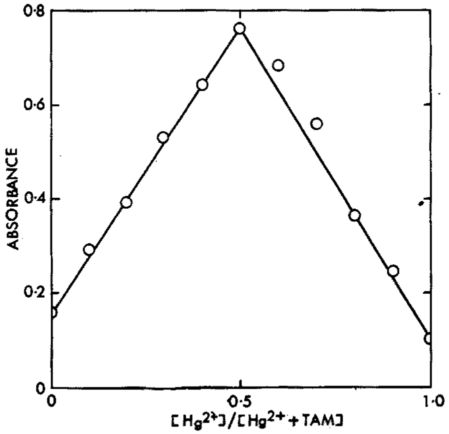

Fig. 3. Continuous variations plot. Total concn. = $1.40 \cdot 10^{-4}$ *M*; pH = 7.39; 625 nm.

TABLE II

ACID DISSOCIATION CONSTANT OF TAM AND FORMATION CONSTANT OF Hg(II)–TAM CHELATE IN 30% (v/v) DIOXANE–WATER SOLUTION

(μ = 0.1 with potassium nitrate; room temp.)

Acid dissociation constant of TAM	*Chelate*			
	Composition	λ_{max} *(nm)*	ε_{max}	*Formation constant*
$pK_{a1} < 0.3$	1:1	630	$1.40 \cdot 10^4$	$\log K_{HgR^+} = 6.62$
$pK_{a2} = 7.90$	1:2	630	$2.79 \cdot 10^4$	$\log K_{HgR_2} = 6.08$

A continuous variations plot at pH 7.39 indicated the formation of the 1:1 chelate (Fig. 3); no 1:2 chelate was found even at higher pH values.

Formation constants of the chelate. The formation constant was defined and calculated as described previously[2]; a value of 6.6_2 was found. The second successive formation constant cannot be calculated directly, but indirectly from the over-all formation constant. The over-all formation constant was estimated as described previously[2]. A value of 12.70 was found, hence the second successive formation constant was 6.08. These values are listed in Table II.

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1 V. CHROMÝ AND L. SOMMER, *Talanta*, 14 (1967) 393.
2 F. KAI, *Anal. Chim. Acta*, 44 (1969) 129.
3 M. TANAKA AND G. NAKAGAWA, *Anal. Chim. Acta*, 32 (1965) 123.

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BOOK REVIEWS

C. A. PARKER, *Photoluminescence of Solutions*, Elsevier Publishing Company, Amsterdam, 1968, xvi+544 pp.,price Dfl. 85,—.

This important new book is concerned with bringing together the large and ever-growing literature on light emission from molecules in solution, and is based on the author's own wide experience in photochemistry and the measurement of photoluminescence.

The text contains an introductory chapter on basic principles followed by a chapter on the kinetics of photoluminescence. Then comes a very large chapter (over half the book) which deals with instrumentation and experimental methods. The next chapter treats special topics and applications from the point of view of the physicist and photochemist, and the final chapter is concerned exclusively with analytical applications of photoluminescence. The text is comprehensively referenced and indexed.

Those who are familiar with the author's contributions to the subject will readily accept this book as the most definitive text available. For many years, Dr. PARKER has involved himself with the design of high-performance instruments for the precise measurement of fluorescence and phosphorescence which his interests in photochemistry and analytical chemistry have demanded.

For the analyst, this is not a compendium of methods of analysis; rather it is a well-balanced account of the entire field of photoluminescence, of which analytical methods form a small, albeit important, part. Thus, the present text will be of considerable value to the analyst who is interested in knowing not only what sort of problems can be solved by measurement of photoluminescence but also how such problems can be tackled. This is undoubtedly a specialist text, but invaluable as a source of instruction and reference. The expanding use of fluorimetric methods of analysis and the availability of reliable commercial spectrofluorimeters make this book a very necessary addition to the library of the modern analytical chemist.

W. I. STEPHEN (Birmingham)

Treatise on Analytical Chemistry. Part III. Vol. 1. Analytical Chemistry in Industry, Edité par I. M. Kolthoff, P. J. Elving et F. H. Stross, John Wiley, New York, 1968, xxiv + 457 pp., price 165 s.

Ce livre est le premier volume de la 3ème partie de cet ouvrage qui traite des applications de la chimie analytique à l'industrie.

Il est l'oeuvre de 19 spécialistes et donne des généralités telles que: la méthodologie dans l'analyse industrielle, où il est question de l'utilité des dosages dans le développement de produits nouveaux, dans l'évaluation de la valeur d'un composé, du choix de la méthode, de la précision et de l'exactitude de l'établissement d'un programme, de l'interprétation des résultats etc. Le 3ème chapitre a pour titre: Organisation de Laboratoires de Chimie Analytique dans la Recherche Industrielle. Un chapitre est consacré aux laboratoires de contrôle et un autre à l'automation. Les précautions à prendre dans un laboratoire de chimie analytique, la préparation industrielle de composés purs et les méthodes de préparation, de purification, sont décrites et les essais des produits commerciaux sont les principaux exposés de ce livre.

On y trouve beaucoup de renseignements intéressants. Par contre, certains chapitres sont peu approfondis. L'automation par exemple est traitée si superficiellement qu'elle est de peu d'intérêt sinon pour les néophytes.

Un volume qui complète bien cet important ouvrage.

D. Monnier (Genève)

Comprehensive Analytical Chemistry. Vol. IIB. Physical Separation Methods, edited by C. L. Wilson and D. W. Wilson, Elsevier Publishing Company, Amsterdam, 1968, xv + 445 pp., price Dfl 70.—.

This volume dealing with four of the fundamental techniques in analytical chemistry (liquid chromatography in columns, gas chromatography, ion exchange and distillation) maintains the high standards set by the previous volumes of this series. Each of the four techniques is reviewed in an excellent and authoritative chapter. The basic theory for each technique and the review of the applications of the technique are discussed in a manner which readily indicates that the authors have both a thorough understanding and a wide experience of the problems involved in modern analytical chemistry. The breadth of the treatment is revealed by the wealth of reference to original literature and to other relevant bibliography.

Whilst one regrets that the other types of chromatography (paper, thin layer, etc.) are not included in this volume, this is certainly a book which will not only become one of the standard textbooks in laboratories where analytical chemistry is practised, but will also be in great demand by the chemist needing to improve his knowledge and understanding of these basic techniques of chemistry.

L. S. Bark (Salford)

H. SIMON UND H. G. FLOSS, *Anwendung von Isotopen in der Organischen Chemie und Biochemie. Band I. Bestimmung der Isotopenverteilung in markierten Verbindungen,* Springer-Verlag, Berlin–Heidelberg–New York, 1967, x+247 pp., gebunden DM 54,–; US $13.50.

Premier ouvrage d'une série de trois qui traiteront successivement de la répartition des isotopes, des effets isotopiques et de l'analyse des molécules marquées.

Ce premier volume traite des méthodes de scission sélective qui permettent de déterminer la répartition des isotopes dans les différentes positions d'une molécule organique. Il se veut essentiellement pratique. Son but est de fournir aux chercheurs une importante bibliographie (plus de 800 références), des méthodes de travail, et d'attirer l'attention sur les nombreuses causes d'erreurs qui peuvent apparaître dans ces réactions de scission.

Après avoir rappelé les différentes méthodes physicochimiques (spectrométrie IR, de masse, RMN) qui permettent l'étude de la répartition d'un isotope dans une molécule et leurs limites, les auteurs attirent l'attention du lecteur sur les méthodes chimiques et biochimiques (enzymatiques) qui permettent de décomposer, en produits facilement identifiables, la molécule étudiée.

Les corps pris en considération sont classés de la manière suivante: acides carboxyliques, hydrocarbures aliphatiques, alcools, amines et dérivés halogénés, aldéhydes et cétones, hydrates de carbone, cycles aromatiques, cycles aliphatiques, isoprenoïdes et stéroïdes, hétérocycles, produits divers (vitamines, alcaloïdes, etc.). Pour chaque corps décrit, plusieurs méthodes sont proposées en fonction du but recherché: isolement d'un groupe d'atomes de carbone ou de chaque atome séparément. Les explications sont très brèves mais claires.

Un tableau synoptique permet, à partir des formules brutes, puis du nom du corps correspondant, de retrouver la référence bibliographique décrivant la méthode de séparation d'un ou de plusieurs atomes caractéristiques.

Si cet ouvrage s'adresse plus particulièrement aux chercheurs qui s'intéressent à des problèmes de structure, il peut néanmoins être, pour un chimiste organicien, une source importante de méthodes de décomposition sélectives.

W. HAERDI (Genève)

J. H. Beynon, R. A. Saunders and A. E. Williams, *The Mass Spectra of Organic Molecules*, Elsevier Publishing Company, Amsterdam, 1968, ix +510 pp., price Dfl. 97.50.

Here is a book written by a team of authors which includes the world authority on the subject of analytical mass spectrometry. Readers will discover in its pages no wild speculations on the origins of ions in complex molecule ion dissociations, no futile rationalisations of cracking patterns and no dubious correlations of mass spectra and chemical behaviour of organic molecules. Instead there is a sober account of the empirical correlations which have been observed by generations of mass spectrometrists between the structure and the mass spectra of the more commonly encountered classes of organic molecules. In addition to the familiar hydrocarbon mass spectra, the authors cover the spectra of molecules containing such hetero atoms as halogen, oxygen, sulphur, nitrogen, boron and silicon. There is a brief but useful introduction to modern instrumentation and an account of the formation of the various types of ions which are responsible for the peaks which constitute a complete mass spectrum.

There are two useful appendices at the end of the book. The first of these consists of a selection of examples of the mass spectrometrists' work which is most frequently the determination of the structure of a molecule from an examination of the mass spectrum of a microscopic and often impure sample. This miniature case book will be of the greatest value to the newcomer and may provide the more experienced with an alternative to the daily crossword puzzle. The second appendix is a table of the masses and abundances of nuclides commonly encountered in organic mass spectrometry.

This book can be most heartily recommended and should be kept in every laboratory where a mass spectrometer is in operation for the enlightenment of the patrons. It has also to be recommended for the teaching of third year and postgraduate students.

J. R. Majer (Birmingham)

H. MATTENHEIMER, *Mikromethoden für das klinisch-chemische und biochemische Laboratorium*, 2. Aufl., Walter de Gruyter & Co., Berlin, 1966, 223 S., DM 30,—.

Wohl wenig Laboratorien, die sich mit der Ausführung von Routineanalysen befassen, sind so auf Mikromethoden angewiesen, wie die klinisch-chemischen und biochemischen Laboratorien. Dies, sowie die Tatsache, dass die Zahl der Mikromethoden ständig zunimmt, machten es nötig, bereits nach fünf Jahren eine Neuauflage des Buches erscheinen zu lassen. In dieser sind zahlreiche Methoden neu aufgenommen und einige veraltete durch moderne ersetzt worden.

Nach einer kurzen Einleitung werden im 2. Kapitel verschiedene handelsübliche Geräte beschrieben, so Photometer verschiedener Firmen, Pipetten, Misch- und Rührvorrichtungen und Büretten. Abschliessend werden auch einige im Handel erhältliche Laboreinrichtungen—mikroanalytische Systeme—für diskontinuierliche Analyse erwähnt. Im 3. Kapitel werden zunächst allgemeine Arbeitsvorschriften (Reinigung von Glasgeräten, Siliconieren, Eichung von Pipetten) gegeben und anschliessend im 4. Kapitel die einzelnen Bestimmungsmethoden in folgender Reihenfolge angeführt: (1) Chemische Methoden, (2) Enzymatische Methoden, (3) Bestimmung von Enzymaktivitäten, (4) Enzymbestimmung in Gewebeproben und (5) Ultramikroverfahren zur Enzymbestimmung. Sämtliche Methoden sind für die Untersuchung von Serum und Gewebe ausgearbeitet, es dürfte aber keinerlei Schwierigkeiten bereiten, sie für die Untersuchung anderer Körperflüssigkeiten anzuwenden. Bei jeder Methode ist zunächst ein kurzer Literaturhinweis gegeben, anschliessend wird das Prinzip der Methode erklärt. Darauf folgen in sehr übersichtlicher Weise die Zusammenstellung der Reagenzien, eine Beschreibung der Durchführung der Bestimmung und die Angabe der Berechnungsformel mit näheren Hinweisen.

Im abschliessenden Kapitel sind Umrechnungstabellen, Vorschriften für die Herstellung von Puffern, sowie verschiedene qualitative Nachweisreaktionen gegeben.

Für die Nomenklatur der Enzyme und Coenzyme wurden die Empfehlungen der Internationalen Union für Biochemie berücksichtigt.

Das Buch gibt in sehr guter übersichtlicher Darstellung eine Zusammenfassung moderner biochemischer und klinisch-chemischer Bestimmungsmethoden und sollte in keinem Laboratorium, das sich mit der Ausführung solcher Analysen befasst, fehlen.

W. SCHÖNIGER (Basel)

Anal. Chim. Acta, 44 (1969) 251

ANNOUNCEMENT

INTERNATIONAL ATOMIC ABSORPTION SPECTROSCOPY CONFERENCE, SHEFFIELD, JULY 1969

An International Atomic Absorption Spectroscopy Conference, organised by the Atomic Absorption Spectroscopy Group of the Society for Analytical Chemistry in association with the Spectroscopy Group of the Institute of Physics, will be held in Sheffield, England, on July 14–18, 1969. This Conference, which is sponsored by I.U.P.A.C., is intended to cover all aspects of atomic absorption and atomic fluorescence spectroscopy, and closely related techniques. Many internationally known workers will be attending, several of whom will be presenting plenary lectures at the start of each session.

The programme of plenary lectures and contributed papers will include sessions on the following topics: theoretical aspects of atomic absorption and allied phenomena; atomic fluorescence spectroscopy; fundamental developments in instrumentation; new developments in the analytical use of flames; new techniques in the analysis of biological, metallurgical and ceramic materials; general analytical development. Contributed papers are cordially invited for the Conference. The last date for receipt of extended abstracts (*ca.* 700 words) is February 28, 1969.

During the Conference there will be a Manufacturer's Exhibition, technical visits, social functions and a comprehensive ladies' programme.

All enquiries should be addressed to: A.A.S. Conference Secretary, Society for Analytical Chemistry, 9/10 Savile Row, London, W.1.

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