ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 42, No. 2, 189–348, August 1968
Published monthly

ANALYTICA CHIMICA ACTA

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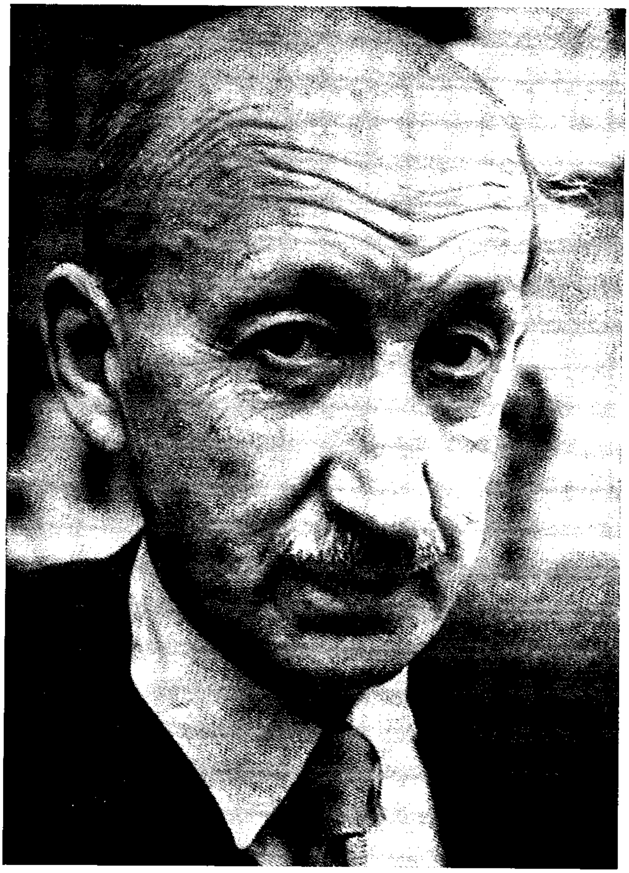

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 42, No. 2, August 1968

ANALYSIS OF TELLURIDES OF LEAD AND TIN BY AUTOMATIC TITRATIONS

An analytical method based on automatic potentiometric EDTA and redox titrations was developed for the analysis of tellurides of lead and tin. First, the sum of lead and tin is titrated at pH 4.5 by adding a known excess of EDTA and back-titrating with a standard lead solution. After addition of ammonium fluoride to mask the tin, the EDTA released from the Sn–EDTA complex is titrated with standard lead solution. Alternatively, after the determination of total lead and tin, lead may be determined by back-titration with standard lead on a separate sample aliquot using tartaric acid to mask the tin. Tellurium is separated as tellurous acid, which is then dissolved in a dilute sulfuric acid solution and oxidized by permanganate at room temperature; the excess permanganate is back-titrated with iron(II) solution automatically. This titration may also be used to determine tellurium in the presence of lead and tin after treatment with perchloric acid. Accuracies of 0.1–0.2% can be obtained.

J. C. Cornwell and K. L. Cheng,
Anal. Chim. Acta, 42 (1968) 189–197

THIN-LAYER SEPARATION AND LOW-TEMPERATURE LUMINESCENCE MEASUREMENT OF MIXTURES OF CARCINOGENS

Low-temperature fluorescence and phosphorescence characteristics of a number of polynuclear aromatic hydrocarbons are reported. Complex mixtures of hydrocarbons are studied to determine the selectivity of low-temperature luminescence measurements. Low-temperature fluorimetry is applied to measure several hydrocarbon carcinogens after ethanolic extraction from thin-layer chromatograms. The method described permits determination of *ca.* 0.1 μg of most of the potent carcinogens.

L. V. S. Hood and J. D. Winefordner,
Anal. Chim. Acta, 42 (1968) 199–205

FRACTIONAL SUBLIMATION OF SOME METAL CHELATES OF THENOYLTRIFLUOROACETONE

Studies on the fractional sublimation of various metal β-diketone chelates have been extended to include the chelates of thenoyltrifluoroacetone (TTA). Many of the common metal chelates were found to be stable, to sublime readily, and to form well-defined zones in the vacuum fractional sublimator. Of the 17 chelates reported only those of manganese(II) and iron(II) were not volatile. The chelates of UO_2(II), Zr(IV), Pb(II), and Cr(III) partially decomposed during sublimation and their recovery was incomplete. The recovery of the sublimed chelates of Ni(II), Mg(II), Al(III), Pd(II), Co(II), Cu(II), Fe(III), Tl(III), Zn(II) and Be(II) ranged from 87 to 100%, with most recoveries being quantitative. The sublimation recrystallization zone temperatures of the various chelates are compared to those of the metal acetylacetonates and the benzoyltrifluoroacetones; in general, the metal chelates of TTA sublime more readily than those of benzoyltrifluoroacetone but are potentially less useful for fractional sublimation separations than the corresponding metal acetylacetonates. Even so, a quantitative separation of iron(III) from Ni(II), Al(III), Mn(II), and Fe(II) is proposed that depends upon the fractional sublimation of the TTA chelates.

E. W. BERG AND K. P. REED,
Anal. Chim. Acta, 42 (1968) 207–212

THE SEPARATION OF FISSION PRODUCTS BY ELECTROPHORETIC FOCUSSING OF IONS. PART II

Electrophoretic focussing of ions was applied to the separation of the long-lived fission products Zr, Nb, Ru, Y, Ce, Sr and Cs. With hydrofluoric acid and nitrilotriacetic acid as the anodic and cathodic electrolytes respectively, a quantitative separation of Zr, Nb, Sr and Cs was obtained whereas Ru, Y and Ce did not focus sharply. The nuclides were detected by γ- and β-counting.

M. PAUWELS, R. GIJBELS AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 213–218

SOLVENT EXTRACTION OF ALKALI METAL IONS WITH CHROMIUM COMPLEXES

Solvent extraction of alkali metal ions by batch and counter-current distribution methods was investigated with tetrathiocyanatodiamminechromate(III) and tetrathiocyanatodianilinechromate(III) as reagents and nitromethane and nitrobenzene as organic solvents. The distribution ratios of alkali metal ions in the various systems were measured. Cesium was readily extracted with the aniline compound and nitrobenzene. The separation of sodium from potassium in trace amounts was possible by the counter-current distribution method.

T. FUJINAGA, M. KOYAMA AND O. TOCHIYAMA,
Anal. Chim. Acta, 42 (1968) 219-224

THE DETERMINATION OF THALLIUM(III) WITH THE 2,2′-BIPYRIDYL–IRON(II) CHELATE

A spectrophotometric determination of thallium(III), based on solvent extraction of an ion-association pair formed between the cationic 2,2′-bipyridyl–iron(II) chelate and the anionic thallium(III) bromide complex is described. The best extractant is 1,2-dichloroethane and extraction is possible over the pH range 2.5–6.7. The composition of the extracted species was confirmed, and conditions were established for the extraction over the concentration range $7.9 \cdot 10^{-6}$–$3.5 \cdot 10^{-5}$ *M* of thallium in aqueous solution.

K. Kotsuji, Y. Yoshimura and S. Ueda,
Anal. Chim. Acta, 42 (1968) 225–231

COMPLEXIMETRIC DETERMINATION OF CALCIUM IN IMPURE CALCIUM CARBONATE AND LIMESTONE

Calcium is determined in impure calcium carbonate and limestone samples by titrating with 0.01 *M* disodium EGTA at pH 12 in the presence of at least 0.6 mg of magnesium and a maximum of 500 μg of iron(III), using a pH 12.5 sodium hydroxide–potassium cyanide–sodium sulfide buffer and Calcon indicator. The results of such titrations are compared with those obtained by titrating at pH 10 the calcium perchlorate solutions derived from calcium oxalate, and with those of a modified Lewis and Melnick method. The results for magnesium (% MgO) obtained by difference are in fair agreement. Magnesium can be titrated compleximetrically as magnesium perchlorate, but the reagent blank must be determined.

J. O. Page,
Anal. Chim. Acta, 42 (1968) 233–238

STABILITY CONSTANTS OF IRON(III)–8-HYDROXYQUINOLINE COMPLEXES

Spectrophotometric determination of the formation constants of iron(III)–8-hydroxyquinoline complexes in 0.1 *M* sodium perchlorate solution at 25° gave the values $K_1 = [\mathrm{FeOx}^{2+}]/([\mathrm{Fe}^{3+}][\mathrm{Ox}^-]) = 4.9 \cdot 10^{13}$, $K_2 = [\mathrm{FeOx_2}^+]/([\mathrm{FeOx}^{2+}][\mathrm{Ox}^-]) = 4.2 \cdot 10^{12}$ and $K_3 = [\mathrm{FeOx_3}]/([\mathrm{FeOx_2}^+][\mathrm{Ox}^-]) = 3.9 \cdot 10^{10}$. $\mathrm{FeOx_2OH}$ and $\mathrm{FeOx(OH)_2}$ are obtainable as solid phases. $\mathrm{FeOx_3}$ ($K_{sp} = 3 \cdot 10^{-44}$, intrinsic solubility $1.6 \cdot 10^{-7}$ *M*) dissolves in basic solutions to form $\mathrm{FeOx_2(OH)_2}^-$. In a solution saturated with $\mathrm{FeOx_3}$, $([\mathrm{FeOx_2(OH)_2}^-][\mathrm{Ox}^-])/[\mathrm{OH}^-]^2 = 7.7 \cdot 10^{-5}$.

T. D. Turnquist and E. B. Sandell,
Anal. Chim. Acta, 42 (1968) 239–245

SCHIFF BASES OF AROMATIC *o*-AMINOKETONES WITH ETHYLENEDIAMINE AND THEIR APPLICATION TO THE DETERMINATION OF NICKEL

(in German)

Schiff bases from ethylenediamine with *o*-aminoacetophenone or *o*-aminobenzophenone were prepared, and their chelating properties towards copper, nickel, cobalt, iron, palladium and platinum were studied. The use of the ligands for the photometric determination of metals was tested. A method for the determination of nickel with N,N′-bis(*o*-aminoacetophenone)-ethylenediimine was developed. Masking agents prevent the interference of iron and copper; a 25-fold amount of palladium and a 10-fold amount of cobalt can be tolerated.

E. Uhlemann and W. Wischnewski,
Anal. Chim. Acta, 42 (1968) 247–252

THE USE OF OXAZINES IN ANALYSIS PART I. THE DETERMINATION OF NITRATE WITH NILE BLUE A

(in German)

The determination of nitrate with the oxazine dyestuff Nile Blue A is described. The dye salt is extracted into 1,2-dichlorobenzene and measured spectrophotometrically. Halide interference is prevented by addition of mercury(II) sulphate. The sensitivity and precision of the method are discussed. Good agreement is found with results obtained by the brucine method. Nitrate can be determined in natural waters.

G. Pokorny and W. Likussar,
Anal. Chim. Acta, 41 (1968) 253–257

A STUDY OF THE REACTION OF SODIUM PEROXIDE ON BERYLLIUM OXIDE BY THERMOGRAVIMETRY, DIFFERENTIAL THERMAL ANALYSIS AND INFRA-RED SPECTROSCOPY

(in French)

Thermogravimetric and differential thermal methods as well as chemical analysis show that sodium peroxide attacks beryllium oxide to form beryllate, apparently in the molecular ratio 1 Na_2O:1 BeO. An unidentified peroxy compound of beryllium is formed at about 165° by the action of the NaO_2 present in the Na_2O_2 sample; it decomposes between 280 and 310°. IR absorption spectroscopy indicates the presence of Be–O bonds in the sodium beryllate which are different from those in the oxide used.

M. Viltange,
Anal. Chim. Acta, 42 (1968) 259–270

NUCLEAR MAGNETIC RESONANCE STUDIES OF EDTA IN THE PRESENCE OF EXCESS CALCIUM OR STRONTIUM

The equilibria which exist between metal ions, ethylenediaminetetraacetic acid (EDTA), and the resulting chelates have been thoroughly investigated by many techniques, emphasis being placed on the study of complexes containing a 1:1 ratio of metal ion to ligand. The results presented here are concerned with the observation of the chemical shift of the nonlabile protons of EDTA when excess calcium or strontium ions are present. The results yield evidence for a 2:1 complex. Formation constants for the equilibria believed to be in effect are given and a possible structure of the 2:1 complex is discussed.

D. E. Leyden and J. F. Whidby,
Anal. Chim. Acta, 42 (1968) 271-278

DETERMINATION OF SILICON, PHOSPHORUS AND SULFUR IN ALLOY STEEL BY NEUTRON ACTIVATION ANALYSIS

Silicon, phosphorus, and sulfur in alloy steel were determined by neutron activation analysis involving rapid radiochemical separation procedures. The standard deviations for silicon, phosphorus, and sulfur were 1.6%, 2.3%, and 2.4% respectively; the sensitivity limits were 3.2, 0.20, and 2.50 p.p.m., respectively. The three constituents could be determined in alloy steel within 2 h of the irradiation.

R. A. Nadkarni and B. C. Haldar,
Anal. Chim. Acta, 42 (1968) 279–284

THE DETERMINATION OF TIN IN TIN ORES AND CONCENTRATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY IN THE NITROUS OXIDE–ACETYLENE FLAME

Tin in tin ores and concentrates can be determined by atomic absorption measurement in the nitrous oxide–acetylene flame. Solutions are prepared by heating the samples with ammonium iodide and dissolving the resulting tin iodide in dilute hydrochloric acid. Calibrating solutions contain ammonium iodide and hydrochloric acid at approximately the concentrations present in the sample solutions. The method has a limit of detection of 0.02% tin in the sample and is suitable for application to geochemical prospecting samples. The results are similar to those obtained by standard chemical methods.

J. A. Bowman,
Anal. Chim. Acta, 42 (1968) 285–291

2-(4-TOLUENESULPHONAMIDO)ANILINE AS AN ANALYTICAL REAGENT

THE NATURE OF THE REACTION WITH COPPER(II)

2-(4-Toluenesulphonamido)aniline, TSA, was examined to evaluate the claim that it is a specific gravimetric reagent for copper(II) and to see if the application of the reagent could be extended. The nature of the reaction and complexes was investigated by potentiometry, solvent extraction, spectrophotometry, polarography and mass spectrometry. A 1:2 copper:TSA complex formed at pH 6 ($K_f = 10^{19.11}$ in 50% (v/v) aqueous dioxane) is suitable for the gravimetric determination, as previously reported. A violet complex ($\lambda_{max.}$ 550 nm, $\varepsilon = 6620$) of uncertain composition is formed at pH 10–11 and may be used for the spectrophotometric determination of copper. The centres of chelation have been deduced from the infrared of the complex and reagent and the causes of the selectivity are discussed.

D. Betteridge and R. Rangaswamy,
Anal. Chim. Acta, 42 (1968) 293–310

METHODS FOR THE STRUCTURAL INVESTIGATION OF XANTHONES

PART II. LOCATION OF HYDROXYL GROUPS BY ULTRAVIOLET AND VISIBLE SPECTROSCOPY

Ultraviolet spectral shifts in presence of certain additives may be used to determine the hydroxylation pattern of xanthones. Thus, 3-hydroxyxanthones are characterized by an intense band around 355 nm which appears in presence of sodium hydroxide. *o*- and *p*-Dihydroxyxanthones decompose in presence of this reagent, the reaction rate depending on the position of the substituents. While the spectra of 1- and 2-hydroxyxanthones do not suffer modification in presence of sodium acetate, 3- and 4-hydroxy groups produce typical shifts which are dependent on the presence of additional oxygen functions. The spectra of 1-hydroxy-, as well as of *o*-dihydroxyxanthones, are affected by the addition of aluminum chloride. 1- and 4-Hydroxy groups with unsubstituted *p*-positions may be detected and distinguished through the visible spectrum (350–750 nm) of the reaction product of the xanthone with 2,6-dichlorobenzoquinone chloroimide (Gibbs test). Relatively acidic hydroxyls give rise to two maxima in this region. Two maxima, even if of different relative intensity, are also obtained with *o*- and *p*-dihydroxy-, as well as with *o*- and *p*-hydroxyallylxanthones.

A. A. Lins Mesquita, D. de Barros Corrêa, O. R. Gottlieb and M. Taveira Magalhães,
Anal. Chim. Acta, 42 (1968) 311–323

DETERMINATION OF IRON IN COPPER–ALUMINUM ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY. USABLE RESONANCE LINES OF IRON

(Short Communication)

K. E. SMITH AND C. W. FRANK,
Anal. Chim. Acta, 42 (1968) 324–326

THE TURBIDIMETRIC DETERMINATION OF SULFATE WITHOUT THE USE OF ADDITIVES

(Short Communication)

J. W. WIMBERLEY,
Anal. Chim. Acta, 42 (1968) 327-329

UTILIZATION OF HYAMINE AS A SELECTIVE EXTRACTION AGENT IN THE SPECTROPHOTOMETRIC DETERMINATION OF COBALT

(Short Communication)

N. GUNDERSEN AND E. JACOBSEN,
Anal. Chim. Acta, 42 (1968) 330–333

THE SPECTROGRAPHIC ANALYSIS OF PLUTONIUM FOR TWENTY-TWO TRACE IMPURITIES BY THE D.C. ARC METHOD

(Short Communication)

R. K. DHUMWAD, M. V. JOSHI AND A. B. PATWARDHAN,
Anal. Chim. Acta, 42 (1968) 334–337

THE USE OF MASS BALANCE CONDITIONS IN CALCULATIONS INVOLVING IONIC EQUILIBRIA

(Short Communication)

D. DYRSSEN AND D. JAGNER,
Anal. Chim. Acta, 42 (1968) 338–339

ADSORPTION OF SOME ELEMENTS IN ACETIC ACID MEDIUM ON DOWEX 1-X8

(Short Communication)

P. VAN DEN WINKEL, F. DE CORTE, A. SPEECKE AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 340

A METHOD OF PRELIMINARY SEPARATION BEFORE THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IN HIGH-PURITY COBALT

(Short Communication; in French)

Tran Van Danh, J. P. Tardif and J. P. Spitz,
Anal. Chim. Acta, 42 (1968) 341–343

SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH 3,5,7,4′-TETRAHYDROXYFLAVONE

(Short Communication)

B. S. Garg K. C. Trikha and R. P. Singh,
Anal. Chim. Acta, 42 (1968) 343–346

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANALYSIS OF TELLURIDES OF LEAD AND TIN BY AUTOMATIC TITRATIONS*

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(Received November 21st, 1967)

The tellurides of lead and tin, which have interesting semiconducting and photosensitive properties, have been intensively investigated as potential electronic materials. Their chemical composition is one of several factors influencing their electrical properties and must be accurately determined. The automatic titration technique, which often offers excellent precision, was used to achieve the necessary accuracy.

The precise titration of lead telluride has been reported by CHENG[1]. Other precise titrations have been reported by BASTIAN *et al.*[2]. GARDELS AND CORNWELL[3] reported the automatic titrations of some tellurides. This paper presents somewhat different approaches. Since tin is difficult to determine by direct titration with EDTA (ethylenediaminetetraacetic acid) because it tends to be hydrolyzed at the pH where it is effectively titrated, a back-titration technique was employed. Tellurium was titrated potentiometrically with potassium permanganate, which is preferred over potassium dichromate or cerate.

The results of the present investigation showed that the tellurides of polyvalent metals may be accurately analyzed by automatic EDTA titrations and that tellurium may be automatically titrated with potassium permanganate. Similar techniques may also be applicable to the analysis of the selenides of these metals.

EXPERIMENTAL

Reagents

Standard solutions. Prepare standard lead and tellurium solutions from 99.999% pure lead and 99.999% pure tellurium. Prepare a standard tin–EDTA solution from 99.999% pure tin and standardized EDTA. Use primary standard-grade potassium dichromate to prepare the dichromate solution. Prepare the 0.05 *N* iron(II) ammonium sulfate solution from its reagent-grade salt and standardize potentiometrically against standard potassium dichromate solution. Prepare a 0.1 *N* potassium permanganate solution from its reagent-grade salt and standardize potentiometrically against the

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* Presented at the XXI International Congress of Pure and Applied Chemistry, Prague, Czechoslovakia, Sept. 4–10, 1967.

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*** Operated with support from the U.S. Air Force.

standardized iron(II) solution. Prepare a 0.05 *M* EDTA solution from its disodium salt and standardize potentiometrically against the standard lead solution.

Ammonium acetate–acetic acid buffer[4]. Dissolve 500 g of ammonium acetate in 1 l of water and add 50 ml of glacial acetic acid.

Sodium acetate–acetic acid buffer[5]. Dissolve 164 g of anhydrous sodium acetate in water with 120 g (114 ml) of glacial acetic acid and dilute to 1 l.

Mercury–EDTA solution, 0.01–0.001 *M*, was purchased from E. H. Sargent or prepared by mixing equivalent amounts of mercury(II) nitrate and EDTA solutions.

Apparatus

The apparatus used was similar to that described by GARDELS AND CORNWELL[3]. The indicator electrode used in the compleximetric titration of lead and tin was the Radiometer P901 mercury cup electrode and for the determination of tellurium a Sargent S-30440 platinum ring electrode. For all titrations the Radiometer K401 saturated calomel electrode was used as the reference electrode.

Sample preparation

Determination of lead and tin in the presence of tellurium. Dissolve 200–250 mg of sample in 4 ml of 3:1 nitric acid–hydrochloric acid and evaporate off the nitrogen oxide fumes. Cool and add a known excess of standardized EDTA solution. Transfer to a 250-ml volumetric flask containing 20 ml of nitric acid and dilute to volume.

Separation of tellurium and subsequent determination of lead, tin and tellurium. Dissolve the sample as described above. After evaporating off the nitrogen oxide fumes, cool and add a known excess of standardized EDTA solution, previously saturated with tellurous acid. Dilute to approximately 100 ml with water saturated with tellurous acid. Adjust the pH to 5.0 with sodium acetate crystals. Wait for several minutes, boil for 1 min, and then cool to room temperature. Filter the tellurous acid precipitate through a fine sintered-glass filter. Wash twice with 5-ml portions of tellurous acid-saturated water and three times with ethanol. Transfer the filtrate to a 250-ml volumetric flask, dilute to volume with water and reserve for the determinations of lead and tin. Dissolve the tellurous acid precipitate in 50 ml of 4 *N* sulfuric acid solution by heating. Transfer to a 250-ml volumetric flask and dilute to volume with 4 *N* sulfuric acid solution for the determination of tellurium.

Recommended procedures

Separate aliquot method. Titration of total lead and tin. To a 250-ml beaker containing 150 ml of water, add a 10–20-ml sample aliquot. Add 10 ml of sodium acetate–acetic acid buffer followed by 3 drops of mercury–EDTA solution. Immerse the mercury indicator electrode and the saturated calomel electrode. After adjusting to pH 4.5 with solid sodium acetate, obtain a potential–titrant curve (Fig. 1) with 0.01000 *M* or 0.00500 *M* standard lead solution. From the potentiometric curve, select the end-point and proportional band settings. Replace the mercury in the indicator electrode cup. After preparing another sample as described above, perform an automatic titration.

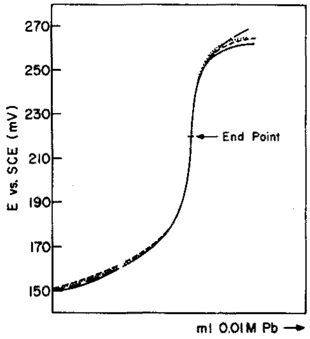
Titration of lead. To a 250-ml beaker containing 150 ml of water and a 10–20-ml sample aliquot add 10 ml of 20% tartaric acid solution. Adjust the pH to 8.5 with concentrated ammonium hydroxide. After 1 min, add 10 ml of ammonium acetate–

acetic acid buffer solution. Adjust to pH 4.5–5.0 with dilute ammonia or dilute nitric acid. Add 3 drops of mercury–EDTA solution. After immersing the electrodes, obtain a potential–titrant curve with standard lead solution. From the potentiometric curve, select the end-point and proportional band settings. Replace the mercury in the indicator electrode cup. After preparing another sample as described above, perform an automatic titration.

Stepwise method. Use the procedure described above for the titration of total lead and tin. After completion of the first automatic titration, add to the solution 5 ml of 10 *M* ammonium fluoride and adjust the pH to 4.5 with dilute nitric acid. Wait for 2 min before obtaining a potential–titrant curve with standard 0.01000 or 0.00500 *M* lead solution as the titrant. Select the end-point and proportional band settings. Take a separate aliquot and perform an automatic titration for total lead and tin. After completion of the titration, add to the solution 5 ml of 10 *M* ammonium fluoride and adjust to pH 4.5 with dilute nitric acid. Make the appropriate end-point and proportional band changes followed by an automatic titration using standard lead solution.

Titration of tellurium after separation as tellurous acid. To a 400-ml beaker containing *ca.* 200 ml of 4 *N* sulfuric acid solution and 5 ml of 85% phosphoric acid, add a suitable aliquot of the sample solution containing 4–10 mg of tellurium. After addition of a known excess of 0.1 *N* standard potassium permanganate solution, wait for 15 min. Using the platinum ring and saturated calomel electrodes and an end-point potential previously determined with a pure tellurite solution, back-titrate the excess of permanganate with a standard 0.05 *N* iron(II) ammonium sulfate solution by the automatic potentiometric titration.

Titration of tellurium in the presence of lead and tin. Weigh a suitable amount of sample containing *ca.* 10 mg of tellurium, dissolve in a mixture of nitric acid and hydrochloric acid, and cool. Add 10 ml of 70% perchloric acid and evaporate to strong fumes. Cool, and add 100 ml of water, 5 ml of 85% phosphoric acid and a known excess of 0.1 *N* standard potassium permanganate solution. After letting stand for 15 min,



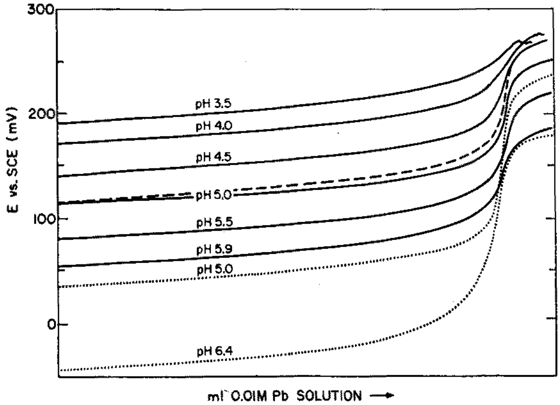


Fig. 1. Potential–titrant curve. (—) Pb+EDTA; (....) Pb+EDTA+x Sn; (- - - -) Pb+EDTA+$2x$ Sn; (— —) Pb+EDTA+$3x$ Sn.

Fig. 2. Effect of pH on the titration of excess EDTA with lead. pH adjusted with: (—) NaOAc–HOAc buffer; (— —) NaOAc; (....) hexamethylenetetramine.

titrate the excess of permanganate with a standard 0.05 *N* iron(II) ammonium sulfate solution by automatic potentiometric titration.

RESULTS AND DISCUSSION

Electrodes

For the automatic EDTA titration of metal ions, either the mercury electrode[6–8] or the gold amalgam electrode[3] may be used. The former is preferred, however, as the latter must frequently be cleaned, reamalgamed and conditioned. It is necessary to replace the mercury in the cup electrode after every titration to obtain precision. For the permanganate titration of tellurium the use of a platinum ring electrode was found to be satisfactory.

pH and buffers

pH is one of the most important factors in achieving a successful EDTA titration. The back-titration of excess of EDTA with a standard lead solution was found to be convenient. For the determination of lead by the separate aliquot method, use of an ammonium acetate–acetic acid buffer gave better potentiometric breaks than those obtained using the sodium acetate–acetic acid buffer. For all titrations, a controlled pH of 4.5–5.0 was chosen. The reason can be easily understood from the potential–titrant curves shown in Fig. 2 for various pH values. These curves show that hexa-

TABLE I

AUTOMATIC TITRATION FOR THE DETERMINATION OF LEAD IN THE PRESENCE OF TIN AND TELLURIUM

Taken (mmole)		*Pb/Sn*	*No Te present*		*0.05 mmole Te present*	
Pb	*Sn*		*Found (mmole) Pb*	*Deviation (mmole)*	*Found (mmole) Pb*	*Deviation (mmole)*
0.04723	0.00169	28.0	0.04725		0.04720	
			0.04723		0.04727	
			0.04720		0.04724	
			0.04727		0.04724	
			0.04721		0.04723	
			0.04724		0.04722	
			Av. 0.04723	None	Av. 0.04723	None
0.04428	0.00506	8.8	0.04426		0.04430	
			0.04430		0.04426	
			0.00427		0.04428	
			0.04429		0.04430	
			0.04426		0.04428	
			0.04431		0.04431	
			Av. 0.04428	None	Av. 0.04427	−0.00001
0.03936	0.01688	2.3	0.03938		0.03935	
			0.03936		0.03935	
			0.03935		0.03938	
			0.03937		0.03937	
			0.03934		0.03934	
			0.03938		0.03936	
			Av. 0.03936	None	Av. 0.03936	None

methylenetetramine gave better breaks than the acetate buffers, but this reagent is not recommended, since it gave poor precision for automatic titrations.

Emf plot

For determining the end-point settings necessary for the automatic titration, preliminary plots of emf *vs.* volume of titrant were obtained (Fig. 2). This may be done with the sample solution or, if the supply is limited, with a synthetic mixture having a composition similar to the sample.

Stepwise method for lead and tin

The separate aliquot method and the stepwise method are proposed here. Both were found to be satisfactory (Tables I and II). When the sample supply is limited, as is often the case, the stepwise method conserves sample and, furthermore, it is time-saving. Unfortunately, tellurium cannot be titrated after completion of the EDTA

TABLE II

STEPWISE AUTOMATIC TITRATION FOR THE DETERMINATION OF LEAD AND TIN IN SYNTHETIC SOLUTIONS

Taken (mmole)			*Pb/Sn*	*Found (mmole)*			
Pb	*Sn*	*Pb+Sn*			*Pb+Sn*	*Pb (by diff.)*	*Sn*
0.04723	0.00169	0.04892	28.0		0.04896	0.04728	0.00168
					0.04892	0.04724	0.00168
					0.04895	0.04728	0.00167
					0.04893	0.04727	0.00166
					0.04896	0.04726	0.00170
					0.04896	0.04726	0.00170
				Av.	0.04895	0.04727	0.00168
				Deviation	+0.00003	+0.00004	−0.00001
0.04428	0.00506	0.04934	8.8		0.04934	0.04426	0.00508
					0.04932	0.04425	0.00507
					0.04936	0.04430	0.00506
					0.04932	0.04428	0.00504
					0.04933	0.04429	0.00504
					0.04933	0.04424	0.00509
				Av.	0.04933	0.04427	0.00506
				Deviation	−0.00001	−0.00001	None
0.03440	0.02110	0.05550	1.6		0.05542	0.03428	0.02114
					0.05552	0.03445	0.02107
					0.05548	0.03434	0.02114
					0.05548	0.03439	0.02109
					0.05543	0.03428	0.02115
					0.05552	0.03446	0.02106
				Av.	0.05548	0.03437	0.02111
				Deviation	−0.00002	−0.00003	+0.00001
0.01968	0.04009	0.05977	0.5		0.05970	0.01970	0.04000
					0.05974	0.01965	0.04009
					0.05980	0.01968	0.04012
					0.05979	0.01967	0.04012
					0.05973	0.01967	0.04006
					0.05982	0.01972	0.04010
				Av.	0.05976	0.01968	0.04008
				Deviation	−0.00001	None	−0.00001

titration of lead and tin because permanganate in a rather highly acidic solution oxidizes EDTA. Obviously, any organic substance such as EDTA, hexamethylenetetramine, or acetic acid must be absent in the permanganate titration of tellurium.

Back-titration

There is no problem in titrating lead directly with EDTA. However, it is impossible to titrate tin directly with EDTA at pH 4–5, where tin is hydrolyzed. As pointed out by CHENG[9], many metal ions are complexed with difficulty by EDTA once they have been hydrolyzed; for instance, the tin–EDTA complex is stable in a slightly acidic medium (pH 5), the complex being decomposed by hydrolysis of tin when it is raised to a pH above 7. The tin hydroxide is not complexed by EDTA even if the solution is readjusted to pH 5. For this reason, not only must a back-titration be used, but the adjustment of pH must be carefully made in order not to exceed a pH of 6.

Interferences

The samples are usually made of pure metals and contain no unexpected impurities. The main disadvantage of the mercury electrode, as pointed out by REILLEY AND SCHMID[7], is the interference from halides; the interference from sulfate is not as serious. The curves of Fig. 4 show the quantitative effects of chloride. A concentration of $3.6 \cdot 10^{-4}$ M chloride could be tolerated but serious interference would result when the concentration exceeded $1 \cdot 10^{-3}$ M.

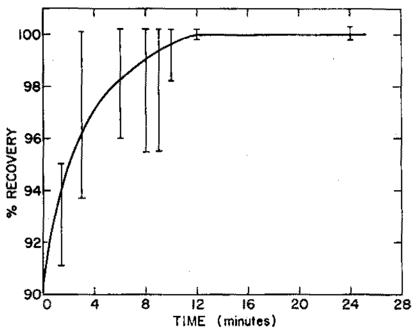


Fig. 3. Effect of time on the oxidation of tellurium with $KMnO_4$.

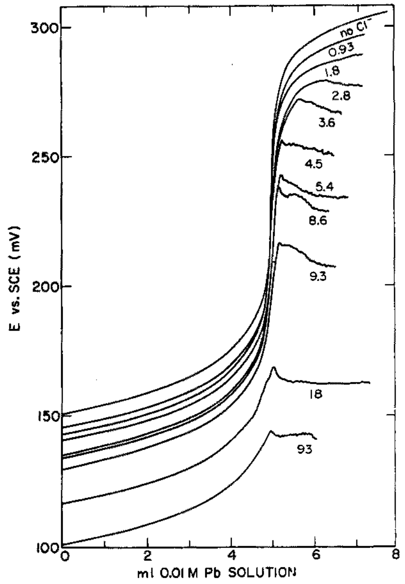


Fig. 4. Effect of chloride on the titration of excess EDTA with lead. Figures at curves in 10^{-4} M.

Titration of tellurium

Dichromate was used by GARDELS AND CORNWELL[3] for potentiometric titration of tellurium; cerium(IV) sulfate has also been used. In the present work, it was found that the permanganate method requires a shorter period of standing (12 min) (Fig. 3) than the dichromate method (60 min) for complete oxidation of tellurium(IV) to tellurium(VI). Because of the solubility of tellurous acid, it is necessary to use a tellurous acid-saturated solution of EDTA for accurate work if separation of the tellurous acid is required. The results obtained in titrating a known amount of tellurium are shown in Table III.

TABLE III

TITRATION OF TELLURIUM AFTER ITS SEPARATION AS TELLUROUS ACID

Te taken (mmole)	*Te found (mmole)*	*Deviation (mmole)*
0.07075	0.07069	
	0.07074	
	0.07077	
	0.07080	
	0.07076	
	0.07078	
	Av. 0.07076	+0.00001

TABLE IV

ANALYSIS OF TELLURIDES OF LEAD AND TIN[a]

Sample	*Weight %*			*Recovery (%)*
	Pb	*Sn*	*Te*	
1	59.14	2.04	38.76	99.94
2	52.98	6.96	40.10	100.04
3	61.26	0.61	38.37	100.24
4	52.11	7.72	40.10	99.93
5	41.98	15.20	42.80	99.98
6	24.76	28.49	46.85	100.10
10 A	55.30	4.51	40.35	100.16
10B	55.21	3.54	41.40	100.15
10C	54.61	4.56	40.87	100.04
10D	55.01	3.88	41.29	100.18

[a] Samples 1–6 were analyzed for lead and tin in the presence of tellurium using the separate aliquot method. Tellurium was subsequently determined after separation as tellurous acid. Samples 10A–10D were analyzed for lead and tin by the stepwise method after tellurium was separated as tellurous acid.

Precision and accuracy

Automatic titration is not a time saver where one or two samples are involved; however, it definitely expedites routine analyses of a large number of samples. It offers, besides, the attractive feature of high precision and accuracy as demonstrated in Tables I and II. By using a constant-rate buret which can be read to 0.002 ml and estimated to 0.001 ml, precision of one to two parts per thousand can generally be obtained with titrant volumes in the 2–10-ml range. This is significantly better than the precision which was achieved by manual titrations of the same systems. The accuracy is about 0.1% as illustrated in Table IV in the results from analyzing the actual samples.

When high accuracy is desired, instrumentation, flasks and pipets must be calibrated. Standardization of solutions against pure metal ion solutions is necessary, and conditions similar to those experienced in an actual determination must be duplicated.

One of the authors (K.L.C.) acknowledges with thanks the School of Graduate Studies, The University of Missouri at Kansas City, for the partial financial support of this work.

SUMMARY

An analytical method based on automatic potentiometric EDTA and redox titrations was developed for the analysis of tellurides of lead and tin. First, the sum of lead and tin is titrated at pH 4.5 by adding a known excess of EDTA and back-titrating with a standard lead solution. After addition of ammonium fluoride to mask the tin, the EDTA released from the Sn–EDTA complex is titrated with standard lead solution. Alternatively, after the determination of total lead and tin, lead may be determined by back-titration with standard lead on a separate sample aliquot using tartaric acid to mask the tin. Tellurium is separated as tellurous acid, which is then dissolved in a dilute sulfuric acid solution and oxidized by permanganate at room temperature; the excess permanganate is back-titrated with iron(II) solution automatically. This titration may also be used to determine tellurium in the presence of lead and tin after treatment with perchloric acid. Accuracies of 0.1–0.2% can be obtained.

RÉSUMÉ

On a mis au point une méthode potentiométrique automatique d'EDTA et de titrages redox pour l'analyse des tellurides de plomb et d'étain. Le plomb et l'étain sont d'abord dosés ensemble au pH 4.5 par addition d'un excès connu d'EDTA et titrage en retour au moyen de plomb étalon. Après addition de fluorure d'ammonium pour masquer l'étain, l'EDTA libéré du complexe Sn–EDTA est titré avec du plomb étalon. Alternativement après dosage plomb–étain, le plomb peut être dosé par titrage indirect à l'aide de plomb étalon sur une prise aliquote séparée, en utilisant l'acide tartrique pour masquer l'étain. Le tellure est séparé comme acide tellureux qui est dissous dans une solution d'acide sulfurique dilué et oxydé par le permanganate, l'excès de permanganate est titré automatiquement en retour par le fer(II). Ce titrage peut également être effectué pour doser le tellure en présence de plomb et d'étain, après traitement à l'acide perchlorique. On arrive à des précisions de 0.1–0.2%.

ZUSAMMENFASSUNG

Es wurde eine analytische Methode, die auf automatischen potentiometrischen AeDTE- und Redox-Titrationen beruht, für die Analyse von Telluriden des

Bleis und Zinns entwickelt. Zuerst wird die Summe von Blei und Zinn bei pH 4.5 durch Zugabe eines bekannten Überschusses von AeDTE und Rücktitration mit einer Bleistammlösung bestimmt. Nach Zugabe von Ammoniumfluorid zur Maskierung des Zinns wird das AeDTE des Zinn-Komplexes mit der Bleistammlösung titriert. Nach der Bestimmung des gesamten Bleis und Zinns kann das Blei durch Rücktitration in einem aliquoten Teil der Probe mit der Bleistammlösung unter Verwendung von Weinsäure zur Maskierung des Zinns bestimmt werden. Tellur wird als Tellursäure abgetrennt und in verdünnter Schwefelsäure mit Permanganat bei Raumtemperatur oxydiert; der Permanganatüberschuss wird mit einer Eisen(II)-Lösung automatisch zurücktitriert. Diese Titration kann ebenso für die Bestimmung des Tellurs in Gegenwart von Blei und Zinn nach Behandlung mit Perchlorsäure verwendet werden. Die Genauigkeiten betragen 0.1–0.2%.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THIN-LAYER SEPARATION AND LOW-TEMPERATURE LUMINESCENCE MEASUREMENT OF MIXTURES OF CARCINOGENS

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(Received February 14th, 1968)

McGLYNN *et al.*[1] have demonstrated the usefulness of measuring low-temperature luminescence for determination of several hydrocarbons of petrochemical interest. Naphthalene, phenanthrene, and 1,2,4,5-tetramethylbenzene were measured in a mixture of the three by judicious choice of fluorescence and phosphorescence excitation and emission wavelengths. In the present work, similar techniques are applied to a number of polynuclear aromatic compounds. Many of these are carcinogens and occur as common environmental contaminants. The need for further investigation of such systems with close attention to measurement techniques is suggested by results of SAWICKI *et al.*[2] in air pollution studies.

There are several distinct advantages in making fluorescence and phosphorescence measurements at low temperatures. McGLYNN *et al.*[1] have discussed the complementary nature and usefulness of low-temperature fluorimetry and phosphorimetry. WINEFORDNER *et al.*[3] have also stressed the analytical utility of combining the two luminescence techniques. In both fluorimetry and phosphorimetry, it is often possible to excite specific species in a mixture and to measure luminescence from certain species. In addition, by means of simple instrumentation, it is possible to use time-resolved phosphorimetry. For example, ST. JOHN AND WINEFORDNER[4] have applied this kinetic approach to the analysis of two-component mixtures of biological importance. MUEL AND LACROIX[5] have stressed that the extremely sharp and numerous fluorescence bands, which characterize the low-temperature fluorescence spectra of polynuclear aromatics, enhance selectivity over room-temperature measurements; the increase in fluorescence intensity with decreasing temperature enhances sensitivity. These authors measured 3,4-benzpyrene in complex mixtures. The major disadvantage of using low-temperature luminescence measurements for quantitative analytical studies is that only solvents which form clear, uncracked glasses[6] can be used. In the present study, ethanol which forms an ideal low-temperature rigid matrix[6], is used as the thin-layer extractant.

EXPERIMENTAL

Apparatus

A fluorescence spectrophotometer (Fluorispec, Model SF-1, Baird-Atomic Inc., Cambridge, Mass.) with X-Y recorder was used for determining all fluorescence and phosphorescence spectra and for measuring limits of detection and analytical curves.

When the smallest slits are used, the spectral bandwidth of the instrument is 2 nm. The low-temperature luminescence unit includes a Dewar flask (normally liquid nitrogen—77°K—is used) and a phosphoroscope which may be moved in or out of the light path, alternately permitting measurement of phosphorescence in the absence of fluorescence or the measurement of fluorescence plus phosphorescence (total luminescence). Sample cells were made from quartz tubing (1 mm I.D. sealed at one end). Phosphorescence decay times were measured with an Aminco-Bowman spectrophotofluorimeter with an Aminco-Keirs phosphoroscope (American Instrument Co., Inc., Silver Spring, Maryland) by manually terminating the exciting light with a shutter and tracing the decay on an X-Y recorder. Commercial thin-layer chromatography equipment (Brinkmann Instruments Inc., Westbury, N.Y.) was used. A long wavelength ultraviolet lamp (Blak-Ray Model XX 15, Ultra Violet Products Inc., San Gabriel, Calif.) was used to locate fluorescent compounds at room temperature on the thin-layer chromatograms.

Materials

The hydrocarbons (Nutritional Biochemicals Corp., Cleveland, Ohio and K and K Laboratories Inc., Plainview, N.Y.) were recrystallized if necessary. Ethanol was distilled as previously described[7]. Hexane was extracted with sulfuric acid, dried over sodium sulfate and passed through a column of silica gel. Pyridine was reagent grade. Silica gel G for thin-layer chromatography (E. Merck A. G., Darmstadt, Germany) was heated at 700° for 12 h before use to reduce luminescence background[8].

Luminescence characteristics

The low-temperature luminescence characteristics (fluorescence and phosphorescence excitation and emission wavelengths, phosphorescence decay times and limits of detection) of a large number of the hydrocarbons were measured. Of the hydrocarbons examined, literature references indicated that eight were carcinogens of varying potency[9–11]: *strong*—3,4-benzpyrene, 20-methylcholanthrene, 1,2,5,6-dibenzanthracene, 3,4,8,9-dibenzpyrene, 3,4,9,10-dibenzpyrene; *intermediate*—1,2,3,4-dibenzpyrene, 1,2,4,5-dibenzpyrene; *weak*—1,2-benzanthracene. Complete analytical curves were prepared for each of these compounds and interferences were studied to determine the selectivity of the luminescence method for measuring complex mixtures.

Thin-layer chromatography

The procedure adopted was similar to that of MATSUSHITA *et al.*[12]. Thin-layer plates (20 cm^2) were coated with a 250 μ layer of silica gel G using standard techniques. The plates were dried for 1 h at 90° and stored in a desiccator. Ethanolic solutions of the hydrocarbons (0.1 μg/μl) were applied with hypodermic syringes. Hexane–pyridine (30:1,v/v) equilibrated for 1 h, was used to develop the separation. Development was carried out in a dark room to minimize hydrocarbon decomposition[13]. The developing solvent was allowed to rise 17 cm (*ca.* 50 min), and then the front was marked and the plates immediately examined under long wavelength ultraviolet light. The hydrocarbon spots were marked and the plates air-dried. A square of adsorbent containing a spot was removed and extracted once with 10 ml of ethanol. The extraction was performed in a centrifuge tube held at 65° in a water bath. The duration of extraction was 15 min, and the solution was frequently stirred. The cooled ethanolic extract was adjusted to 10.00 ml and centrifuged. A small portion of the resulting solution was transferred to a luminescence sample tube for measurement.

RESULTS AND DISCUSSION

In Table I, the R_F values for the thin-layer separation and the low-temperature luminescence characteristics obtained in this investigation are given. The trend in the R_{F_B} values (R_F relative to 3,4-benzpyrene) is consistent with literature results[2,12,14]. A more complete separation of all the hydrocarbons, or complete separation of certain pairs could probably be perfected by an exhaustive investigation of the chromatographic procedure. The present separation study, however, does indicate where interference problems might occur in an actual experimental situation. Luminescence wavelengths cited are those at which the limits of detection were determined and are in general the most intense peaks. The limit of detection was defined as that concentration giving a signal twice the mean fluctuation in background[15]. Fluorimetric limits of detection were obtained under conditions of maximum resolution (2 nm spectral bandwidth). By using wider slits, these limits of detection could be lowered considerably[16]. High spectral resolution, however, was required for the analysis of complex mixtures studied here, and therefore a spectral bandwidth of 2 nm was a good compromise. Phosphorescence limits of detection were determined with a spectral bandwidth of 8 nm. The four compounds for which no phosphorescence data are presented gave no significant luminescence at a concentration of 10^{-3} M. The phosphorescence

TABLE I

R_{F_B} VALUES AND LOW-TEMPERATURE LUMINESCENCE CHARACTERISTICS OF POLYNUCLEAR AROMATIC HYDROCARBONS

Compound	R_{F_B}[a]	*Fluorescence*[b,d]			*Phosphorescence*[c,d]			
		λ_{ex} *(nm)*	λ_{em} *(nm)*	*L. of D. (μg/ml)*	λ_{ex} *(nm)*	λ_{em} *(nm)*	*L. of D. (μg/ml)*	τ *(sec)*
Pyrene	1.40	338	374	0.002	328	595	0.4	0.46
2,3-Benzfluorene	1.40	320	342	0.01	315	507	0.4	2.8
1,2-Benzanthracene	1.30	348	387	0.03	310	505	0.05	1.4
20-Methylcholanthrene	1.10	300	396	0.008	—	—	—	—
Triphenylene	1.10	288	354	0.3	285	460	0.003	16.2
1,2-Benzpyrene	1.00	333	390	0.03	325	544	0.02	2.1
3,4-Benzpyrene	1.00	369	405	0.003	330	517	2.0	2.3
Perylene	0.90	438	470	0.002	—	—	—	—
1,2,5,6-Dibenzanthracene	0.90	300	396	0.008	295	554	0.02	1.5
1,12-Benzperylene	0.80	386	421	0.005	295	556	0.09	0.67
1,2,3,4-Dibenzanthracene	0.77	290	377	0.007	287	565	0.09	0.90
1,2,3,4-Dibenzpyrene	0.73	331	504	0.07	—	—	—	—
3,4,9,10-Dibenzpyrene	0.73	421	473	0.05	295	530	0.5	2.7
3,4,8,9-Dibenzpyrene	0.70	313	453	0.003	—	—	—	—
1,2,4,5-Dibenzpyrene	0.67	305	397	0.007	379	609	0.6	0.67
Coronene	0.67	341	446	0.004	310	557	0.004	9.6

[a] R_F values relative to 3,4-benzpyrene.
[b] Spectral bandwidth 2 nm.
[c] Spectral bandwidth 8 nm.
[d] All limits of detection (L. of D.) were measured at excitation, λ_{ex}, and emission, λ_{em}, wavelengths given. The wavelengths are generally peak values uncorrected for instrumental response.

decays were exponential for all compounds studied except 1,2-benzanthracene which gave a non-exponential decay even after several recrystallizations. The fluorimetric and phosphorimetric limits of detection cannot be directly compared since different spectral bandwidths were used, but it is evident that low-temperature fluorimetry is *considerably more sensitive* than phosphorimetry for the measurement of most of these compounds. At concentrations where both techniques give analytically useful signals, it is convenient to measure phosphorescence as well as fluorescence. Analytical curves for both techniques were linear over three or more decades. The curves extended to lower concentrations for the fluorescence measurements and to higher concentrations for the phosphorescence measurements. By combining the two techniques, an analytical range of over four decades resulted.

In Fig. 1, some of the advantages of low-temperature fluorimetry are indicated

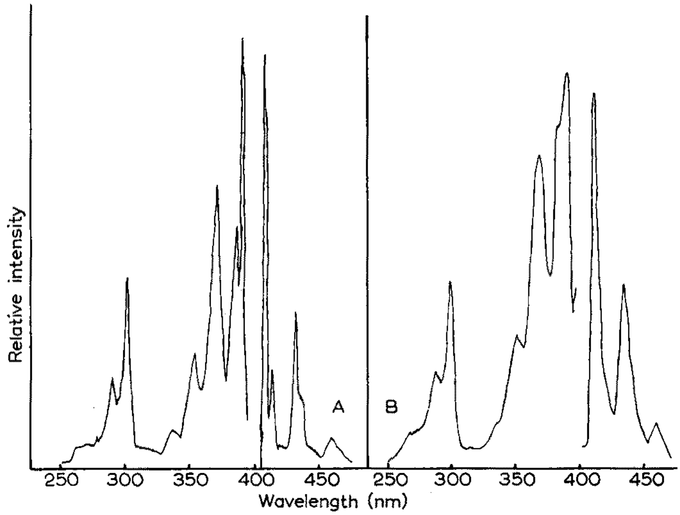

Fig. 1. Fluorescence excitation and emission spectra of 3,4-benzpyrene (10 μg/ml). (A) At 77°K (low-temperature luminescence assembly with liquid N_2); (B) at 298°K (low-temperature luminescence assembly without liquid N_2; instrumental sensitivity 10 times greater than for A). Other instrumental settings which were the same for A and B are: λ_{ex} = 390 nm; λ_{em} = 405 nm; 1-mm sample tube; spectral bandwidth = 2 nm.

TABLE II

DETERMINATION OF 1,2-BENZANTHRACENE AND 20-METHYLCHOLANTHRENE IN A FIVE-COMPONENT MIXTURE[a]

Carcinogen (1 μg/ml)	*Fluorescence wavelengths*		*% Error in measured concn. Interferent concn.*	
	λ_{ex}[b] *(nm)*	λ_{em}[b] *(nm)*	*(1 μg/ml)*	*(5 μg/ml)*
1,2-Benzanthracene	348[c]	387	−4.3	+5.0
20-Methylcholanthrene	300	396	−2.1	0

[a] Mixture consists of 1,2-benzanthracene, 20-methylcholanthrene, 2,3-benzfluorene, pyrene, triphenylene.

[b] All wavelengths were chosen to achieve maximum selectivity with minimum loss in sensitivity. Other instrumental conditions were as given in Table I.

[c] Excitation wavelength is one edge of sharp peak which requires tedious adjustment.

by comparison of the spectra of 3,4-benzpyrene obtained at 77°K and at room temperature. In Tables II–IV, results are given of interference studies for low-temperature fluorescence measurement of mixtures of compounds having similar R_{F_B} values. In most cases, the carcinogens could be determined in the presence of a large number of interfering compounds even when these compounds were present in excess. The wavelengths chosen for these measurements were those which gave the least interference and not necessarily the greatest sensitivity. Absorption of the exciting light and absorption of emitted fluorescence by interfering species resulted in the most severe limitation for excesses of interfering species. Interference studies were not practical when phosphorimetry was used, because the wider spectral beandwidth needed resulted in poor selective excitation of multi-component mixtures. Phosphorimetry would appear to be most useful in cases where the species of concern is in a mixture of strongly fluorescent but weakly phosphorescent interfering species. For example, perylene will interfere in the fluorimetric determination of 3,4,9,10-dibenzpyrene (see Table IV) but should give negligible interference in the phosphorimetric determination. No attempt was made to apply time-resolved phosphorimetry to these systems since the life-times of the carcinogens were too similar.

TABLE III

DETERMINATION OF 3,4-BENZPYRENE, 20-METHYLCHOLANTHRENE, AND 1,2,5,6-DIBENZANTHRACENE IN AN EIGHT-COMPONENT MIXTURE

Carcinogen (1 μg/ml)	*Fluorescence wavelengths*		*% Error in measured concn. Interferent concn.*	
	λ_{ex}[b] *(nm)*	λ_{em}[b] *(nm)*	*(1 μg/ml)*	*(5 μg/ml)*
3,4-Benzpyrene	389	406	−1.8	−17.5
20-Methylcholanthrene	382	396	−5.8	−14.2
1,2,5,6-Dibenzanthracene	325	396	+8.0	+50

[a] Mixture consists of 3,4-benzpyrene, 20-methylcholanthrene, 1,2,5,6-dibenzanthracene, triphenylene, 1,2-benzpyrene, perylene, 1,12-benzperylene, 1,2,3,4-dibenzanthracene.

[b] See footnote in Table II.

TABLE IV

DETERMINATION OF 1,2,5,6-DIBENZANTHRACENE, 1,2,3,4-DIBENZPYRENE, 1,2,4,5-DIBENZPYRENE, 3,4,8,9-DIBENZPYRENE, 3,4,9,10-DIBENZPYRENE IN A NINE-COMPONENT MIXTURE[a]

Carcinogen (1 μg/ml)	*Fluorescence wavelengths*		*% Error in measured concn. Interferent concn.*	
	λ_{ex}[b] *(nm)*	λ_{em}[b] *(nm)*	*(1 μg/ml)*	*(5 μg/ml)*[c]
1,2,5,6-Dibenzanthracene	300	396	0	0
1,2,3,4-Dibenzpyrene	332	503	+4.0	+47
1,2,4,5-Dibenzpyrene	379	397	−1.0	−8.7
3,4,8,9-Dibenzpyrene	313	454	+2.0	−17.8
3,4,9,10-Dibenzpyrene	393	463	+320	+930

[a] Mixture consists of 1,2,5,6-dibenzanthracene, 1,2,3,4-dibenzpyrene, 1,2,4,5-dibenzpyrene, 3,4,8,9-dibenzpyrene, 3,4,9,10-dibenzpyrene, 1,12-benzperylene, 1,2,3,4-dibenzanthracene, perylene, coronene.

[b] See footnote in Table II.

[c] Coronene concentration 2 μg/ml.

The recovery results given in Table V were obtained using the thin-layer separation and the low-temperature fluorescence measurement techniques described above. Each result is the average of four or more complete determinations. Recoveries for all of the carcinogens except 20-methylcholanthrene and 3,4,8,9-dibenzpyrene were greater than 85%. The luminescence background of the ethanol blank and the silica gel G blank (ethanol extraction) were negligible at the instrumental settings employed in this study. The results are similar to those of LAM AND BERG[14] for ethanol extraction of larger quantities of some of the same compounds. Although ethanol was the most desirable extractant because of its low-temperature matrix properties, other solvents could be used. For instance, methanol which should be a slightly better eluting solvent, will form a suitable matrix when mixed with ethanol[6]. The ethanol extraction does appear adequate and could be improved by using several extractions with smaller volumes. However, one 10-ml extraction is fast and good recoveries result. By using the procedures given in this paper, it is possible to determine approximately 0.1 μg of most of the carcinogens with good precision. Therefore, the described procedures would seem to be well suited for application in environmental studies of hydrocarbon pollution.

TABLE V

RECOVERY OF CARCINOGENS FROM THIN-LAYER CHROMATOGRAMS BY FLUORESCENCE MEASUREMENT AT 77°K

Carcinogens	*% Recovery*[a]	
	0.5 μg applied	*2 μg applied*
3,4-Benzpyrene	91 ± 3	86 ± 4
1,2,5,6-Dibenzanthracene	97 ± 4	101 ± 1
1,2-Benzanthracene	82 ± 5	86 ± 7
1,2,4,5-Dibenzpyrene	86 ± 6	87 ± 2
1,2,3,4-Dibenzpyrene	—	103 ± 5
3,4,9,10-Dibenzpyrene	86 ± 4	—
3,4,8,9-Dibenzpyrene	Not	extracted
20-Methylcholanthrene	42 ± 5	48 ± 10

[a] Each result is average of 4 or more complete determinations.

This research was carried out as part of a study on the phosphorimetric analysis of drugs in blood and urine supported by a U. S. Public Health Service Grant (GM-11373-05).

SUMMARY

Low-temperature fluorescence and phosphorescence characteristics of a number of polynuclear aromatic hydrocarbons are reported. Complex mixtures of hydrocarbons are studied to determine the selectivity of low-temperature luminescence measurement. Low-temperature fluorimetry is applied to measure several hydrocarbon carcinogens after ethanolic extraction from thin-layer chromatograms. The method described permits determination of *ca.* 0.1 μg of most of the potent carcinogens.

RÉSUMÉ

On fait un rapport des caractéristiques de fluorescence et de phosphorescence à basse température d'un certain nombre d'hydrocarbures aromatiques polynucléaires. Des mélanges complexes d'hydrocarbures sont étudiés en vue de déterminer la sélectivité des mesures de luminescence à basse température. La fluorimétrie à basse température est appliquée à la mesure de plusieurs hydrocarbures carcinogènes après extraction éthanolique de chromatogrammes sur couche mince. La méthode décrite permet le dosage d'environ 0.1 μg de la plupart des carcinogènes.

ZUSAMMENFASSUNG

Über die Tieftemperatur-Fluoreszenz und -Phosphoreszenz einer Anzahl polynuklearer aromatischer Kohlenwasserstoffe wird berichtet. Um die Selektivität der Tieftemperatur-Lumineszenz-Messungen zu bestimmen, werden komplexe Mischungen von Kohlenwasserstoffen untersucht. Die Tieftemperatur-Fluorometrie wird zur Messung verschiedener Kohlenwasserstoffcarcinogene nach äthanolischer Extraktion aus Dünnschichtchromatogrammen angewandt. Die beschriebene Methode erlaubt die Bestimmung von etwa 0.1 μg der meisten möglichen Carcinogene.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

FRACTIONAL SUBLIMATION OF SOME METAL CHELATES OF THENOYLTRIFLUOROACETONE

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(Received February 14th, 1968)

The initial work of BERG AND TRUEMPER[1-3] and BERG AND DOWLING[4] confirmed the general volatility of the metal chelates of the β-diketones. BERG AND HARTLAGE[5-7] then reported the separation of a number of mixtures of metal β-diketone chelates by a vacuum fractional sublimation technique which they developed. More recently, BERG AND CHIANG[8,9] reported on the volatility and fractional sublimation of the dipivaloylmethane chelates of the lanthanide and related elements. The β-diketones which have been investigated most extensively in these studies are listed in Table I. These investigations have indicated that the chelates of acetylacetone provided the most satisfactory separations and that the β-diketones which contained aromatic groups did not lead to favorable results, although many of these chelates were volatile. For example, the chelates of benzoylacetone and benzoyltrifluoroacetone generally recrystallized in diffuse zones of microcrystals or condensed as liquids, and good separations were not possible. In addition, benzoylacetone formed few volatile chelates.

TABLE I

β-DIKETONES INVESTIGATED

Name	*IUPAC name*	*Symbol*
Acetylacetone	2,4-Pentanedione	AA
Trifluoroacetylacetone	1,1,1-Trifluoro-2,4-pentanedione	TFAA
Hexafluoroacetylacetone	1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	HFAA
Benzoylacetone	1-Phenyl-1,3-butanedione	BA
Benzoyltrifluoroacetone	1-Phenyl-4,4,4-trifluoro-1,3-butanedione	BTA
Dipivaloylmethane	2,2,6,6-Tetramethyl-3,5-heptanedione	DPM

It would be advantageous, however, to use the aryl β-diketonates in fractional sublimation separation methods for several reasons. First, these chelates form very insoluble complexes in aqueous systems. This would result in more complete and easier separations of the metals from their initial environment. Second, the aryl chelates are usually more stable than those of the aliphatic β-diketones. Such stability would be helpful under the experimental conditions of fractional sublimation. Third,

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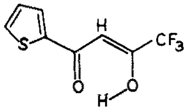
an increase in separation of the recrystallized zones might be anticipated. Thenoyltrifluoroacetone (TTA; 1-(2-thenoyl)-4,4,4-trifluoro-1,3-butanedione)



reacts readily with metal ions in aqueous solution, and forms chelates which are both quite stable and insoluble in water. TTA combines the effects of the thienyl group, which is aromatic, and the trifluoromethyl group which has been demonstrated by BERG AND HARTLAGE to enhance the volatility of the β-diketone chelates. The chelates of TTA have been well characterized and have been demonstrated to be volatile[1-3]. The extension of fractional sublimation separation studies to include the chelates of TTA is both logical and warranted.

EXPERIMENTAL

Apparatus and procedures

The schematic diagrams for the sublimation apparatus employed in these studies and the specifications, construction details and operating procedures were reported by BERG AND HARTLAGE[5]. Briefly, the apparatus consists of a pyrex tube (12 mm o.d.; length 120 cm) along which a nearly linear temperature gradient is maintained. The pressure inside the tube is held at approximately 1 mm Hg by means of an air throttle-valve at the hot end of the tube, while a vacuum is applied at the cool end. Samples are introduced in small aluminum boats at the hot end before the pressure is reduced. The sublimed chelate is entrained in a stream of air and passed through the tube until recrystallization occurs. The recrystallized chelate usually is found in discrete zones in the sublimation tube. The temperature range which corresponds to this zone is defined as the recrystallization zone temperature. The chelate can be removed from the tube by cutting the tube into appropriate segments and scraping out the chelate, or by dissolving the complex in a suitable solvent.

The recovery calculations are determined on the basis of the weight lost by the sample on sublimation. Since the chelates are for the most part all stable at the temperatures involved in the sublimator and since no traces of the sublimed chelate could be found anywhere else in the apparatus, the recrystallized zone was assumed to contain all the chelate which was volatilized. In the case of the chelates which decomposed as they sublimed, the yield was determined by recovering and weighing the chelate.

Preparation of the chelates

The metal chelates of TTA were prepared according to the method of BERG AND TRUEMPER[2]. An excess of a hot 5% aqueous solution of the metal nitrate (except for Be) was added to 10 ml of a hot 1% ethanolic solution of TTA and immediately buffered with sodium acetate. If precipitation did not occur on cooling, the solution was evaporated on a steam bath until the first indication of the separation of solid, and then cooled. The precipitates were filtered, washed with water and air-dried. The chelates were purified by recrystallization from the minimum amount of boiling ethanol.

The beryllium chelate was prepared by shaking 50 ml of a 5% aqueous solution of beryllium chloride with 5 g of sodium acetate and 40 ml of a 1% solution of TTA in ether. The diethyl ether layer was separated, washed with water until neutral, dried over sodium sulfate and evaporated to dryness. The crude product was recrystallized from ethanol as above.

The chelates were characterized by their melting points when possible, and all were confirmed by their infrared spectra.

DISCUSSION AND RESULTS

The sublimation recrystallization zone data and the recovery data for the TTA chelates are summarized in Table II. An examination of these data shows that the chelates of TTA formed well-defined crystalline zones, and when no decomposition occurred, the recovery of the chelates was quite good, often quantitative. The chelates of iron(II) and manganese(II) were not volatile and the chelate of cadmium was only slightly volatile. The chelates of uranyl(II), zirconium(IV), lead(II), and chromium(III) decomposed during the sublimation process, even when lower sublimator temperatures were employed. Even though decomposition accompanied the sublimation of these complexes, some recovery of the pure chelate was found. The sublimation recrystallization temperatures for the TTA chelates are graphically presented in Fig. 1.

TABLE II

SUBLIMATION RECRYSTALLIZATION ZONE TEMPERATURES AND RECOVERY DATA OF VARIOUS METAL THENOYLTRIFLUOROACETONATES

(1.0 mm Hg pressure)

Metal ion	*Maximum T(°) in the sublimator*	*Recrystallization zone temperatures*	*mg chelate taken*	*Recovery (%)*
Cd(II)	210	180–170	5.5	3.1
Ni(II)	201	175–140	13.9	99.5
Mg(II)	201	175–145	15.8	100
UO_2(II)	185	168–160	4.8	35.5 (dec.)
Al(III)	184	160–145	25.4	91.7
Zr(IV)	185	155–127	3.7	15.3 (dec.)
Pd(II)	200	152–138	2.5	88.0
Pb(II)	210	152–125	16.7	71.5 (dec.)
Co(II)	192	147–110	8.2	100
Cu(II)	175	145–123	18.5	100
Fe(III)	158	140–112	19.2	100
Fe(II)	160	Not volatile	10.1	0.0
Mn(II)	175	Not volatile	7.4	0.0
Tl(III)	184	138–118	11.6	87.1
Cr(III)	170	135–123	13.1	10.7 (dec.)
Zn(II)	210	134–90	4.8	100
Be(II)	165	127–102	29.9	100

dec. = decomposition along with sublimation.

The recrystallization zone temperatures of the chelates of TTA are compared to those of the acetylacetonates and the benzoyltrifluoroacetonates in Table III. The differences between the highest temperatures of the recrystallization zones indicate in a qualitative way the ease with which a given separation may be effected. For most metal chelates, the differences between these temperatures are found to be most advantageous in the case of the acetylacetonates. However, some separations are possible with the chelates of TTA which are not possible with the chelates of acetyl-

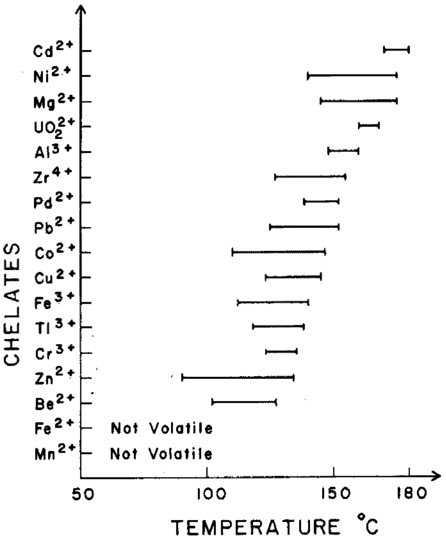


Fig. 1. Sublimation recrystallization temperatures for various metal 2-thenoyltrifluoroacetonates.

TABLE III

COMPARISON OF THE RECRYSTALLIZATION ZONE TEMPERATURES OF VARIOUS METAL CHELATES OF TTA, AA AND BTA

Metal ion	*TTA*	*AA*	*BTA*
Cd(II)	180–170	137–117	Liquid
Ni(II)	175–140	111–88	Liquid
Mg(II)	175–145	141–120	Liquid
UO_2(II)	168–160	146–114	—
Al(III)	160–145	81–60	128–120
Zr(IV)	155–127	102–77	Liquid
Pd(II)	152–138	94–74	133–103
Pb(II)	152–125	—	—
Co(II)	147–110	88–67	Liquid
Cu(II)	145–123	102–82	126–101
Fe(III)	140–112	85–66	Liquid
Fe(II)	Not volatile	—	—
Mn(II)	Not volatile	90–70	Liquid
Tl(III)	138–118	—	—
Cr(III)	135–123	106–80	—
Zn(II)	134–90	38–31	119–103
Be(II)	127–102	31–15	97–71

acetone. For example, iron(III) can be quantitatively separated from Al(III), Mg(II), Ni(II), Mn(II), and Fe(II) by fractional sublimation of their TTA chelates, but not their acetylacetonates. On the other hand, Mg(II), Al(III), Zn(II) and Be(II) can be separated as the acetylacetonates but not as the chelates of TTA.

The effect of the thienyl ring on chelate volatility can be shown by comparing the sublimation results of the TTA chelates with the benzoyltrifluoroacetonates. Many of the chelates of BTA condensed as liquids and were not suitable for sublimation studies, whereas the volatile chelates of TTA crystallized in well-defined zones. Also, the chelates of TTA were less volatile than the corresponding ones of BTA. The combination of the thienyl group and the trifluoromethyl group in TTA apparently strikes a balance in which the trifluoromethyl group increases the volatility of the diketone while the thienyl group contributes to the formation of crystalline sublimates.

One may conclude from the recrystallization zone data that many chelates of TTA are sufficiently volatile and stable to be fractionally sublimed in vacuum and recovered with high yields. The differences in the recrystallization zone temperatures observed among the chelates studied indicate that a number of mixtures can be resolved by the fractional sublimation of the TTA chelates. Still, the best overall separability of metal chelates by fractional sublimation has been found with the acetylacetonates. The results with the TTA chelates compare quite favorably with, and in some respects are superior to, the results reported for the chelates of trifluoroacetylacetone, hexafluoroacetylacetone and benzoylacetone.

This work was supported in part by a National Science Foundation Science Faculty Fellowship awarded K.P.R.

SUMMARY

Studies on the fractional sublimation of various metal β-diketone chelates have been extended to include the chelates of thenoyltrifluoroacetone (TTA). Many of the common metal chelates were found to be stable, to sublime readily, and to form well-defined zones in the vacuum fractional sublimator. Of the 17 chelates reported only those of manganese(II) and iron(II) were not volatile. The chelates of UO_2(II), Zr(IV), Pb(II), and Cr(III) partially decomposed during sublimation and their recovery was incomplete. The recovery of the sublimed chelates of Ni(II), Mg(II), Al(III), Pd(II), Co(II), Cu(II), Fe(III), Tl(III), Zn(II) and Be(II) ranged from 87 to 100%, with most recoveries being quantitative. The sublimation recrystallization zone temperatures of the various chelates are compared to those of the metal acetylacetonates and the benzoyltrifluoroacetonates; in general, the metal chelates of TTA sublime more readily than those of benzoyltrifluoroacetone but are potentially less useful for fractional sublimation separations than the corresponding metal acetylacetonates. Even so, a quantitative separation of iron(III) from Ni(II), Al(III), Mn(II), and Fe(II) is proposed that depends upon the fractional sublimation of the TTA chelates.

RÉSUMÉ

Une étude est faite sur la sublimation fractionnée de divers chélates métalliques de β-dicétone comprenant également les chélates de thénoyltrifluoroacétone (TTA). La plupart des chélates de métaux courants sont stables et donnent des zones bien définies dans le sublimateur à vide fractionné. Des 17 chélates examinés, seuls ceux de manganèse(II) et de fer(II) ne sont pas volatils. Les chélates de UO_2(II), Zr(IV), Pb(II) et Cr(III) sont partiellement décomposés au cours de la sublimation; leur rendement est incomplet. Les zones de températures de la recristallisation par sublimation de divers chélates sont comparées à celles des acétylacétonates métalliques et des benzoyltrifluoroacétonates. En général, les chélates métalliques de TTA subliment plus rapidement que ceux de la benzoyltrifluoroacétone, mais ils sont moins utilisés pour des séparations fractionnées que les chélates correspondants des acétylacétonates. Une séparation quantitative du fer(III) d'avec Ni(II), Al(III), Mn(II) et Fe(II) est proposée, basée sur la sublimation fractionnée des chélates TTA.

ZUSAMMENFASSUNG

Untersuchungen der fraktionierten Sublimation verschiedener Metall-β-Diketon-Chelate wurde auf die Chelate von Thenoyltrifluoroaceton (TTA) ausgedehnt. Viele der gebräulichen Metallchelate sind stabil, sublimieren schnell und bilden wohldefinierte Zonen im Vakuumsublimator. Von den 17 Chelaten, über die berichtet wird, sind nur die von Mangan(II) und Eisen(II) nicht flüchtig. Die Chelate von UO_2(II), Zr(IV), Pb(II) und Cr(III) zersetzen sich während der Sublimation teilweise und sind nur unvollständig wiederzugewinnen. Die Ausbeuten der sublimierten Chelate von Ni(II), Mg(II), Al(III), Pd(II), Co(II), Cu(II), Fe(III), Tl(III), Zn(II) und Be(II) liegen zwischen 87 und 100% und sind meist quantitativ. Im allgemeinen sublimieren die Chelate von TTA schneller als die von Benzoyltrifluoroaceton, sie sind jedoch möglicherweise für eine Trennung durch fraktionierte Sublimation weniger geeignet als die entsprechenden Metall-Acetylacetonate. Eine quantitative Trennung des Eisen(III) von Ni(II), Al(III), Mn(II) und Fe(II), die auf der fraktionierten Sublimation der TTA-Chelate beruht, wird vorgeschlagen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SEPARATION OF FISSION PRODUCTS BY ELECTROPHORETIC FOCUSSING OF IONS. PART II

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In a previous paper [1], the authors described a fast separation of the fission products by means of electrophoretic focussing of ions (E.F.I.). The principles of this separation method have been fully explained by SCHUMACHER AND STREIF[2,3]. Cerium, strontium, cesium and yttrium were separated quantitatively but ruthenium, zirconium and niobium were left as one focus.

In the present paper special attention is paid to the separation of these elements by E.F.I. This method has also been applied to the separation of fission products by other authors[4-6].

Choice of experimental conditions

For the separation of a mixture of the long-lived fission products, a 0.08 *M* solution of the diammonium salt of nitrilotriacetic acid (NTA) containing 0.06 *M* sodium acetate and adjusted to pH 7, was chosen as the cathodic solution; 0.5 *M* hydrochloric acid was chosen as the anodic electrolyte. Before the mixture of the fission products was applied, the metal ions were complexed with a solution of 0.08 *M* NTA, adjusted to pH 7 by means of ammonium hydroxide. An aliquot of 25 µl was focussed for 6–10 min at 500 V. Zirconium, niobium and ruthenium could not be separated although the molarity of the anodic electrolyte was widely varied[1].

TABLE I

CROSS-CONTAMINATIONS OF THE SEPARATION OF Zr + Nb FROM Ru

Focus	*Nuclide*	*% found*	
		after 7.5 min	*after 15 min*
Zr + Nb	^{95}Zr(^{95}Nb)	35.4	100.0
	^{106}Ru	0.6	0.4
Ru	^{95}Zr(^{95}Nb)	64.6	0.0
	^{106}Ru	99.4	99.6

With hydrofluoric acid as anodic electrolyte, an improvement was expected, as niobium and zirconium form soluble complexes in this medium. When 0.5 *M* hydrofluoric acid was used as the anodic electrolyte and the mixture of Zr, Nb and Ru was applied after complexation with a solution of 0.005 *M* NTA, zirconium and

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* Aspirant N.F.W.O.

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niobium could be separated from ruthenium (Table I), but ruthenium gave rise to a double focus. In these conditions, Zr, Nb and Ru could be quantitatively separated from one another, when the 0.005 *M* complexing solution of NTA was adjusted to pH 2.25, *i.e.* practically a saturated solution of NTA.

Obviously, the mixture of zirconium, niobium and ruthenium must be completely evaporated to dryness, to remove traces of free acid before addition of the adjusted complexing solution.

TABLE II

INFLUENCE OF THE pH OF THE COMPLEXING SOLUTION ON THE SEPARATION OF ^{95}Zr FROM ^{95}Nb

pH of the complexing solution	*ratio* $\frac{\text{activity in Nb focus}}{\text{activity in Zr focus}}$
1.5	1.81
2.0	2.36
2.5	2.07
3.0	1.55

At higher or lower pH values of the complexing solution, the separation of zirconium from niobium became worse as shown in Table II, whereas the quality of the separation of ruthenium from Zr + Nb was independent of the pH of the 0.005 *M* NTA complexing solution.

It also appeared that the tailing of ruthenium led to a higher cross-contamination with the other fission products, especially with yttrium. The extent of tailing was inversely proportional to the time ruthenium was boiled under reflux with the complexing solution. No substantial improvement was obtained for boiling times longer than 1 h, which allowed recovery of *ca.* 85% of the ruthenium between the foci of niobium and yttrium.

TABLE III

INFLUENCE OF THE AMOUNT OF URANIUM ON THE SEPARATION ^{95}Zr/^{95}Nb/^{106}Ru

Amount of U per focussing experiment (μg)	*Ratio* $\frac{\text{activity in Nb focus}}{\text{activity in Zr focus}}$	*%^{95}Zr(^{95}Nb) found in Ru fraction*	*%^{106}Ru found in Zr and Nb fractions*
10	2.05	0.8	1.1
60	1.99	1.1	4.1
200	No separation	24.6	31.9

Separate experiments showed that the amount of uranium present should not exceed 60 μg per 25 μl. Table III shows the influence of increasing amounts of uranium on the separation of zirconium, niobium and ruthenium.

As described in the previous article[1], carrier-free fission products do not focus very sharply and stay partly in the applied zone together with the broad uranium focus. Carriers were therefore added to the mixture of the fission products so that adsorption on the glass walls and the formation of radiocolloids was avoided. Up to

10 mg of zirconium or niobium can readily be dissolved in 25 ml of 0.005 *M* NTA (pH 2.25) in the presence of 60 mg of uranium.

Under the conditions mentioned, a practically quantitative separation of zirconium, niobium and ruthenium can be obtained if 500 V is applied during 10–15 min. Yttrium and cesium are, however, not sharply focussed so that rather high cross-contaminations are observed. This is obviously due to the presence of hydrofluoric acid, which forms insoluble fluorides with these metals.

The separation of strontium and cesium is of the same quality as reported in the previous paper[1]. The separation of a synthetic mixture of long-lived fission

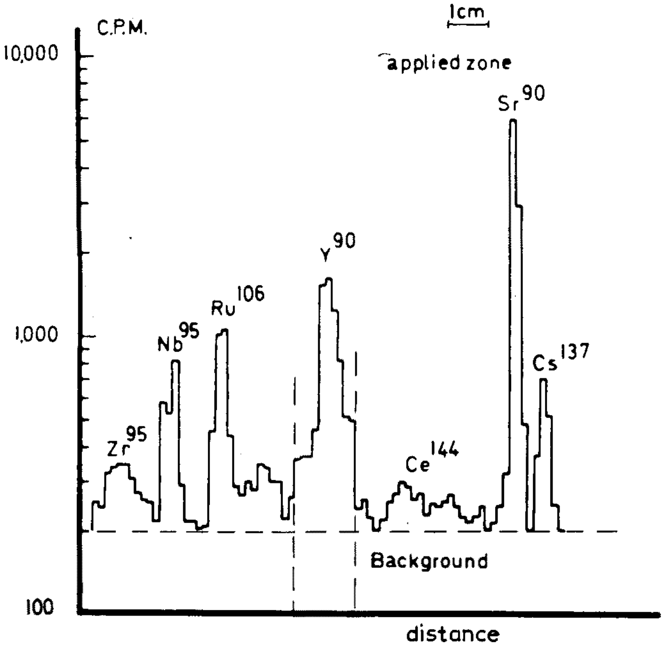

Fig. 1. The separation of a synthetic mixture of long-lived fission products by means of E.F.I.

TABLE IV

CROSS-CONTAMINATIONS OF THE FOCI

Focus	*Nuclide*	*% found*	*Standard deviation*[a]	*Focus*	*Nuclide*	*% found*	*Standard deviation*[a]
Cs	^{137}Cs	99.1	0.9	Ru	^{106}Ru	72.8	9.0
	^{90}Sr	0.4	1.0		^{90}Y	4.2	3.5
Sr	^{90}Sr	99.6	1.0		^{144}Ce	2.6	1.5
	^{137}Cs	0.9	0.9		^{95}Zr + ^{95}Nb	0.8	0.5
Ce	^{144}Ce	93.7	2.1	Nb	^{95}Nb	97.3	1.4
	^{90}Y	7.5	6.6		^{95}Zr	−0.6	5.5
	^{106}Ru	5.2	6.6		^{106}Ru	5.6	1.2
Y	^{90}Y	84.0	8.0	Zr	^{95}Zr	100.6	5.5
	^{144}Ce	2.5	0.6		^{95}Nb	2.7	1.4
	^{106}Ru	16.3	9.7		^{106}Ru	0.0	

[a] Standard deviation for a single separation as determined from 6 experiments.

products in the presence of 60 μg of U per 25 μl, is shown in Fig. 1. The cross-contaminations of the individual fractions were determined by γ-ray spectrometry for the γ-emitters and by following the decay and the growth of ^{90}Y in freshly separated ^{90}Sr. The values are given in Table IV. They show the relative distribution of each fission product over the different foci.

Figure 1 shows the γ-spectra of freshly separated ^{95}Zr and ^{95}Nb fractions as well as a mixture of both isotopes in equilibrium.

Measurements

To identify the foci, the paper strip was cut into 1-mm strips and counted in a well-type NaI (Tl) detector. The cross-contaminations were determined by γ-ray spectrometry for γ-emitting isotopes. The strips were also counted with a G.M.-tube to calculate the cross-contamination of the pure β-emitters.

Purity checks of the zirconium and niobium foci were done by comparing the ratio of the activities of the niobium and zirconium fractions after the separation, with the theoretically expected $^{95}Nb/^{95}Zr$ ratio in the original mixture at equilibrium, namely 2.16. It must be borne in mind that equality does not necessarily prove the quantitative separation of niobium from zirconium as compensation of errors is possible.

Further investigations with a high resolution Ge(Li) detector connected to a 4000-channel analyser, made it possible to calculate the cross-contaminations of the zirconium and niobium fractions with more certainty.

EXPERIMENTAL

In a 100-ml beaker, add to *ca.* 1 μc of a nitric acid solution of a fuel element, containing not more than 60 mg of uranium, 1 mg of each of the following carriers: Cs, Sr, Ce, Y, Ru (as the chlorides in 1 *M* hydrochloric acid), and Zr and Nb (as NTA-complexes). Add 10 ml of 12 *M* hydrochloric acid and take to dryness on a hot plate. Dissolve the residue in 12 *M* hydrochloric acid and take to dryness again. Add to the residue 25 ml of a 0.005 *M* NTA solution. Adjust the pH at 2.25 by means of hydrochloric acid. Cover the beaker and boil for 1 h. After reducing the volume to *ca.* 20 ml, dilute to 25 ml in a measuring flask. Spot 25 μl at the center of a 34 × 2 cm paper-strip (Whatman paper no. 1). Place the ends of the strip in the cathode and anode compartments containing 0.08 *M* $(NH_4)_2HNTA$ + 0.06 *M* sodium acetate, and 0.5 *M* hydrofluoric acid respectively. Immerse the central part in the carbon tetrachloride cell. Allow the anode and cathode solution to diffuse to the applied zone. Apply the 500-V potential to the platinum electrodes during 10–15 min. Stir the carbon tetrachloride slowly by means of a magnetic stirrer to provide more efficient cooling. Remove the paper strip and dry under a warm air blower. Cut the paper strip into pieces of 1–3 mm width. Place the pieces into counting vials for the γ-emitters or mount on planchets for G.M.-counting in the case of pure β-emitters.

DISCUSSION

As can be seen in Fig. 1, clearly defined foci are obtained for zirconium, niobium, strontium and cesium, resulting in a quantitative separation of these elements. Yttrium and cerium are however not sharply focussed and ruthenium forms a double focus. It appears from Table IV that the present separation method combined with the one described previously[1], allows a rapid determination of each of the long-lived fission products.

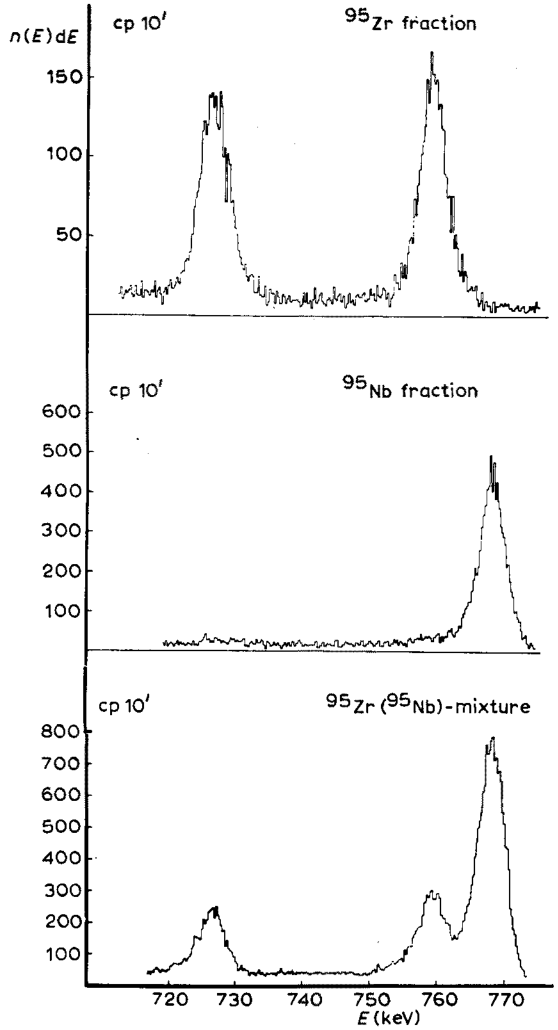

Fig. 2. The γ-spectra of freshly separated ^{95}Zr and ^{95}Nb fractions and of a mixture of both isotopes in equilibrium.

This work is part of the research sponsored by the "Nationaal Fonds voor Wetenschappelijk Onderzoek" and the I.I.K.W.

SUMMARY

Electrophoretic focussing of ions was applied to the separation of the long-lived fission products Zr, Nb, Ru, Y, Ce, Sr and Cs. With hydrofluoric acid and nitrilotriacetic acid as the anodic and cathodic electrolytes respectively, a quantitative separation of Zr, Nb, Sr and Cs was obtained whereas Ru, Y and Ce did not focus sharply. The nuclides were detected by γ- and β-counting.

RÉSUMÉ

On propose une séparation de produits de fission à longue période Zr, Nb, Ru, Y, Ce, Sr et Cs par "focussing" electrophorétique. On peut ainsi obtenir une séparation quantitative de Zr, Nb, Sr et Cs à l'aide d'acide fluorhydrique et d'acide nitrilotriacétique comme électrolytes, anodique et cathodique respectivement. Les nuclides sont détectés par comptage γ et β.

ZUSAMMENFASSUNG

Die elektrophoretische Fokussierung von Ionen wurde zur Trennung der langlebigen Spaltprodukte Zr, Nb, Ru, Y, Ce, Sr und Cs angewendet. Mit Fluorwasserstoffsäure und Nitriloessigsäure als anodischen bzw. kathodischen Elektrolyten wurden Zr, Nb, Sr und Cs quantitativ getrennt, während Ru, Y und Ce nicht scharf fokussiert wurden. Die Nuklide wurden durch Messung ihrer γ- bzw. β-Strahlung nachgewiesen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SOLVENT EXTRACTION OF ALKALI METAL IONS WITH CHROMIUM COMPLEXES

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(Received November 21st, 1967)

The close similarity in the chemical behavior of heavy alkali metal ions has led to numerous attempts to separate one from the other. Precipitation as tetraphenylborate[1] offers an excellent separation of alkali metal ions heavier than potassium from sodium and alkali earth metal ions. Ion-exchange methods have proved efficient for the mutual separations, especially for traces of cesium in radiochemical work [2-5].

Extraction processes have some advantages over precipitation or ion exchange; both trace and major amounts of materials can be handled and the short separation periods required are especially important in the treatment of short-lived radioisotopes. However, the method is very restricted for alkali metals because of their highly ionic character, which makes extraction into organic solvents difficult. The chelating reagents, thenoyltrifluoroacetone (TTA)[6] and a heteropolyacid, molybdophosphate[7] have been examined for the extraction. Ion-association systems with dipicrylamine[8,9], tetraphenylborate[10], hexafluorophosphate[11], polyiodide[12], and phenols[13] have been investigated for analytical purposes. FRIEDMAN AND HAUGEN [14] investigated the partition of alkali salts of Reineckate and perrhenate between the aqueous and organic phases to calculate thermodynamic constants, *i.e.* free energy of transfer of electrolytes and the ion-pair formation constants. These experiments suggested the potential use of the related compounds for the analytical purpose.

In a previous report[15], tetrathiocyanatodianilinechromate ($Cr(C_6H_5NH_2)_2(NCS)_4^-$, TAnCr$^-$) and tetrathiocyanatodiamminechromate ($Cr(NH_3)_2(NCS)_4^-$, TAmCr$^-$) which have been commonly used as precipitants for basic amino acids were shown to be useful for the solvent extraction of cesium ion in tracer to macro quantities. These compounds possess absorption bands in the visual spectral region, hence cesium could be determined spectrophotometrically after its extraction with the reagents into nitrobenzene.

The present paper describes an investigation of the behavior of alkali metal ions with these complexes, when batch and counter-current methods are used with different organic solvents.

EXPERIMENTAL

Apparatus

The γ-ray activity was measured with a single-channel pulse-height analyzer TPA-3 (Aloka), and γ-ray spectra were measured with a 400-channel pulse-height analyzer (RCL).

Reagents

$NH_4Cr(NH_3)_2(NCS)_4$ and $NH_4Cr(C_6H_5NH_2)_2(NCS)_4$ were prepared[16] and stored as the crystalline ammonium salts. The absorption spectra of their aqueous solutions showed clear absorption maxima which agreed fairly well with those reported previously[17].

For the experiments, an aqueous solution of NH_4TAmCr or NH_4TAnCr was shaken with ether with a slight excess of hydrochloric acid, and the resulting acid form of the complex was extracted into ether. After the phases had been separated, the ether solution was shaken with an aqueous solution of calcium carbonate in order to back-extract $TAnCr^-$ or $TAmCr^-$; this aqueous solution was used as the extracting reagent. The final concentration of calcium ion in the aqueous solution was 10^{-2} *M*. Under these conditions, the pH of the aqueous solution was 4–5.

All substances used were of reagent-grade purity. Alkali metal ion solutions were prepared by dissolving the chloride in water, and were stored in polyethylene bottles.

^{137}Cs, ^{86}Rb, ^{42}K and ^{24}Na were used as tracers. Carrier-free ^{137}Cs was supplied by Oak Ridge National Laboratory. ^{86}Rb, ^{42}K and ^{24}Na were prepared by neutron irradiation of rubidium chloride, potassium hydroxide and sodium hydroxide at Kyoto University Reactor; the potassium hydroxide and sodium hydroxide were first neutralized with hydrochloric acid. The radiochemical purity of these isotopes was checked by their γ-ray spectra.

Procedures

Solutions of alkali and of the calcium salt of $TAnCr^-$ or $TAmCr^-$ were placed in a 30-ml separatory funnel; the final volume of the aqueous phase was 10 ml throughout the experiments. An equal volume of the organic solvent (10 ml) was used for extraction. Variations in the shaking time from 30 sec to 10 min had little effect on the extraction percentages. A shaking time of 1 min was chosen, because prolonged shaking caused some difficulties in phase separation.

Experiments involving counter-current distribution were carried out using 10 separatory funnels. Aliquots (10 ml) of aqueous $4 \cdot 10^{-3}$ *M* $TAmCr^-$ or $TAnCr^-$ solution were added to each of the funnels, and extraction was performed with 10-ml portions of nitrobenzene as the moving phase. In both cases, partition of alkali metal ions was measured by counting γ-ray activity in both aqueous and organic phases.

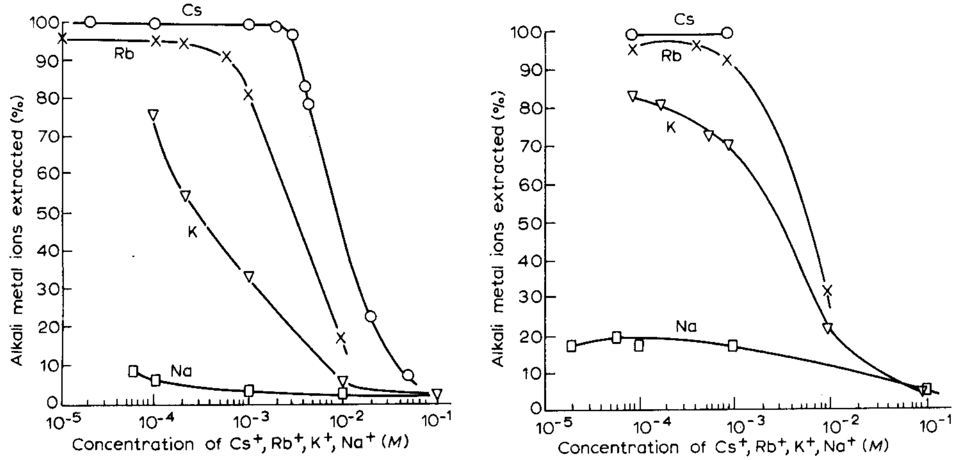
RESULTS AND DISCUSSION

The influence of pH on the extraction of cesium

The influence of pH on the extraction of cesium ion was examined by means of carrier-free ^{137}Cs (*ca.* 10^{-11} *M*) and a γ-ray spectrometer. The pH of the aqueous solution was adjusted with hydrochloric acid and/or lithium hydroxide solution. A slight change in the pH of the aqueous phase was observed before and after the extraction with nitrobenzene. The ^{137}Cs in the aqueous and organic phases was measured 30 min after the extraction, when ^{137m}Ba had decayed and equilibrium between ^{137}Cs and ^{137m}Ba had been established. The percentage extraction was found to be 100 ±2% over the pH range 2–9. The organic phase became turbid at pH values above 10. A pH range of 2–8 is recommended for practical work.

The influence of the concentration of alkali metal ion

The percentage extraction of alkali metal ions into nitrobenzene or nitromethane in the presence of $4 \cdot 10^{-3}$ *M* reagents is shown in Figs. 1 and 2. The extraction percentages of cesium and rubidium ions reached nearly constant values when the concentration was less than 10^{-3} *M*. Extraction percentages decreased for concentrations above 10^{-2} *M* alkali metal ion, because there was insufficient reagent to form the extractable species. However, the extraction percentages of potassium ion did not attain a constant value even when the concentration of potassium ion was less than 10^{-3} *M*.



Figs. 1–2. Extraction of alkali metal ions. Reagent: (1) $TAnCr^-$, (2) $TAmCr^-$, $4 \cdot 10^{-3}$ *M*; solvent: nitrobenzene.

TABLE I

EXTRACTION OF ALKALI METAL IONS

(Concentration of alkali metal ion, 10^{-4} *M*; concentration of reagent, $4 \cdot 10^{-3}$ *M*)

Reagent	*Solvent*	*Extraction percentages of*			
		Na^+	*K^+*	*Rb^+*	*Cs^+*
$TAnCr^-$	Nitromethane	——	——	95.2	98.9
$TAmCr^-$	Nitromethane	26.6	82.3	94.6	98.2
$TAnCr^-$	Nitrobenzene	5.6	75.1	94.3	99.1
$TAmCr^-$	Nitrobenzene	1.5	17.2	70.5	91.6

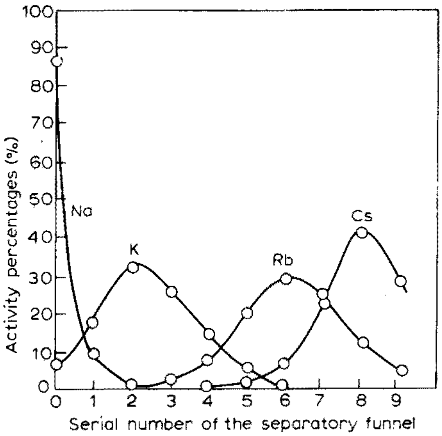
The percentage extraction of the 4 alkali metal ions in the presence of $TAnCr^-$ or $TAmCr^-$ into nitrobenzene or nitromethane is shown in Table I. It is clear that the percentage extraction improves as the apparent radius of the alkali metal ion increases. The Table also shows that the species formed by $TAnCr^-$ with alkali metal ions are more readily extracted than those formed by $TAmCr^-$. Moreover, these ion pairs can be extracted more efficiently into nitromethane than into nitrobenzene. When $TAnCr^-$ is used as the reagent and nitromethane as the organic solvent, $TAnCr^-$ moves completely into the organic solvent, presumably as a calcium salt, even if the alkali ions are not present. However, the fact that the extraction of alkali metal ions proceeds efficiently with this system indicates that the exchange of ions in the organic solvent takes place preferentially for all alkali metal ions.

There is a large difference in the percentage extraction between Na$^+$ and K$^+$ when TAnCr$^-$ and nitrobenzene or TAmCr$^-$ and nitromethane are used. When TAmCr$^-$ and nitrobenzene are used, the difference in the percentage extraction is larger between Rb$^+$ and K$^+$ than between Na$^+$ and K$^+$. Accordingly, the separation of Na$^+$ and K$^+$ is more efficient when TAmCr$^-$ and nitromethane or TAnCr$^-$ and nitrobenzene are used, whereas the separation of potassium and rubidium is more efficient when TAmCr$^-$ and nitrobenzene are used.

Counter-current distributions of Na, K, Rb and Cs

Counter-current distribution tests were made with 10 separatory funnels for each alkali metal ion. The concentration of each alkali metal ion in the starting separatory funnel was 10^{-4} *M*, and 10 ml of $4 \cdot 10^{-3}$ *M* TAmCr$^-$ aqueous solution was added to each funnel. Nitrobenzene was used as the organic solvent.

The results are shown in Fig. 3. The distribution curves are in reasonable agreement with the theoretical curves based on the partition coefficients (Na: 2%, K: 20%, Rb: 60%, Cs: 85%) derived from Table I. The Figure indicates that sodium and cesium or rubidium ions can be separated by means of 10 separations, and that potassium and cesium ions can be separated by using a few additional extractions.



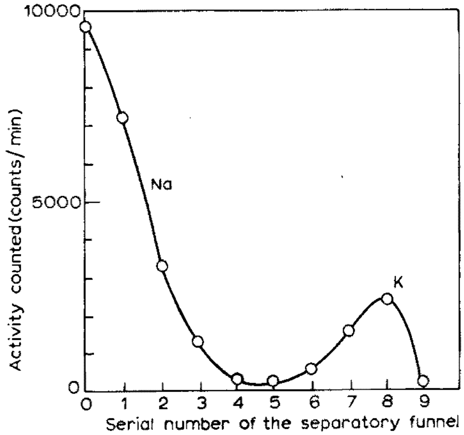


Fig. 3. Distribution of Na$^+$, K$^+$, Rb$^+$, Cs$^+$. Reagent: TAmCr$^-$; solvent: nitrobenzene.

Fig. 4. Separation of sodium and potassium by couter-current distribution method. Reagent: TAnCr$^-$; solvent: nitrobenzene.

The counter-current method was applied with $4 \cdot 10^{-3}$ *M* TAnCr$^-$ solution in each funnel and nitrobenzene as the moving phase in order to separate sodium and potassium ions at concentrations of 10^{-4} *M* labelled with radioisotopes. Figure 4 shows the distribution of these activities; the ^{24}Na activity appears before the fourth funnel and the activities after the fifth funnel are ^{42}K. Complete separation of sodium and potassium ions at about 10^{-4} *M* concentration is therefore possible.

Back-extraction of cesium

The back-extraction of cesium ion from the organic phase was investigated in order to obtain aqueous solutions of purified cesium free from the reagents.

Carrier-free ^{137}Cs was extracted into nitrobenzene with TAnCr$^-$ by a single pass. The organic phase containing ^{137}Cs was then shaken with an aqueous phase of different acidity, adjusted with hydrochloric acid. Figure 5 shows the results for the percentage extraction *versus* acid concentration in the ordinary scale and for the partition coefficient *versus* acid concentration in the logarithmic scale. The linear relationship with unit slope between D_{Cs} and hydrochloric acid concentration indicates that an exchange reaction of proton and cesium ion takes place:

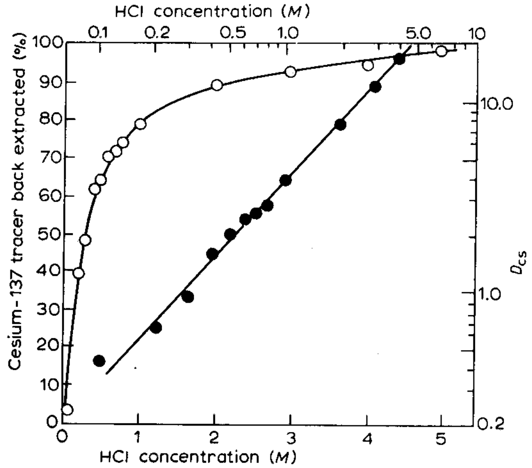


Fig. 5. Back-extraction of cesium-137 tracer. (○) cesium-137 back-extracted, %. (●) D_{Cs} = cesium-137 in aqueous phase/cesium-137 in organic phase. Reagent: TAnCr$^-$, $8 \cdot 10^{-3}$ *M*; solvent: nitrobenzene.

$$H^+ + CsTAnCr \overset{K}{\rightleftarrows} HTAnCr + Cs^+ \qquad (1)$$

where $K = [H^+]\,[CsTAnCr]/[HTAnCr]\,[Cs^+]$

If it is assumed that hydrogen and cesium ions move into the aqueous phase and that CsTAnCr and HTAnCr remain in the organic phase, then the distribution ratio D_{Cs} can be defined as:

$$D_{Cs} = \frac{[Cs^+]}{[CsTAnCr]} = \frac{1}{K}\,\frac{[H^+]}{[HTAnCr]}$$

Thus $\log D_{Cs} = \log [H^+] - \log K - \log [HTAnCr] = \log [H^+] - \text{const.}$ where $\log K$ and log HTAnCr are constant under the experimental conditions used. If one plots $\log D_{Cs}$ *versus* $\log H^+$, a linear relationship with unit slope will thus be obtained. The experimental values agree very well with the theoretical ones, hence it can be concluded that the back-extraction of cesium(I) proceeds as expressed in eqn. (I).

The authors gratefully acknowledge the valuable help and suggestions of Professor S. IWATA and the members in Hot-Laboratory of Research Reactor Institute Kyoto University in the preparation of isotopes.

SUMMARY

Solvent extraction of alkali metal ions by batch and counter-current distribution methods was investigated with tetrathiocyanatodiamminechromate(III) and tetrathiocyanatodianilinechromate(III) as reagents and nitromethane and nitrobenzene as organic solvents. The distribution ratios of alkali metal ions in the various systems were measured. Cesium was readily extracted with the aniline compound and nitrobenzene. The separation of sodium from potassium in trace amounts was possible by the counter-current distribution method.

RÉSUMÉ

On examine les méthodes d'extraction dans un solvant (à contre-courant et autres) des ions de métaux alcalins à l'aide de tétrathiocyanatodiammino-chromate-(III) et de tétrathiocyanatodianiline-chromate(III) comme réactifs, de nitrométhane et de nitrobenzène comme solvants organiques. On a mesuré les coefficients de partage des métaux alcalins dans les divers systèmes. Le césium est rapidement extrait avec le dérivé aniline et le nitrobenzène. La séparation du sodium d'avec le potassium à l'état de traces est possible par la méthode à contre-courant.

ZUSAMMENFASSUNG

Die Extraktion von Alkalimetallen mit den Reagenzien Tetrathiocyanatodiamin-chromat(III) und Tetrathiocyanatodianilin-chromat(III) und Nitromethan und Nitrobenzol als Lösungsmittel wurde untersucht. Die Verteilungskoeffizienten der Alkalimetall-Ionen in verschiedenen Systemen wurden gemessen. Cäsium wurde mit der Anilinverbindung und Nitrobenzol extrahiert. Die Trennung von Spuren des Natrium vom Kalium ist möglich.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF THALLIUM(III) WITH THE 2,2'-BIPYRIDYL–IRON(II) CHELATE

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(Received November 21st, 1967)

Various dyestuffs which are sensitive to thallium, such as rhodamine B[1-3], methyl violet[4], ethyl violet[5] and brilliant green[6], have been suggested for the determination of thallium(III). These methods are based on the formation of a coloured ion-association complex between a halide complex anion of thallium(III) and a large cationic dyestuff.

Chelate cations such as the 2,2'-bipyridyl–iron(II) chelate[7] and the 1,10-phenanthroline–iron(II) chelate cation[8,9], have been proposed for the spectrophotometric determination of perchlorate, in place of cationic dyestuffs such as methylene blue[10] and crystal violet[11]. Moreover, it has been shown[12] that 2,2'-bipyridyl–iron(II) chelate cations can be extracted with halide complex anions of mercury(II) into 1,2-dichloroethane. The absorbance of the organic layer showed a linear relationship to the quantity of mercury(II) initially present in the aqueous solution.

In the present paper, a similar method is suggested for the determination of thallium(III) by extracting it into 1,2-dichloroethane with the 2,2'-bipyridyl–iron(II) chelate as a counter ion, from aqueous solution in the presence of a large excess of bromide. The proposed method is convenient and accurate for the determination of thallium in the range $7.9 \cdot 10^{-6}$–$3.5 \cdot 10^{-5}$ *M*. The species predominating in the extraction was also ascertained.

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were made with a Hitachi Model EPU-2A spectrophotometer with 10-mm glass cells. The shaking was done with an Iwaki Model KM shaker with a time switch. The pH measurements were made with a Hitachi-Horiba M 3 pH meter.

Reagents

Thallium solution. A standard solution containing 1 mg of thallium per ml was prepared by dissolving thallium(I) nitrate in distilled water[2]. This standard solution was then diluted to the concentration required for the experiments.

2,2'-Bipyridyl–iron(II) chelate solution. Iron(II) ammonium sulfate and 2,2'-bipyridyl solutions were prepared as described previously[7]. The two solutions were mixed well, the mole ratio of bipyridyl to iron(II) being kept at 4:1, and the pH of the mixture was adjusted to 3–5. The solution was diluted with distilled water to make a $3 \cdot 10^{-3}$ *M* chelate solution.

The molar concentration of the chelate solution was assumed to be equal to that of the iron(II) added because of the high stability of the chelate[13].

Solvent. 1,2-Dichloroethane was purified by distillation.

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

All other reagents (analytical grade) were used without further purification.

Standard procedure

Add the required amount of saturated bromine water and dilute sulfuric acid to an aliquot of the working thallium solution containing up to 180 μg of thallium. Heat the solution to *ca.* 90° until the colour due to bromine disappears, and then cool to room temperature[14]. To the solution, add 5 ml of aqueous $6 \cdot 10^{-2}$ *M* potassium bromide solution, 1 ml of 3 *M* sodium acetate solution and 1 ml of the bipyridyl–iron(II) chelate solution. Adjust the pH of the solution to 4.5–5 with a dilute sulfuric acid solution or a dilute sodium hydroxide solution, and dilute it to 25 ml with distilled water. To this, add 5.0 ml of dichloroethane and shake for 4 min.

After 15 min, transfer the organic layer to a flask containing 1 g of anhydrous sodium sulfate and shake it vigorously in order to make the solution transparent. Measure the absorbance of the extracted solution at 524 nm with a reagent blank as reference.

RESULTS AND DISCUSSION

Absorption spectrum

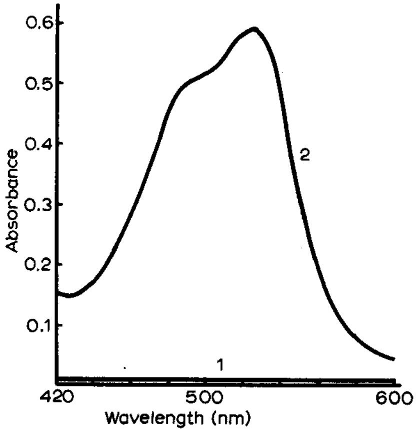
Figure 1 shows the absorption spectra; curve 1 is a spectrum of the extract when thallium(III) is absent, while curve 2 is that of the extract with thallium(III). It is well known that thallium(III) in halide media forms anionic complexes of the type TlX_4^-, where X indicates a halogen atom. The bipyridyl–iron(II) chelate cation is quite extractable into dichloroethane when a small amount of thallium(III) as bromide complex anion is present in the aqueous phase, hence thallium(III) can be determined. The maximum absorbance of the extracted species in dichloroethane occurs at a wavelength of 524 nm, although the maximum of the tris(2,2′-bipyridyl)–iron(II) species is at 522 nm in the aqueous phase. The slight red shift of the spectrum in the organic phase may be attributed to an association between the cations and anions.

Effect of 2,2′-bipyridyl–iron(II) chelate concentration

The extraction was carried out for a series of solutions (pH 5), in which the final concentrations of thallium, potassium bromide and sodium acetate were kept at $1.98 \cdot 10^{-5} M$, $1.2 \cdot 10^{-2} M$ and $0.12 M$ respectively but that of the bipyridyl–iron(II) chelate was varied from $6.0 \cdot 10^{-6}$ to $3.6 \cdot 10^{-4} M$, and the absorbance of the extracts was measured. The absorbance of the extracts at 524 nm remained essentially constant provided that the concentration of the chelate is more than $6.0 \cdot 10^{-5}$ *M*. The concentration of the chelate was therefore usually kept at $1.2 \cdot 10^{-4}$ *M* in this work.

Effect of mole ratio of 2,2'-bipyridyl to iron (II)

The final concentrations of bipyridyl–iron(II) chelate, potassium bromide, sodium acetate and thallium in the experiments were kept at $1.2 \cdot 10^{-4}$ *M*, $1.2 \cdot 10^{-2}$ *M*, 0.12 *M* and $1.98 \cdot 10^{-5}$ *M* respectively. However, the chelate solutions used here were prepared by varying the mole ratio of bipyridyl to iron(II) from 3:1 to 8:1, by a method similar to that described above. The results are shown in Fig. 2. When the mole ratio of bipyridyl to iron(II) exceeded 5:1, a decrease in the absorbance of the extract at 524 nm was observed. This may be caused by the formation of a colourless bipyridyl–thallium(III) chelate, which is more stable than the thallium(III) bromide complex [15,16], by the reaction of excessive amounts of bipyridyl with the thallium(III) bromide complex. However, a slight excess of bipyridyl is necessary for the stoichiometric formation of the bipyridyl–iron(II) chelate, and this mole ratio was maintained at 4:1.



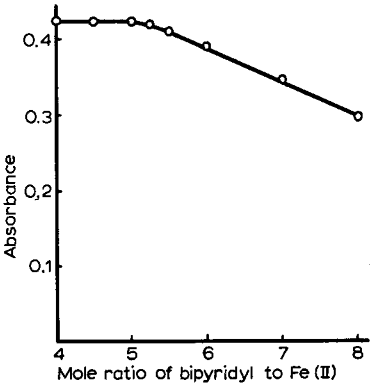


Fig. 1. Absorption spectra against dichloroethane as reference. (1) Spectrum of organic phase extracted from the aqueous solution (25 ml) kept at $1.2 \cdot 10^{-4}$ *M* $Fe(bip)_3$, $1.2 \cdot 10^{-2}$ *M* KBr and 0.12 *M* NaAc, but Tl is absent, pH 5. (2) Spectrum of organic phase extracted from the aqueous solution (25 ml) contained the same component as that of curve 1, and $2.77 \cdot 10^{-5}$ *M* Tl, pH 5.

Fig. 2. Effect of mole ratio of bipyridyl to iron(II). Tl: $1.98 \cdot 10^{-5}$ *M*. Fe(II): $1.2 \cdot 10^{-4}$ *M*, KBr: $1.2 \cdot 10^{-2}$ *M*, NaAc: 0.12 *M*, pH of the aqueous phase: 5. Absorbance at 524 nm *vs.* reagent blank.

Effect of potassium bromide concentration

Thallium ($1.98 \cdot 10^{-5}$ *M*) was reacted with a varying amount of potassium bromide, the required excess of bipyridyl–iron(II) chelate and other reagents. The extraction was done for each aqueous solution at pH 5 as described above. The absorbance of the extracts was measured at 524 nm, and was found to remain constant for bromide concentrations exceeding $0.7 \cdot 10^{-2}$ *M* up to at least $1.7 \cdot 10^{-2}$ *M*. An excess of bromide was necessary to obtain a constant absorbance, and a concentration of $1.2 \cdot 10^{-2}$ *M* was chosen for later work.

Effect of pH

The effect of the pH on the extraction was investigated by measuring the absorbance of the extracts obtained from aqueous solutions, containing $1.98 \cdot 10^{-5}$ *M* thallium, $1.2 \cdot 10^{-2}$ *M* potassium bromide, 0.12 *M* sodium acetate and $1.2 \cdot 10^{-4}$*M* bipyridyl–iron(II) chelate, at different pH values from 2 to 7.5. Maximum, and essentially constant, absorbance was obtained over the pH range 2.5–6.7. The pH of the aqueous solution was therefore adjusted to between 4.5 and 5 by using 1 ml of 3 *M* sodium acetate solution. No effect of the concentration of sodium acetate on the extraction was observed over the tested range of 0.06–0.18 *M*.

Effect of shaking time on extraction

The shaking time was varied from 1 to 5 min, while the other variables were kept constant. It was found that shaking for 1 min sufficed; for safety, a shaking time of 4 min was selected.

Colour stability

The colour intensity of the extract was not influenced by temperature in the range 10–18° and was stable for at least 2 h if the absorption cells were closed to prevent the evaporation of dichloroethane.

Choice of organic solvent

Various water-immiscible organic solvents were tested for the extraction: nitrobenzene, bromobenzene, chlorobenzene, benzene, 1,2-dichloroethane, chloroform, carbon tetrachloride, benzonitrile, *n*-butyronitrile, *n*-butyl alcohol, isoamyl alcohol, *n*-butyl acetate, cyclohexanone and methyl isobutyl ketone. Nitrobenzene proved to give the highest difference in absorbance between the reagent blank and the bipyridyl–iron(II) chelate–thallium(III) bromide complex, and dichloroethane the next highest. Unfortunately, nitrobenzene gave a higher absorbance of the reagent blank and, moreover, produced a positive error with even a small amount of nitrate. Thus dichloroethane was chosen as the organic solvent.

Extraction efficiency

The efficiency of the extraction of thallium was checked by stripping thallium from an aliquot of the dichloroethane extract into 10 ml of 2% sodium sulfite solution (pH 5) by shaking for 10 min. The amount of stripped thallium was determined as follows. After the separation, the aqueous sulfite layer was heated with a dilute sulfuric acid in order to remove sulfur dioxide. The solution was cooled and diluted with distilled water. Then an aliquot containing less than 20 μg of thallium was taken. Thallium was determined by the photometric rhodamine B method[3].

The percentage extraction with 5.0 ml of dichloroethane was about 94%. For convenience, a single extraction was used in this work.

Calibration curve and precision

On the basis of the above results, the procedure was worked out. The absorbance of each extract from aqueous solutions containing various amounts (1–9 ml) of thallium solution ($9.90 \cdot 10^{-5}$ *M*) was measured at 524 nm against the reagent blank. A linear relationship was obtained over the tested range of $7.9 \cdot 10^{-6}$ to $3.5 \cdot 10^{-5}$ *M* of thallium in an aqueous solution, and the sensitivity was 0.424 in absorbance for $1.98 \cdot 10^{-5}$ *M* thallium in aqueous solution.

The reproducibility of the proposed method was estimated from the results of

8 sample solutions, each $1.98 \cdot 10^{-5}$ *M* in thallium. The standard deviation was calculated to be 0.004 absorbance unit from a mean value of 0.424, *i.e.*, a relative error of 1%.

Interferences

The influence of diverse ions on the extraction was examined under experimental conditions similar to those used for the calibration curve. Table I illustrates the degree of interference of diverse ions added to a solution containing $1.98 \cdot 10^{-5}$ *M* of thallium (4 p.p.m.). Complexing ions, such as citrate and tartrate, had no effect on the extraction and determination of thallium, even when present in 100-fold amounts, whereas small amounts of EDTA seriously inhibited the extraction. The presence of the following ions caused no interference: a 5-fold excess of Cu(II), Fe(III), Mo(VI) and W(VI); a 10-fold excess of Al, As(V), Cd, Ge(IV), In(III) and Pb(II); a 20-fold excess of Ga(III) and Zn. Mercury(II), gold(III) and iodide must be absent as they form extractable red complexes with bipyridyl–iron(II) chelate.

TABLE I

EFFECT OF DIVERSE IONS ON THE EXTRACTION OF THALLIUM
(Concentration of thallium: $1.98 \cdot 10^{-5}$ *M* (4 p.p.m.))

Ion	*Concn. (p.p.m.)*	*Abs.*	*Ion*	*Concn. (p.p.m.)*	*Abs.*
None	None	0.424	Pb(II)	40	0.421
Al(III)	40	0.424	W(VI)	20	0.424
As(V)	40	0.421	Zn(II)	80	0.424
Au(III)	2	0.622			
Bi(III)	4	0.432	SO_4^{2-}	2000	0.426
Cd(II)	40	0.426	NO_3^-	1800	0.426
Cu(II)	40	0.431	Cl^-	700	0.418
Fe(III)	20	0.424	PO_4^{3-}	400	0.424
Ga(III)	80	0.427	PO_4^{3-}	2000	0.376
Ge(IV)	40	0.428	Tartrate	1400	0.422
Hg(II)	4	0.696	Citrate	400	0.424
In(III)	40	0.424	Citrate	2000	0.407
Mo(VI)	20	0.425			

Although bromine is a satisfactory reagent to oxidize univalent thallium to tervalent, excess of bromine produced a positive error, hence the bromine must be removed by either heating or adding of 3 drops of 2% phenol solution. The addition of 2% phenol solution had no effect on the determination of thallium and gave the same results as those obtained by heating.

An attempt was made to separate thallium(III) from mercury(II). To a solution containing 50 μg of thallium(III) and 1 mg of mercury(II) under optimum acidity (2 *N* hydrobromic acid), 25 ml of isopropyl ether was added and the mixture was shaken for 1 min[3]. After the separation, the organic layer was warmed on a water bath to evaporate isopropyl ether and treated as described above for the determination of thallium. It was found that although the mercury was removed, only about 90% of the thallium was recovered.

Composition of extracted species

The ratio of thallium to the bipyridyl–iron(II) chelate in the extracted species was determined by the continuous variations method. Equimolar solutions of thallium and the chelate were mixed so that the mole fraction of the chelate was varied from 0.0 to 1.0, keeping the total concentration of the two variables at $4.0 \cdot 10^{-5}$ *M*. The resulting curve (Fig. 3) indicated that the metal and the chelate combine in a ratio of 2:1. This suggests that a 1:2 associated ion pair is formed in the dichloroethane phase between the bipyridyl–iron(II) chelate cation and the bromide complex anion of thallium(III), and thus the chemical formula of the extracted species is assumed to be $[Fe(bip)_3] \cdot (TlBr_4)_2$.

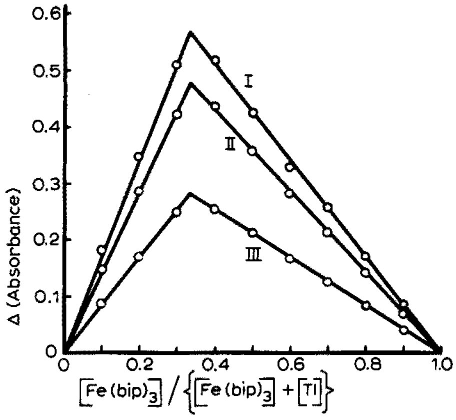


Fig. 3. Continuous variation plots at pH 5. $[Fe(bip)_3]+[Tl]$: $4.0 \cdot 10^{-5}$ *M*, KBr: $2.2 \cdot 10^{-2}$ *M*, NaAc: 0.12 *M*. Reference: reagent blank. (I) 524 nm, (II) 490 nm, (III) 550 nm.

The authors wish to express their thanks to Professor SHIGEHIKO HAYASHI of Fukui University and Professor YUROKU YAMAMOTO of Hiroshima University for their kind guidance and encouragement throughout this work.

SUMMARY

A spectrophotometric determination of thallium(III), based on solvent extraction of an ion-association pair formed between the cationic 2,2′-bipyridyl–iron(II) chelate and the anionic thallium(III) bromide complex is described. The best extractant is 1,2-dichloroethane and extraction is possible over the pH range 2.5–6.7. The composition of the extracted species was confirmed, and conditions were established for the extraction over the concentration range $7.9 \cdot 10^{-6}$–$3.5 \cdot 10^{-5}$ *M* of thallium in aqueous solution.

RÉSUMÉ

On décrit un dosage spectrophotométrique du thallium(III) basé sur extraction dans un solvant d'un chélate associé, 2,2′-bipyridyl–fer(II) et le complexe anionique thallium(III) bromure. Le meilleur réactif d'extraction est le dichloro-1,2-éthane à un pH compris entre 2.5 et 6.7. La composition des espèces extraites est déterminée; les conditions permettent des extractions de thallium en solution aqueuse à des concentrations de $7.9 \cdot 10^{-6}$ à $3.5 \cdot 10^{-5}$ *M*.

ZUSAMMENFASSUNG

Es wird eine spektralphotometrische Bestimmung des Thallium(III) beschrieben, bei der das Ionenpaar aus dem kationischen 2,2′-Bipyridyl–Eisen(II)-Chelat und dem anionischen Thallium(III)-bromid-Komplex extrahiert wird. Die Extraktion erfolgt im pH-Bereich von 2.5–6.7 mit 1,2-Dichloräthan. Die Zusammensetzung der extrahierten Spezies wurde bestätigt und Bedingungen für die Extraktion von $7.9 \cdot 10^{-6}$ bis $3.5 \cdot 10^{-5}$ *M* Thallium aus wässriger Lösung aufgestellt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COMPLEXIMETRIC DETERMINATION OF CALCIUM IN IMPURE CALCIUM CARBONATE AND LIMESTONE

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(Received November 29th, 1967)

High and variable results were obtained for calcium when samples of impure calcium carbonate were decomposed with dilute hydrochloric acid, and titrated with 0.02 N disodium EDTA at pH 10 in the usual manner. The iron(III) ions present in the sample solutions "blocked" the eriochrome black T by means of irreversible chelation[1]. This phenomenon caused large positive errors. In addition to calcium carbonate, the samples contain magnesium carbonate, iron(III) compounds, silica, and alkali salts. The limestone samples also contained a small amount of organic matter.

LEWIS AND MELNICK[2] adsorb iron(III) ions from phosphate-containing solutions on a column of Dowex 50W-X8 resin (H form), as a preliminary to compleximetrically determining the calcium and magnesium ions. FRITZ AND SCHENK[1] extract the chloroferrate(III) ions with methyl isobutyl ketone from 6 M hydrochloric acid[3] solution, before compleximetrically determining the calcium and magnesium ions.

In order to determine calcium compleximetrically without separation of the iron(III), a number of reagents were studied for capability of complexing or precipitating the iron. The reagents tested in this study were potassium cyanide, sodium dithionite, potassium ferrocyanide, sodium sulfide, sodium thiosulfate, mercaptoacetic acid (neutralized with ammonium hydroxide solution), 2,4-pentanedione, thioacetamide, and thiourea. Homogeneous precipitation techniques were studied in the case of thioacetamide. Except for sodium sulfide, the results for calcium were not quantitative, because an excess of the reagent interfered with the end-point indication, or because the iron(III) complex formed was insufficiently stable.

The method of LEWIS AND MELNICK[2] was modified in three ways: iron was separated as iron(III) hydroxide at pH 9 with ammonium hydroxide in the presence of 0.25 g of ammonium chloride; and iron was separated by adsorbing the chloroferrate(III) ions from 11.5 M hydrochloric acid solution on a column of Dowex 1-X8 anion-exchange resin, eluting calcium and magnesium ions with 110 ml of 11.5 M hydrochloric acid. Also, 0.01 M disodium EGTA titrant was used in place of 0.01 M disodium EDTA. Disodium EGTA reagent was investigated as the titrant because it chelates calcium ion selectively[4] in the presence of magnesium.

Method B: Calcium ion in an amount of 4–28.1 mg was titrated at pH 12 by 0.01 M disodium EGTA, in the presence of at least 0.6 mg of magnesium and a maximum of 500 μg of iron(III), using a pH 12.5 5 M sodium hydroxide–0.2 M potassium cyanide–0.128 M sodium sulfide buffer, and Calcon indicator. *Method A*:

TABLE I

DETERMINATION OF CALCIUM AND MAGNESIUM IN IMPURE CALCIUM CARBONATE AND LIMESTONE

(Results are expressed as % CaO or MgO; each result is the average of duplicate determinations)

Sample	*Method A* Ca(ClO$_4$)$_2$ pH 10 Di-Na EDTA	*Method B* Di-Na EGTA pH 12.5 NaOH–KCN–Na$_2$S buffer	*Method C* Modified LEWIS–MELNICK[2] pH 12.5 Di-Na EDTA	*Titrimetric* Ca(II) + Mg(II), as % CaO pH 10, di-Na EDTA	*% MgO calcd. by difference*	
					Method A	*Method B*
Impure CaCO$_3$	41.20	41.36	41.78^a	42.63^a	1.03	0.96
A	41.20	41.24	41.67^b	42.55^b	0.97	0.90
	Av. 41.20	41.30	41.73	42.59	1.00	0.93
B	38.00	38.18	38.66^a	39.28^a	0.92	0.83
	38.00	38.12	38.54^b	39.27^b	0.91	0.82
	37.99	38.08				
	Av. 38.00	38.13	38.60	39.28	0.92	0.83
C	39.99	40.00	40.22^a	41.08^a	0.79	0.82
	39.97	39.95	40.15^b	41.02^b	0.75	0.78
		39.85				
	Av. 39.98	39.93	40.19	41.05	0.77	0.80
D	35.12	35.15	35.28^a			
	35.11	35.15	35.16^b	36.16	0.75	0.73
	Av. 35.12	35.15	35.22			
E	33.49	33.42	33.69^b			
	33.45	33.39	33.63^a	34.33	0.62	0.67
	Av. 33.47	33.41	33.66			
F	36.79	36.73	37.04^b			
	36.75	36.70	37.03^a	37.80	0.74	0.80
	Av. 36.77	36.72	37.04			
G	41.09	41.11	41.38^a			
	41.04	41.09	41.30^b	42.27	0.86	0.86
	Av. 41.07	41.10	41.34			
Limestone A	43.36	43.48	43.60^a	55.60^a	8.84^c	8.78
	43.28	43.30	43.52^a	55.45^a	8.74	8.67
	43.27			55.53	8.79	8.73
	Av. 43.30	43.39	43.56			
Limestone B	35.32	35.28	35.45^a	58.31^a	16.55^d	16.59
	35.26	35.16		58.31	16.55	16.59
	Av. 35.29	35.24	35.45			

[a] Iron(III) separated by anion exchange.
[b] Iron(III) separated as Fe(OH)$_3$.
[c,d] % MgO, titrated as Mg(ClO$_4$)$_2$*:
[c] 9.23, 9.09, 9.01, av. 9.11 %.
[d] 16.73, 16.67, av. 16.70 %.
* reagent blank was $6.3 \cdot 10^{-3}$ mequiv.

After iron had been separated from the sample solutions by adsorbing chloroferrate(III) ions on a Dowex 1-X8 anion-exchange column, or by precipitation as iron(III) hydroxide with ammonium hydroxide solution, double precipitation of calcium ions as calcium oxalate was performed in the usual way. The hydrochloric acid solution of the calcium oxalate was evaporated to a small volume, oxidized with 8 ml of 16 *M* nitric and 1 ml of 12 *M* perchloric acid, and evaporated to dryness and the absence of fumes. The white crystalline residue was dissolved with distilled deionized water, and diluted to volume. An aliquot of the calcium perchlorate solution was titrated with 0.01 *M* disodium EDTA at pH 10, in presence of eriochrome black T indicator, as is customary. The magnesium ions in the combined calcium oxalate filtrates of the limestone samples were converted to magnesium perchlorate with concentrated nitric and perchloric acids. After evaporation to the absence of fumes, the white crystalline residue was dissolved with distilled deionized water, and diluted to volume. The magnesium ion in an aliquot was titrated at pH 10 with 0.01 *M* disodium EDTA to the eriochrome black T end-point, as usual. The reagent blank of the entire sample (0.2500–0.3000 g) was 1.48 ml of 0.0210 *N* disodium EDTA; for the aliquot titrated, this was 0.30 ml or $6.3 \cdot 10^{-3}$ mequiv. of cations, expressed as magnesium. The results of the limestone magnesium determinations are given in Table I (footnote).

EXPERIMENTAL

Reagents and chemicals

Buffer solutions. A pH 12.5 5 *M* sodium hydroxide–0.2 *M* potassium cyanide buffer was prepared as described by LEWIS AND MELNICK[2]. A pH 12.5 5 *M* sodium hydroxide–0.2 *M* potassium cyanide–0.128 *M* sodium sulfide buffer was prepared by dissolving 200 g of sodium hydroxide in 800 ml of deionized water, cooling, adding and dissolving 13 g of potassium cyanide and 10 g of sodium sulfide, and diluting to 1 l with deionized water. The buffer was kept in a polyethylene bottle.

A pH 10 ammonium hydroxide–ammonium chloride buffer was prepared as described by SKOOG AND WEST[5].

0.01 M Disodium EGTA solution. This was prepared by dissolving 8.1260 g of EGTA (Chel De, Geigy) in 42.8 ml of *N* sodium hydroxide and deionized water, diluting to 2 l with deionized water, and storing in a polyethylene bottle[4]. The reagent was standardized with 0.020 *N* calcium chloride, adding 1 ml of a 0.5% solution of magnesium chloride hexahydrate, 5 ml of pH 12.5 5 *M* sodium hydroxide–0.2 *M* potassium cyanide buffer[2] and 0.25 g of dry Calcon-KCl (1:250) indicator[2] to the calcium chloride solution before titrating. Sulfide-containing buffer can also be used, the results being the same.

Ion-exchange column. A 30-ml (23 g) column of Dowex 1-X8 resin (100–200 mesh) was placed in a 50-ml buret, in the usual way; a prepared polycello grease was the stopcock lubricant. Elution was facilitated by means of a water aspirator, connected by way of a safety flask. Before use, the column was prepared by washing successively with 100-ml volumes of 0.5 *M* and 11.5 *M* hydrochloric acid at a flow rate of 1–2 ml per min.

Procedures

Calcium in impure calcium carbonate (Method B of Table I). Wet 0.5–0.7500 g of the powdered dried sample with a few ml of deionized water, add 1.5–2 ml of 11.5 *M* hydrochloric acid through the lip of the beaker, evaporate the solution to moist dryness without baking, rinse the walls of the beaker with deionized water from a polyethylene bottle, and again evaporate the solution to moist dryness. Dissolve the salts with deionized water, and wash the solution, with the silica, into a 500-ml volumetric flask; dilute to 500 ml with deionized water and mix. Store the solution at pH 3–5 before titrating. To a 50-ml aliquot, add 1 ml of 0.5% magnesium chloride hexahydrate solution, and 7–7.5 ml of pH 12.5 hydroxide–cyanide–sulfide buffer. Cover the mouth of the conical flask with a small watch glass, and mix by swirling occasionally for 5 min. Add 0.25 g of Calcon-KCl (1:250) indicator and titrate with 0.01 *M* disodium EGTA until the mixture changes from pink to dark navy blue (with no purple). The end-point is stable for 30 min; after this time, the color may change to purple.

Calcium in limestone. Prepare a 0.5–0.700 g sample exactly as described for the impure calcium carbonate, and dilute the solution of the salts, plus silica, to 500 ml with deionized water. Titrate a 10–25 ml aliquot, containing no more than 500 µg of iron(III), with 0.01 *M* disodium EGTA in the conditions described above. The intense blue end-point is stable.

If the limestone contains more than a small amount of insoluble organic material, decompose a 0.5–0.700 g sample with 1 ml each of 11.5 *M* hydrochloric, 16 *M* nitric, and 12 *M* perchloric acid in mixture. Evaporate the solution to the absence of fumes, dissolve the red residue with 1 ml of 11.5 *M* hydrochloric acid, evaporate the solution to moist dryness, and dissolve the salts with 4 drops of 11.5 *M* hydrochloric acid and deionized water. Filter the hot solution through fluted Whatman No. 42 paper into a 500-ml volumetric flask, wash the white silica with a large volume of hot deionized water, allow the filtrate to cool to 25°, and dilute to 500 ml with deionized water. Complete the determination as described above. The blue end-point is stable.

DISCUSSION

In the presence of *ca.* 0.8–1.1 mg (3.3–$4.5 \cdot 10^{-4} M$) of total magnesium, the blue Calcon end-point must be stabilized with cyanide ion, which is added in the pH 12.5 buffer. The Calcon end-point is stable in titrated limestone aliquots, containing total magnesium in amounts of 1.5–5.6 mg (1.2–$4.5 \cdot 10^{-3}$ *M*). However, the same buffer is used at the higher magnesium ion concentration. If iron(III) is present in excess of about 500 µg, traces of calcium ion may be coprecipitated with the magnesium hydroxide and insoluble sulfide.

The apparent calcium in impure calcium carbonates, titrated in the presence of 0.5 g of potassium cyanide, was 0.72–1.06% (average 0.88 % as CaO) higher than the actual value determined by titrating the calcium perchlorate solutions at pH 10 with 0.01 *M* disodium EDTA. Addition of 2–3 ml of aqueous 80% mercaptoacetic acid (neutralized with ammonium hydroxide solution) to the prepared sample aliquots gave apparent calcium oxide results that were 0.37–0.72% (average 0.53%) too high.

After iron(III) had been separated from the impure calcium carbonate and limestone solutions as described, the coefficients of variation of the results of the modified LEWIS AND MELNICK[2] pH 12.5 titration of calcium ions with 0.01 *M* disodium EDTA, and those of the analogous method with 0.01 *M* disodium EGTA, with the calcium values determined by titrating the corresponding calcium perchlorate (from calcium oxalate) solutions were +0.7 and +0.3%, respectively.

The coefficient of variation of the calcium determined in the impure calcium carbonate and limestone samples by titrating with 0.01 *M* disodium EGTA under the given conditions, with the calcium values determined by titrating the calcium perchlorate solutions with 0.01 *M* disodium EDTA, was 0.17% (Table I). The relative standard deviations of the calcium determination in the presence of iron(III), by titrating with 0.01 *M* disodium EGTA under the given conditions were 0.0–0.29%, with an average of ±0.14%.

TABLE II

DETERMINATION OF IRON IN IMPURE CALCIUM CARBONATE

Sample	*% Fe*	*Sample*	*% Fe*
Impure $CaCO_3$			
A	0.058[a]	F	0.0223
B	0.036	G	0.041
C	0.038	Limestone	
D	0.018	A	2.29
E	0.030	B	1.72

[a] Average of duplicate results.

The percentages of magnesium oxide by difference from Method A and of Method B (Table I) were calculated from the total percent calcium(II) and magnesium(II) (expressed as % CaO) found by titrating at pH 10 with 0.01 *M* disodium EDTA, less the percent calcium(II) titrated, times the factor MgO/CaO. For the calcium determinations by Method B, the microgram amount of iron(III) present in each titration mixture was calculated from the iron(III) results in Table II. The iron(III) was determined in 2-g samples of impure calcium carbonate and 0.5-g samples of limestone, by titrating with 0.02 *N* potassium dichromate using 0.2% sodium diphenylamine sulfonate indicator solution[5]. The silica present in samples was not determined.

We are happy to acknowledge the courtesy of the Dow Chemical Co., in giving a supply of Dowex 1-X8 resin.

SUMMARY

Calcium is determined in impure calcium carbonate and limestone samples by titrating with 0.01 *M* disodium EGTA at pH 12 in the presence of at least 0.6 mg of magnesium and a maximum of 500 μg of iron(III), using a pH 12.5 sodium hydroxide–potassium cyanide–sodium sulfide buffer and Calcon indicator. The results of such titrations are compared with those obtained by titrating at pH 10 the calcium perchlorate solutions derived from calcium oxalate, and with those of a modified LEWIS AND MELNICK method. The results for magnesium (% MgO) obtained by difference are in fair agreement. Magnesium can be titrated compleximetrically as magnesium perchlorate, but the reagent blank must be determined.

RÉSUMÉ

On propose une méthode de titrage du calcium dans du carbonate de calcium impur et dans du calcaire par titrage au moyen d'EGTA disodique 0.01 *M*, au pH 12, en présence de quantités de magnésium supérieures à 0.6 mg et de 500 μg de fer(III) au maximum; on utilise un tampon pH 12: hydroxyde de sodium–cyanure de potassium–sulfure de sodium et le Calcon comme indicateur. Les résultats sont comparés avec ceux obtenus par titrage, au pH 10, du perchlorate de calcium provenant de l'oxalate et par la méthode modifiée de Lewis et Melnick. Les résultats pour le magnésium (% MgO) obtenus par différence sont satisfaisants. Le magnésium peut être titré par complexométrie comme perchlorate de magnésium, mais il faut faire un essai à blanc.

ZUSAMMENFASSUNG

Calcium wird in unreinem Calciumcarbonat und Kalkstein mit 0.01 *M* Dinatrium-EGTA bestimmt. Die Titration erfolgt beim pH 12 in Gegenwart von wenigstens 0.6 mg Magnesium und höchstens 500 μg Eisen(III) unter Verwendung eines Natriumhydroxid–Kaliumcyanid–Natriumsulfid-Puffers und Calcon als Indikator. Die Ergebnisse werden mit denen verglichen, die durch Titration des bei pH 10 aus perchlorsaurer Lösung gefällten Oxalats und mit denen, die nach der modifizierten Methode von Lewis und Melnick erhalten wurden. Die aus der Differenz erhaltenen Ergebnisse für das Magnesium stimmen gut überein. Magnesium kann komplexometrisch wie Magnesiumperchlorat titriert werden, jedoch muss der Blindwert des Reagenzes bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

STABILITY CONSTANTS OF IRON(III)-8-HYDROXYQUINOLINE COMPLEXES*

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(Received February 12th, 1968)

Evaluation of the precipitability and extractability of iron(III) oxinate as a function of the pH and oxine concentration requires values for the constants

$K_1 = [FeOx^{2+}]/[Fe^{3+}][Ox^-]$ (HOx = 8-hydroxyquinoline = oxine)

$K_2 = [FeOx_2^+]/[FeOx^{2+}][Ox^-]$

$K_3 = [FeOx_3]/[FeOx_2^+][Ox^-]$

$K_{s22} = [FeOx_2(OH)_2^-][Ox^-]/[OH^-]^2$ ($FeOx_3$ as solid phase)

$K_{sp} = [Fe^{3+}][Ox^-]^3$ ($FeOx_3$ as solid phase)

When the work summarized here was begun, only approximate values of K_1, K_2 and K_3 in aqueous solution were available[1,2]. Values of these constants (for $\mu = 0.5$), obtained from liquid–liquid extraction of iron(III) oxinate, have lately been reported[3]. The constant K_{s22} has not previously been determined.

K_1, K_2, K_3

These constants were determined spectrophotometrically. Absorbance measurements were made, as a function of the oxinate ion concentration, of mixtures of iron(III) and oxine at 3 different pH values, at which the predominant iron species are

(1) Fe^{3+}, $Fe(OH)^{2+}$, $FeOx^{2+}$ (pH 1.5)

(2) $FeOx^{2+}$, $FeOx_2^+$ (pH 2.5)

(3) $FeOx_2^+$, $FeOx_3$ (pH 3.85)

The total iron concentrations in the 3 series were $4.5 \cdot 10^{-4}$, $3 \cdot 10^{-5}$ and $1.5 \cdot 10^{-5}$ *M* respectively. Measurements in solutions having appreciable concentrations of $FeOx_3$ were possible only because supersaturated solutions were formed. All solutions were entirely aqueous. Absorbance measurements were made in 10-cm cells.

K_1, K_2 and K_3 were calculated iteratively. The data and calculations will not be given here. The following auxiliary constants (25°) were used in the calculations:

$[FeOH^{2+}](H^+)/[Fe^{3+}] = 2.8 \cdot 10^{-3}$ ($\mu = 0.10$, (H^+) is hydrogen-ion activity)

$[HOx](H^+)/[H_2Ox^+] = 0.98 \cdot 10^{-5}$ ($\mu = 0.10$, calc. from ref. 4)

$(H^+)[Ox^-]/[HOx] = 1.94 \cdot 10^{-10}$ ($\mu = 0.10$)[4]

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[*] Based on the Ph.D. thesis of T. D. TURNQUIST, University of Minnesota, July, 1965.
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The concentration of the species $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ were small enough to neglect in all solutions.

The following values were obtained for the constants at 0.10 M ionic strength (adjusted with $HClO_4$ and $NaClO_4$) at 25° from absorbance measurements made at various wave lengths:

$K_1 \cdot 10^{-13} = 4.7, 5.0, 5.1, 4.8$ (absorbance measurements at 550, 600, 645 and 700 nm); avg. 4.9

$K_2 \cdot 10^{-12} = 3.9, 3.9, 4.4, 4.4$ (550, 600, 645 and 700 nm); avg. 4.2

$K_3 \cdot 10^{-10} = 3.8, 3.8, 4.1$ (475, 525 and 575 nm); avg. 3.9

It will be realized that small experimental errors will have rather large effects on the values of the constants. Considering that an error of ± 0.02 unit may be made in measuring the pH and an error of 1% may be made in absorbance measurement, the error in K_1 could well be 15%. The value of K_2 depends on K_1; an error of 15% in K_1 results in an error of approximately 30% in K_2.

The β formation constants determined by ZOLOTOV AND KUZ'MIN[3] and in the present work (25°) compare as follows:

	T. and S. *(μ = 0.10)*	*Z. and K.* *(μ = 0.50)*
$\log \beta_1 = \log K_1$	13.69	12.85
$\log \beta_2 = \log K_1K_2$	26.3	25.45
$\log \beta_3 = \log K_1K_2K_3$	36.9	36.95
	36.7 (from K_{sp})	

The molar absorptivity curves of $FeOx^{2+}$, $FeOx_2^+$ and $FeOx_3$ in water are shown in Fig. 1. Only the curve for $FeOx_3$ was obtained by direct measurement.

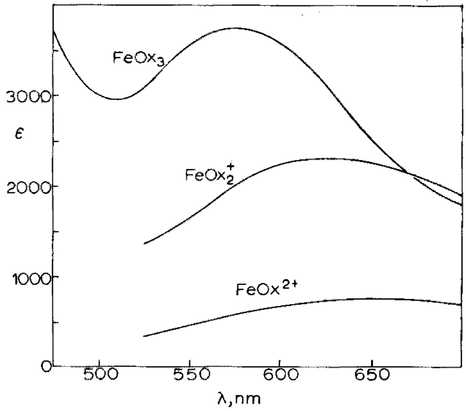


Fig. 1. Molar absorptivity curves of $FeOx_3$, $FeOx_2^+$ and $FeOx^{2+}$ in water.

S_0, K_{sp} *and* β_3

The intrinsic solubility, S_0, of $FeOx_3$ in water was determined by shaking solid iron(III) oxinate with an acetate-buffered solution (pH 5.0) containing oxine in sufficient concentration to make $[Ox^-] > 10^{-9}$. Above this oxinate ion concentration, $FeOx_3$ accounts for the solubility, provided that the solution is not alkaline. The solid iron(III) oxinate used was first aged by digesting at 100°, then filtered off, washed with water and dried at 110°. Analysis of the solid gave 11.5% Fe and 87.8% Ox, compared to the theoretical values 11.4% and 88.6%.

Saturated iron(III) oxinate solutions were obtained by shaking the solid and solution for 4 or 5 days. The filtrate was analyzed for iron by adding additional oxine to make its concentration $8 \cdot 10^{-4}$ *M*, extracting $FeOx_3$ from 500 ml of solution with 10 ml of chloroform and measuring the absorbance of the extract at 580 nm. A standard curve was established similarly. The results in Table I demonstrate that the solubility remains unchanged as the oxinate ion concentration is increased 4-fold (or as $[Ox^-]^3$ is increased about 70 times).

TABLE I

INTRINSIC SOLUBILITY OF IRON(III) OXINATE

($\mu = 0.10$, 25°)

Σ [*oxine*] $\cdot 10^4$	[*Ox*⁻] $\cdot 10^9$	S_0 (*M*) $\cdot 10^7$	Σ [*oxine*] $\cdot 10^4$	[*Ox*⁻] $\cdot 10^9$	S_0 (*M*) $\cdot 10^7$
2.0	1.9	1.6	8.2	7.9	1.6
2.0	1.9	1.4	8.2	7.9	1.6
4	3.8	1.6	8.2	7.9	1.6
4.5	4.3	1.5			Avg. 1.6

TABLE II

SOLUBILITY PRODUCT OF IRON(III) OXINATE

($\mu = 0.10$, 25°)

pH	Σ [*Fe*] $\cdot 10^3$	[*Oxine*] $\cdot 10^2$	$[Ox^-]^3 \cdot 10^{41}$	$[Fe^{3+}] \cdot 10^4$	$K_{sp} \cdot 10^{44}$
1.42	1.74	2.89	5.53	5.41	3.0
1.51	1.02	2.71	15.9	2.35	3.7
1.59	1.17	1.50	8.13	3.25	2.6
1.37	2.41	3.05	3.28	8.47	2.8
1.42	1.49	3.32	8.40	4.10	3.4
1.35	2.02	3.95	5.32	6.28	3.3
					Avg. 3.1

The solubility product of $FeOx_3$ was obtained from its solubility in acidic oxine solutions (pH ~ 1.5), in which Fe^{3+} and $FeOx^{2+}$ are the principal species (Table II). Iron was determined in the filtered saturated solution by chloroform extraction of $FeOx_3$ after adding additional oxine ($1 \cdot 10^{-3}$ *M*) and adjusting the pH to 5; the absorbance was measured at 580 nm. ε for $FeOx_3$ in $CHCl_3$ was found to be 3720 at 580 nm, agreeing well with 3700 reported by UMLAND AND HOFFMANN[5]. The concentration of Ox^- was calculated with the aid of the formation constants of $FeOx^{2+}$, $FeOx_2^+$ and the measured pH.

The average value of K_{sp}, $3.1 \cdot 10^{-44}$, agrees fairly well with OOSTING's[6] value $4.3 \cdot 10^{-44}$ obtained by recalculating his data with the values $pK_{1_{Ox}} = 4.91$ and $pK_{2_{Ox}} = 9.82$ for HOx.

A value for β_3 ($= K_1K_2K_3$) was calculated from the intrinsic solubility and K_{sp} of $FeOx_3$:

$$\beta_3 = S_0/K_{sp} = 1.6 \cdot 10^{-7}/3.1 \cdot 10^{-44} = 5.2 \cdot 10^{36}$$

The value of β_3 from K_1, K_2 and K_3 is $8 \cdot 10^{36}$. These two values are not entirely independent, however, because K_1 must be used to calculate $[Fe^{3+}]$ in the K_{sp} measurements, in which *ca.* 50% of the iron is present as $FeOx^{2+}$. $FeOx_2^+$ makes up about 10% of the total iron, so that β_3 is not greatly dependent on K_2.

Iron(III) hydroxo-oxine complexes

In alkaline oxinate solutions, iron(III) forms yellow or orange-yellow species of the type $FeOx_m(OH)_n^{-m-n+3}$. At a suitable pH (8.4), it is easy to show by the use of the molar ratio method that complexes having Ox/Fe ratios of 1, 2 and 3 are formed. A series of iron(III) solutions having a final concentration of $1.5 \cdot 10^{-5}$ *M* were treated with increasing amounts of oxine and buffered at pH 8.4. Plots of absorbances at 430, 580 and 620 nm *versus* [Ox]/[Fe] (not reproduced here) showed breaks at the ratios $^1/_1$, $^2/_1$ and $^3/_1$. At pH 11, Job's continuous variation method indicated the formation of a complex having Ox/Fe = 2. Electromigration experiments showed the presence of one or more yellow anionic iron(III) hydroxo-oxine complexes in solutions having $[OH^-] \sim 10^{-2}$ and $[Ox^-] \sim 3 \cdot 10^{-4}$. These species were adsorbed on a strong base anion-exchange resin. At lower hydroxyl ion concentrations (pH 8.4–9.7), with $\sim 10^{-4}$ *M* oxine, the colored species were predominantly uncharged. The formation of uncharged and anionic hydroxo-8-hydroxyquinoline-5-sulfonic acid complexes with iron(III) has already been demonstrated[7].

Taking the coordination number of iron(III) as 6, one may postulate the existence of the complexes

$FeOx_2OH$ $FeOx(OH)_2$
$FeOx_2(OH)_2^-$ $FeOx(OH)_3^-$
$FeOx(OH)_4^{2-}$

but not $FeOx_4^-$.

The two uncharged complexes written above can be obtained in solid form. The 1 Fe:1 Ox complex was precipitated by slowly adding with stirring 0.1 *M* ammonia to 250 ml of a solution containing 0.61 mmole each of iron(III) and H_2Ox^+ until a pH of 8.5 was reached. The 1 Fe:2 Ox complex was prepared similarly except that a solution containing 0.36 mmole of iron(III) and 0.72 mmole of H_2Ox^+ was used. The precipitates were filtered off, washed with water, and dried at 110° for 1 h. The solids were dark brown in color, intermediate between the red-brown of iron(III) hydroxide and the black of iron(III) oxinate. Analysis of the dried 1:1 complex gave the values

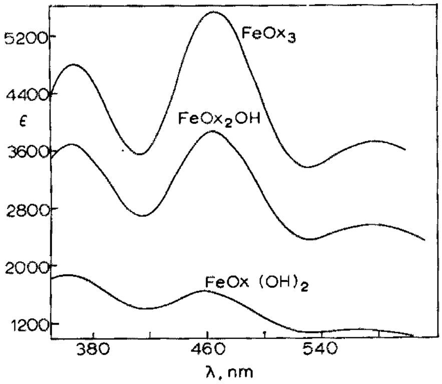
	Experimental	*Calculated for $FeOx(OH)_2$*	*Calculated for FeOxO*
Fe(%)	25.0	23.9	25.8
Ox(%)	64.3	61.6	66.7
Ox/Fe (mole ratio)	1.01	1.00	1.00

The Fe/Ox ratio is close to the theoretical, but some OH has been converted to O on drying.

The 1 Fe : 2 Ox complex gave the analysis:

	Experimental	*Calculated for $FeOx_2OH$*
Fe(%)	15.5	15.5
Ox(%)	80.8	79.9
Ox/Fe (mole ratio)	2.02	2.00

Both solids dissolve in chloroform to some extent, the 1Fe:2Ox complex more readily than the 1:1 complex. The chloroform solutions are brown, unlike the black of $FeOx_3$. The molar absorptivity curves (based on 1 gram atom of iron per liter of chloroform solution) are shown in Fig. 2.



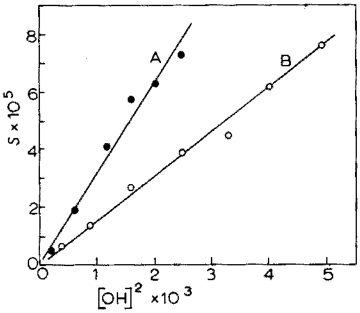


Fig. 2. Molar absorptivity curves of $FeOx_3$, $FeOx_2OH$ and $FeOx(OH)_2$ (the latter largely as FeOxO) in chloroform.

Fig. 3. Molar solubility (*S*) of iron(III) oxinate in basic oxinate solutions as a function of $[OH^-]^2$. (A) $[Ox^-]$ $2.5 \cdot 10^{-3}$, (B) $[Ox^-]$ $5.0 \cdot 10^{-3}$.

The existence of the anionic complex $FeOx_2(OH)_2^-$ was established and the equilibrium constant

$$K_{s22} = [FeOx_2(OH)_2^-][Ox^-]/[OH^-]^2 \text{ (solution saturated with } FeOx_3\text{)}$$

was determined by obtaining the solubility of $FeOx_3$ in basic solutions as a function of the oxinate and hydroxyl ion concentrations. The solubility contributions from $FeOx_3$, $FeOx_2OH$ and $FeOx(OH)_2$ can be neglected when the total iron concentration is greater than 10^{-5} *M*. Then, the solubility is given by

$$S = [FeOx_2(OH)_2^-] + [FeOx(OH)_3^-] + [FeOx(OH)_4^{2-}]$$
$$= K_{s22}[OH^-]^2/[Ox^-] + K_{s13}[OH^-]^3/[Ox^-]^2 + K_{s14}[OH^-]^4/[Ox^-]^2$$

Two series of solubility determinations were run in which the oxinate ion concentration was held constant at $2.5 \cdot 10^{-3}$ *M* and $5.0 \cdot 10^{-3}$ *M* and the hydroxyl ion concentration was varied. The ionic strength was maintained constant at 0.10 *M* with sodium perchlorate. The solid iron(III) oxinate used in the determination of K_{sp} was also used here. The solutions were deaerated with nitrogen and brought to equilibrium by shaking with iron(III) oxinate for a week. After filtration, the iron content of the solution was determined by adding more oxine, adjusting the pH to 5 and extracting $FeOx_3$ into chloroform for photometric determination.

In the range of oxinate ion concentrations and hydroxyl ion concentrations (maximum 0.07 *M*) covered, the solubility increases as the square of the hydroxyl ion concentration and inversely as the oxinate ion concentration (Fig. 3). Within the limits of experimental error, the solubility conforms with the formation of only the ion $FeOx_2(OH)_2^-$. The slopes of the lines in Fig. 3 give the values $7.8 \cdot 10^{-5}$ and $7.6 \cdot 10^{-5}$ for K_{s22}. The formation of a polynuclear ion such as $Fe_2Ox_5(OH)_2^-$ (which would not be revealed by the method) is unlikely because of the low iron concentration. The possibility of the formation of the ions $FeOx(OH)_3^-$ and $FeOx(OH)_4^{2-}$ at higher hydroxyl ion concentrations was not investigated.

Other constants

Incidentally, the partition coefficient $[HOx]_{CHCl_3}/[HOx]_{H_2O}$ was determined at 25°, for alcohol-free chloroform solutions with an equilibrium oxine concentration of 0.01–0.02 *M*. The aqueous phase was a potassium dihydrogen phosphate buffer of pH 7.1 and 0.1 *M* ionic strength. Six runs gave the values 334, 337, 335, 329, 341 and 339, average 336. Previously reported values range from 350 (25°) to 720 (18°). ZOLOTOV AND KUZ'MIN[3] found the partition coefficient to be 353 when the aqueous phase was 0.5 *M* sodium perchlorate.

Seven determinations of the chloroform (alcohol-free) solubility of $FeOx_3$ at 25° gave the values ($\cdot 10^2 M$): 1.92, 1.93, 1.89, 1.92, 1.91, 1.87 and 1.89 or an average of $1.90 \cdot 10^{-2}$ *M*. A solubility of $1.5 \cdot 10^{-2} M$ has recently been recorded[6].

Grateful acknowledgement is made to the National Aeronautics and Space Administration for fellowships received by T. D. TURNQUIST in the years 1962–1965.

SUMMARY

Spectrophotometric determination of the formation constants of iron(III)-8-hydroxyquinoline complexes in 0.1 *M* sodium perchlorate solution at 25° gave the values $K_1 = [FeOx^{2+}]/([Fe^{3+}][Ox^-]) = 4.9 \cdot 10^{13}$, $K_2 = [FeOx_2^+]/([FeOx^{2+}][Ox^-]) = 4.2 \cdot 10^{12}$ and $K_3 = [FeOx_3]/([FeOx_2^+][Ox^-]) = 3.9 \cdot 10^{10}$. $FeOx_2OH$ and $FeOx(OH)_2$ are obtainable as solid phases. $FeOx_3$ ($K_{sp} = 3 \cdot 10^{-44}$, intrinsic solubility $1.6 \cdot 10^{-7}$ *M*) dissolves in basic solutions to form $FeOx_2(OH)_2^-$ In a solution saturated with $FeOx_3$, $([FeOx_2(OH)_2^-][Ox^-])/[OH^-]^2 = 7.7 \cdot 10^{-5}$.

RÉSUMÉ

La détermination spectrophotométrique des constantes de formation des complexes fer(III)–hydroxy-8-quinoléine en solution perchlorate de sodium 0.1 *M* à 25° a fourni les valeurs $K_1 = [FeOx^{2+}]/([Fe^{3+}][Ox^-]) = 4.9 \cdot 10^{13}$, $K_2 = [FeOx_2^+]/([FeOx^{2+}][Ox^-]) = 4.2 \cdot 10^{12}$ et $K_3 = [FeOx_3]/([FeOx_2^+][Ox^-]) = 3.9 \cdot 10^{10}$.

$FeOx_2OH$ et $FeOx(OH)_2$ sont obtenus comme phases solides. $FeOx_3$ se dissout en solution basique pour former $FeOx_2(OH)_2^-$. Dans une solution saturée avec $FeOx_3$, $([FeOX_2(OH)_2^-][Ox^-])/[OH^-]^2 = 7.7 \cdot 10^{-5}$.

ZUSAMMENFASSUNG

Die spektralphotometrische Bestimmung der Bildungskonstanten der Eisen-(III)-8-hydroxychinolin-Komplexe in 0.1 M Natriumperchlorat-Lösung bei 25° ergaben folgende Werte: $K_1 = [FeOx^{2+}]/([Fe^{3+}][Ox^-]) = 4.9 \times 10^{13}$, $K_2 = [FeOx_2^+]/([FeOx^{2+}][Ox^-]) = 4.2 \times 10^{12}$ und $K_3 = [FeOx_3]/([FeOx_2^+][Ox^-]) = 3.9 \times 10^{10}$. $FeOx_2OH$ und $FeOx(OH)_2$ können als feste Phasen vorliegen. $FeOx_3$ ($K_{sp} = 3 \times 10^{-44}$, wirkliche Löslichkeit 1.6×10^{-7} M) löst sich in basischen Lösungen unter Bildung von $FeOx_2(OH)_2^-$. Für eine Lösung die mit $FeOx_3$ gesättigt ist gilt:

$$([FeOx_2(OH)_2^-][Ox^-])/[OH^-]^2 = 7.7 \times 10^{-5}.$$

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DERIVATE VON SALICYLKETONEN[1]

II. MITT. SCHIFFSCHE BASEN AROMATISCHER *o*-AMINOKETONE MIT ÄTHYLENDIAMIN UND IHRE ANALYTISCHE ANWENDUNG ZUR NICKELBESTIMMUNG

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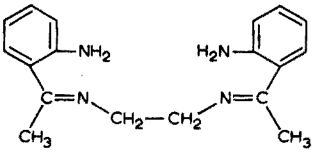
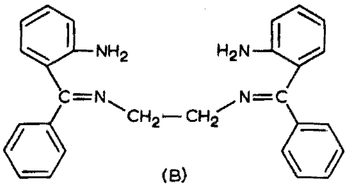
(Eingegangen den 20. Februar, 1968)

Schiffsche Basen von Äthylendiamin mit *o*-Aminobenzaldehyd[2] und 2-Pyrrolaldehyd[3] können für die spektrophotometrische Bestimmung von Nickel bzw. Kobalt genutzt werden. Die für die Synthese dieser Reagenzien nötigen Aldehyde sind jedoch schwierig zugänglich oder nur wenig stabil. Deshalb wurden die Schiffschen Basen des *o*-Aminoacetophenons (A) und *o*-Aminobenzophenons (B) dargestellt und auf ihre analytische Eignung geprüft.



(A)



(B)

EXPERIMENTELLES

Darstellung der Reagenzien und ihrer Metallchelate

14 g *o*-Aminoacetophenon[4] bzw. 20 g *o*-Aminobenzophenon[5] wurden in 25 ml wasserfreies Äthylendiamin eingetragen, 1 g Äthylendiaminhydrobromid (Katalysator nach REDDELIEN[6]) zugegeben und 12 Stunden im Paraffinbad (Badtemperatur 130–140°) am Rückfluss erhitzt. Nach beendeter Reaktion wurde das überschüssige Äthylendiamin im Vakuum abdestilliert und die noch heisse Mischung in 80 ml heissem Alkohol eingetragen. Beim Abkühlen fielen die Schiffschen Basen kristallin an.

*N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin (A)*. Hellgelbe Kristalle (Benzol), Schmp. 153–156°, Ausbeute: 45%d. Th. Analyse: ber. C 73.47% H 7.48% N 18. 96%: gef. C 73.09% H 7.53% N 18.44%.

*N,N'-Bis(*o*-aminobenzophenon)-äthylendiimin (B)*. Gelblichweisse Kristalle (Alkohol), Schmp. 136–137°, Ausbeute: 62% d. Th. Analyse: ber. C 80.39% H 6.22%: gef. C 80.50% H 6.61%.

Zur Darstellung der Metallchelate wurden jeweils 3 mMol der Schiffschen Basen in 100 ml Alkohol gelöst und unter Rühren die äquivalente Menge Metallsalz, gelöst in Äthanol ($Ni(CH_3COO)_2 \cdot 4H_2O, Cu(CH_3COO)_2 \cdot H_2O, Co(CH_3COO)_2 \cdot 4H_2O$) oder Wasser ($PdCl_2$, K_2PtCl_4) zugegeben. Bei der Komplexbildung mit den Platinmetallen wurden die Reaktionslösungen mit alkoholischer Kalilauge neutralisiert. Alle Chelate wurden aus Xylol umkristallisiert.

Hydrolyse der Schiffschen Basen

Das Hydrolyseverhalten der Schiffschen Basen A und B wurde unter pH—stat—Bedingungen am Autotitrator der Fa. Radiometer, Kopenhagen untersucht. Die Messungen erfolgten bei 25° in 50%igen Dioxan. Zur Titration des freiwerdenden Amins wurde 0.05 *N* Salzsäure verwendet. Die Konzentration an Schiffscher Base betrug 10^{-3} Mol/l.

Spektroskopische Messungen

Die Spektren der Metallchelate wurden mit dem Spektralphotometer USP-2 nach GEPPERT aufgenommen. Für die photometrische Nickelbestimmung kam das Kolorimeter nach HAVEMANN zum Einsatz.

Lösungen

Zur Ermittlung der Eichkurve wurde eine 10^{-3} *M* Nickelsulfatlösung verwendet, deren Gehalt massanalytisch gesichert war. Als Pufferlösung diente eine Mischung von Ammoniak und Ammoniumchlorid im Verhältnis 1:1. Die 0.02 *M* Reagenzlösung von A wurde unter Verwendung von Benzol p.a. hergestellt.

ERGEBNISSE UND DISKUSSION

N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin (A) und N,N'-Bis (*o*-aminobenzophenon)-äthylendiimin (B) stimmen in ihren chemischen Eigenschaften weitgehend überein. Beide Substanzen sind in den meisten organischen Lösungsmitteln gut löslich, in Wasser unlöslich. Schwach saure Lösungen von A und B zeigen eine intensive gelbe Farbe, die auf die Protonisierung der Schiffschen Basen zurückzuführen ist. Die Protonenaddition verläuft reversibel. In stärker saurer Lösung setzt Hydrolyse ein, die nach dem Zeitgesetz einer Reaktion 1. Ordnung abläuft. A ist oberhalb pH 4 relativ hydrolysebeständig; diese Eigenschaft ist bedeutungsvoll für die Verwendung der Substanz als Extraktionsmittel. Einige kinetische Daten für die Hydrolyse der Schiffschen Basen A und B sind in Tabelle I zusammengestellt.

N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin (A) und N,N'-Bis(*o*-amino-

TABELLE I

HYDROLYSE DER SCHIFFSCHEN BASEN BEI 25° IN 50%IGEM DIOXAN

	pH 2.70	*pH 3.36*
A	$K = 0.022$ min^{-1} $t_{\frac{1}{2}} = 30.9$ min	Geringfügige Hydrolyse
B	$K = 0.114$ min^{-1} $t_{\frac{1}{2}} = 6.7$ min	$K = 0.053$ min^{-1} $t_{\frac{1}{2}} = 13.2$ min

benzophenon)-äthylendiimin (B) bilden mit Kupfer(II), Nickel(II), Kobalt(II), Palladium(II) und Platin(II) Innerkomplexverbindungen planarquadratischen Aufbaus. Eine Übersicht über die dargestellten Metallchelate wird in Tabelle II gegeben. Die Farbigkeit der Metallchelate sowie die gute Löslichkeit in Lösungsmitteln wie Benzol und Chloroform ermöglichen ihre Nutzung zur photometrischen Metallanalyse. Besonders günstige Bedingungen sind für Nickel und Palladium gegeben (s. Fig. 1). Das Spektrum des Kobalt(II)-Komplexes (Fig. 1) ist durch eine intensive charge-transfer-Bande bei 444 nm charakterisiert, die auf die leichte Oxydierbarkeit dieses Chelates hindeutet. Tatsächlich gehen die Kobalt(II)-Verbindungen der Liganden A und B in Lösung rasch in tiefgrüne Kobalt(III)-Chelate über. Von anderen dreiwertigen Metallen bildet Eisen(III) mit beiden Liganden weinrote Komplexverbindungen. Störungen der extraktionsphotometrischen Bestimmung von Nickel (oder Palladium) mit A und B durch Kobalt(III) und Eisen(III) sind wegen der geringen Löslichkeit der entsprechenden Kobalt(III)- und Eisen(III)-Chelate in Lösungsmitteln geringer Polarität nicht zu erwarten.

TABELLE II

ÜBERSICHT ÜBER DIE DARGESTELLTEN METALLCHELATE

Ligand	*Metall*	*Farbe Eigenschaften*	*Analyse (%)*
A	Ni(II)	Rote, glänzende Kristalle[a]	Ni: ber.: 16.74 gef.: 16.91
A	Cu(II)	Olivbraune Kristalle[a]; der Komplex fällt erst nach Zugabe alkoholischer Kalilauge aus	Cu: ber.: 17.87 gef.: 17.71
A	Pd(II)	Orangefarben[a]	Pd: ber.: 26.70 gef.: 27.14 N: ber.: 14.06 gef.: 14.27
B	Ni(II)	Dunkelrote Kristalle; Schmp. 321–322°	Ni: ber.: 12.39 gef.: 12.17
B	Cu(II)	Braungrüne Kristalle; Schmp. 217–219°	Cu: ber.: 13.25 gef.: 13.01
B	Co(II)	Weinrot mikrokristallin[a]	Co: ber.: 12.43 gef.: 12.17
B	Pd(II)	Orangefarben[a]	Pd: ber.: 20.39 gef.: 20.07
B	Pt(II)	Weinrot[a]	Pt: ber.: 31.92 gef.: 31.60

[a] Die Substanz zeigt keinen eindeutigen Schmelz- oder Zersetzungspunkt.

Extraktion und photometrische Bestimmung von Nickel

Die Extraktion der Nickelchelate der beiden Schiffschen Basen A und B ist stark pH-abhängig. Für A sind die günstigsten Extraktionsbedingungen im pH-Intervall 6–8 gegeben (s. Tabelle III), während B maximale Extraktion bei pH 8 zeigt. Für die analytische Bestimmung von Nickel ist es zweckmässig, auf pH 8 einzustellen, um die Bildung der gelben Protonisierungsprodukte der Schiffschen Basen zu vermeiden. Die Abhängigkeit der Nickelextraktion vom Überschuss an Reagenz wird in Tabelle IV gezeigt. Danach bleibt bei B die Extraktion des Metalls auch bei Anwendung eines grossen Überschusses des Liganden unbefriedigend. Selbst durch Steigerung der Extraktionszeiten kann keine quantitative Extraktion erreicht werden. Während durch die Schiffsche Base A Nickel bei pH 8 und einem 50fachen Reagenzüberschuss bereits nach 2 Minuten Schüttelzeit quantitativ extrahiert wird, muss man dafür mit B

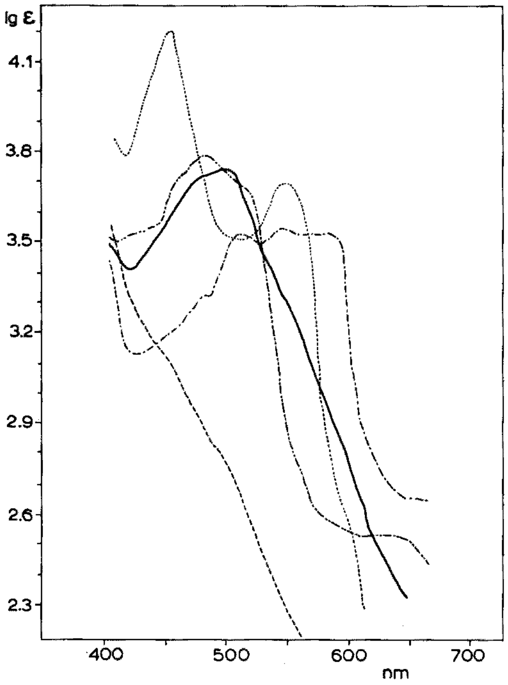


Fig. 1. Absorptionsspektren von Metallchelaten des N,N′-Bis (*o*-aminobenzophenon)-äthylendiimins in Chloroform. ——— Nickel(II), ·–·–·– Palladium(II), – – – – Kupfer(II), ······ Kobalt(II); (in Benzol) —·—·—· Platin(II).

TABELLE III

EXTRAKTION VON NICKEL (%) MIT SCHIFFSCHEN BASEN AUS ÄTHYLENDIAMIN UND *o*-AMINOACETOPHENON (A) bzw. *o*-AMINOBENZOPHENON (B)

pH	*A* *20facher Überschuss; 2 min*	*B* *128facher Überschuss; 15 min*
3	—	7.3
4	7.4	17.7
5	61.2	23.8
6	75.9	24.0
7	75.8	30.0
8	75.8	39.0
9	51.6	16.7
10	64.9	2.8
11	28.3	2.3

bei einem 130fachen Überschuss an Ligand dreimal 20 Minuten schütteln. Somit ist nur der Ligand A für eine analytische Nutzung geeignet.

Für die Nickelchelate beider Liganden ist das Lambert–Beersche Gesetz im Bereich von 0.5–25 μg Ni/ml erfüllt: 0.5 μg Ni/ml waren noch gut nachweisbar. Die Extinktionswerte der Nickelchelate von A in Benzol und von B in Chloroform sind bis zu 8 Tagen konstant.

TABELLE IV

BEEINFLUSSUNG *T* DER NICKELEXTRAKTION DURCH DIE LIGANDENKONZENTRATION (in %)

	A	*B*
1:20	75.8	—
1:30	88.5	—
1:40	93.0	—
1:50	100.0	—
1:64	100.0	17.0
1:128	100.0	31.5
1:256	100.0	40.2

Arbeitsvorschrift zur Nickelbestimmung

Zur Durchführung der Nickelbestimmung werden 10 ml Analysenlösung, die 0.5–25 μg Ni/ml enthalten soll, in einen 50-ml Schütteltrichter überführt. Dazu gibt man 10 ml 0.02 *M* Reagenz- und 2 ml Pufferlösung und schüttelt 2 Minuten kräftig durch. Nun wird die wässrige Phase abgetrennt und die gelbrote organische Schicht über wasserfreies Natriumsulfat in einen 25-ml Messkolben filtriert. Der Schütteltrichter wird mit etwa 5 ml Benzol nachgespült. Die vereinigten benzolischen Lösungen füllt man im Masskolben auf 25 ml auf. Die Gehaltbestimmung wird mit Hilfe einer Eichkurve durchgeführt, die aus einer Verdünnungsreihe von 0.5–25 μg Ni/ml zugänglich ist. Die Extinktionsmessungen erfolgen bei 496 nm. Die Genauigkeit der Bestimmung liegt bei 2% (relativer Fehler bei $2 \cdot 10^{-5}$ Mol/l).

Störung durch Fremdionen

Kupfer, Eisen, Kobalt und Palladium stören die Nickelbestimmung. Von ihnen kann Eisen bei pH 8 mit Seignettesalz maskiert werden und darf dann bis zum 100-fachen Überschuss zugegen sein. Jedoch muss dabei die Reagenzkonzentration erhöht werden (Verhältnis Nickel:Ligand = 1:90). Die Maskierung des Kupfers gelingt bis zum 100fachen Überschuss mit Natriumthiosulfat. Palladium wird aus ammoniakalischer Lösung nicht mit extrahiert, auf diese Weise kann Nickel bis zum 25fachen Überschuss an Palladium sicher bestimmt werden. Störungen der Nickelbestimmung durch Kobalt sind auf oxydativem Wege teilweise zu umgehen, da das Kobalt(III)-Chelat des Reagenzes in der organischen Phase nur wenig löslich ist. Man arbeitet dann mit einer Extraktionszeit von 15 Minuten im ammoniakalischen Medium, als Oxydationsmittel dient Wasserstoffperoxid. Kobalt stört so bis zum zehnfachen Überschuss nicht mehr.

Herrn Prof. Dr. H. HOLZAPFEL danken wir für die Möglichkeit zur Durchführung dieser Untersuchungen, dem VEB Laborchemie Apolda für gute Zusammenarbeit und grosszügige Unterstützung. Unser Dank gilt weiter Herrn Prof. Dr.

E. Hoyer für wertvolle Hinweise bei der Arbeit am Autotitrator und Frau Plath für die Durchführung von Testanalysen.

ZUSAMMENFASSUNG

Es wurden die Schiffschen Basen aus Äthylendiamin und *o*-Aminoacetophenon bzw. *o*-Aminobenzophenon dargestellt und die Komplexbildung dieser Liganden mit Kupfer, Nickel, Kobalt, Eisen, Palladium und Platin untersucht. Die Verwendung der Liganden zur photometrischen Metallanalyse wurde geprüft und ein Verfahren zur Bestimmung von Nickel mit N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin ausgearbeitet.

SUMMARY

Schiff bases from ethylenediamine with *o*-aminoacetophenone or *o*-aminobenzophenone were prepared, and their chelating properties towards copper, nickel, cobalt, iron, palladium and platinum were studied. The use of the ligands for the photometric determination of metals was tested. A method for the determination of nickel with N,N'-bis(*o*-aminoacetophenone)-ethylenediimine was developed. Masking agents prevent the interference of iron and copper; a 25-fold amount of palladium and a 10-fold amount of cobalt can be tolerated.

RÉSUMÉ

On a preparé des bases de Schiff à partir d'*o*-aminoacétophénone ou d'*o*-aminobenzophénone. Une étude est effectuée sur les propriétés de leurs chélates avec cuivre, nickel, cobalt, fer, palladium et platine. La possibilité d'utiliser ces ligands pour le dosage photométrique des métaux est examinée. Une méthode de dosage du nickel avec la N,N'-bis(*o*-aminoacétophénone)-éthylènediimine est développée. Des agents de masquage permettent d'éviter les interférences du fer et du cuivre, une teneur 10 fois supérieure de cobalt et 25 fois supérieure de palladium peut être tolérée.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ÜBER DIE VERWENDUNG VON OXAZINEN IN DER ANALYTIK

I. MITTEILLUNG. NILBLAU A ZUR BESTIMMUNG VON NITRAT

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(Eingegangen den 2. Januar, 1968)

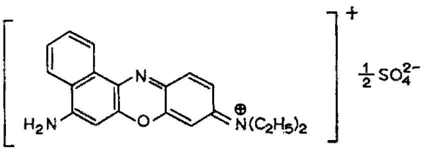
Die analytische Bedeutung von Oxazinen beschränkte sich bis vor kurzem fast ausschliesslich auf die Verwendung als pH- und Redoxindikatoren in wässrigem Medium[1-4]. Auch in wasserfreien Lösungen wie Eisessig werden Oxazine als Säure–Base Indikatoren eingesetzt[5,6]. Der Farbumschlag erfolgt hier sehr scharf. Ausführliche Untersuchungen über die Verwendung von Oxazinderivaten als acidobasische Indikatoren werden von STUŽKA *et al.*[7-9] angestellt.

Ein zweites Anwendungsgebiet dieser Stoffe liegt in ihrer Verwendung als komplexirnetrische Indikatoren. So beschreiben MILNER[10] und BARNARD *et al.*[11] die chelatometrische Titration von Gallium mit Gallocyanin.

Eine andere Möglichkeit der analytischen Verwendung von Oxazinen besteht darin, dass Farbänderungen, hervorgerufen durch ihre Reaktion mit anorganischen Ionen, photometrisch ausgewertet werden. So beschreibt EEGRIWE[12] schon 1927 das Verhalten von wässrigen Oxazinlösungen bei der Einwirkung von Antimon(V)-chlorid. Die Lösungen reagieren mit Antimon(V) unter Farbwechsel, zum Teil treten auch gefärbte Niederschläge auf.

KORENMAN *et al.*[13] berichten über die Reaktion von Indium mit dem Oxazinfarbstoff Gallocyanin und MILNER[10] über die von Gallium mit demselben Farbstoff. SKAAR[14] untersuchte 8 Oxazinderivate auf ihre Fähigkeit mit Bortetrafluoridion extrahierbare Komplexe zu bilden. Brillantkresylblau, Capriblau und Nilblau bilden solche Komplexe und können als empfindliche photometrische Reagenzien für Bor verwendet werden. GAGLIARDI UND WOLF[15] fanden in Nilblau ein geeignetes Reagens zur Bestimmung von Bor und Tantal.

Bei dem von uns untersuchten Oxazinderivat handelt es sich um Nilblau A der Struktur:



Der Farbstoff ist in Wasser gut löslich und wird von einigen organischen Lösungsmitteln wie Benzol, Chlorbenzol, *o*-Dichlorbenzol und *n*-Butylacetat nur geringfügig extrahiert. Enthält die wässrige Phase jedoch Nitrat, so nimmt die Extrahierbarkeit des Farbstoffes zu. Die Zunahme der Farbintensität in der organischen Phase ist der

Nitratkonzentration in der wässrigen Lösung proportional. Dies kann zwanglos durch das Massenwirkungsgesetz gedeutet werden. Nilblausulfat dissoziiert in weit stärkerem Masse als Nilblaunitrat. Nur der Bruchteil des undissoziiert gelösten Farbsalzes wird in das organische Lösungsmittel extrahiert. Dieser Anteil wächst zwangsläufig mit Erhöhung der Nitratmenge in der wässrigen Phase. Farbgebende Komponente ist das Farbstoffkation. Quantitative Messungen haben diese Annahme bestätigt und wurden zu einer Nitratbestimmung ausgearbeitet.

EXPERIMENTELLES

Apparate

Die Absorptionskurven wurden mit einem Perkin-Elmer Spektralphotometer 137 UV aufgenommen. Die Einzelmessungen erfolgten mit einem Zeiss Spektralphotometer PMQ II in 1-cm Glasküvetten.

Reagenzien

Nile blue A (G.F. Smith Chemical Co., Columbus, Ohio). Schwefelsäure, Quecksilber(II)-acetat, Thallium(I)-acetat, Salpetersäure, Methanol, p.A. Merck. 1,2-Dichlorbenzol purum (Fluka), wurde durch Destillation gereinigt.

Standardlösungen

Quecksilberschwefelsäure. 6.35 g Quecksilber(II)-acetat werden in 200 ml 1 *N* Schwefelsäure unter Rühren gelöst und mit Wasser auf 1 l aufgefüllt; die Lösung ist nun 0.2 *N* an Schwefelsäure und enthält 4 mg Quecksilber(II)/ml.

Thalliumstammlösung. 28.5 g Thallium(I)-acetat werden mit Wasser zu 1 l gelöst; die Stammlösung enthält 20 mg Thallium(I)/ml. Zur Aufstellung der Eichgeraden wird Salpetersäure so verdünnt, dass pro ml 10 μg Nitrat enthalten sind.

Einfluss der Reaktionsbedingungen

Um die günstigsten Bedingungen für die Nitratbestimmung festzustellen wurde die Absorptionskurve des Farbsalzes in 1,2 Dichlorbenzol–Methanol (Fig. 1) aufgenommen und die Abhängigkeit der Extraktion von der Acidität und der Farbstoffkonzentration der wässrigen Lösung untersucht.

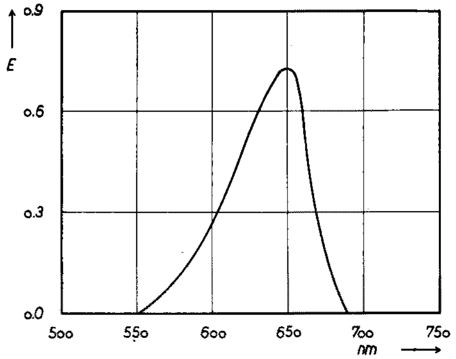
In einem 50-ml Messkolben wurden 25 ml verschieden normaler Schwefelsäure, 5 ml 0.02 %-ige wässrige Nilblaulösung und 200 μg Nitrat vorgelegt und mit Wasser bis zur Marke aufgefüllt, in einen Schütteltrichter überführt und dreimal mit je 5 ml 1,2-Dichlorbenzol extrahiert; die organischen Extrakte in einem 25-ml Messkolben gesammelt und mit Methanol bis zur Marke aufgefüllt. Die Extinktion wurde bei 650 nm in 1-cm Küvetten gegen den jeweiligen Blindwert gemessen.

Der Einfluss der Farbstoffmenge auf die Extinktionswerte wurde unter den gleichen Arbeitsbedingungen wie zuvor ermittelt, jedoch wurde die Normalität der wässrigen Phase mit 0.1 eingehalten und nunmehr die zugesetzte Farbstoffmenge variiert (Fig. 2).

Arbeitsvorschrift

In einem 50-ml Messkolben werden 25 ml 0.2 *N* Schwefelsäure, 5 ml 0.02 %-ige wässrige Nilblaulösung und die schwach saure, nitrathaltige Probe (0–250 μg NO_3^-)

gebracht und mit Wasser bis zur Marke aufgefüllt. Man überführt in einen Schütteltrichter und extrahiert dreimal mit je 5 ml 1,2-Dichlorbenzol. Die organischen Extrakte sammelt man in einem 25-ml Messkolben und füllt mit Methanol bis zur Marke auf. Die Extinktion wird in 1-cm Glasküvetten bei 650 nm gegen einen analog hergestellten Blindwert gemessen.



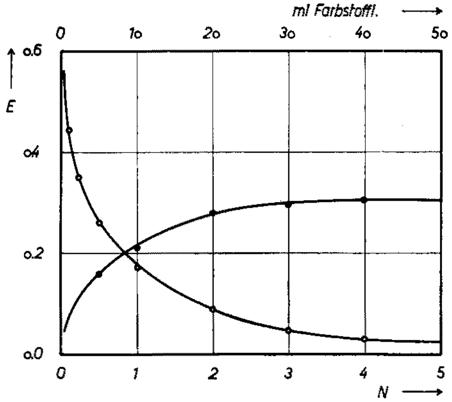


Fig. 1. Lichtabsorption von Nilblausulfat in 1,2-Dichlorbenzol–Methanol.

Fig. 2. Abhängigkeit der Nitratbestimmung von der Säurenormalität (○) und der Farbstoffmenge (●).

Die Empfindlichkeit der Methode beträgt 0.02 $\mu g\ NO_3^-\ ml^{-1}.cm$ bei einer Extinktion von 0.001, der molare dekadische Extinktionskoeffizient $\varepsilon_{650} = 3100$ $l.mol^{-1}.\ cm^{-1}$.

Störeinflüsse

Die Halogenide Fluorid, Chlorid, Bromid und Jodid stören die Nitratbestimmung. Bei Anwesenheit dieser Ionen nimmt die Extrahierbarkeit des Farbstoffes in die organische Phase stark zu. Bei der angegebenen Arbeitsvorschrift ist eine Menge von 10 mg Fluorid noch ohne Einfluss auf die Extinktion, während Jodid empfindlicher zu erfassen ist als Nitrat. Der Störeinfluss steigt in der Reihe F^-, Cl^-, Br^-, J^-. Durch Zugabe von Quecksilber(II)-salzen bilden sich die kaum dissoziierten Hg(II)-halogenide und eine Störung der Nitratbestimmung wird vermieden. Bei Verwendung der unter *Standardlösungen* beschriebenen "Quecksilberschwefelsäure", anstelle der in der *Arbeitsvorschrift* angegebenen 0.2 N Schwefelsäure, bleiben Mengen von 5 mg Chlorid, 10 mg Bromid beziehungsweise 20 mg Jodid ohne Einfluss auf die Extinktion. Grössere Mengen an Halogeniden sind vorher durch Fällung mit Thallium(I)-acetat abzutrennen. Da die Löslichkeit von Thalliumchlorid recht beträchtlich ist ($pK_L = 3.8$), verwendet man auch in diesem Fall "Quecksilberschwefelsäure".

Starke Oxydationsmittel wie Chromat, Permanganat, Chlorat und Reduktionsmittel wie Sulfid und Nitrit beeinflussen die Nitratbestimmung ebenfalls durch ihre Reaktion mit dem Farbstoff. Der Einfluss von Nitrit wird vermieden, indem man die Lösung mit Natriumazid versetzt.

Keinen Störeinfluss bewirken die in natürlichen Wässern vorkommenden

Anionen Borat, Phosphat, Silikat, Sulfat und das zur Maskierung der Halogenide zugesetzte Quecksilber(II)-acetat. Kationen wie Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+} und Cu^{2+}, die ebenfalls in Mineralwässern enthalten sind, bleiben ohne Einfluss.

BESTIMMUNG VON NITRAT IN MINERALWASSER

Wässer mit einem Gehalt von weniger als 5 mg Nitrat/kg

Man wiegt eine ausreichende Menge der Probe ein und versetzt bis zur schwach sauren Reaktion mit Schwefelsäure um die Kohlensäure zu vertreiben. Anschliessend engt man ein und fällt nach dem Erkalten mit der Thalliumacetatlösung die Halogenide. Nun filtriert man in einen Messkolben und entnimmt einen aliquoten Teil. Die Bestimmung erfolgt nach der angegebenen Arbeitsvorschrift unter Verwendung von "Quecksilberschwefelsäure".

Wässer mit einem Gehalt von mehr als 5 mg Nitrat/kg

5–15 g der Probe werden mit Schwefelsäure bis zur schwach sauren Reaktion versetzt, die Kohlensäure durch Erwärmen vertrieben und in einen 50-ml Messkolben filtriert. Um eine Störung durch Halogenide zu vermeiden, wird wiederum "Quecksilberschwefelsäure" verwendet. Die Messungen erfolgen jeweils gegen den analog hergestellten Blindwert in 1- oder 5-cm Küvetten bei 650 nm. Vergleichsweise wurde der Nitratgehalt von 4 Mineralwässern auch nach der Brucinmethode bestimmt. Es ergab sich befriedigende Übereinstimmung. Die Genauigkeit der Methode wird in Tabelle I aufgezeigt.

TABELLE I

GENAUIGKEIT DER NITRATBESTIMMUNG MIT NILBLAU A

Wasser	*Störende Begleitionen (mg/kg)*			*Brucinmethode (mg NO_3^-/kg)*	*Nilblaumethode (mg NO_3^-/kg)*	*N*[a]	*s*[b] *(mg)*	*V*[c] *(%)*
	Cl^-	*Br^-*	*I^-*					
A	280	0.5	0.2	0.160	0.173	8	0.011	6.3
B	290	2.5	0.1	0.985	1.10	8	0.05	4.5
C	300	1.5	0.2	4.22	4.32	5	0.10	4.3
D	515	1.1	0.3	12.20	12.30	5	0.47	3.8

[a] N = Anzahl der Bestimmungen.
[b] s = Standardabweichung
[c] V = Varianz.

ZUSAMMENFASSUNG

Eine Bestimmung von Nitrat mit dem Oxazinfarbstoff Nilblau A wird beschrieben. Das Farbsalz wird in 1,2-Dichlorbenzol extrahiert und spektralphotometrisch ausgewertet. Störungen der Bestimmung durch Halogenide werden durch Zusatz von Quecksilber(II)-salzen ausgeschaltet. Die Empfindlichkeit und Genauigkeit der Methode werden angegeben. Vergleichsweise Bestimmung von Nitrat nach der Brucinmethode ergab befriedigende Übereinstimmung. Das Verfahren ist zur Nitratbestimmung in natürlichen Wässern geeignet.

SUMMARY

The determination of nitrate with the oxazine dyestuff Nile Blue A is described. The dye salt is extracted into 1,2-dichlorobenzene and measured spectrophotometrically. Halide interference is prevented by addition of mercury(II) sulphate. The sensitivity and precision of the method are discussed. Good agreement is found with results obtained by the brucine method. Nitrate can be determined in natural waters.

RÉSUMÉ

On décrit un dosage de nitrate à l'aide d'un colorant oxazine Bleu Nil A. Le sel colorant est extrait dans le dichloro-1,2-benzène et dosé par spectrophotométrie. L'interférence due aux halogènes est évitée par addition de sulfate de mercure(II). On discute de la sensibilité et de la précision de la méthode. Les résultats correspondent bien à ceux obtenus à l'aide de la brucine. Les nitrates peuvent être ainsi dosés dans les eaux naturelles.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
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ETUDE PAR THERMOGRAVIMETRIE, ANALYSE THERMIQUE DIFFERENTIELLE ET SPECTROGRAPHIE D'ABSORPTION INFRA-ROUGE DE LA REACTION DU PEROXYDE DE SODIUM SUR L'OXYDE DE BERYLLIUM

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(Reçu le 2 février, 1968)

A l'état solide, les béryllates minéraux sont peu connus. L'hydroxyde de béryllium se dissout bien dans les solutions concentrées de soude ou de potasse en formant les espèces $Na[BeO_2H] \cdot H_2O$ et K_2BeO_2 [1]. Il est reconnu, par contre, que ni les carbonates ni les hydroxydes de sodium ou de potassium n'agissent sur l'oxyde[1]. A température élevée, celui-ci est attaqué par l'oxyde de sodium en donnant Na_6BeO_4 [2]. De leur côté, PRASAD ET SRIVASTAVA[3] ont préparé les béryllates de magnésium, calcium, strontium, baryum, zinc, cobalt et nickel à haute température en le calcinant avec les oxydes correspondants. Après séparation, ils ont analysé des composés répondant aux formules dualistiques: $M(II)O \cdot 3$ BeO, 2 $MO \cdot 3$ BeO et $MO \cdot BeO$. RAFTER[4] a suivi, par analyse thermique différentielle, l'attaque du béryl par le peroxyde de sodium à partir de 283°. Le produit formé était formulé Na_2BeO_2.

Nous avons voulu reprendre la question en étudiant l'action du peroxyde de sodium, Na_2O_2, sur l'oxyde de béryllium, BeO, à l'aide de la thermogravimétrie, de l'analyse thermique différentielle et de la spectrographie d'absorption infra-rouge. Nous avons rappelé récemment[5] que le peroxyde de sodium commercial contenait du superoxyde, NaO_2. Au cours du travail présent, nous avons utilisé deux échantillons de peroxyde Prolabo R.P., de dates de fabrication différentes. L'un contenait 13% de superoxyde (échantillon A) et l'autre 4.5% (échantillon B). Seul ce dernier a été employé pour les dosages.

L'oxyde de béryllium a été préparé par chauffage à 500° de l'hydroxyde $Be(OH)_2$ β selon l'étude de DUPUIS[6]. Il a été lui-même obtenu par barbotage d'un lent courant d'air chargé d'ammoniac dans une solution de nitrate ou de sulfate de béryllium[7].

TECHNIQUES EXPÉRIMENTALES ET CONDITIONS OPÉRATOIRES

Thermogravimétrie

De 100 à 200 mg de produits à l'état de poudres ont été mélangés et chauffés dans le four de thermobalances A.D.A.M.E.L. à enregistrement électronique, dans l'air ou sous circulation d'azote. L'échauffement a été de 300° par heure. Les creusets étaient en aluminite.

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Analyse thermique différentielle

Le micro-analyseur thermique différentiel du type Mazières, commercialisé par Bureau de Liaison, et équipé avec une sonde et des creusets de platine a servi à chauffer de 0.2 à 0.4 mg au maximum de substance dans l'air ou l'azote. La température montait à 300–350° en 1.5–2 h. Jusqu'à 450°, le platine n'est pas attaqué.

Analyse gazométrique

L'oxygène actif résiduel contenu dans les mélanges chauffés a été dosé par gazométrie après décomposition catalytique par un sel cuivrique dans des conditions identiques à celles qui ont été décrites précédemment[5].

Spectrographie d'absorption infra-rouge

Les spectres d'absorption infra-rouge ont été enregistrés à l'aide d'un spectrographe Beckman IR 12. Les cuves étaient constituées par des lamelles de CsBr transparentes entre 300 et 650 cm^{-1} (de 33 à 15 μ) ou de NaCl (entre 650 et 4000 cm^{-1} ou de 15 à 2.5 μ). Quelques parcelles du résidu de chauffage aussi finement broyées que possible étaient disposées entre les lamelles, à sec ou mêlées de vaseline ou d'hexachlorobutadiène, suivant le domaine spectral exploré. Les cuves ont été souvent préparées dans une enceinte asséchée à l'anhydride phosphorique et débarrassée de l'anhydride carbonique par de la chaux sodée et de l'Ascarite.

RÉSULTATS DE L'ÉTUDE THERMOGRAVIMÉTRIQUE ET DE L'ANALYSE THERMIQUE DIFFÉRENTIELLE

Réaction Na_2O_2 (échantillon A) + BeO, dans la proportion 1/1 ou 2/1

La courbe thermogravimétrique (Fig. 1, courbe IIa) enregistrée au cours du chauffage dans l'air se confond pratiquement jusque vers 200° avec celle du peroxyde non mélangé (Fig. 1, courbe Ia). Au-dessous de 130°, tous les pics d'ATD (courbe IIb) sont attribués à la seule décomposition d'hydrates ou de peroxydrates du peroxyde de sodium ou encore de percarbonates[5]. Ils n'ont pas été représentés sur les Figs. et nous n'y ferons plus allusion au cours de cet exposé. Entre 130 et 200°, se dessine (courbe IIb) un phénomène exothermique complexe de maximum situé à 180°. Il est sectionné à 166° par un pic endothermique d'assez faible intensité qui serait dû à la transformation habituelle du superoxyde de sodium en une solution solide, $Na_2O_{3.6}$[8]. Le poids varie extrêmement peu entre 200 et 300°: la décomposition habituelle de $Na_2O_{3.6}$ en peroxyde ne doit pas se réaliser. L'absence de pic endothermique correspondant vers 282° (voir courbe I b) en est une autre preuve, tout au moins dans le cas du mélange équimoléculaire. C'est dire que $Na_2O_{3.6}$ doit réagir avec l'oxyde de béryllium au-dessous de 200°, sans dégagement appréciable d'oxygène.

La soude provenant principalement d'une hydrolyse partielle du peroxyde de sodium fond normalement à 290°. Une perte de poids assez rapide se produit ensuite entre 330 et 400–430°. Après un certain ralentissement, elle reprend à partir de 490°. Un pic exothermique très intense entre 330 et 372° est encadré d'un côté par un crochet et une dépression endothermiques respectivement à 303 et 326° et de l'autre par un pic exothermique moins développé de 372 à 400° environ. Plusieurs réactions peuvent se produire, avec une certaine simultanéité: décomposition de la substance formée entre 130 et 180°, du peroxyde en excédent (on sait qu'elle doit être endothermique), d'une certaine quantité de soude (même signe thermique), formation de béryllate de sodium par exemple.

Notons que la réaction décelée entre 326 et 372° est trop fortement exothermique pour correspondre à la décomposition de peroxyde de béryllium. WILCOX ET BROMLEY[9] ont en effet estimé à +142 kcal la chaleur de formation de cette substance encore hypothétique, à partir de ses éléments, dans les conditions standards. Elle serait ainsi fort voisine de celle de l'oxyde de béryllium (de +136 à +145 kcal selon les auteurs[1]).

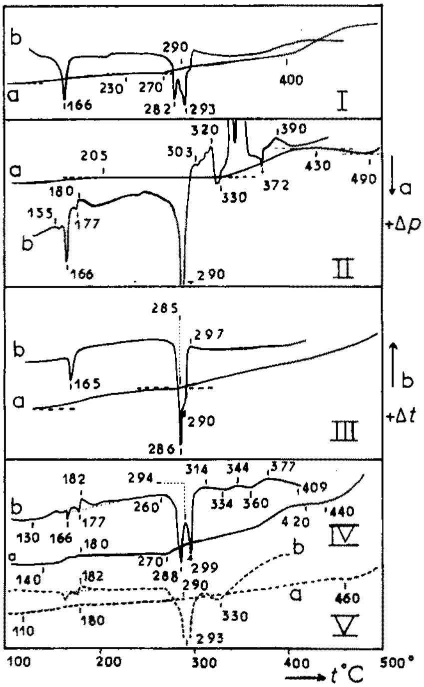

Fig. 1. Courbes de thermogravimétrie (a) et d'analyse thermique différentielle (b) de: (I) Na_2O_2 échantillon A, (II) Na_2O_2 échantillon A + BeO, (III) Na_2O_2 échantillon B, (IV) Na_2O_2 échantillon B + BeO, (V) Na_2O_2 B soumis à un préchauffage + BeO.

Réaction 1 ou 2 Na_2O_2+BeO (échantillon B) (Fig. 1, courbes IV a et IV b)

Entre 130 et 180°, le mélange perd plus de poids que le peroxyde seul (courbe III a), puis il semble y avoir stabilisation jusque 215°. Ensuite, une nouvelle diminution s'amorce; elle augmente d'importance à partir de 260–270°. Vers 450°, on observe un ralentissement sur quelques dizaines de degrés. A partir de 630–650°, le poids ne varie plus jusqu'au début de la décomposition du carbonate de sodium (850°).

Au-dessous de 270°, la courbe d'analyse thermique différentielle (courbe IV b) montre les mêmes phénomènes que pour les mélanges plus riches en superoxyde (courbe II b). A cette température, commence un pic endothermique de maximum situé à 299 ou 308° suivant les expériences. Il est coupé par le pic de fusion de la soude vers 285–290° et se termine à 310–320°. Une dépression endothermique d'assez faible intensité le suit, puis un pic exothermique jusqu'à 410–430°.

On observe des courbes absolument semblables lorsque l'échantillon A de peroxyde de sodium ne contient plus que quelques % de superoxyde, après avoir séjourné quelques mois à la température ordinaire.

Réaction Na_2O_2 (B) + BeO, après préchauffage de Na_2O_2 sous azote (Fig. 1, courbes V a et V b)

Au cours de quelques expériences, le superoxyde a été détruit par chauffage du peroxyde dans l'azote jusqu'à 305–308°. Après refroidissement, on a ajouté rapidement de l'oxyde de béryllium, en quantité calculée, puis le mélange a été soumis à une nouvelle chauffe dans l'air.

De 135 à 180°, la perte de poids est plus faible que précédemment (courbe IV a). La partie de la courbe d'ATD située entre 165 et 175° environ est dans le prolongement de la ligne de base de l'ensemble du pic exothermique; il ne semble pas y avoir de dégagement de chaleur sensible dans cet intervalle d'une dizaine de degrés. Le pic endothermique de 270–304° est absent. Il semble donc que les réactions dues au superoxyde, ou à ses sous-produits, et à l'oxyde de béryllium se produisent surtout entre 165 et 175° d'une part, et 270 et 304° d'autre part.

RÉSULTATS DES DOSAGES GAZOMÉTRIQUES ET GRAVIMÉTRIQUES

La méthode gazométrique utilisée pour doser l'oxygène actif est analogue à celle de SEYB ET KLEINBERG[10]. Les résultats sont donnés en nombres d'équivalents-grammes (n) d'oxygène actif contenus dans les résidus de chauffage à l'air de 100 g de peroxyde de sodium (B) primitivement mélangés à 16 g d'oxyde de béryllium (soit $n_{1/1}$) ou à 32 g (soit $n_{2/1}$). Ils sont comparés aux résultats des dosages du même échantillon de peroxyde chauffé seul ($n_{1/0}$), pour compenser en première approximation les effets d'hydrolyse et de carbonatation (voir Tableaux I et II).

On a également essayé de doser la quantité d'oxyde de béryllium attaquée au cours du chauffage, après reprise par l'eau. Les gravimétries classiques à l'oxinate

TABLEAU I

RÉSULTATS DES DOSAGES GAZOMÉTRIQUES ET GRAVIMÉTRIQUES DES RÉSIDUS DE CHAUFFAGE DES MÉLANGES DE 2 MOLES DE PEROXYDE DE SODIUM ET D'UNE D'OXYDE DE BÉRYLLIUM

t (°)	$n_{1/0}$	$n_{2/1}$	*% BeO total attaqué*	*% BeO attaqué au chauffage*	$\Delta n_{\text{grav.}}$ *calculé*	$n_{1/0}-n_{2/1}$	*Ecart*	*% BeO*	
								Be(II)	*Autre composé*
20	2.62	2.62	12.9	0	0	0	0	0	0
130	2.50	2.52				−0.02		0	0
167	2.37	2.29	19.3	6.4	0.08	0.08	0	6.4	0
180	2.33	2.21	29.0	16.1	0.20	0.12	0.08	9.5	6.6
210	2.24	2.08	29.5	16.6	0.21	0.16	0.05	10	6.6
260	2.07	1.92	30	17.0	0.22	0.15	0.07	10.4	6.6
280	2.00	1.84				0.16	0.07	10.4	6.6
300	1.92	1.61	31	18	0.23	0.31	−0.08		
320	1.84	1.58	33	20	0.26	0.26	0	20	0
340	1.72	1.48	33	20	0.26	0.24	0.02	20	0
400	1.40	0.77	54.5	41.6	0.53	0.63	−0.10	41.6	0
570	0	0	58	45	0.58			45	0

TABLEAU II

RÉSULTATS DES DOSAGES GAZOMÉTRIQUES ET GRAVIMÉTRIQUES DES RÉSIDUS DE CHAUFFAGE DE MÉLANGES D'UNE MOLE DE PEROXYDE DE SODIUM ET D'UNE MOLE D'OXYDE DE BÉRYLLIUM

t (°)	$n_{1/0}$	$n_{1/1}$	*% BeO total attaqué*	*% BeO attaqué au chauffage*	*$\Delta n_{grav.}$ calculé*	$n_{1/0}-n_{1/1}$	*Ecart*	*% BeO*	
								Be(II)	*Autre composé*
20	2.62	2.62	9	0	0	0	0	0	0
130	2.50	2.50	9	0	0	0	0	0	0
167	2.37	2.19	16	7	0.18	0.18	0	7	0
175	2.35	2.17	17.9	8.9	0.23	0.18	0.05	7	1.9
180	2.33	2.16	18.0	9.0	0.23	0.17	0.06	6.7	2.3
260	2.07	1.88	20.5	9.7	0.29	0.19	0.10	7.2	2.5
300	1.92	1.62	21.6	12.6	0.32	0.30	0.02	11.9	0.7
350	1.72	1.39	22.5	13.5	0.34	0.33	0.01	12.9	0
400	1.40	0.90	30.5	21.5	0.55	0.50	−0.05	21.5	

ou au pyrophosphate ammoniacobéryllien n'ont pas donné de résultats reproductibles: il semble qu'une partie au moins du béryllium dissous soit dissimulée à ces réactifs. Cette propriété cesse par ébullition prolongée de la solution mais fait courir le risque d'une hydrolyse. Notons qu'une telle dissimulation des ions Be^{2+} n'existe pas en présence d'eau oxygénée. Il a fallu se contenter de peser le résidu d'oxyde de béryllium non attaqué, après filtration, sur creuset de porcelaine et séchage. Par le même procédé, on a constaté que la reprise par l'eau du mélange faisait passer en solution une certaine quantité de béryllium, avant tout chauffage. A partir de ces derniers résultats, on a calculé la perte d'oxygène actif ($\Delta n_{grav.}$) que devrait provoquer la production d'un béryllate de sodium du type Na_2BeO_2 et l'on a comparé les valeurs ainsi trouvées aux quantités expérimentales $n_{1/0}-n_{x/1}$ représentant l'oxygène dégagé par action du peroxyde sur l'oxyde de béryllium à une température déterminée.

Essayons maintenant d'interpréter les résultats consignés dans les Tableaux I et II, en particulier pour le mélange 2 Na_2O_2 + 1 BeO.

Jusqu'à 130°, seuls les effects consécutifs à la pollution par l'air semblent se produire, en accord avec la thermogravimétrie et l'analyse thermique.

Entre 130 et 167°, 6.4% de BeO sont attaqués. Cent grammes de peroxyde chauffés avec 16 g de BeO perdent 0.23 équivalent-gramme d'oxygène. La diminution correspondante de $n_{1/0}$ est de 0.13. La différence, soit 0.08, équivaut exactement à l'attaque des 6.4% d'oxyde de béryllium (résultat fourni par la gravimétrie), dans la mesure où l'on suppose qu'il se forme exclusivement un béryllate du type Na_2BeO_2.

Entre 167 et 180°, le peroxyde seul perd 0.04 équivalent-gramme et le mélange 2/1, le double. L'écart est trop faible pour correspondre à l'attaque des 9.7% (dosés) d'oxyde métallique. Il devrait être égal à 0.12.

On peut envisager la formation d'un béryllate plus "acide" que Na_2BeO_2. Les valeurs trouvées grâce à la gazométrie s'accorderaient avec la formation de l'espèce $Na_2O \cdot 3$ BeO (ou $Na_2Be_3O_4$ ou $Na_2BeO_2 \cdot 2$ BeO) analogue aux béryllates M(II)O·3 BeO de PRASAD ET SRIVASTAVA[3].

L'examen des courbes thermogravimétriques et d'analyse thermique différentielle nous a laissé prévoir la formation possible, entre 130 et 180°, de substances oxygénées. Par conséquent, l'écart de 0.08 équivalent-gramme trouvé entre les valeurs gazométriques et gravimétriques peut s'expliquer par la production de perbéryllate ou de peroxyde de béryllium (6.6% comptés en BeO), à côté de béryllate tel que $Na_2O \cdot BeO$ (3.1% de BeO), pour l'intervalle de températures 167–180°. Grâce au Tableau II, il est possible de le restreindre encore à une dizaine de degrés: de 167 à 175° environ. Les dosages gravimétriques montreront plus loin qu'il se forme, entre 340 et 400° du béryllate par la seule entremise du peroxyde de sodium *avec dégagement de chaleur.* Donc l'ensemble du pic exothermique qui s'étale entre 130 et 180° doit être attribué à la formation de béryllate, tandis que celle du composé plus oxygéné est limitée entre les deux dépressions de 166 et de 177° (courbe IV b). Elle est également exothermique. Le phénomène a une plus grande intensité dans le cas de mélanges plus riches en superoxyde de sodium (courbe II b).

Jusqu'à présent, les essais destinés à préparer un peroxyde de béryllium semblent avoir échoué[1], soit par action de l'oxygène sous pression sur BeO, soit par action de l'eau oxygénée sur les diméthyl et diéthylbéryllium[11]. Par contre, KOMAROWSKI[12] a obtenu le composé $2\ BeO_2 \cdot 3\ BeO \cdot 8.5\ H_2O$ à partir du carbonate basique. VOL'NOV[13] a identifié, dans le système $Be(OH)_2$–H_2O_2–H_2O, des composés tels que $3\ Be(OH)_2 \cdot 4\ H_2O_2 \cdot 5\ H_2O$ et $n\ BeO_2 \cdot n'\ BeO \cdot n''H_2O$. De son côté, HAAS[14] a isolé un hydroperoxyde de béryllium, $3\ BeO \cdot 4\ H_2O_2 \cdot 8\ H_2O$, à partir de l'hydroxyde.

De 180 à 280°, le mélange $2\ Na_2O_2 + 1\ BeO$ perd 0.04 équivalent-gramme de plus que l'essai témoin. Il se forme encore du béryllate (1% compté en BeO). La perte théorique est de 0.03.

De 280 à 320°, le peroxyde de sodium chauffé en perd 0.16, le mélange 0.26. La différence est trop grande pour correspondre à la seule attaque de 2% de BeO (théoriquement 0.03). La substance peroxydée, formée à plus basse température, peut en libérer 0.08 précisément en se décomposant.

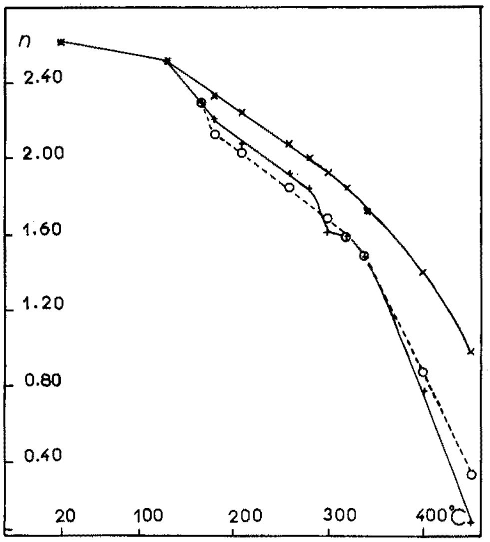

Fig. 2. Nombres d'équivalents-grammes d'oxygène actif dans le résidu de chauffage de 100 g de peroxyde de sodium (B) en fonction de la température: (×) dosages gazométriques pour Na_2O_2 seul, (+) dosages gazométriques des mélanges $2\ Na_2O_2 + BeO$, (○) détermination par calcul à partir de $n_{1/0}$ et des dosages gravimétriques.

De 320 à 340°, il ne se produit pratiquement rien, en dehors du début de la décomposition de la soude.

De 340 à 400°, 21.6% de BeO sont attaqués ($\Delta n_{\text{grav.}} = 0.27$ équivalent-gramme). Le mélange en perd effectivement 0.71. Si l'on tient compte de l'essai-témoin (0.32), cela montre qu'une partie du peroxyde de sodium se décompose sans réagir (0.12 équivalent au minimum). La courbe $n_{\text{grav.}}$ (Fig. 2) construite à partir des calculs passe au-dessus de la courbe gazométrique $n_{2/1}$ entièrement expérimentale.

Au-delà de 450°, la perte de poids reprend, la soude termine sa décomposition.

Nous venons de voir que le peroxyde de sodium attaquait bien l'oxyde de béryllium avec formation de béryllate. Le superoxyde contenu dans l'échantillon fait passer une petite partie de l'oxyde de béryllium à une forme peroxydée. L'ordre de grandeur de la quantité d'oxygène impliquée est compatible avec la teneur initiale en superoxyde (4.5%). La substance est soluble au moment de la reprise par l'eau du résidu de chauffage. Elle est dosable par oxydimétrie au permanganate: le mélange équimoléculaire porté à 260° puis traité à l'eau glacée et immédiatement dosé, conduit à une valeur de l'indice $n_{\text{oxyd.}}$ égale à 1.89. Celle de $n_{1/1}$ fournie par la gazométrie est de 1.88 pour la même température. Rappelons que ni le superoxyde de sodium ni les produits assimilés ne peuvent être dosés par le permanganate[15].

Ce produit est assez stable: à la sortie du four, le creuset peut être conservé dans un poudrier au réfrigérateur pendant 2 h sans perdre d'oxygène. Il est formé exclusivement par l'action de l'espèce $Na_2O_{3.6}$. Un contrôle quantitatif a été effectué après préchauffage à 300–330° avant addition d'oxyde de béryllium. Un chauffage ultérieur à 220° conduit aux résultats suivants:

$n_{2/1\,(\text{gazométrie})} = 1.89$
$n_{1/0\,(\text{gazométrie})} = 2.02$
différence = 0.13
% BeO attaqué = 23.6% au total
% BeO attaqué = 10.7% au cours du chauffage
$\Delta n_{(\text{gravimétrie})} = 0.13$ (valeur calculée).

A cause du préchauffage, il y a concordance entre les valeurs gazométrique et gravimétrique. Cela montre, que, dans de telles conditions, il ne se forme pas de composé plus oxygéné que le béryllate de sodium, l'oxyde de béryllium ou le résidu de peroxyde de sodium. La quantité de béryllate formée est du même ordre de grandeur que celle produite par le peroxyde non débarrassé de son superoxyde (soient 10%), mais ce n'est peut-être qu'une coïncidence.

Au cours d'un travail publié en 1960[16], nous avions admis la formation entre 80 et 100°, de composés peroxygénés du molybdène, du tungstène, de l'uranium et du vanadium en quantité importante, en plus des molybdate, tungstate, uranate et vanadate de sodium. Ainsi, dans le cas de l'anhydride molybdique, 42% de celui-ci étaient transformés par le peroxyde de sodium en un composé renfermant un atome d'oxygène actif par mole et 44% étaient simplement à l'état de molybdate normal. A 320°, l'oxygène actif se dégageait presque instantanément, il ne restait dans le creuset que du molybdate normal et un excès de peroxyde de sodium.

Les résultats de l'étude actuelle sont assez différents pour les raisons suivantes.

(*1*) Les échantillons de peroxyde de sodium utilisés autrefois devaient contenir peu de superoxyde: les courbes de thermolyse ne montraient en effet aucune perte de poids appréciable entre 260 et 310°.

(*2*) La forte proportion d'oxygène actif fixé sur l'oxyde métallique ne pouvait provenir, en majeure partie, que du peroxyde de sodium lui-même. Dans le cas de l'oxyde de béryllium, le produit peroxydé formé est dû exclusivement à la présence de superoxyde de sodium.

On peut se demander si, dans le mélange étudié, il existe un seul composé peroxygéné du béryllium: avec l'échantillon A, riche en superoxyde, la perte de poids ne débute pas avant 330°. Il ne peut donc pas y avoir production de béryllate avant cette température. Sur la courbe correspondante d'analyse thermique, on observe un crochet endothermique très peu intense à 303° et un pic fortement exothermique entre 330 et 360°. Avec l'échantillon A vieilli ou B, on constate l'existence d'un pic endothermique assez intense vers 300°, attribué à une perte d'oxygène actif, grâce aux dosages et un accident exothermique extrêmement faible vers 340°, qui disparaissent tous deux après préchauffage.

RÉSULTATS DE LA SPECTROGRAPHIE D'ABSORPTION INFRA-ROUGE

Nous ne connaissons pas de spectres d'absorption infra-rouge de béryllates métalliques. Par contre, les bandes de vibrations fondamentales des liaisons Be–O d'un certain nombre de composés ont été publiées:

(*1*) pour l'acétylacétonate[17,18] de symétrie T_d, à 826 cm^{-1} (ν_{as}) et 380 cm^{-1} (δ_{as}) en absorption infra-rouge, 700–746 cm^{-1} (ν_s) et 443 cm^{-1} (δ_s) en diffusion Raman,

(*2*) pour les groupements tétraédriques BeO_4 de l'oxyde de béryllium[17,19] de symétrie C_{3v}, à 960 cm^{-1} (ν_2), 885 cm^{-1} (ν_4), 735 cm^{-1} (ν_1), 695 cm^{-1} (ν_3) et 610 cm^{-1} (ν_6),

(*3*) pour les groupements $[BeO_2(H_2O)_2]^{2-}$ de l'oxalate[20] (C_{2v}), avec levée de la dégénérescence de la vibration de valence antisymétrique à 898, 830 et 812 cm^{-1},

(*4*) pour les groupements $[Be(H_2O)_4]^{2-}$ des sels minéraux hydratés de béryllium[20–22] à 856, 775 et 690 cm^{-1} (ν_{as}) et la bande de rotation gênée de l'eau à 900–975 cm^{-1} et δ_{as} à 312 cm^{-1}. Sur les spectres de diffusion du sulfate tétrahydraté cristallisé, on relève la bande δ_s à 533 cm^{-1},

(*5*) pour l'hydroxyde de béryllium, de symétrie C_1[19,23], avec ν_2 à 880 cm^{-1}, ν_6 à 826 cm^{-1}, ν_8 à 780 cm^{-1}, ν_1 à 755 cm^{-1}, ν_4 à 720–685 cm^{-1} et ν_7 à 618–580 cm^{-1}.

On sait maintenant que ni les ions peroxyde O_2^{2-} ni les ions superoxyde O_2^- alcalins et alcalino-terreux ne peuvent donner lieu à une absorption du rayonnement infra-rouge à cause de leur caractère homopolaire. GIGUÈRE[24] a estimé que la vibration de valence O–O des peroxydes ou hydroperoxydes devait se situer à 877 cm^{-1}. Or, la présence, inévitable, de la bande de déformation symétrique des carbonates dans cette région ne permet pas une attribution irréfutable, sauf dans le cas des peroxydes organiques[25]. VANNERBERG[26] est arrivé aux mêmes conclusions après avoir étudié les spectres d'absorption des hydrates et peroxydrates des peroxydes de sodium, magnésium, baryum, strontium et zinc. Dans ces conditions, l'identification d'un peroxyde de béryllium doit être illusoire, à supposer qu'une telle substance se forme dans les mélanges étudiés.

Nous avons enregistré les spectres du peroxyde de sodium commercial, de l'oxyde de béryllium, des mélanges de ces deux produits après chauffage à diverses températures dans l'air ou l'azote et, à titre de comparaison, sans chauffage préalable. Nous les avons comparés à ceux du peroxyde de baryum et des béryllates de baryum préparés à partir de l'oxyde[3] ou du peroxyde de baryum. Les bandes d'absorption sont peu intenses, les rendements des préparations étant relativement faibles. De plus, les résidus sont souillés de carbonate de sodium, de soude et, dans certains cas de percarbonates.

Spectres des béryllates de baryum (Figs. 3 et 4)

Résidus des réactions 2 BaO_2+BeO (courbes IIa et IIb de la Fig. 3). On sait que le carbonate de baryum absorbe principalement à 858 (δ_s) et 697 (δ_{as}) cm^{-1}. Après chauffage à 800°, il n'y a plus d'oxygène actif dans le résidu. La bande de 960 cm^{-1}, relevée sur les spectres des produits bruts, disparaît après lessivage à l'eau chaude et séchage. Elle doit être due à la présence d'eau captée et combinée au cours du transfert du creuset dans le caisson. Les bandes relevées à 795–807 cm^{-1}, 710 cm^{-1}, 495 cm^{-1} et 370–380 cm^{-1} subsistent au contraire. Elles se situent dans les mêmes régions d'absorption que celles des groupements BeO_4 ou $Be(H_2O)_4$ déjà mentionnés. On peut toutefois se demander si celle de nombre d'onde 710 cm^{-1} n'est pas due simplement à l'existence d'une certaine quantité d'oxyde de béryllium.

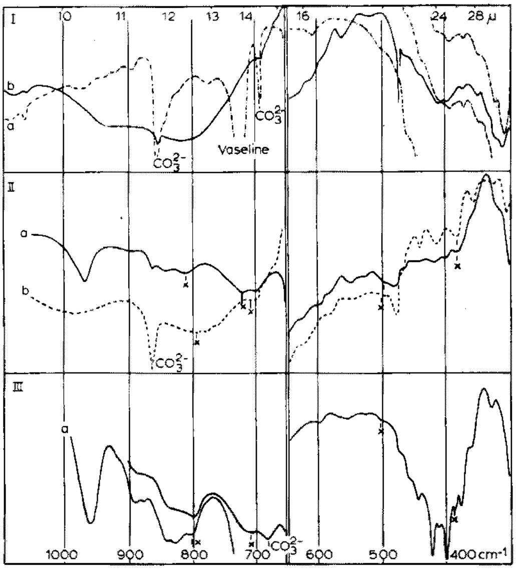

Fig. 3. Spectres d'absorption infra-rouge entre 300 et 1100 cm^{-1} de: (I a) BaO_2, (I b) BaO_2 + BeO à 20°, (II a) BaO_2 + BeO chauffé à 800°, (II b) BaO_2 + BeO chauffé à 800° et lavé à l'eau, (III) BaO_2 + BeO chauffé à 1000°.

Après chauffage à 1000°, on retrouve les mêmes bandes à 800, 700–710, 500 et 384 cm^{-1}. D'autres, à 890–878 et 825 cm^{-1} se retrouvent sur le spectre du mélange non chauffé et, de ce fait, peuvent être causées par la présence d'impuretés (courbe III de la Fig. 3).

Des bandes semblables (Fig. 4) se pointent sur les spectres des béryllates de baryum de PRASAD ET SRIVASTAVA[3]:

BaO·3 BeO	828	(730)	490	? cm^{-1}
2 BaO·3 BeO	805–838	(715)	500	388 cm^{-1}
BaO·BeO	830	(740)	492	381 cm^{-1}

Spectres des résidus de la réaction du peroxyde de sodium avec l'oxyde de béryllium (Fig. 5)

Bien que ne devant pas absorber, le peroxyde de sodium commercial présente un certain nombre de bandes d'absorption infra-rouge identiques à celles que Brame *et al.*[27] ont enregistrées. Sur la Fig. 5, sont reproduits les spectres des résidus de

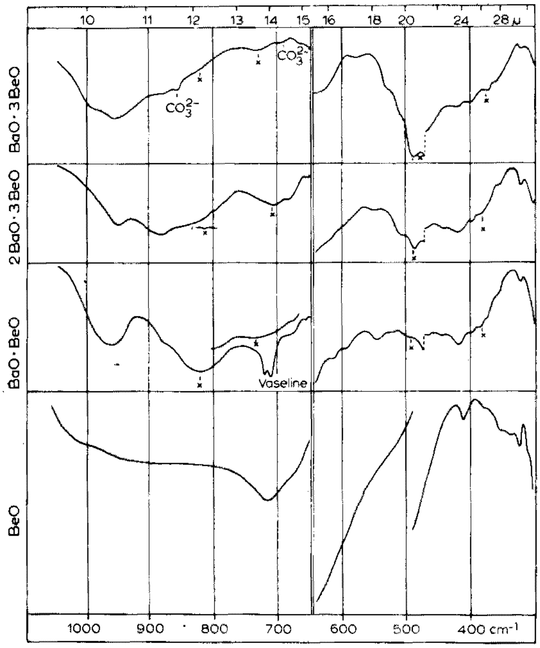

Fig. 4. Spectres d'absorption infra-rouge entre 300 et 1100 cm^{-1} de: BaO·3 BeO, 2 BaO·3 BeO et BaO·BeO obtenus par chauffage de BaO avec BeO et spectre de BeO.

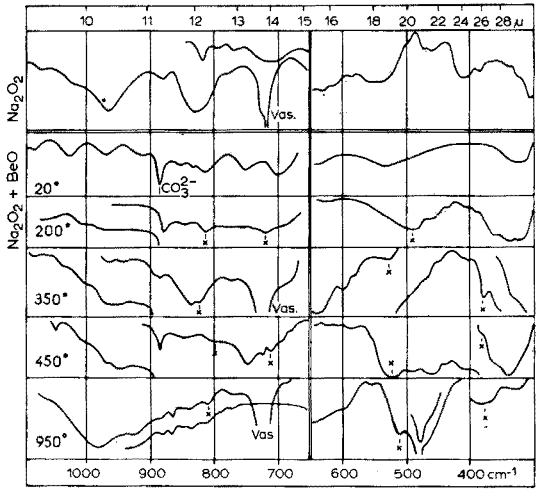

Fig. 5. Spectres d'absorption infra-rouge entre 300 et 1100 cm^{-1} de Na_2O_2, Na_2O_2 + BeO à 20°, Na_2O_2 + BeO après chauffage à 200, 350, 450 et 950°.

chauffage dans l'azote à 200, 350, 450 et 950° du peroxyde mélangé d'oxyde de béryllium. Rappelons que les bandes d'absorption du carbonate de sodium se situent vers 880 (intensité moyenne) et 695 (intensité faible) cm^{-1}.

On pointe quatre bandes vers 790–810, 710–720, 490–510 et 380–385 cm^{-1}. Elles semblent être absentes des spectres témoins. Leur nombre d'onde correspond assez bien à celui des béryllates de baryum. En outre, celle de 790–810 cm^{-1} semble être différente de la large bande pointée à 820–840 cm^{-1} sur les spectres du peroxyde de sodium et de son octohydrate. Ainsi qu'il avait été prévu, rien n'indique, sur ces spectres, l'existence d'un composé peroxygéné du béryllium, après arrêt du chauffage à 200°.

S'il devait se former un béryllate du type Na_2BeO_2, nous devrions nous attendre à trouver en absorption infra-rouge trois vibrations fondamentales, deux de valence et une de déformation, par analogie avec les spectres bien connus des nitrites, chlorites[28] et iodites[29] de structure angulaire C_{2v}, ou seulement une vibration de valence et une vibration de déformation antisymétriques dans le cas d'une molécule linéaire de symétrie $D_{\infty h}$. Or, nous pensons avoir relevé quatre bandes d'absorption qui s'apparentent à celles des liaisons Be–O de groupements tétracoordinés. L'apparition des vibrations symétriques de valence (710–720 cm^{-1}) et de déformation (490–510 cm^{-1}) traduirait une symétrie moins élevée que T_d. Les nombreuses bandes dues à la présence d'impuretés rendent douteuse une recherche plus approfondie. En s'appuyant sur les résultats obtenus par analyse chimique, on peut envisager que le béryllate de sodium formé répond peut-être à une formule du type $(Na_2O \cdot BeO)_n$.

CONCLUSION

L'impossibilité d'isoler les substances produites à diverses températures, au cours de la réaction du peroxyde de sodium sur l'oxyde de béryllium ne nous a pas permis de les caractériser définitivement. Cependant nous pensons que la confrontation des résultats de la thermogravimétrie, de l'analyse thermique différentielle et de l'analyse chimique montre bien la formation de béryllate de sodium et d'une autre substance plus riche en oxygène par la seule action de l'espèce $Na_2O_{3.6}$ contenue dans l'échantillon. Quelques expériences ont montré qu'il ne pouvait être confondu avec les composés oxygénés connus du sodium. La difficulté rencontrée jusqu'à présent pour préparer le peroxyde de béryllium en employant des agents oxydants tels que l'oxygène ou l'eau oxygénée explique que l'existence du produit obtenu ici soit due exclusivement à un composé du sodium jouissant d'un plus grand pouvoir oxydant.

RÉSUMÉ

L'étude entreprise par thermogravimétrie, analyse thermique différentielle et analyse chimique montre que le peroxyde de sodium attaque l'oxyde de béryllium avec production de béryllate, vraisemblablement dans le rapport moléculaire 1 Na_2O pour 1 BeO. Un composé peroxygéné du béryllium, non identifié, se forme vers 165° par la seule action du superoxyde de sodium contenu dans l'échantillon de peroxyde et se décompose entre 280 et 310°. La spectrographie d'absorption infra-rouge indique l'existence de liaisons Be–O du béryllate de sodium différentes de celles de l'oxyde utilisé.

SUMMARY

Thermogravimetric and differential thermal methods as well as chemical analysis show that sodium peroxide attacks beryllium oxide to form beryllate, apparently in the molecular ratio 1 Na_2O:1 BeO. An unidentified peroxy compound of beryllium is formed at about 165° by the action of the NaO_2 present in the Na_2O_2 sample; it decomposes between 280 and 310°. IR absorption spectroscopy indicates the presence of Be–O bonds in the sodium beryllate which are different from those in the oxide used.

ZUSAMMENFASSUNG

Sowohl mit thermogravimetrischen und differentialthermischen Methoden als auch mit der chemischen Analyse konnte gezeigt werden, dass Natriumperoxid Berylliumoxid angreift und Beryllat bildet, wahrscheinlich im Molverhältnis 1 Na_2O: 1 BeO. Ist NaO_2 im Na_2O_2 enthalten, so wird bei etwa 165° eine nicht identifizierte Peroxiverbindung des Berylliums gebildet, die sich zwischen 280 und 310° zersetzt. Im IR-Spektrum beobachtet man die Anwesenheit einer Be–O-Bande beim Natriumberyllat, welche sich von derjenigen im Oxid unterscheidet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NUCLEAR MAGNETIC RESONANCE STUDIES OF EDTA IN THE PRESENCE OF EXCESS CALCIUM OR STRONTIUM*

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(Received December 29th, 1967)

Metal chelates of ethylenediaminetetraacetic acid (EDTA) have received much attention and the stability constants for the formation of a large number of metal–EDTA chelates have been tabulated in numerous publications. In most of these chelates, the principal species present in aqueous solution is the one with an 1:1 metal–EDTA ratio, but some exceptions such as molybdenum do exist[1]. However, the similarity of structure between the two iminodiacetate groups of EDTA and iminodiacetic acid suggests the possibility of a less stable species containing two metal ions, each chelated by an iminodiacetate group. Such structures have been suggested[2] as intermediates in electrophilic substitution (S_E) ligand-exchange reactions

$$M_AY + M_B \rightleftarrows [M_AY\ M_B] \rightleftarrows M_A + M_BY$$

Unsymmetrical S_E ($M_A \neq M_B$) reactions involving EDTA have been studied using spectrophotometric methods[3] and polarographic techniques[4-6]. Symmetrical S_E ($M_A = M_B$) reactions have been investigated using radiochemical methods[3] and nuclear magnetic resonance techniques[2].

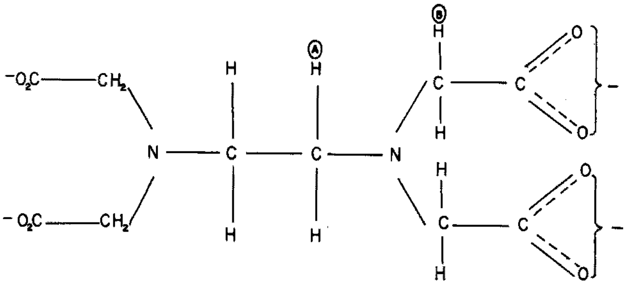

Fig. 1. Structure of ethylenediaminetetraacetic acid.

KULA *et al.*[7] have studied the nuclear magnetic resonance spectra of metal–EDTA solutions with metal-to-ligand ratios of 1:3 and 1:1. These authors state that in the case of a 1:3 calcium–EDTA mixture, a single set of sharp resonance lines is observed above pH 11.5 which is attributed to the ethylenic (A) and methylenic (B) protons which are labeled in Fig. 1. These lines broaden with decreasing pH and two sets of two resonance lines appear between pH 9.5 and 6. One set of lines is assigned

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* Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Atlanta, Georgia in November, 1967.

to the complexed ligand and the other to the free ligand. The collapse of the signal to one set of lines is said to be a result of rapid nucleophilic ligand exchange. Strontium exhibits only one set of lines over the pH range 5–13.

This report is concerned with a study of the behavior of the nuclear magnetic resonance spectrum of EDTA over a range of metal-to-ligand ratios in the region of excess metal. The chemical shifts of inert protons adjacent to an acidic or metal binding site are dependent upon changes in the electronic environment caused by protonation[8] or metal bond formation. Consequently, the chemical shift of such protons may be used as an indication of the extent of reaction of the functional sites. In this paper, the chemical shift data of the protons of EDTA as a function of calcium or strontium ion concentration are used to obtain formation constants for complexes of higher than 1:1 metal to EDTA ratios.

EXPERIMENTAL

The nuclear magnetic resonance spectra were recorded using a Varian HA-100 high-resolution spectrometer. Chemical shift measurements were made using the methyl protons of *tert.*-butanol as an internal reference. The chemical shift values reported were obtained using the usual frequency difference calibration technique and are the average of several measurements. Estimated precision is ±0.1 Hz. A sweep rate of 0.1 Hz per sec was employed and the radiofrequency power was adjusted for maximum signal-to-noise ratio. The spectra were recorded at an ambient probe temperature of 29±0.5°. The pH measurements were made at room temperature using a Leeds and Northrup model 7403 line-operated pH meter. The meter was standardized using National Bureau of Standards buffer solutions.

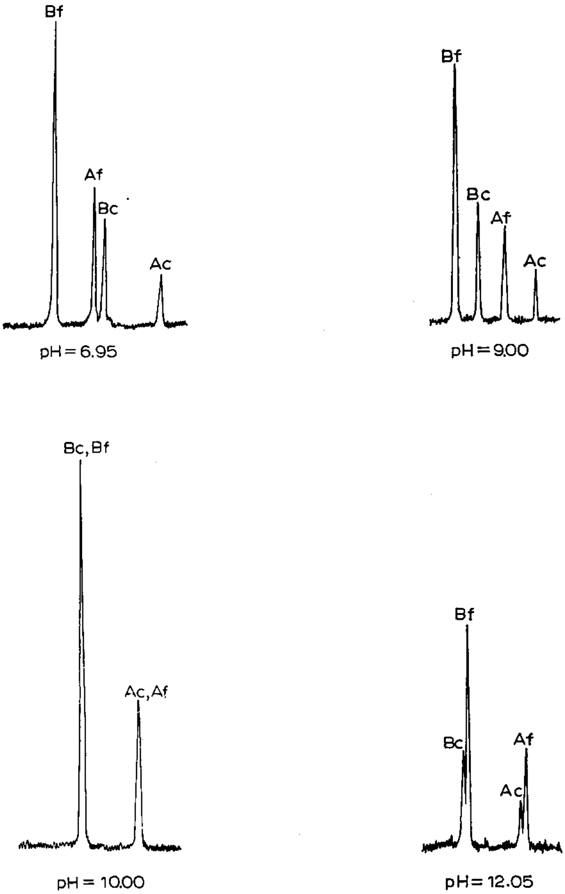
Stock solutions were prepared using reagent-grade ethylenediaminetetraacetic acid disodium salt, and the chlorides of calcium or strontium. A standard zinc chloride solution was prepared by dissolving a weighed amount of reagent-grade zinc metal in hydrochloric acid. The EDTA solutions were standardized by titrating an aliquot of the zinc chloride solution with the EDTA solution using eriochrome black T as the visual indicator. The calcium chloride and strontium chloride were subsequently standardized by titration with the EDTA stock solution.

Samples for nuclear magnetic resonance spectra were prepared by mixing predetermined volumes of the stock metal ion solution with a constant volume of the stock EDTA solution and diluting the mixture with water such that the final total ligand concentration was constant in all samples. The pH of the solution was adjusted to 12.5±0.1 with carbon dioxide-free potassium hydroxide before a final small volume adjustment was made. In order to obtain a reasonable signal-to-noise ratio, the EDTA concentration in the sample was approximately 0.2 *F*.

RESULTS AND DISCUSSION

Before discussing the species present in aqueous solutions containing calcium-to-EDTA ratios greater than 1:1, it is important to comment briefly on the structure of the 1:1 chelate. The evidence concisely summarized by GARVAN[9] indicates an octahedral structure in which EDTA is hexadentate in the solid and in solution at pH 5–10. However, the chelate undergoes proton dissociation[9] with a pK_a value of

11.39, which may be explained if one of the carboxyl groups is detached at high pH to form $[Ca(EDTA)OH]^{3-}$. These pH data correspond to the changes in the n.m.r. spectra with pH variation as shown by KULA *et al.*[7]. However, the results obtained in the present study show that the spectra of the complex and the free ligand in a 1:3 metal-to-ligand ratio do not coalesce in the high pH region when observed with a spectrometer operating at 100 MHz. Repetition of KULA's work, with a spectrometer operating at 60 MHz, gave the impression of the formation of a single spectrum in the limit of high pH. The spectra appear to coalesce at pH 10 with a 60-MHz spectrometer[7], but they only appear to overlap when a spectrometer operating at 100 MHz is used as shown in Fig. 2. Because the chemical shift ratio of the spectrum taken at 100 MHz to the one taken at 60 MHz is 100/60, an increase in the rate of ligand exchange by a factor of approximately 1.67 times the rate at which the 60-MHz spectrum coalesced would cause the 100-MHz spectrum to coalesce. This increase in rate should not be difficult to obtain. However, no variation in pH or temperature could effect a coalescence in the 100-MHz spectrum. It is concluded that the coalescence observed at 60



pH = 6.95
pH = 9.00
pH = 10.00
pH = 12.05

Fig. 2. N.M.R. spectra of 1:3 calcium to EDTA solutions at various pH values.

MHz is an overlap of the two spectra as a result of chemical shift change with pH variation. The explanation is that the chemical shift of the complex in the pH range 6–12 is essentially independent of pH, whereas the spectrum of the ligand shifts to higher field with increasing pH. This distinction is not easily made with the 60 MHz spectrometer available to Kula when his results were obtained. These results do not preclude the opinion that one of the carboxyl groups is, on the time average, detached from the calcium ion in the high pH region. Kula has proposed that in the species $H[CaEDTA]^-$ only one of the iminodiacetate groups chelates the calcium[10].

In light of the evidence presented above, the existence of a measurable concentration of a 2:1 calcium-to-EDTA chelate seems quite probable. The n.m.r. evidence[7] suggests the same conclusion for the strontium chelate. Nuclear magnetic resonance was chosen as the tool for the investigation because it permits direct observation of a physical parameter (chemical shift) which is dependent upon the electronic environment of the metal-binding sites. Other metal ions, with a few exceptions, could not be studied because of the high stability of the hexadentate chelate preventing formation of sufficient concentration of the 2:1 chelate. In still other cases, slow ligand-exchange rates or the fact that the metal ion was paramagnetic prevented use of the n.m.r. technique. The n.m.r. method has one major disadvantage in studies of the type presented in this paper. The solutions must be more concentrated than those permitted for equilibrium studies if thermodynamic values are sought. For this reason, the total concentration and pH of the solutions could not be varied over a meaningful range and the results must be interpreted as "formal" or applicable only to the conditions used.

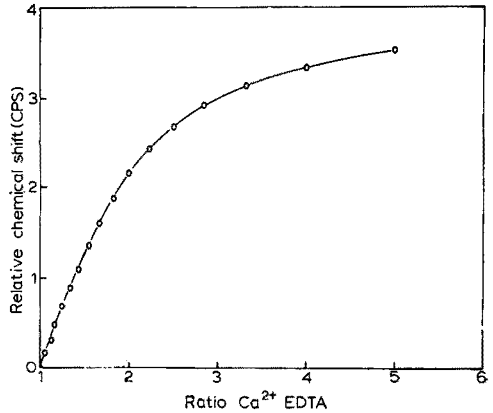


Fig. 3. Relative chemical shift of B protons *versus* the ratio of total calcium ion concentration to total EDTA concentration.

Figure 3 is a plot of the chemical shift of the methylenic protons of EDTA *versus* the ratio of total calcium ion concentration to total EDTA concentration in a solution of pH 12.5. The chemical shift values shown are relative to the 1:1 complex and are given for the coalesced spectra resulting from rapid electrophilic ligand exchange. The plot shows that the coalesced spectra of the species present in the solutions containing excess of metal ion undergo a shift to lower field with increasing calcium-to-EDTA ratio. The ethylenic protons undergo a similar, but smaller, shift and were not used.

These chemical shift changes were attributed to the formation of a complex containing a ratio of calcium-to-EDTA greater than 1:1. A structure such as that shown in Fig. 4 is proposed in which each calcium ion is chelated by one of the iminodiacetate groups in EDTA. The calcium ion is expected to be more effective in deshielding the methylenic protons in this structure than in the 1:1 complex. Such a structure is compatible with the observations given above. There are undoubtedly hydroxyl ions bonded to one or both of the calcium ions and to this extent the complete structure of the species has not been determined.

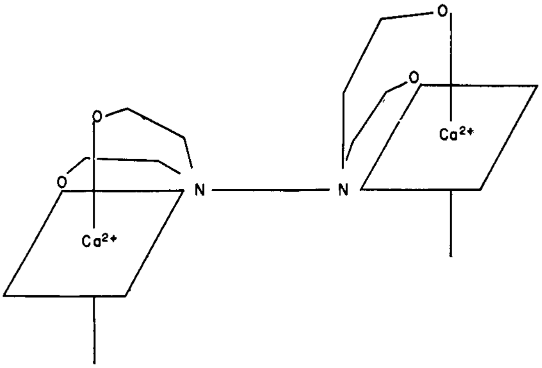


Fig. 4. Proposed structure of $Ca_2(EDTA)$.

The quantitative relationship between the observed chemical shift of a proton on the ligand and the stability constant for the complex has been derived elsewhere[11]. If the equilibria represented by eqns. (1) and (2):

$$MY + M \rightleftarrows M_2Y \qquad (1)$$

$$M_2Y + M \rightleftarrows M_3Y \qquad (2)$$

are considered, the corresponding concentration equilibrium constants are

$$K_2 = [M_2Y]/[M]\,[MY] \qquad (3)$$

$$K_3 = [M_3Y]/[M]\,[M_2Y] \qquad (4)$$

The calculated chemical shift is then given by eqn. (5)

$$\delta_{calc} = ([M_2Y]/C)\,\delta_{M_2Y} + ([M_3Y]/C)\,\delta_{M_3Y} \qquad (5)$$

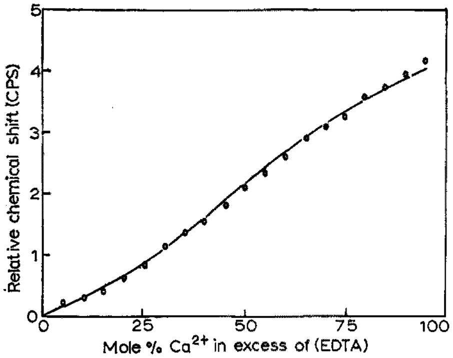
where C is the analytical concentration of MY, and $[M_2Y]$ and $[M_3Y]$ are the equilibrium concentrations of the respective species.

Each of these values is calculated with assumed values for K_2 and K_3 and the usual expressions for simultaneous equilibria. The values of δ_{M_2Y} and δ_{M_3Y} represent the chemical shift of the respective species in p.p.m. measured from the resonance of MY. Estimates were made for δ_{M_2Y} and δ_{M_3Y} with limiting values for the observed chemical shift at high metal-to-ligand ratios.

In order to compute the calculated chemical shift as a function of mole fraction of ligand, a program was written in FORTRAN and processed on an IBM 1620 digital computer. Variation were made in K_2 and K_3 until the "best" overall fit was obtained.

The function was relatively insensitive to δ_{M_2Y} and δ_{M_3Y} but quite sensitive to K_2 and K_3. This, of course is advantageous inasmuch as the choice of the chemical shift parameters was not excessively critical. A true value of the chemical shift parameter cannot be obtained unless the species can be made to be predominate, or the formation constants are previously known. The arguments for including the species M_3Y, which represents three metal ions per ligand, will be discussed later.

Figure 5 shows a plot of the relative chemical shift of the methylenic protons of EDTA *versus* the mole percent of calcium in a calcium–Ca(EDTA) mixture. The circled points are the experimental data, whereas the solid line represents the calculated curve obtained from eqn. (5). Figure 6 is a similar plot for the strontium–EDTA system. The formation constants, K_2 and K_3 which gave the best comparison between the experimental and computed chemical shift values are given in Table I.



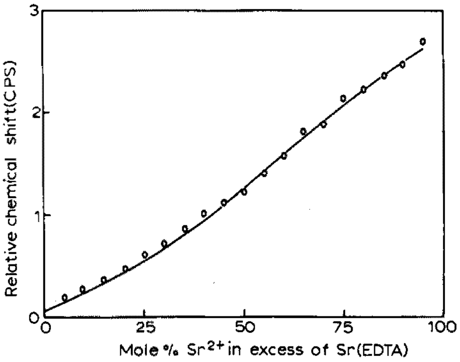


Fig. 5. Relative chemical shift of B protons *versus* mole percent calcium in a calcium–Ca(EDTA) mixture (pH 12.5).

Fig. 6. Relative chemical shift of B protons *versus* mole percent strontium in a strontium–Sr(EDTA) mixture (pH 12.5).

TABLE I

STABILITY CONSTANTS FOR CALCIUM AND STRONTIUM COMPLEXES OF EDTA

	log K_1	*log* K_2	*log* K_3
Ca	10.57[a]	1.1 ± 0.1	−0.4 ± 0.1
Sr	8.63[a]	1.0 ± 0.1	−0.4 ± 0.1

[a] L. G. Sillén and A. E. Martel, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, 1964, p. 634.

The formation constants for the 2:1 metal-to-EDTA species are relatively small as expected. The similar numerical values for K_2 for Ca_2(EDTA) and Sr_2(EDTA) are also reasonable in view of the formation constants of the iminodiacetic acid chelates with these ions. In order to obtain the best correlation between the computed curves shown in Figs. 5 and 6 and the experimental data it was necessary to include a small value represented by K_3 which is larger than the estimated error of ±0.1 for all the values given in Table I. However, there is no evidence at present to permit other than speculation about the structure of a species with a calcium-to-EDTA ratio of 3:1.

The results presented here give reasonable evidence for the existence of compounds with ratios of metal to EDTA higher than 1:1 in the cases of calcium and strontium. The stability of these species is certainly of sufficient magnitude to permit their participation in ligand-exchange reactions. Although the use of n.m.r. in studies of this type has certain limitations as discussed earlier, information such as that presented here would be difficult to obtain by other techniques.

This investigation was supported in part by Public Health Service Research Grant GM-13935 from the National Institutes of Health.

SUMMARY

The equilibria which exist between metal ions, ethylenediaminetetraacetic acid (EDTA), and the resulting chelates have been thoroughly investigated by many techniques, emphasis being placed on the study of complexes containing a 1:1 ratio of metal ion to ligand. The results presented here are concerned with the observation of the chemical shift of the nonlabile protons of EDTA when excess calcium or strontium ions are present. The results yield evidence for a 2:1 complex. Formation constants for the equilibria believed to be in effect are given and a possible structure of the 2:1 complex is discussed.

RÉSUMÉ

Les équilibres existant entre ions métalliques, acide éthylènediaminotétracétique (EDTA) et les chélates correspondants ont été examinés en détails par de nombreuses techniques. L'étude effectuée ici est basée sur la résonance nucléaire magnétique de l'EDTA en présence d'un excès de calcium et de strontium. Les résultats permettent d'admettre l'existence du complexe 2:1. On donne les constantes de formation pour l'équilibre supposé, on discute de la structure possible du complexe 2:1.

ZUSAMMENFASSUNG

Das Gleichgewicht, welches zwischen Metallionen, AeDTE und den resultierenden Chelaten besteht, ist eingehend mit verschiedenen Methoden untersucht worden. Besonders untersucht wurden die Komplexe, bei denen das Verhältnis von Metallionen zum Liganden 1:1 beträgt. Die hier angegebenen KMR-Ergebnisse beschäftigen sich mit der Beobachtung einer chemischen Verschiebung des nichtlabilen Protons von AeDTE, wenn ein Überschuss von Calcium- oder Strontium-Ionen anwesend sind. Es wird daraus auf das Vorliegen eines 2:1-Komplexes geschlossen. Es werden die Bildungskonstanten für das angenommene Gleichgewicht angegeben und eine mögliche Struktur des 2:1-Komplexes wird diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF SILICON, PHOSPHORUS AND SULFUR IN ALLOY STEEL BY NEUTRON ACTIVATION ANALYSIS

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(Received January 15th, 1968)

Neutron activation methods involving radiochemical separation are known for the estimation of silicon, phosphorus, and sulfur in a variety of matrices[1–6]. The method[7] for the determination of silicon in high-purity iron takes about 1.5 h and since the end product is not radiochemically pure it is necessary to subtract the activity due to long-lived impurities from the measured activity of silicon-31. Many workers [1,8,9] have determined sulfur by measuring the phosphorus-32 activity resulting from the reaction of ^{32}S with fast neutrons because this technique has a better sensitivity than the thermal neutron activation method and it avoids the difficulty associated with the measurements of the weak β-activity of sulfur-32. However, it is not sufficiently accurate when the ratio of P to S in the sample is large.

The present paper describes the determination of sulfur, phosphorus and silicon in alloy steels by thermal neutron activation followed by rapid radiochemical separation and measurements of sulfur-35, phosphorus-32 and silicon-31 activities. The characteristics of these nuclides are summarised in Table I.

TABLE I

THE RADIOACTIVE NUCLIDES OF SILICON, PHOSPHORUS AND SULFUR

Radio-nuclide	*Half-life*	*Radiations and energy (MeV)*	*Parent nuclide and reaction*	*%Natural abundance of parent*	*Neutron activation cross-section*
^{31}Si	2.65 h	β^-,1.47	$^{30}Si(n,\gamma)$	3.05	0.11 b
		γ, 0.17	^{31}P (n,p)	100	77 mb
		0.52	^{34}S (n,α)	4.2	140 mb
^{32}P	14.3 d	β^-,1.7	^{31}P (n,γ)	100	0.23 b
			^{32}S (n,p)	95.1	0.065 b
			$^{35}Cl(n,\alpha)$	75.4	0.05 mb
^{35}S	87.1 d	β^-,0.167	^{34}S (n,γ)	4.2	0.26 b
			^{35}Cl (n,p)	75.4	0.17 b

EXPERIMENTAL

Irradiation procedure

Samples (10–125 mg) of alloy steel in the form of fine turnings were enclosed in aluminium foils and irradiated along with standard samples of silicon (*ca.* 5 mg), ammonium dihydrogen phosphate (2 mg) and sodium sulfate (5 mg), for 2–168 h at a thermal neutron flux of $1\text{–}2 \cdot 10^{12}$n/cm^2/sec in the Apsara Reactor of Bhabha Atomic Research Centre, Trombay. The samples were kept in close proximity in a polyethylene tube placed in a standard aluminium can. Metallic silicon, ammonium dihydrogen phosphate, and sodium sulfate of purity better than 99.99, 99.0, and 99.5%, respectively, were used as standards. All other reagents and solvents used were of Analar grade. The carrier solutions were prepared by dissolving appropriate salts in water to give solutions of 10 mg/ml concentration.

Radiochemical procedures

The irradiated steel was accurately weighed and was dissolved in a mixture of 10 ml of concentrated hydrochloric acid, 2 ml of concentrated nitric acid, and 2 ml of saturated bromine water containing 10–20 mg of silicon(IV), 3–5 mg of sulphur and 2–3 mg of phosphorus(V) as carriers. To the hot solution, 10% barium chloride solution was added and the precipitated barium sulphate was centrifuged. The supernate (solution I) was reserved for silicon and phosphorus determination, and the precipitate was washed twice with 10 ml of 2 *N* hydrochloric acid. It was transferred to a platinum crucible and fused with anhydrous sodium carbonate, and the melt was extracted with hot water. The precipitated barium carbonate was centrifuged off and the solution was scavenged successively with hydrated iron(III) oxide and silver chloride. It was treated with 5 ml of 0.1 *M* disodium-EDTA solution and barium sulphate was precipitated by the addition of 10% barium chloride solution. The precipitate was centrifuged, and washed twice with 10 ml of 2 *N* hydrochloric acid. After drying at 120° and weighing, the precipitate was transferred to a filter paper, fixed with polymethylacrylate solution and counted on a 2 π-proportional counter.

The solution I (reserved for the separation of silicon and phosphorus) was treated with 25 ml of concentrated sulphuric acid and then heated to boiling for a minute or so. After cooling, the precipitated silica was centrifuged and the supernatant solution (II) was kept for the determination of phosphorus. The precipitate was washed with 2 *N* hydrochloric acid and then dissolved in 5 ml of 10 *N* sodium hydroxide. The solution was scavenged twice with hydrated iron(III) oxide and once with silver chloride. It was then treated with 10 ml of 0.1 *N* disodium-EDTA solution and 25 ml of concentrated sulphuric acid and boiled for a minute. The precipitated silica was centrifuged, washed twice with 10 ml of 2 *N* hydrochloric acid, transferred to an aluminium planchet, fixed with a drop of cement and counted on a thin end-window G.M. counter. After the completion of activity measurements, the sample of silica was ignited at 900–1000°, cooled, and weighed to obtain the chemical yield.

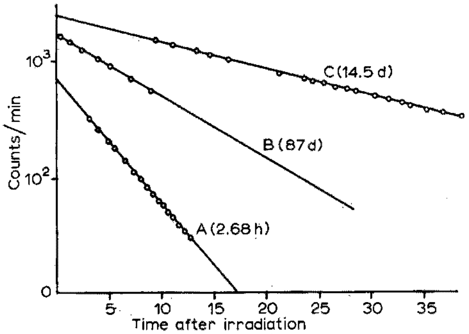
The solution (II) (containing phosphorus along with other steel constituents) was made 6.5 *N* with respect to hydrochloric acid and extracted twice with 25 ml of ethyl ether to remove iron(III) and molybdenum(IV). The aqueous phase was scavenged with hydrated iron(III) oxide and treated with 5 ml of concentrated nitric acid and 20 ml of 10% ammonium molybdate to precipitate ammonium phosphomolybdate. The precipitate was centrifuged and washed twice with 20 ml of 2 *N* nitric acid. The slurry of the precipitate was shaken twice with 10 ml of *n*-butanol in 2 *N* nitric acid solution. Ammonium phosphomolybdate was back-extracted from the organic phase by equilibration with 10 ml of 4 *N* sodium hydroxide. The solution was scavenged twice with hydrated iron(III) oxide and acidified with hydrochloric acid. The precipitated ammonium phosphomolybdate was centrifuged, washed, and prepared for counting in the usual way. The activity of ^{32}P was measured on a thin end-window G.M. counter.

The irradiated standards were also processed through the entire procedure outlined above. Silicon standard was brought into solution by fusion with solid sodium hydroxide and sodium nitrate and leaching with water. The phosphate and sulphate standards were simply dissolved in water.

Corrections for chemical yield, back-ground, coincidence loss, self-absorption, self-scattering and decay corrections were applied, wherever necessary.

RESULTS AND DISCUSSION

The radiochemical purity of samples of silicon-31, phosphorus-32 and sulfur-35 were confirmed by half-life determinations (Fig. 1) and β-energy measurements (Fig. 2). The results in Tables II–IV indicate that decontaminations from some of the nuclides occurring in steels are fairly high. Synthetic mixtures prepared from varying amounts of Mo, Fe, Ni, Cr, Mn, Si, P and S, and a standard alloy steel (Bureau of Analysed Samples, England) were analysed by following the procedure described



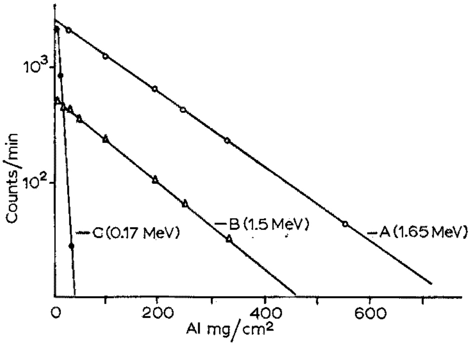


Fig. 1. Half-lives of ^{31}Si, ^{32}P and ^{35}S. (A) ^{31}Si (2.62 h); x-axis scale in h, (B) ^{35}S (87 d); x-axis scale in 14-day periods; (C) ^{32}P (14.3 d); x-axis scale in days.

Fig. 2. Aluminium absorption curves for ^{31}Si, ^{32}P and ^{35}S. (A) ^{32}P (1.701 MeV); (B) ^{31}Si (1.48 MeV); (C) ^{35}S (0.167 MeV).

TABLE II

DECONTAMINATION STUDIES WITH SILICA PRECIPITATE

Activity used (counts/min ·10^{-5})	*Weight of SiO$_2$ recovered (mg)*	*Chemical yield (%)*	*Decontamination factor*
^{59}Fe 7.3	34.4	55	4.0·10^5
^{35}S 2.4	11.7	51	2.9·10^4
^{99}Mo 1.8	34.3	50	1.8·10^5
^{32}P 7.2	41.6	54	5.8·10^5
^{187}W 1.8	37.9	50	2.8·10^3
^{51}Cr 3.6	58.2	65	3.7·10^4

above. An artificial mixture containing only Mo, Fe, Ni, Cr and Mn was also irradiated by the thermal neutrons to test for the presence of Si, P or S, and these were found to be

TABLE III

DECONTAMINATION STUDIES WITH AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE

Activity used (counts/min $\cdot 10^{-5}$)	*Weight of ppt. recovered (mg)*	*Chemical yield (%)*	*Decontamination factor*
^{59}Fe 7.9	22.5	59	$2.2 \cdot 10^5$
^{99}Mo 1.80	55.0	55	$1.8 \cdot 10^5$
^{35}S 2.4	43.3	58	$1.3 \cdot 10^5$
^{187}W 3.1	54.9	55	$7.7 \cdot 10^4$
^{51}Cr 3.6	30.3	55	$1.8 \cdot 10^4$

TABLE IV

DECONTAMINATION STUDIES WITH BARIUM SULFATE PRECIPITATE

Activity used (counts/min $\cdot 10^{-5}$)	*Weight of $BaSO_4$ recovered (mg)*	*Chemical yield (%)*	*Decontamination factor*
^{59}Fe 6.7	60.3	68	$6.7 \cdot 10^5$
^{99}Mo 1.1	54.4	65	$1.1 \cdot 10^5$
^{32}P 0.13	24.6	65	$6.7 \cdot 10^5$
^{187}W 2.8	61.9	66	$1.0 \cdot 10^4$
^{51}Cr 3.8	53.6	70	$3.8 \cdot 10^5$

TABLE V

DETERMINATION OF SILICON, PHOSPHORUS AND SULFUR BY NEUTRON ACTIVATION ANALYSIS

Duration of irradiation (h)	*Amount of steel or artificial mixture irradiated*	*%Si*		*%P*		*%S*	
		Present	*Found*	*Present*	*Found*	*Present*	*Found*
2–4	27–44 mg	0.25	0.247[b] ±0.011	—	—	—	—
168	10 mg	0.25	0.238[a]	0.014	0.013[a] ±0.001	0.036	0.035[c] ±0.003
73–168	31–125 mg	—	—	0.014	0.014[d] ±0.001	—	—
160–5	Artificial mixture	—	—	—	—	1.49 p.p.m.	1.44 p.p.m.
160–5	Artificial mixture	—	—	3.80 p.p.m.	3.56 p.p.m.	5.5 p.p.m.	5.29 p.p.m.

[a] Mean of duplicate analysis.
[b] Average of 4 determinations
[c] Average of 5 determinations
[d] Average of 6 determinations

The variations of the mean are calculated on the basis of 95% confidence limits[10].

absent. The results (Table V) of activation analysis are in good agreement with the reported values. The chemical yields for silicon, phosphorus and sulfur are 50%, 55% and 65% respectively. Purification and counting of samples requires 30 min for silicon, 45 min for sulfur and 60 min for phosphorus. All the three constituents in a sample can be determined within 2 h from the end of the irradiation.

To evaluate the amounts of silicon-31 and phosphorus-32 produced by the reactions ^{31}P (n,p) ^{31}Si, ^{34}S (n,α) ^{31}Si and ^{32}S (n,p) ^{32}P, samples of alloy steel and standards wrapped in 2 g of cadmium foil were irradiated along with alloy steel and standard samples without cadmium wrapping. The samples were processed through the recommended radiochemical purification steps and counted. The results suggest that 0.01% and 0.002% P are produced by fast-neutron reactions in the steel examined; accordingly, the necessary corrections were applied before including the values in Table V.

The standard deviations for silicon, phosphorus and sulfur were found to be ±1.6%, ±2.3% and ±2.4%, respectively. The sensitivity limits for the determinations of the three elements are 3.2, 0.20 and 2.5 p.p.m., respectively. These limits are calculated on the basis of the production of 50 dps, irradiation for 2 h in the case of silicon and one week in the case of phosphorus and sulfur at a flux of $2 \cdot 10^{12}$ n/cm^2/sec, and counting 2 h after the end of irradiation.

The authors are grateful to the University Grants Commission, New Delhi, for the award of a Senior Research Fellowship to one of them (R.A.N.).

SUMMARY

Silicon, phosphorus, and sulfur in alloy steel were determined by neutron activation analysis involving rapid radiochemical separation procedures. The standard deviations for silicon, phosphorus, and sulfur were 1.6%, 2.3%, and 2.4% respectively; the sensitivity limits were 3.2, 0.20, and 2.50 p.p.m., respectively. The three constituents could be determined in alloy steel within 2 h of the irradiation.

RÉSUMÉ

Le silicium, le phosphore et le soufre dans un acier sont dosés par activation neutronique avec séparations radiochimiques rapides. Les déviations standards pour Si, P et S sont respectivement 1.6%, 3.2%, et 2.4%, et les limites de sensibilité 3.2, 0.2 et 2.5 p.p.m. Le dosage de ces 3 constituants dans un acier se fait en 2 heures à partir de l'irradiation.

ZUSAMMENFASSUNG

Silicium, Phosphor und Schwefel wurden in Stählen mit der Neutronenaktivierungsanalyse einschliesslich einer schnellen radiochemischen Trennung bestimmt. Die Standardabweichung für Silicium, Phosphor und Schwefel beträgt 1.6%, 2.3% bzw. 2.4%. Die Nachweisgrenzen sind 2.3, 0.2 bzw. 2.5 p.p.m. Die drei Elemente konnten zwei Stunden nach der Bestrahlung bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF TIN IN TIN ORES AND CONCENTRATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY IN THE NITROUS OXIDE–ACETYLENE FLAME

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(Received February 23rd, 1968)

The standard methods available for determining tin in tin ores and concentrates are too time-consuming to enable large numbers of geochemical prospecting samples to be analysed rapidly and economically. As the technique of atomic absorption has proven successful for the determination of many elements in rocks and soils, it was decided to investigate the possibility of using this technique to provide a rapid and reliable method for determining tin in the whole range of samples from ores to concentrates.

GATEHOUSE AND WILLIS[1] measured the sensitivity of tin absorption in the air/acetylene flame, and ALLAN[2] later reported on the use of the air/hydrogen flame for increasing the sensitivity. Tin down to 0.05 mg/l in 90-vol hydrogen peroxide solutions has been determined by AGAZZI[3] by means of atomic absorption measurements in an oxy–hydrogen direct injection flame. CAPACHO-DELGADO AND MANNING[4] used an air/hydrogen flame to determine tin in N.B.S. standard alloys of brass, lead and zirconium. Tin in N.B.S. non-ferrous alloys has also been determined by SATTUR[5]. SLAVIN AND SLAVIN[6] have reported on the fully automatic determination of tin in used lubricating oil by atomic absorption in the air/acetylene flame. The air/hydrogen flame gives greater sensitivity than the air/acetylene flame for tin absorption but interferences are greater. AMOS AND WILLIS[7] measured tin absorption in the hotter nitrous oxide/acetylene flame and found that the sensitivity was intermediate between that given by the air/hydrogen flame and that given by the air/acetylene flame. AMOS[8] found more recently that the interferences which occur in the air/hydrogen flame seem to be completely eliminated when the nitrous oxide/acetylene flame is used.

An ammonium iodide attack followed by dissolution of the sublimed tin iodide in 2 *N* hydrochloric acid was found to be the most rapid and convenient method of dissolving the tin samples for the determination.

EXPERIMENTAL

Instrumentation

The instrumental conditions which were used for measuring the absorption of tin are shown in Table I. A Techtron AA4 Spectrophotometer was used with the read-out meter on the W.M.A. unit replaced by a spot galvanometer with a 12-in scale. Working scales for the spot galvanometer for each of the 4 ranges of samples could then be calibrated directly in percentage tin in the sample. Five-fold expansion of the 0–20 %T range was used to enable lower dynode volts to be applied to the photomultiplier detector, thereby considerably reducing the effect of flame instability. This was particularly useful for the 2246 Å, 2335 Å and 2422 Å resonance lines which are relatively weak in intensity.

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF TIN IN TIN ORES AND CONCENTRATES

Source: A.S.L. Neon-filled tin hollow-cathode lamp operated at 7.5 mA.
Flame: Nitrous oxide–acetylene.

Sn in sample range (%)	*Spectral line (Å)*	*Spectral S.W. (Å)*	*Sensitivity for 50% absorption (μg/ml)*
0–4.0	2246.1	3.3	108
4.0–8.0	2706.5	1.7	265
8.0–19.0	2334.8	3.3	635
19.0–80.0	2421.7	3.3	2460

The tin absorption was measured in a nitrous oxide/acetylene flame as this was found to give the best sensitivity with freedom from interference from other metals present in the solutions. A Techtron high-temperature burner with a 5 × 0.038 cm slot was used with a standard Techtron nebulizer operating at 18 psi. The acetylene pressure was adjusted to give the maximum "red feather" without the flame becoming luminous. With this type of flame very little carbon deposited in the burner slot. Maximum absorption was obtained by raising the burner about 2 mm into the light path.

Four spectral lines were used to avoid having to dilute sample solutions high in tin.

Materials

Analytical-reagent grade hydrochloric acid and laboratory-reagent grade ammonium iodide were used. Standard tin solutions were prepared with granulated tin (99.6%) and spectrographically pure tin(IV) oxide was used for recovery experiments.

A stock standard solution containing 5000 μg Sn/ml was prepared by gently heating 5.0000 g of tin in 200 ml 1:1 hydrochloric acid until dissolved. This was then diluted to 1 l with distilled water and hydrochloric acid to give a final solution 2 N in hydrochloric acid.

Development of method

Ammonium iodide in 2 N hydrochloric acid solution did not disturb the structure of the nitrous oxide/acetylene flame but the ammonium iodide did result in slight enhancement of the absorbance of tin in 2 N hydrochloric acid (Fig. 1). The lower curves show the "absorbance" of ammonium iodide alone in 2 N hydrochloric acid. Owing to the slight enhancement of tin absorbance by ammonium iodide, calibrating solutions were prepared to contain approximately the ammonium iodide concentration present in the sample solutions.

Procedure

Weigh a 0.200-g sample of finely ground tin ore or concentrate into an 18 × 150 mm pyrex test tube and add 1 g of ammonium iodide crystals. Mix the contents and rotate the tube in and out of the flame from a Meker burner so that only the end is heated and the sublimate containing the tin iodide condenses on the walls of the tube.

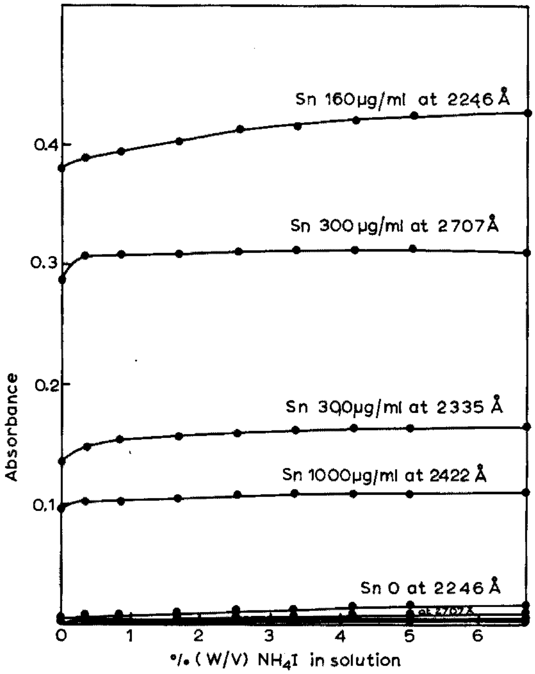

Fig. 1. The effect of ammonium iodide on the absorbance of tin in 2 *N* hydrochloric acid at the 4 resonance lines 2246 Å, 2707 Å, 2335 Å, 2422 Å.

When the reaction has ceased, allow the tube to cool and dissolve the tin iodide in 10 ml of 2 *N* hydrochloric acid by heating on a water bath at 70–75° for *ca.* 20 min. Add 20 ml of 2 *N* hydrochloric acid, mix thoroughly and allow any undissolved residue to settle before measuring the tin absorbance of the supernatant liquor.

Prepare calibrating solutions by diluting the stock 5000-µg Sn/ml standard with 2 *N* hydrochloric acid and incorporating 3.3%(w/v) ammonium iodide into the solutions. Prepare a blank solution containing 3.3%(w/v) ammonium iodide in 2 *N* hydrochloric acid.

Measure the absorbances of the calibrating solutions and blank in triplicate for each of the 4 ranges, setting zero absorbance while spraying water. From the average absorbances of the calibrating solutions corrected for blank absorption, construct working scales calibrated directly in percentage tin in the sample, for use with the spot galvanometer.

Starting at the most sensitive spectral line, 2246 Å, for the range 0–4% tin in the samples, set full-scale deflection while spraying the blank solution. Then adjust the position of the burner by rotating slightly in a horizontal plane so that the calibrating solutions give the correct reading on the calibrated working scale of the spot galvanometer; two calibrating solutions are used to check the sensitivity. Then spray the sample solutions and read the tin concentration from the calibrated working scale, checking the sensitivity after every 10 samples and spraying blank solution after every sample until it reads zero. Measure any sample solutions which show greater than 4% tin in the sample again for absorption using one of the less sensitive resonance lines.

For samples containing greater than 30% tin, repeat the attack with 2 g of ammonium iodide to ensure that all the tin in the sample is converted to the iodide. Then dissolve the attacked samples in 10 ml of 2 N hydrochloric acid and add 50 ml of 2 N hydrochloric acid, instead of the 20 ml added for samples with less than 30% tin.

RESULTS AND DISCUSSION

Figure 2 shows a comparison of the results obtained by this atomic absorption method with results obtained in two different laboratories by standard chemical meth-

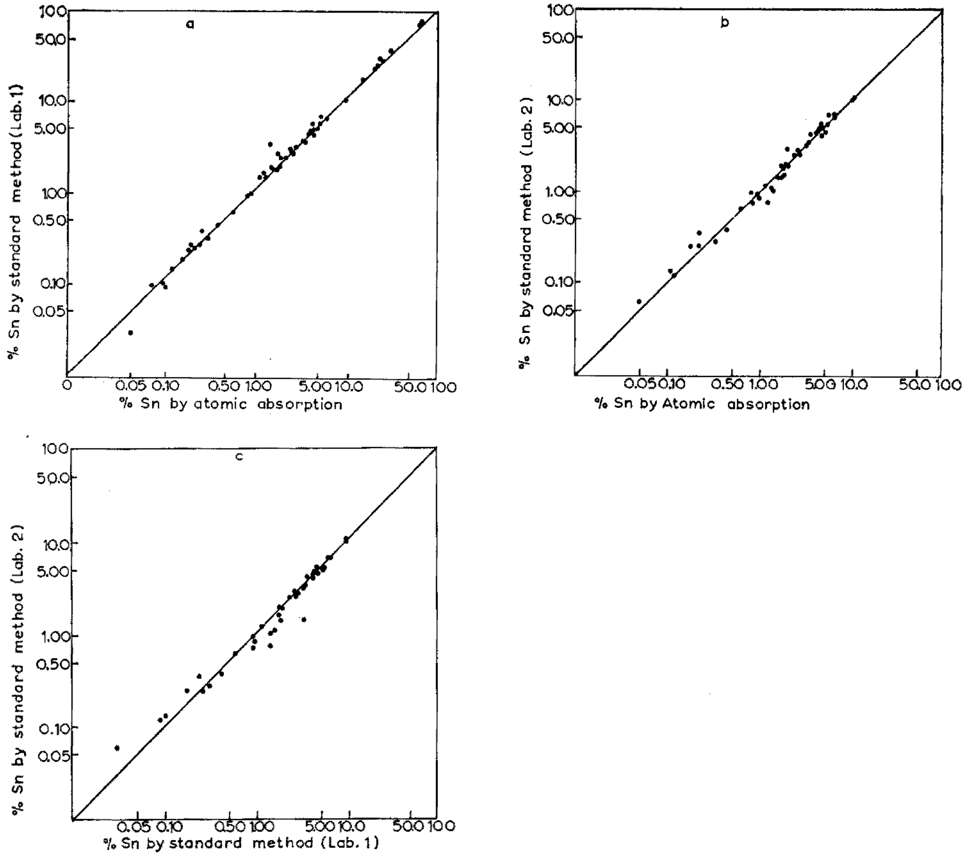

Fig. 2. Comparison of results obtained by atomic absorption with those obtained by standard chemical methods for tin in tin ores and concentrates. (a) Atomic absorption results compared with results obtained by standard chemical method in Lab. 1. (b) Atomic absorption results compared with results obtained by standard chemical method in Lab. 2. (c) Results obtained by standard chemical method in Lab. 1 compared with Lab. 2.

ods involving sodium carbonate/sodium peroxide fusion followed by iodimetric determination. As it was not possible to obtain more accurate results by standard chemical methods for these samples, it is not known how accurate the atomic absorption results are. However, they are in as good agreement with either of the two results obtained by standard chemical methods as these are with each other.

Typical calibration curves of absorbance *vs.* concentration for tin in solutions containing 3.3%(w/v) ammonium iodide in 2 *N* hydrochloric acid are shown in Fig. 3.

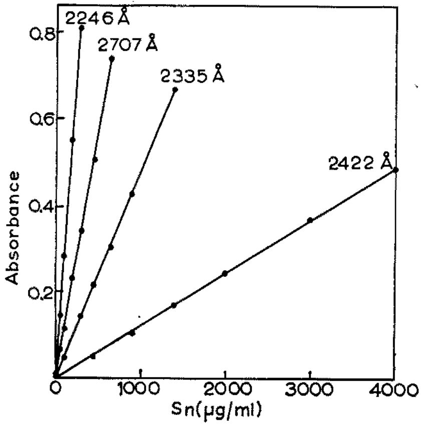

Fig. 3. Calibration curves at 2246 Å, 2707 Å, 2335 Å and 2422 Å for Sn in 2 *N* HCl containing 3.3% (w/v) NH$_4$I.

The presence of the large concentration of ammonium iodide in the tin solution causes a marked "memory" effect of tin absorption. It is necessary to spray with water and blank for quite some time after a solution which gives a high absorbance has been sprayed, before the spray chamber walls are washed free of tin and the blank absorbance returns to zero. Tin solutions in 2 *N* hydrochloric acid alone show no memory effect.

Results obtained with different dilutions of sample and different concentra-

TABLE II

RECOVERY EXPERIMENTS FOR THE ATOMIC ABSORPTION METHOD

Sn in sample (%)	*SnO$_2$ in 0.2-g sample (mg)*	*SnO$_2$ added (mg)*	*SnO$_2$ total (mg)*	*SnO$_2$ recovered (mg)*	*Recovery (%)*
0.23	0.58	2.0	2.58	2.59	100
0.52	1.32	2.5	3.82	3.78	99
0.93	2.35	2.0	4.35	4.20	97
1.83	4.65	10.0	14.65	14.2	99
4.75	12.05	12.0	24.05	23.4	97
10.6	26.90	25.0	51.9	51.2	99
10.9	27.60	25.0	52.6	52.0	97
66.0[a]	84.0	50.0	134.0	135.0	101
67.7[a]	85.8	50.0	135.8	136.0	100
					Av. 99

[a] 0.1-g sample used.

tions of ammonium iodide in solution were in agreement. To show further that any interelement interference was insignificant, some recovery experiments were carried out with spectrographically pure tin(IV) oxide added to the weighed sample. The results of these experiments are shown in Table II. For geochemical prospecting samples, this level of recovery is completely acceptable.

The reproducibility of the atomic absorption method is shown in Table III. Ten replicate samples were weighed and the relative standard deviation calculated on the 10 single atomic absorption readings taken on the same day. These results are well within the limits of reproducibility necessary for geochemical prospecting for tin.

TABLE III

REPRODUCIBILITY OF ATOMIC ABSORPTION METHOD ON 10 REPLICATE SAMPLES MEASURED CONSECUTIVELY

Sn in sample (%)	*Relative std. deviation (%)*	*Sn in sample (%)*	*Relative std. deviation (%)*
0.05	17.5	10.2	1.0
0.22	4.8	18.8	1.7
0.63	3.8	21.2	3.9
1.18	2.3	31.8	4.5
2.66	1.9	60.5	2.9
4.36	1.4	62.7	4.5
6.48	1.3	64.9	4.5

This method has been in routine use for several months at Sampey Exploration Services for the analysis of tin ores containing tin in the 0.25–5.0% range and concentrates containing up to 79% tin. It is sufficiently rapid to allow several hundred determinations to be carried out within a week. The only problem experienced so far has been the rather rapid failure of Techtron nebulizers owing to attack of the end of the capillary and the Venturi by the highly oxidizing conditions.

The author wishes to thank Mr. D. SAMPEY and Mr. C. N. MACLIVER for helpful discussions and Sampey Exploration Services for permission to publish this paper.

SUMMARY

Tin in tin ores and concentrates can be determined by atomic absorption measurement in the nitrous oxide–acetylene flame. Solutions are prepared by heating the samples with ammonium iodide and dissolving the resulting tin iodide in dilute hydrochloric acid. Calibrating solutions contain ammonium iodide and hydrochloric acid at approximately the concentrations present in the sample solutions. The method has a limit of detection of 0.02% tin in the sample and is suitable for application to geochemical prospecting samples. The results are similar to those obtained by standard chemical methods.

RÉSUMÉ

L'étain dans des minerais d'étain peut être dosé par mesure d'absorption atomique dans la flamme oxyde nitreux–acétylène. Les solutions sont préparées par chauffage des échantillons avec de l'iodure d'ammonium et dissolution de l'iodure d'étain formé dans l'acide chlorhydrique dilué. Les solutions de calibrage renferment de l'iodure d'ammonium et de l'acide chlorhydrique à des concentrations correspondant approximativement à celles de l'échantillon à analyser. La méthode a une limite de détection de 0.02 % d'étain dans l'échantillon et peut être appliquée à des échantillons géochimiques. Les résultats correspondent à ceux obtenus par des méthodes chimiques standard.

ZUSAMMENFASSUNG

Zinn kann in Zinnerzen und in Konzentraten mit der Flammenabsorptionsanalyse unter Verwendung einer Stickstoffoxyd–Acetylen-Flamme bestimmt werden. Dazu werden die Proben mit Ammoniumjodid erhitzt und das dabei entstehende Zinnjodid in verdünnter Salzsäure gelöst. Die Eichlösungen enthielten Ammoniumjodid und Salzsäure in nahezu den gleichen Konzentrationen wie die Probelösungen. Die Methode besitzt eine Nachweisgrenze von 0.02 % Zinn in der Probe und ist für geochemische Untersuchungen geeignet. Die Ergebnisse sind ähnlich denen, die mit chemischen Standardverfahren erhalten wurden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

2-(4-TOLUENESULPHONAMIDO)ANILINE AS AN ANALYTICAL REAGENT

THE NATURE OF THE REACTION WITH COPPER(II)

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(Received December 20th, 1967)

Despite a great deal of research, the causes of specificity and selectivity of organic reagents are only understood in a few examples: nickel dimethylglyoxime[1], where a unique crystal structure has been established; iron(II) and copper(I) 1,10-phenanthrolines, where ligand field stabilisation leads to intense absorption maxima[2]; competitive equilibria, which can reduce side reactions, *e.g.* substoichiometry, lead diethyldithiocarbamate for copper(II)[3-5]. The Irving–Williams order of stabilities of complexes of divalent post-manganese transition metal ions leads one to doubt that a specific reagent for copper(II) exists, hence the discovery that 2-(4-toluenesulphonamido)aniline is a specific reagent for copper(II)[6], is of great interest.

The study described here was initiated to investigate the claims of the original workers, to explain the nature of the reaction and the reasons for its selectivity, and to try to establish whether the reagent could be used for the selective extraction of copper(II) and for its spectrophotometric determination. This last objective was realised by BILLMAN[7] after this study had started, but his method differs markedly from that described below.

EXPERIMENTAL

Apparatus

A Unicam SP800 and a Perkin Elmer 257 were used for recording spectra in the ultraviolet, visible and infrared regions of the spectrum and a Unicam SP500 was used for measurements at fixed wavelengths.

A Cambridge pH meter was used for spectrophotometric work and a Radiometer M4c was used for stability constant work. A glass–saturated calomel electrode pair was used.

Titration cell. A glass-jacketed titration cell was constructed from a 250-ml and a 600-ml beaker. A temperature constant to ±0.20° was maintained by circulating water from a Hetotherm thermostat through the jacket. The cell stopper had inlets for two 10-ml microburettes, two nitrogen flow tubes, a thermometer and the electrodes.

A Gallenkamp shaking incubator was used. The temperature was controlled to within ±0.5°. Many (40–60) solutions were equilibrated at a time by placing them in 20-ml bottles with polythene-lined screw caps and laying them in a plastic box, which was then put in the shaker.

A scintillation counter with a NaI(Tl) crystal was attached to an IDL 1700 scaler for use in counting γ-ray activity.

A Tinsley recording polarograph was used. Mr. R. C. ROONEY of Southern Analytical kindly ran a polarogram on the Southern Analytical Differential Cathode Ray Polarograph.

Reagents

Reagent-grade chemicals and demineralised water were used throughout.

2-(4-Toluenesulphonamido)aniline. The reagent is commercially available, but tests showed that it was only 80% pure. It was recrystallised twice from 1:1 water–ethanol and shown to be pure by elemental analysis and determination of the equivalent weight. A stock solution, 0.5%(w/v) in 3:7 water–ethanol, was stored in an amber glass bottle in a refrigerator. It was diluted to $1.57 \cdot 10^{-3}$ *M* for use in the spectrophotometric procedure. The stock solution is stable for at least a week when kept under these conditions, but decomposes within a few hours at room temperature.

Copper solutions. A stock solution was prepared by dissolving 0.5 g of electrolytic copper in 25 ml of 1:3 nitric acid, boiling to remove the oxides of nitrogen and diluting to 500 ml with water. The solution was standardised titrimetrically by standard iodimetric and EDTA procedures.

Copper-64, obtained from the Radiochemical Centre, Amersham, was used in the solvent extraction work. The specific activity was so low that carrier copper was not necessary.

Buffer solutions. Standard perchloric acid, phthalate, acetate, phosphate, borate and sodium hydroxide buffer solutions were prepared to cover the pH range 1–12. The solutions were adjusted to an ionic strength of 0.10 ± 0.01 with sodium nitrate where necessary.

Sodium hydroxide solution. This was prepared carbonate-free by diluting 50%(w/v) solution of sodium hydroxide and was tested by addition of barium chloride solution.

Dioxane. Commercially available dioxane was refluxed over metallic sodium for 24 h and then fractionated thrice through a glass column packed with glass helices, the 99–100° fraction being collected. It was stored in the dark for not more than a week, and tested for peroxide formation with potassium iodide before use.

Determination of acid dissociation constants by potentiometric titration[8]

Fifty ml of 0.01 *M* reagent solution and 50 ml of 0.01 *M* perchloric acid were placed in the titration vessel. The solution was deaerated with nitrogen for 10 min, the temperature checked and the titration with standard sodium hydroxide begun. An equal volume of dioxane was added for each addition of titrant. An atmosphere of nitrogen was maintained during the titration. The pH was read at appropriate intervals after equilibrium had been reached; the readings were corrected by adding 0.07 to the observed reading to take into account the effects of the mixed solvent[9].

The acid dissociation constants were calculated from points on the titration curve. They are sufficiently separated to allow the following formulae to be used:

$$K_{a1} = [HR][H^+]/[H_2R^+] = [H^+][T_R - S]/S \qquad (1)$$

$$K_{a2} = [H^+][R^-]/[HR] = [H^+][S']/[T_R - S'] \qquad (2)$$

where HR is TSA, H_2R^+ and R^- its protonated and deprotonated forms respectively,

T_R is the analytical concentration of TSA, $S = [ClO_4^-] - [H^+] - [Na^+]$, and $S' = [H^+] + [Na^+] - [ClO_4^-] - [OH^-]$.
The dissociation constant of water was taken[10] as $10^{-16.14}$.

Determination of stability constants by potentiometric titration[8]

The procedure was that described for the determination of acid dissociation constants except that 1–5 ml of 0.01 *M* metal ion solution, sufficient sodium nitrate solution to adjust the ionic strength to that desired and an equal volume of dioxane were added. The metal ion itself was titrated in the absence of reagent to confirm that complex formation was being observed, and the stability constant was determined at different copper : TSA ratios to confirm that the complex was not polynuclear under the conditions of measurement.

The stoichiometry of the complex with copper has been established gravimetrically[6] as 1:2, and two protons were released on chelation, suggesting that the reaction between pH 2–4.5 can be written,

$$Cu(II) + 2\ HR = CuR_2 + 2\ H^+$$

The other metal ions examined released two protons but did not precipitate. The acid dissociation constants are well separated so the following formulae could be used to calculate the stability constants of the complexes:

$$\bar{n} \cdot T_M = T_R - S''\ ([H^+] + K_{a1})/(2[H^+] + K_{a1}) \tag{3}$$

$$[R^-] = S'' K_{a1} K_{a2}/\{[H^+] + (K_{a1} + 2\ [H^+])\} \tag{4}$$

and

$$\bar{n}/(\bar{n}-1)\ [R^-] = \{(2-\bar{n})/(\bar{n}-1)\}[R^-](k_1k_2 - k_1) \tag{5}$$

where, $\bar{n}$ is the formation function of the system = (total concentration of bound ligand)/(total concentration of metal), k_1 and k_2 are the stepwise stability constants,

$$k_1 = [MR^+]/[M^{2+}][R^-] \qquad k_2 = [MR_2]/[MR^+][R^-],$$

the overall stability constant being $K_f = k_1k_2$, T_M is the analytical concentration of metal ion and

$$S'' = (T_R - 2T_M - [H^+] - [Na^+] + [OH^-] + [ClO_4^-]).$$

Other terms are used as defined above.

The values were calculated from a least squares fit of $(\bar{n}/(\bar{n}-1)[R^-])$ *vs.* $\bar{n}(2-\bar{n})[R^-]/(\bar{n}-1)$ by an IBM 1600 computer with the aid of a programme devised and supplied by Professor QUINTUS FERNANDO of the University of Arizona. They were also calculated by the method of POULSEN, BJERRUM AND POULSEN[11]. The values of k_1 and k_2 are too similar to enable the simpler method of interpolation at half $\bar{n}$ values to be used, but calculated values of the constants were used to compute values of $\bar{n}$ as a function of $[R^-]$ from eqn. (5a)

$$\bar{n} = \{k_1[R^-] + 2k_1k_2[R^-]^2\}/\{1 + k_1[R^-] + k_1k_2[R^-]^2\} \tag{5a}$$

and compared with the experimental points to check that the results were free from gross error.

Determination of acid dissociation constants by solvent extraction

TSA (1 mg) was equilibrated between benzene and a buffered aqueous layer of constant ionic strength (0.10 ± 0.01) and temperature in the shaker. The concentration of TSA in the benzene layer was determined spectrophotometrically at 295 nm. The distribution ratio ($D = [\mathrm{TSA}]_{\mathrm{org}}/[\mathrm{TSA}]_{\mathrm{aq}}$) was determined over the pH range 0.2–12 and the acid dissociation constants and the partition coefficient of undissociated TSA, K_{DR}, were calculated from eqn.(6):

$$D = K_{\mathrm{DR}} K_{\mathrm{a1}}[\mathrm{H}^+]/([\mathrm{H}^+]^2 + K_{\mathrm{a1}}[\mathrm{H}^+] + K_{\mathrm{a1}} K_{\mathrm{a2}}) \qquad (6)$$

Determination of the stability constant of the complex and stoichiometry of the reaction by solvent extraction

The distribution of copper between benzene and aqueous solutions of constant ionic strength (0.10 ± 0.01) was determined for systems of pH 3–12 with TSA concentrations of 10^{-2}–10^{-5} M. The concentration of copper in the organic and aqueous phases was determined by measuring the γ-activity of copper-64 or spectrophotometrically with 1-(2-pyridylazo)-2-naphthol. If the total amount of copper found was less than 80% of the actual amount taken, the result was discarded; many results had to be rejected because the copper precipitated or gathered at the interface between the two phases or adhered to the glass walls. The copper concentration was varied between $5 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$ M to confirm that the distribution ratio was independent of copper concentration. These limits were fixed by the specific activity of the copper-64 and solubility of TSA. The following equations[12] were used to calculate the overall stability constant, stoichiometry and partition coefficient, K_{DX}, of the complex formed at pH 4–7 and to make deductions about the nature of the violet complex at pH 10–11:

$$D = [\mathrm{Cu_{tot}}]_{\mathrm{org}}/[\mathrm{Cu_{tot}}]_{\mathrm{aq}} = K_f \cdot K_{\mathrm{DX}} \cdot \beta \cdot \alpha_{2(D)}{}^n [\mathrm{TSA}]_{\mathrm{tot}}{}^n \qquad (7)$$

where $[\mathrm{TSA}]_{\mathrm{tot}}$ is the analytical concentration of TSA assuming, notionally, that it were present in the aqueous phase,

$$\alpha_{2(D)} = K_{\mathrm{a1}} K_{\mathrm{a2}}/([\mathrm{H}^+]^2 + [\mathrm{H}^+]K_{\mathrm{a1}}(1 + K_{\mathrm{DR}}) + K_{\mathrm{a1}} K_{\mathrm{a2}}), \text{ and}$$

$$1/\beta = 1 + k_{1(\mathrm{R})}[\mathrm{R}^-] + k_1 k_{2(\mathrm{R})}[\mathrm{R}^-]^2 + k_{1(\mathrm{OH})}[\mathrm{OH}^-] + \ldots + k_{1(\mathrm{tart})}'[\mathrm{tart}] + \ldots$$

where $k_{i\,(\mathrm{X})}'$ is the ith stepwise conditional stability (formation) constant for the reaction between copper and X, and tart stands for tartrate. Equation 7 under appropriate conditions simplifies to

$$D = K_f \; K_{\mathrm{DX}}\{K_{\mathrm{a2}}[\mathrm{TSA}]_{\mathrm{org}}/K_{\mathrm{DR}}[\mathrm{H}^+]\}^n \qquad (7a)$$

so that the slope of a plot of log D *vs.* pH or $\log[\mathrm{HR}]_{\mathrm{org}}$ is n, the number of protons released on, or the number of reagent molecules involved in the chelation per mole of copper.

Attempted determination of stoichiometry of the violet complex formed at high pH

The mole ratio[13], slope ratio[14] methods and the method of continuous variations[15] were used to try to ascertain the nature of the violet complex formed at about pH 10. The medium was 30% (v/v) ethanol, the concentration of the stock solutions of copper and TSA was 1–$2 \cdot 10^{-4}$ M, varying volumes being taken, and the pH was controlled by addition of 5 ml of borate buffer pH 10 per 25 ml of total solution. The order of addition of reactants is critical, the best being: copper, reagent, buffer, diluent. Difficulties were encountered because of the low solubility of the copper complex and the instability of the colour under these conditions. The wavelength of maximum absorption is 530 nm.

Polarography

Polarograms of ethanolic solutions of the violet complex were run. The inert electrolyte was potassium nitrate. A plot of E *vs.* $\log i/(i_d - i)$, where the symbols have their usual significance, was made.

Spectrometry

Infrared spectra were run on solid samples in potassium bromide discs.

Mass spectra were measured on the AEI MS9 mass spectrometer. Solid samples were employed; the green complex was precipitated as detailed below, and the violet complex was isolated after extraction followed by evaporation of the solvent (benzene).

THE NATURE OF THE COMPLEX

Preliminary experiments established that at least two complexes could be formed: a stable green complex, sparingly soluble in aqueous solution, was formed over the pH range 4.5–10 and an intensely violet complex was formed at pH 10–11. The stability of the latter complex varied markedly with solvent; the complex decomposed instantly in 70% ethanol but was stable for 24 h in benzene. These complexes were studied by a variety of methods as described below.

Potentiometric titration

The acid dissociation constants of the reagent and the stability constants of the reagent with several divalent transition metal ions at various ionic strengths were measured by potentiometric titration; the results are given in Tables I and II. From the evidence of other methods it seems reasonable formally to assign K_{a1} to the loss

TABLE I

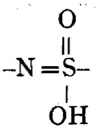
ACID DISSOCIATION CONSTANTS OF TSA

Method	*Solvent*	*Ionic strength (KNO_3)*	pk_1	pk_2
I Potentiometry	50% (v/v) dioxane: water	0.01	2.24 ± 0.04	10.16 ± 0.02
	50% (v/v) dioxane: water	0.1 ± 0.01	2.88 ± 0.02	9.98 ± 0.04
	50% (v/v) dioxane: water	0.2 ± 0.01	2.85 ± 0.01	9.96 ± 0.06
	50% (v/v) dioxane: water	0.3 ± 0.01	2.79 ± 0.02	9.87 ± 0.04
	50% (v/v) dioxane: water	0.4 ± 0.01	2.74 ± 0.06	9.77 ± 0.03
II Solvent extraction	Water saturated with benzene	0.1 ± 0.01	1.72 ± 0.1	10.49 ± 0.08
III Spectrophotometry	30% ethanol in water	0.1 ± 0.01	2.01 ± 0.04	9.20 ± 0.06

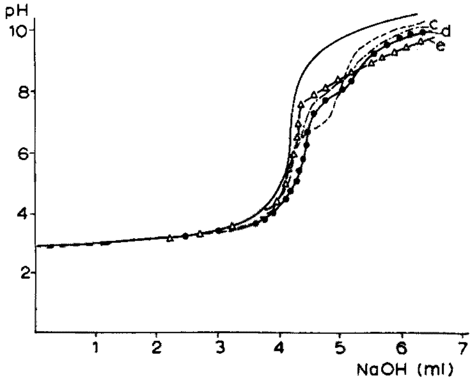
TABLE II

STABILITY CONSTANTS OF METAL–TSA COMPLEXES

Method	*Metal*	*Solvent*	*Ionic strength (KNO_3)*	*log k_1*	*log k_2*	*log K_f*
I Potentiometry	Cu(II)	50%(v/v)dioxane: water	0.01	9.50	9.61	19.11 ± 0.06
	Fe(II)	50%(v/v)dioxane: water	0.01	9.31	8.14	17.45 ± 0.04
	Co(II)	50%(v/v)dioxane: water	0.01	9.57	9.16	18.73 ± 0.03
	Ni(II)	50%(v/v)dioxane: water	0.01	9.67	9.27	18.94 ± 0.08
	Zn(II)	50%(v/v)dioxane: water	0.01	9.33	8.91	18.24 ± 0.07
II Solvent extraction	Cu(II)	Water saturated with benzene	0.1 ± 0.01	8.03	8.03	16.06 ± 0.05

of a proton from the $-NH_3^+$ group and K_{a2} to the loss of a proton from the  $-\mathrm{N}{=}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{S}}}-$ group. The pK value of aniline in 50% ethanol[16] is 4.42, which suggests that hydrogen bonding is prevalent within the system stabilising the enol, –C–N =S–O–H, form, and this is confirmed by the infrared spectra.

The stability constants follow the normal sequence, but the value for the copper system is lower in relation to the other values than might have been expected, possibly because different coordinating sites are being used. The green copper complex precipitates during the titration, but the other complexes do not. The precipitation is



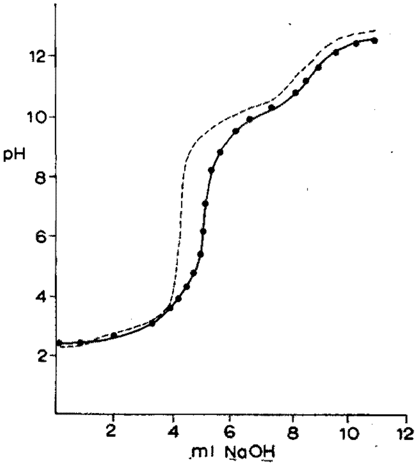


Fig. 1a. Potentiometric titration for the determination of stability constants of some divalent metal ions with TSA in 50%(v/v) 1,4-dioxane/water (0.1228 M NaOH) (——) 50.0 ml of 0.01 M reagent + 50 ml of 0.01 M $HClO_4$; (– – –) as (a) + 5 ml 0.01 M zinc(II); (–.–.) as (a) + 5 ml 0.01 M nickel(II); (●—●) as (a) + 5 ml 0.01 M cobalt(II); (△—△) as (a) + 5 ml 0.01 M iron(II).

Fig. 1b. As Fig. 1a curve (——) + 5 ml 0.01 M copper(II).

apparently affected by the nature of the supporting electrolyte; a much heavier precipitate was observed when hydrochloric acid was used than with nitric or perchloric acids. The stoichiometry of the complexes other than the copper one has not been independently established, but has been inferred from the titration curves (Fig. 1) and the $\bar{n}$ curves (Fig. 2).

Even at high pH the violet copper complex was not formed under the conditions of the titration, probably because the concentrations were too high.

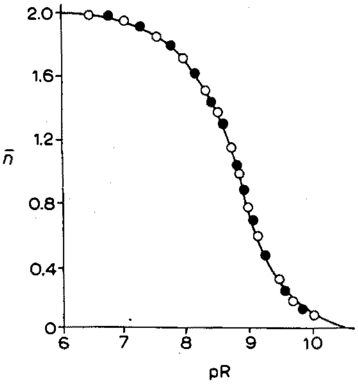


Fig. 2. Formation curve for copper(II)–TSA complex. (●) experimental $\bar{n}$ values, (O) calculated $\bar{n}$ values.

Solvent extraction

The results of distribution studies are shown in Table III. These clearly indicate that a 1:2 complex is formed (eqn.(7a)) and since the distribution ratio was found to be independent of copper concentration it is probably mononuclear. The overall stability constant is given in Table II. Insufficient results were obtained to

TABLE III

DISTRIBUTION OF TSA AND COPPER IN BENZENE/WATER SYSTEM

TSA as function of pH									
pH:	0.22	0.39	0.79	1.30	1.52	1.69	2.00	2.34	2.91
log D:	$\bar{1}.58$	$\bar{1}.74$	0.05	0.43	0.62	0.73	0.76	0.82	1.00
pH:	3.36	3.94	4.34	5.10	6.08	7.16	7.63	8.09	8.94
log D:	1.12	1.13	0.88	0.88	1.51	0.82	0.88	0.82	0.86
pH:	9.92	10.40	11.00	11.61	12.00				
log D:	0.62	0.50	0.21	$\bar{1}.74$	$\bar{1}.51$				
Copper as function of pH, [TSA] = $5\cdot10^{-3}M$, [Cu] = $1.58\cdot10^{-4}M$									
pH:		4.77	5.13	5.35	5.90	6.48	6.96	7.46	7.71
log D:		$\bar{2}.65$	$\bar{2}.85$	$\bar{1}.04$	0.23	1.04	1.27	1.77	1.77
pH:	8.30	8.75	9.20	9.81	10.08				
log D:	1.77	1.77	1.71	1.77	0.69				
Copper as function of [TSA], pH = 7.66, [Cu] = $4.46\cdot10^{-5}M$, [tartrate] = $4\cdot10^{-4}M$									
log[TSA]$_{org}$:	−2.00	−3.69	−3.47	−3.39	−3.30	−3.00	−4.47		
log D:	0.41	0.99	1.15	1.34	1.38	1.45	1.40		
log[TSA]$_{org}$:	−4.00	−5.47	−5.00						
log D:	0.15	−0.91	−1.36						

calculate the stepwise stability constants reliably, but curves of log D *vs.* pH were plotted using eqn.(7) for $k_1/k_2 = 10^{0.5}$, $k_1 = k_2$ and $k_1/k_2 = 10^{-0.5}$, k_1k_2 being kept equal to the experimentally determined value. These curves when compared with the experimental curves suggested that $k_1 \triangleq k_2$. In this respect, there was good agreement with the result from the potentiometric titration. The actual value of K_t does not seem in quite such good agreement, although the difference is of the order and direction expected for the different solvent systems used.

Despite the high value of the stability constant, considerable experimental difficulty was experienced when lower reagent concentrations and/or higher pH values were used. The situation can be improved by the addition of tartrate, but this was not used for the stability constant work. At lower reagent concentrations and above pH 7.5, it is possible that there is a minimum of the sort noticed in other systems[17]; it is not due to the buffer.

At high pH the violet complex was sometimes formed, but the results did not allow a detailed description of it. However, the fact that extraction occurs at high pH and to the same extent as at lower pH suggests that another $Cu(TSA)_2$ species is being formed. Several other possible species were considered ($Cu^IR_3M^I$, Cu^IR, $Cu^IR_2X^-$) but rejected for the following reasons. A 1:3 complex or a copper(I) complex, other than a 1:2, would show a different dependence on pH. A 1:1 copper(I) complex would probably show a marked difference in solubility and a 1:2 copper(I) complex would require an associated univalent cation to give an electrically neutral species. The results preclude hydrogen ion and suggest that it is unlikely that sodium ion would be effective. A 1:3 copper(II) complex would require an associated anion. To see whether the extraction depended upon an anion, the buffer concentration was varied as far as practicable in some equilibrations, but there was no effect on the distribution ratios. This test is not necessarily conclusive because the minimum buffer concentration which could be achieved, might be greater than that required to effect the maximum extraction, but it indicates that CuR_3X is not likely to be the extracted species.

The acid dissociation constants shown in Table I were calculated from the results shown in Table III. These results also show that K_{a1} is associated with the loss of a proton from a charged species to give an uncharged species, and that K_{a2} is associated with the loss of a proton from an uncharged species. This rules out the possibility of both K_a's being due to protonated nitrogen atoms. If a doubly protonated species is formed it is only stable below pH 0.22. It seems that there must be keto–enol tautomerism with the enol form predominating under the conditions of these experiments.

Spectrophotometry

In 90% ethanol a broad band was observed in the ultraviolet region of the TSA spectrum with peaks at 215 and 231 nm. In hexane the peaks shifted to 211 and 228 nm and altered in relative intensity, the peak at lower wavelength being the most intense in hexane and *vice versa* in ethanol; this suggests tautomerism. The acid dissociation constants are given in Table I. Attempts to detect a doubly protonated species at high acidity were unsuccessful.

The molar absorptivity of the green complex was too low to permit spectrophotometric study of the complex.

TABLE IV

STABILITY OF THE ABSORBANCE OF THE COPPER(II) COMPLEX IN VARIOUS SOLVENTS[a]

Time (min)	*30% ethanol*	*Hexone*	*Diethyl ether*	*Benzene*
0	0.430[b]	0.187	0.160	0.201
5	0.516[c]	0.200	0.165	0.205
10	0.580	0.211	0.167	0.200
15	0.600	0.220	0.175	0.200
20	0.610	0.234	0.180	0.200
25	0.610	0.245	0.180	0.201
30	0.617	0.254	0.208	0.200
40	0.620	0.281	0.210	0.201
50	0.644	0.292	0.175	0.205
60	0.658	0.308	0.130	0.210
120	0.700	0.465	0.120	0.205

[a] 10 ml (100 μg) copper + 10 ml reagent ($1.57\cdot10^{-3}M$) + 5 ml buffer pH 10, $\lambda = 530$ nm.
[b] Absorbance readings.
[c] Complex decomposes with the appearance of a broad peak at 430 nm which increases the absorbance at 530 nm.

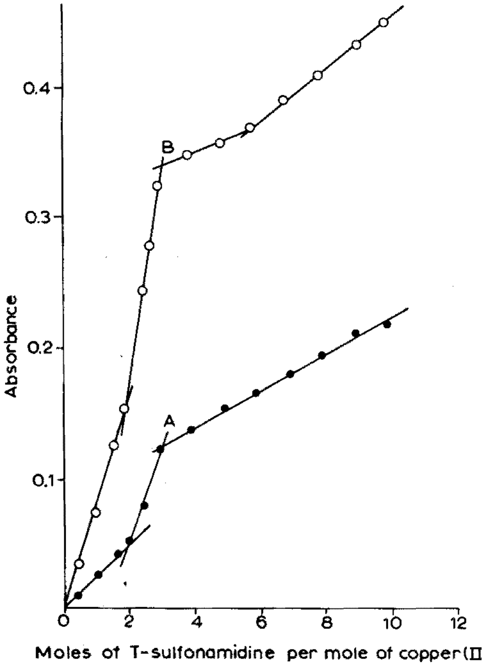


Fig. 3. Mole ratio method, pH 10. (A) $4\cdot10^{-3}M$ Cu(II); (B) $8\cdot10^{-3}M$ Cu(II).

The formation of the violet complex was accompanied by a big shift in the absorption maximum from 295 to 530 nm in 30% ethanol or to 560 nm in benzene. The reaction was very dependent upon pH, maximum absorbance being obtained over the range pH 10–11. The colour changed from violet to yellow at a rate greatly influenced by the solvent, the change being accompanied by an increase in absorbance

(Table IV). Despite this, the results of the studies of stoichiometry carried out in 30% ethanol with measurements being made immediately, were reproducible. It was noted that a large excess (14-fold) of reagent prevented colour formation, but not the reaction with copper, since copper could be extracted at concentrations of TSA sufficient to prevent colour formation.

The stoichiometry of the violet complex is uncertain. The mole ratio[13] (Fig. 3) and method of continuous variations[15] (Fig. 4) indicate that a 1:3 copper:TSA complex is the coloured species but that 2:1 and 1:1 complexes are also formed, as well as a 1:2 species. The slope ratio[16] within 95% confidence limits is 5.33 ± 0.081. The 1:3 stoichiometry is not supported by the evidence from the solvent extraction experiments. It is impossible to make any estimate of the stability constants for the system, but it was noted that the colour was quenched by various complexing agents which would not be expected to interfere if the stability constant were $\geqslant 10^{18}$, *e.g.* triethanolamine, oxalate. In the presence of the minimum amount of ammonia required to buffer the solution, coloration was observed, but in more concentrated ammonia it was not.

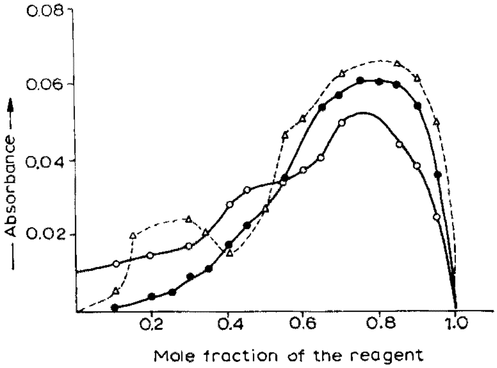


Fig. 4. Method of continuous variations, pH 10. Total volume 25 ml. Buffer 5 ml x and $20-x$ ml of $1.57 \cdot 10^{-4}$ M Cu(II) and TSA. (○) 530 nm; (●) 580 nm; (△) 480 nm.

The intensity of the colour indicates that an allowed transition is taking place. The possibility that this might be due to copper(I), formed with oxidation of the reagent at high pH was considered, but the results of solvent extraction and polarographic experiments both suggest that copper(II) is predominant. The transition might be due to charge transfer, which could lead to kinetic instability[18]. The possibility of a series of reactions initiated or catalysed by the copper leading to the decomposition of the reagent and the formation of a coloured intermediate cannot be completely dismissed.

The evidence accumulated indicated the complexity of the system and suggested that an immense amount of work would be needed to understand it fully. The conditions for a useful analytical reaction had been established and so further work on the violet complex was abandoned.

Polarography

These results apply only to the violet complex. The slope of the curve of E *vs.* $\log i/(i_d - i)$ was 0.0156. For a reversible curve this would suggest that the number of electrons involved in the reduction was 3.84. The reduction is irreversible, as confirmed by the cathode-ray polarograph. Since the "degree of irreversibility"[19] is usually about 0.3−0.5 the number of electrons involved in the reduction, it is probably a 2-electron reduction. This conclusion was also reached by Mr. R. C. ROONEY after a brief examination with the cathode-ray polarograph.

Mass spectrometry

The mass spectra of the green and violet complexes were markedly different. The peak of highest mass number in the spectrum of the green complex was at 421, suggesting that it is a 1:2 complex, although the parent peak would be at 585. Other peaks can be interpreted by postulating that the copper atom is knocked out and that this is followed by a rearrangement to give the ditosylate[20]. Whereas the spectrum for the green complex showed peaks well separated into bands, whose probable structure can be reasonably deduced, that of the violet complex showed peaks for every mass number from 485 downwards. The pattern was cyclic, consisting of a series of bands centred 12–14 mass units apart, the intensity of the peaks falling off almost symmetrically on both sides. The maximum recorded mass number, whilst not necessarily representing the parent peak, was sufficiently greater than 324 to confirm unambiguously that the violet complex is not Cu(TSA).

Infrared spectra

Spectra were obtained in the solid state only, because of the low solubility of the complexes in solvents suitable for infrared spectroscopy. The regions of absorption associated with $-NH_2$, $-NH-$, and $-SO_2-$ groups are well known [21–23], and it is possible to check the assignments by equations relating the ratios of ν_s and ν_{as} frequencies[22,23]. The position of the absorption maxima observed is given in Table V, with the given assignments. This Table includes all the bands of reasonable intensity above 1100 cm^{-1} which are affected by complex formation except a strong peak at 1405 cm^{-1} which was observed with the reagent but not the complex. Spectra recorded at lower frequency did not add to the interpretation.

TABLE V

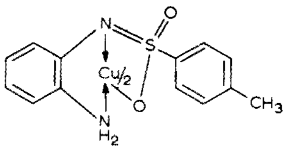
MAIN ABSORPTION BANDS IN INFRARED SPECTRA OF TSA AND GREEN $Cu(TSA)_2$ COMPLEX

TSA		*$Cu(TSA)_2$ green*	
Absorption(cm^{-1})	*Assignment*	*Absorption(cm^{-1})*	*Assignment*
3470 (m)	ν_a $-NH_2$	3290 (m)	ν_a $-NH_2$
3390 (s)	ν_s $-NH_2$	3260 (s)	ν NH
3200 (vs)	N...H intra H bond	3110 (w)	
1618 (vs)	δ_t $-NH_2$	1600 (m)	δ_t $-NH$
1315 (vs)	ν_{as} $-SO_2$	1280	ν_{as} $-SO_2$
1142 (vs)	ν_s $-SO_2$	1130 1115 } (vs)	ν_s $-SO_2$

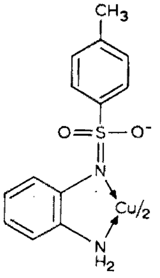
The bands associated with the $-NH_2$ group in the reagent disappear on chelation when the green complex is formed. At the same time the $-NH-$ bands obscured in the reagent spectrum, are clear in that of the complex. The $-SO_2-$ group is also affected. The bonding in the green complex, therefore, is almost certainly through the nitrogen of the aniline amino group and the oxygen of the $-SO_2-$ group.

Conclusions

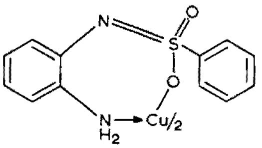
The nature of the green complex formed in neutral or nearly neutral solution is fairly clear. The complex is formed through the enol form of the reagent reacting with copper(II) to form a 1:2 complex with displacement of hydrogen. The bonding is through the nitrogen atom *ortho* to the sulphonamide group and through an oxygen atom of that group. The overall stability constant depends upon the nature of the solvent, but is of the order of 10^{16}–10^{18}. Other divalent transition metal ions form complexes of similar stability.



(I)



(II)



(III)

Some of these findings are initially surprising; one might have thought that coordination would have given rise to either a five-membered and a four-membered ring (I) or a five-membered ring only (II), rather than a seven-membered ring (III), and that the stability constant for the copper complex would be higher in relation to the other complexes. We believe that these observations may help to explain the selectivity of the reagent towards copper. It is shown below that the reagent is selective, but not so selective as previously claimed.

It seems probable from the stability constants that the chief cause of the selectivity is lattice structure which cannot be deduced from the available data. However, with the aid of Framework Molecular Models inferences can be made about the structure of chelate molecules and their likely crystal packing. It is obvious that structure I is impossible; bonding is possible between the two nitrogen atoms or between the amino nitrogen and the oxygen (III) but not between all three. Both structures II and III are free from strain, and II would normally be favoured thermodynamically. It is possible that II is the structure favoured by the other transition metal ions. At pH 6 it is probable that such complexes would be charged and therefore soluble; it is significant that all errors from interferences in the analytical applications of the reagent are negative, suggesting that complex formation is taking place without precipitation. Structure III is more open than II, because of the larger ring. Complexes of copper(II) show Jahn–Teller distortion, and if a reasonable value is taken for the copper–copper bond (3.3 Å)[24], there is a likelihood of copper–copper bonding in the complex accompanied by intermolecular hydrogen bonding. This possibility does not exist for structure II, because of steric hindrance. The other metal ions examined are not distorted to the same degree and are thus unable to form the metal–metal bonds, which could stabilise structure III relative to structure II in the solid state. They probably form complexes of structure II, which are more stable thermodynamically and more soluble. Thus, the selectivity in the gravimetric determination may be due to lattice effects, *i.e.* very similar to the gravimetric selectivity towards dimethylglyoxime.

The exact nature of violet complex is not known, but the cause of the selectivity is probably electronic in that its main absorption band in the visible region is much more intense and centred at a very different wavelength from that of other TSA complexes.

ANALYTICAL ASPECTS

The results obtained from the theoretical study were used to select the optimum conditions for the determination of copper. The effect of interferences and the analytical worth of the reagent were investigated. The procedures and results are given below.

Analytical procedures for the determination of copper with TSA. Recommended procedures

Gravimetry. The procedure of BILLMAN *et al.*[6] was followed.

Spectrophotometry with solvent extraction. Dissolve 1–2 g of alloy either in 25 ml of 1:1 nitric acid or in a 1:1 mixture of nitric acid and hydrochloric acid and evaporate the solution to 10 ml. If iron is present, extract into diethylether in presence of 6 *M* hydrochloric acid. If antimony or bismuth is present, filter the solution and wash the precipitate with distilled water. Roughly neutralise the solution with 10% sodium hydroxide and dilute to contain about 10 p.p.m. of copper. Transfer x ml of solution into a 100-ml separating funnel, add 10 ml of $1.57 \cdot 10^{-3}$ *M* reagent solution in 70% ethanol and 5 ml of pH 10 borate buffer, and make up to 25 ml with 70% ethanol. Extract immediately with 25 ml of AR benzene. Break the emulsion with a pinch of sodium nitrate and let the layers settle. Measure the absorbance of the benzene layer at 560 nm and read the copper content from a calibration curve prepared by taking known amounts of copper (20–100 μg) through the same procedure.

Spectrophotometry without extraction. Follow the above procedure to the point of diluting the solution to 25 ml. Measure the absorbance at 530 nm within 2 min. Prepare a calibration curve under the same conditions.

Interference from foreign ions

Over forty ions were examined to determine their effect on the spectrophotometric determination of copper. The levels of tolerance were established in the procedures with and without extraction. The results obtained are shown in Table VI. The extraction procedure was more effective, because highly coloured cations were not extracted into benzene, and has the advantage that the colour is stable in the benzene layer. In all cases 100 μg of copper and the relevant amount of diverse ion were put through the general procedures. In some instances tartrate was successfully added to prevent hydroxide formation, but the potentialities of masking were limited, because the masking agents either formed stronger copper complexes than the reagent or they reacted with the borate buffer; 1 ml of 0.01 *M* tartrate could be used, with some loss of intensity, and 5 ml of 0.1 *M* fluoride masked up to 1 mg of aluminium, but EDTA, iminodiacetic acid, triethanolamine, citrate and salicylate could not be used.

TABLE VI

STUDY OF INTERFERENCE IN T. SULPHONAMIDO METHODS

Foreign element	*Amount added ($\mu g/25$ ml)*	*Relative error (%)*	
		Solvent extraction[a]	*30% ethanol*
Al(III)	100	0	0[b]
	200	−10	−18
	1000	0	0[c]
Ag(I)	1000	−4	−5
As(III)	1000	0	0
	1500	−2	−4
Be(II)	1000	0	0
	2000	−3	−6
Bi(III)	500	0	0
	1000	+3	+4
Ca(II)	1000	0	0
	2000	+3	+2
Cd(II)	500	0	0
	1000	−10	−15
Cs(I)	1000	0	0
	2000	−2	−2
	5000	−4	−6
Co(II)	100	0	0[b]
	200	−4	−10[b]
	1000	−2[d]	−15
Cr(III)	500	0	−100
	1000	−9	
Fe(III)	100	0	−60
	200	−3[b]	
Fe(II)	100	0	0[b]
	500	−2[b]	−7[b]
Hg(I)	1000	0	0
	2000	0	0
	3000	−3	−5
Hg(II)	1000	+2	+3
K(I)	10000	0	0
Li(I)	700	0	0
	1000	−5	−10
Mg(II)	500	0	0
	1000	−6[b]	−8
Mn(II)	100	0	0[b]
	200	−8	−7[b]
Na(I)	4000	0	0
	10000	−3	−3
NH_4^+	1000	0	0
	2000	−4	0
Ni(II)	100	0	0[b]
	1000	−1[d]	−80
Pb(II)	1000	0[b]	0[b]
	2000	−6	−8
Sb(III)	500	0	0[b]
	1000	−7	−8
Sn(II)	100	0[b]	0[b]
	1000	−1[d]	−5[b]

TABLE VI (Continued)

Foreign element	*Amount added ($\mu g/25$ ml)*	*Relative error (%)*	
		Solvent extraction[a]	*30% ethanol*
Sn(IV)	100	0	0[b]
	500	−2	−4
Sr(II)	1000	0	0
	2000	−1	0
Ti(IV)	100	0	0
	200	−9	−12
Tl(IV)	500	0	0
	1000	−2	0
V(IV)	1000	0	0
	3000	0	−2
	3500	−2	−5
V(V)	2000	0	0
	5000	−3	−6
Zn(II)	500	0[b]	−7[b]
	1000	−17	−20
	1000	−3[d]	−20
BO_3^{3-}	16000	0	0
ClO_4^-	100	0	0
	500	−33	−40
CO_3^{2-}	1000	0	0
$C_2O_4^{2-}$	2000	−1	−3
	400	−3	−5
F^-	3000	0	0
IO_3^-	5000	0	0
NO_3^-	10000	0	0
PO_4^{3-}	4000	−2	0
SO_4^-	6000	−2	0

[a] Each solution contains 100 μg of Cu(II), 10 ml of complexing solution and 5 ml of buffer per 25 ml. Copper(II) complex is extracted into benzene. Absorbance values measured after leaving the two layers for 15 min.

[b] Same as (a) plus 1 ml of 0.01 *M* sodium tartrate.

[c] Same as (a) plus 5 ml of 0.1 *M* sodium fluoride.

[d] The complex is extracted after shaking overnight.

The levels of interference in the gravimetric procedure were established by determining 10 mg of copper(II) in the presence of varying amounts of foreign ion. The following ions gave an error of 1% relative, usually negative, when present in the indicated milligram amounts: Ni(II), 80; Co(II), 70; Fe(III), 150; Fe(II), 250; Mn(II), 100; Pb(II), 150; Zn(II), 200; Al(III), 200; Sb(III), 200; Bi(III), 150; Sn(II), 150; Na(I), 10,000; K(I), 10,000; tartrate, 10,000; nitrate, 10,000. This is a different procedure to that used by BILLMAN *et al.*[6], who determined copper in a wide range of alloys. Aluminium and zinc were found to interfere to a greater extent than is implied from BILLMAN's results. However, this is a marginal criticism and there is no doubt that TSA is a selective and convenient gravimetric reagent for the determination of copper.

To confirm the utility of the reagent for practical purposes copper was determined in several alloys with satisfactory results. The results obtained are shown in Table VII.

TABLE VII

DETERMINATION OF COPPER IN ALLOYS BY THE SOLVENT EXTRACTION METHOD

Alloy	*Composition* (%)	*No. of detns.*	*% Copper found*		
			EDTA	*Solvent extn.*	*Standard deviation*[a]
1	Cu 7.0[b] Pb 3.47[b] Sn 74.6[b]	3	7.0	6.93	∓ 0.035
2	Cu 3–4[b] Sb 6.5–7.5[b] Sn remainder	3	3.63	3.55	∓ 0.059
BCS 307 Ce–Zn–Zr magnesium alloy[c]	Cu 0.005	3		0.004422	∓ 0.00021
BCS 260/2 high-purity iron[d]	Cu 0.002	3		0.00172	∓ 0.00008

[a] Based on the range.
[b] Approximate value.
[c] Zn 2.08, total rare earths 2.84, Zr 0.56, Mn 0.006, Fe 0.002.
[d] Si 0.003, S 0.008, P 0.004, Mn 0.013, Ni 0.011, Co 0.009.

TABLE VIII

SENSITIVITY OF COPPER REAGENTS

Reagent	*Molar extinction coefficient*	*Reference*
2,2′-Dipyridyl	4550	26
1,10-Phenanthroline	7150	26
2,2′-Biquinoline	5490	27
2,9-Dimethyl-1,10-phenanthroline	7950 8500	28
4,7-Diphenyl-1,10-phenanthroline	12140	29
2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline	14160	30
Fast Sulphon Black F	14000	31
Diethyl dithiocarbamate	12340	32
1,5-Diphenylcarbohydrazide	158000	33
o-(*p*-Toluenesulphonamido)aniline pH 6.5	2150	7
o-(*p*-Toluenesulphonamido)aniline pH 10, 30% ethanol	6618	This work
Solvent extraction (benzene)	6780	This work

White-metal alloys. Dissolve 1 g of the white metal in 25 ml of 1:1 nitric acid and evaporate to about 10 ml to remove nitrogen oxides. Dilute to about 50 ml. Digest the precipitate for 15 min and filter whilst hot. Wash the precipitate with hot water and transfer the washings and filtrate to a standard flask. Take a suitable aliquot and put through the extraction procedure.

High-purity iron alloy BCS 260/2. Dissolve 2.5 g of the alloy in a 1:1 mixture of 5 *M* nitric acid and 5 *M* hydrochloric acid and evaporate to about 10 ml. Add 40 ml of 6 *M* hydrochloric acid and extract the iron into diethylether. Repeat the extractions until iron has been quantitatively removed. Evaporate the aqueous solution to about 10 ml and then apply the extraction procedure.

Ce–Zn–Zr magnesium alloy BCS 307. Dissolve 1 g of the alloy in 25 ml of dilute aqua regia and evaporate to about 10 ml. Then apply the extraction procedure. Extract the copper complex by shaking overnight.

Discussion

Comparison with other reagents shows that *o*-(*p*-toluenesulphonamido)aniline used under the recommended conditions has a useful selectivity and sensitivity (Table VIII). It would seem fair to class it with 2,9-dimethyl-1,10-phenanthroline which was recommended by the Analytical Methods Committee. Fast Sulphon Black F and 1,5-diphenylcarbohydrazide, however, are more sensitive than *o*-(*p*-toluenesulphonamido)aniline.

SUMMARY

2-(4-Toluenesulphonamido)aniline,TSA, was examined to evaluate the claim that it is a specific gravimetric reagent for copper(II) and to see if the application of the reagent could be extended. The nature of the reaction and complexes was investigated by potentiometry, solvent extraction, spectrophotometry, polarography and mass spectrometry. A 1:2 copper:TSA complex formed at pH 6 ($K_f = 10^{19.11}$ in 50% (v/v) aqueous dioxane) is suitable for the gravimetric determination, as previously reported. A violet complex ($\lambda_{max.}$ 550 nm, $\varepsilon = 6620$) of uncertain composition is formed at pH 10–11 and may be used for the spectrophotometric determination of copper. The centres of chelation have been deduced from the infrared spectra of the complex and reagent and the causes of the selectivity are discussed.

RÉSUMÉ

Une étude est effectuée sur l'utilisation de la 2-(4-toluènesulfonamido)aniline (TSA) pour le dosage gravimétrique spécifique du cuivre(II); on a envisagé également la possibilité d'étendre l'application de ce réactif. On examine la nature de la réaction et des complexes par potentiométrie, extraction dans un solvant, polarographie et spectrophotométrie. Un complexe cuivre/TSA (1:2) formé au pH 6 convient au dosage gravimétrique comme déjà mentionné. Un complexe violet ($\lambda_{max.}$ 550 nm, $\varepsilon = 6620$) de composition mal définie est formé au pH 10 et peut être utilisé pour le dosage spectrophotométrique du cuivre. Les centres de chélation sont déduites des spectres infrarouges du complexe et du réactif.

ZUSAMMENFASSUNG

Es wurde geprüft, ob 2-(4-Toluolsulfonamido)anilin, TSA, sich als spezifisches, gravimetrisches Reagenz für Kupfer(II) eignet und inwieweit die Anwendung des Reagenzes erweitert werden kann. Die Reaktion wurde potentiometrisch, durch

Extraktion, spektralphotometrisch, polarographisch und massenspektrometrisch untersucht. Ein 1:2-Kupfer:TSA-Komplex der beim pH 6 gebildet wird, ist für die gravimetrische Bestimmung geeignet, wie früher bereits berichtet wurde. Ein violetter Komplex ($\lambda_{max.}$ 550 nm, $\varepsilon = 6620$) unsicherer Zusammensetzung wird bei pH 10 gebildet und kann zur spektralphotometrischen Bestimmung von Kupfer verwendet werden. Der Komplex und das Reagenz wurden im IR untersucht und die Ursachen der Selektivität diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

METHODS FOR THE STRUCTURAL INVESTIGATION OF XANTHONES

PART II. LOCATION OF HYDROXYL GROUPS BY ULTRAVIOLET AND VISIBLE SPECTROSCOPY[1]

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(Received January 12th, 1968)

Ultraviolet spectra are used extensively for the elucidation of structural problems in the xanthone series. In spite of a valuable contribution by DREYER[2], the approach continues to be largely by empirical correlations involving similarity and dissimilarity of spectra, which may provide information on the general oxygenation patterns of the carbon skeleton[3]. The location of free hydroxyl groups within this framework is feasible by the observation of spectral shifts in presence of certain additives. In this context, some general observations, obtained by the examination of a number of natural and synthetic xanthones are discussed in the present paper.

Addition of sodium hydroxide ionizes hydroxyl groups at all positions of the xanthone skeleton, resulting in profound alterations of the absorption spectrum. Data for various xanthones are shown in Figs. 1–12. For 1-hydroxyxanthones, the changes involve a reduction of the intensity of the second principal maximum, as well as bathochromic shifts of this and the other maxima at higher wavelengths (Figs. 1, 9, 10). 3-Hydroxyxanthones in alkaline media give rise to intense bands at 345–365 nm (Figs. 3, 9) where other xanthones, including the relatively acidic (see below) 4-hydroxy derivatives (Figs. 4, 10), absorb feebly even in the alkaline medium. After registration of the spectrum, the addition of hydrochloric acid to the alkaline solution is advisable in order to verify the stability of the substance under basic conditions. Xanthones which possess *ortho-* or *para-*quinolic systems decompose in presence of sodium hydroxide. The rate of this reaction is significantly higher for 1,2- (Fig. 5) and 1,4-dihydroxyxanthones (Fig. 6) than for their 3,4-analogues (Fig. 8), while 2,3-dihydroxyxanthones (Fig. 7) are surprisingly stable.

Addition of sodium acetate also provides selective information. Being a weaker base, it ionizes only the hydroxyl at C-3 to much the same extent as does sodium hydroxide. Accordingly, 3-hydroxyxanthones (I) give rise to identical bathochromic shifts of the UV maxima in presence of either sodium hydroxide or sodium acetate (Fig. 3). The same phenomenon is observed with 1,6-dihydroxyxanthones (II) (Fig. 5 of ref. 4). The 1,3-dihydroxy system (III), however, is less acidic, since the curves in presence of the two additives are not quite superimposable (Fig. 9). Thus, the pronounced acidity of the 3-(or equivalent 6-) hydroxyl group, due to charge stabilization,

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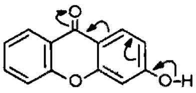
is seen to be somewhat diminished, if such mesomeric withdrawal of electrons also engages a hydroxyl *ortho* to the carbonyl situated on the same ring. If this interpretation is correct, 3-hydroxy-1-methoxyxanthones should display the usual high acidity of the 3-hydroxy derivatives. This is indeed the case; their curves in presence of sodium hydroxide and of sodium acetate are superimposable.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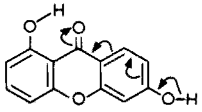
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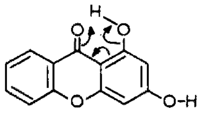
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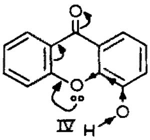
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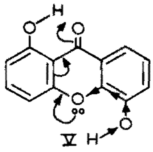
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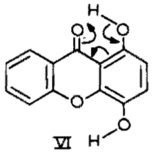
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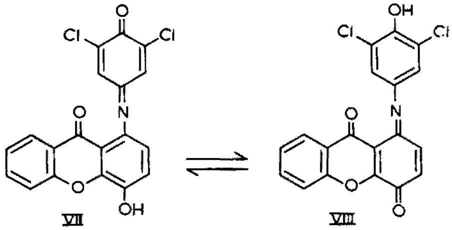
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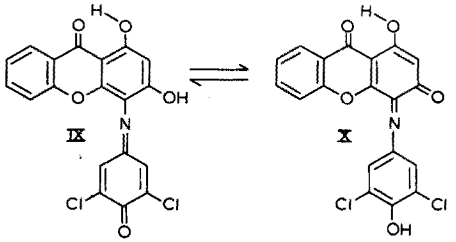

IX X

Derivatives of all the three series are soluble in aqueous sodium carbonate. Indeed, it has been stated repeatedly[4] that the solubility of a xanthone in sodium carbonate is evidence for a 3-hydroxy group. We have found, however, that hydroxyls at position 4 are also sufficiently acidic to confer to a xanthone considerable solubility in sodium carbonate[3]. The UV spectra of 4-hydroxyxanthones in presence of sodium hydroxide or sodium acetate are very close[5] (Fig. 4) and almost superimposable. In this case, in order to distinguish between 3- and 4-hydroxyxanthones it suffices to observe alterations of band intensity in the 345–365-nm region after addition of sodium acetate. As happens also with sodium hydroxide (see above), a hyperchromic effect characterizes only 3-hydroxy derivatives (compare Figs. 3 and 4, 9 and 10). The concomitant presence of 4- and 1- or 8-hydroxy groups produces even more striking alterations than in the 3-hydroxy series. Thus the UV spectra of 4,8-(equivalent to 1,5-) dihydroxy-

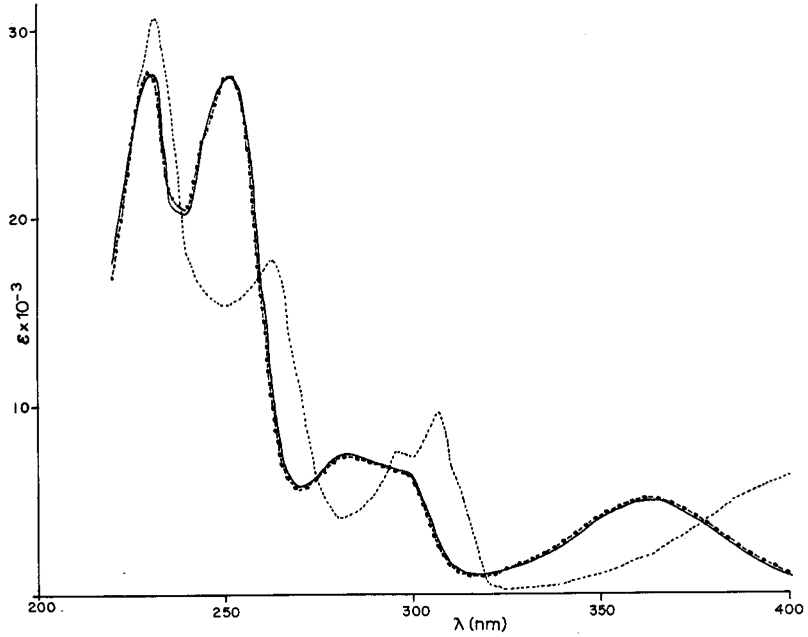


Fig. 1. Ultraviolet spectra of 1-hydroxyxanthone in EtOH (———), in EtOH + NaOAc (–·–·–), in EtOH + NaOH (· · · · · ·).

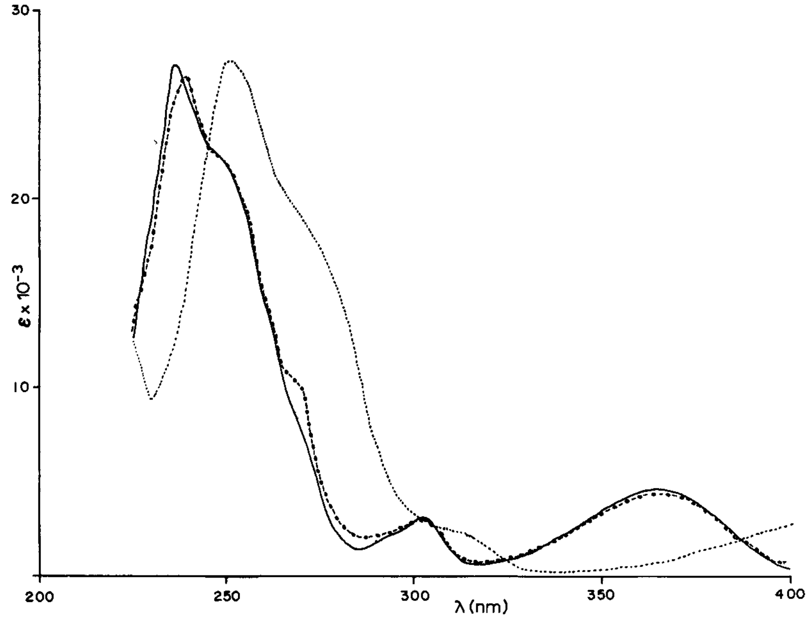


Fig. 2. Ultraviolet spectra of 2-hydroxyxanthone in EtOH (———), in EtOH + NaOAc (–·–·–), in EtOH + NaOH (· · · · · ·).

xanthones in presence of sodium acetate reveal features belonging to the spectra in neutral *and* in sodium hydroxide medium (Fig. 10, Fig. 6 of ref. 4), whereas the spectra of 1,4-dihydroxyxanthones in sodium acetate are superimposable on the spectra in

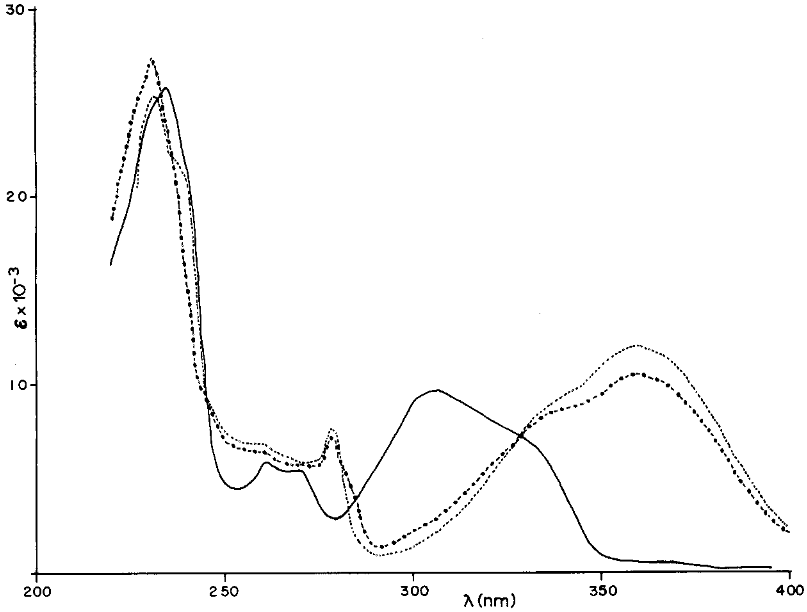


Fig. 3. Ultraviolet spectra of 3-hydroxyxanthone in EtOH (———), in EtOH + NaOAc (·—·—), in EtOH + NaOH (······).

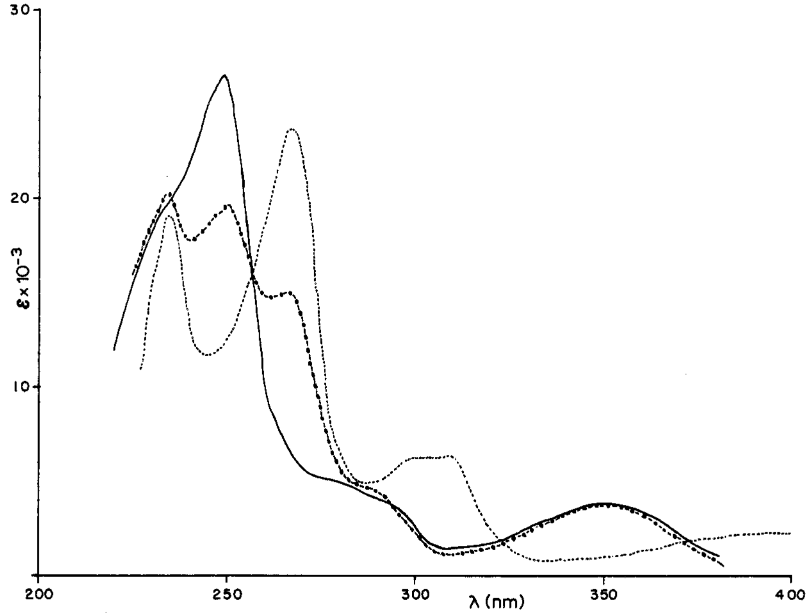


Fig. 4. Ultraviolet spectra of 4-hydroxyxanthone in EtOH (———), in EtOH + NaOAc (–·–·–), in EtOH + NaOH (······).

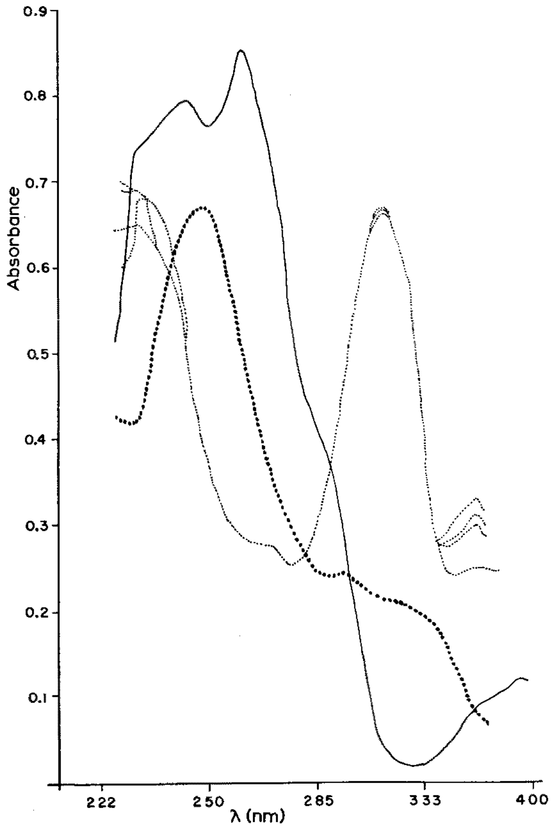


Fig. 5. Ultraviolet spectra of 1,2-dihydroxyxanthone in EtOH(————), in EtOH + NaOH (······) (curve of highest intensity read immediately after addition of alkali; other curves, from top to bottom, read at successive 5-min intervals), in EtOH + NaOH + HCl (••••••).

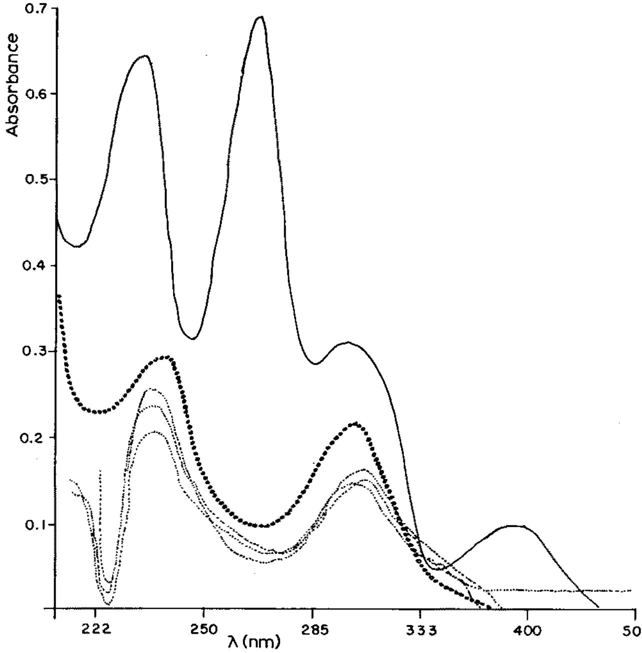


Fig. 6. Ultraviolet spectra of 1,4-dihydroxy-3-methoxyxanthone in EtOH (————), in EtOH + NaOH (······) (curve of highest intensity read immediately after addition of alkali; other curves, from top to bottom, read at successive 5-min intervals), in EtOH + NaOH + HCl (••••••).

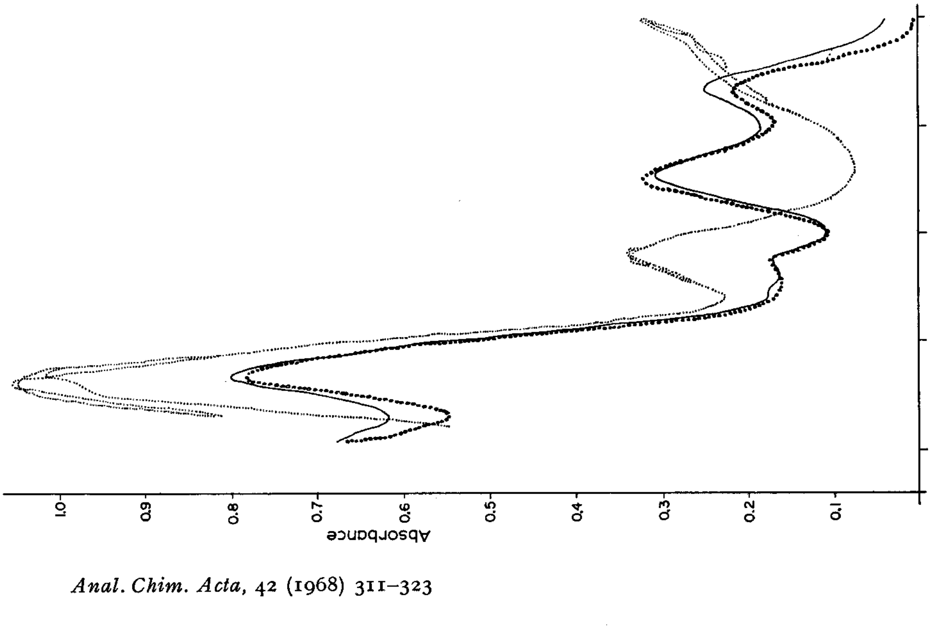


Fig. 7. Ultraviolet spectra of 2,3-dihydroxyxanthone in EtOH (———), in EtOH + NaOH (······) (curve of highest intensity read immediately after addition of alkali; other curves, from top to bottom, read at successive 5-min intervals), in EtOH + NaOH + HCl (•••••).

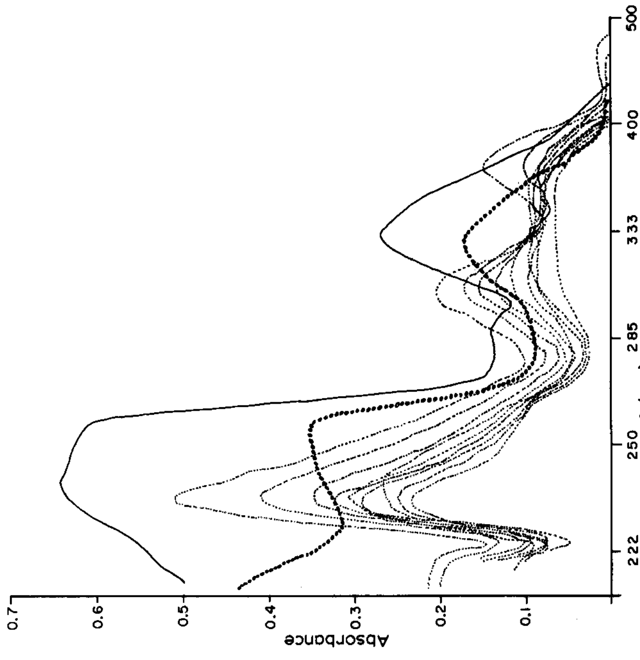
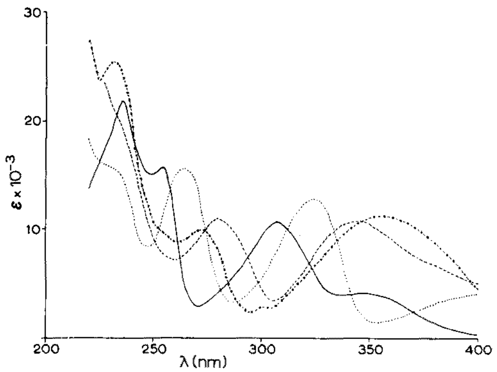


Fig. 8. Ultraviolet spectra of 3,4-dihydroxy-2-methoxyxanthone in EtOH (———), in EtOH + NaOH (······) (curve of highest intensity read immediately after addition of alkali; other curves, from top to bottom, read at successive 5-min intervals), in EtOH + NaOH + HCl (•••••).



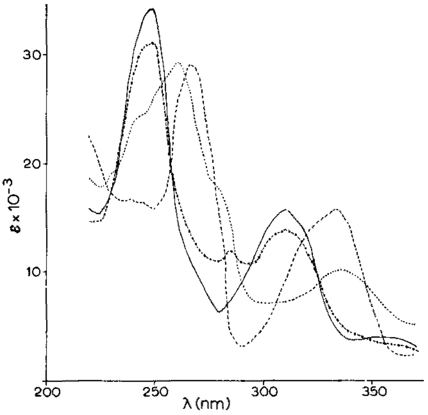
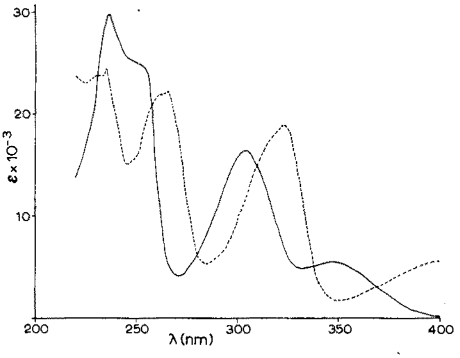


Fig. 9. Ultraviolet spectra of 1,3-dihydroxyxanthone in EtOH (———), in EtOH + NaOH (······), in EtOH + NaOAc (–·–·–), in EtOH + $AlCl_3$ (––––).

Fig. 10. Ultraviolet spectra of 1,5-dihydroxy-3-methoxyxanthone in EtOH (———), in EtOH + NaOH (······), in EtOH + NaOAc (–·–·–), in EtOH + $AlCl_3$ (––––).



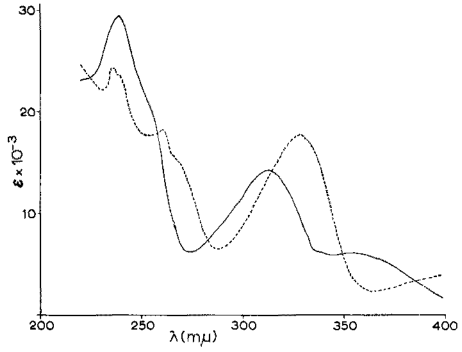


Fig. 11. Ultraviolet spectra of 1-hydroxy-3-methoxyxanthone in EtOH (———), in EtOH + $AlCl_3$ (––––).

Fig. 12. Ultraviolet spectra of 2,3-dihydroxy-1-methoxyxanthone in EtOH (———), in EtOH + $AlCl_3$ (––––).

neutral medium. Accordingly, 4,8-dihydroxyxanthones are soluble in sodium carbonate, while 1,4-dihydroxyxanthones are insoluble. In this way, complete, partial and no ionization are taken to occur respectively when sodium acetate is added to derivatives of IV, V and VI. Since here the *meta* relation to the carbonyl group makes formation of mesomeric anions of type I impossible, enhancement of the acidity in the 4(or 5)-hydroxyxanthone system can only be ascribed to an inductive effect of the vicinal ether oxygen, triggered by the carbonyl group. Whereas an 8-hydroxy group decreases this inductive effect only partially, a 1-hydroxyl seems to suppress it completely.

2-Hydroxyxanthones are insoluble in sodium carbonate and their spectra in neutral and sodium acetate media are superimposable (Fig. 2). Indeed, this is to be expected, since mesomeric conjugation with the carbonyl group is impossible and the etheric oxygen is too far removed to exert its inductive action.

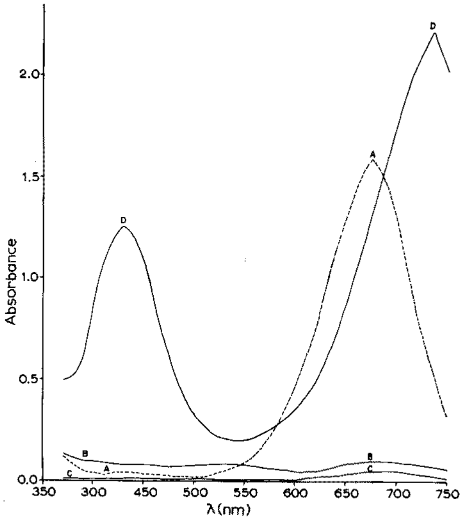
Owing to chelation, hydroxyl groups at C-1 show greatly diminished acidity. All 1-hydroxyxanthones are insoluble even in sodium hydroxide and their UV spectra, as well as those of 1,8-dihydroxyxanthones, are unaffected by addition of sodium acetate.

The bathochromic shifts of UV maxima caused by addition of aluminum trichloride are well known and may also be used in the xanthone series for detection of a free hydroxyl group at C-1. A strong reduction of intensity and a bathochromic shift of about 20 nm of the second principal maximum is observed (Fig. 11). It should be noted, however, that exactly the same spectral modifications are also characteristic of *ortho*-dihydroxyxanthones (Fig. 12). The presence of an *o*-dihydroxy group may be confirmed by observing spectral shifts after addition of boric acid and sodium acetate, a well-known expedient.

It is felt appropriate to consider Gibbs test, since this was introduced into organic analysis in its present spectrometric form in order to elucidate the structure of a xanthone[6], and has been applied frequently. Its aim is to demonstrate the existence of an unsubstituted position *para* to a free hydroxyl group through an absorption band between 500 and 700 nm due to the blue indophenol chromophore. More recently, however, the test has been reported frequently to be misleading[7]. It has now been found, nevertheless, that the indophenol reaction may be applied with confidence, at least in the xanthone field, if a differential technique is adopted and if the absorption curve is measured throughout the 350–750-nm range. Indeed, analysis of this curve is capable of yielding even more information than the Gibbs test intended in its original form.

In the xanthone series, hydroxyl groups with unsubstituted *para*-positions may be situated either at C-1 or at C-4. These types are easily distinguished by the Gibbs test, giving rise, respectively, to curves with maxima between 660 and 700 nm and between 710 and 750 nm. Only this high wavelength maximum is observed with slightly acidic xanthones, such as 1-hydroxyxanthone (Fig. 13, curve A) and 1,7-dihydroxyxanthone (Fig. 14, curve C). If, however, an additional structural feature, such as a *peri*-hydroxyl (Fig. 15, curve A) or a 3-alkoxyl (Fig. 15, curves C,D,E), diminishes the strength of chelation, a second maximum of relatively low intensity appears between 430 and 460 nm. Since the Gibbs test spectra of 4-hydroxyxanthones (Fig. 13, curve D; Fig. 16, curves A–D) also include this additional absorption peak, the mobility of a hydroxyl proton, with the consequent establishment of an equilibrium between two tautomeric forms (VII–VIII), may be considered to be the cause of the appearance of the two maxima. An analogous explanation (IX–X) may justify the occurrence of two maxima also in the Gibbs test spectra of 1,3-dihydroxyxanthones (Fig. 15, curve F). Their intensity is relatively low, a fact which may be ascribed to steric hindrance of the 4-position, and which also characterizes the spectra of tests performed on 1-hydroxy-3-alkoxyxanthones (Fig. 15, curves C,D,E).

While xanthones which possess only hydroxyls with unsubstituted *ortho*-positions (Fig. 13, curves B,C) do not absorb in the 350–750 nm region under the conditions of the test, *o*- or *p*-dihydroxy derivatives (Fig. 17, curves A–E) give rise to two maxima. Nervertheless, the low intensity of the corresponding curves and the brown colour of the reaction mixture, translated by the intensity ratio of the two peaks which now favours the maximum around 450 nm, makes distinction from positive Gibbs tests an easy matter. This observation is valid also in the case of compounds belonging



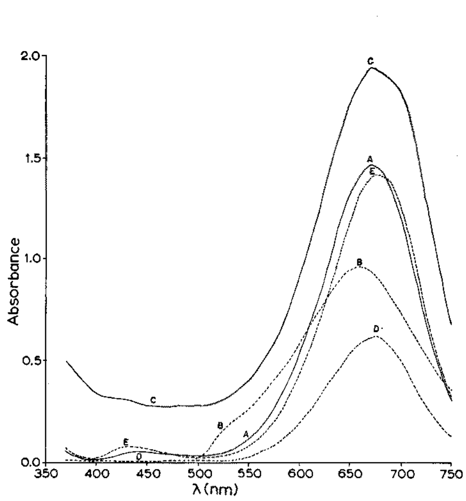
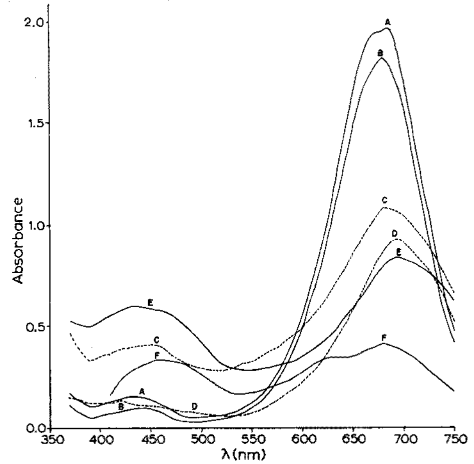


Fig. 13. Gibbs test spectra of 1-hydroxyxanthone (A), 2-hydroxyxanthone (B), 3-hydroxyxanthone (C), 4-hydroxyxanthone (D).

Fig. 14. Gibbs test spectra of 1-hydroxy-7,8-dimethoxyxanthone (A), 1,7-dihydroxy-8-methoxyxanthone (B), 1,7-dihydroxyxanthone (C), 1-hydroxy-5,6-dimethoxyxanthone (D), 1-hydroxy-7-methoxyxanthone (E).



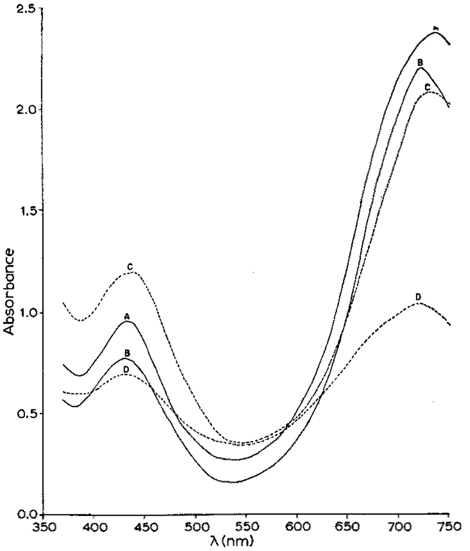
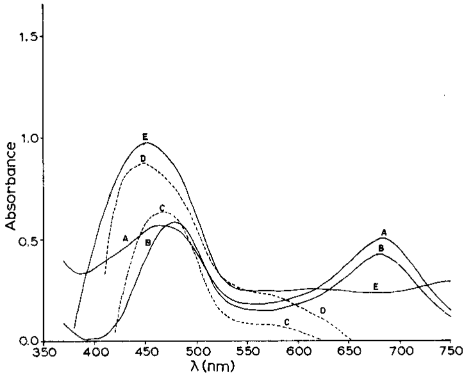


Fig. 15. Gibbs test spectra of 1,8-dihydroxyxanthone (A), 1-hydroxy-8-methoxyxanthone (B), 1,7-dihydroxy-3-methoxyxanthone (C), 1-hydroxy-3-methoxyxanthone (D), 1,7-dihydroxy-(6′,6′-dimethylpyrano-2′,3′, 3,2)-xanthone (E), 1,3-dihydroxyxanthone (F).

Fig. 16. Gibbs test spectra of 1,5-dihydroxy-3-methoxyxanthone (A), 5-hydroxy-1,3-dimethoxyxanthone (B), 1,5-dihydroxy-(6′,6′-dimethylpyrano-2′,3′,3,2)-xanthone (C), 4-hydroxy-2,3-dimethoxyxanthone (D).

to other structural classes (Table I, samples 1–7). Quinonic oxidation products formed through the action of the reagent upon the substrates are considered to be responsible for the absorption.

Xanthones which contain *o*- or *p*-hydroxyallylbenzene moieties give rise to similar curves, possibly because of oxidation to quinone methides. This observation can also be extended to substances of different structural classes (Table I, sample 8).



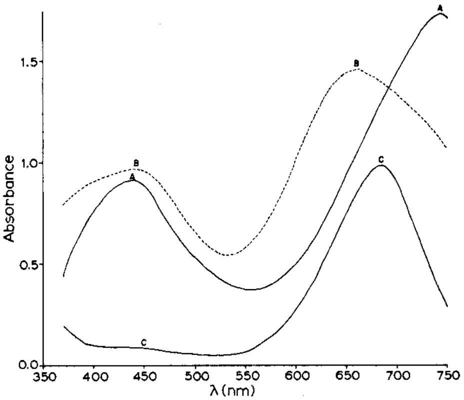


Fig. 17. Gibbs test spectra of 1,4-dihydroxyxanthone (A), 1,2-dihydroxyxanthone (B), 3,4-dihydroxy-2-methoxyxanthone (C), 2,3-dihydroxy-1-methoxyxanthone (D), 1,5,6-trihydroxy-(6′,6′-dimethylpyrano-2′,3′, 3,2)-xanthone (E).

Fig. 18. Gibbs test spectra of 1,5-dihydroxy-6-(3′,3′-dimethylallyl)-xanthone (A), 1,5-dihydroxy-8-(3′,3′-dimethylallyl)-xanthone (B), 1-hydroxy-(2′,2′-dimethylchromane-6′,5′,5,6)-xanthone (C).

TABLE I

APPARENT GIBBS TEST MAXIMA OF NON-XANTHONIC SUBSTRATES

Sample	*Compound*	λ_{max}*(nm)*	*Absorbance*	λ_{max}*(nm)*	*Absorbance*
1	1,2-Dihydroxybenzene	410	1.68	580	0.94
2	1,4-Dihydroxybenzene	390	0.84	550	0.88
3	1,4-Dihydroxy-2,6-dimethoxybenzene	460	0.85	660	0.05
4	2,5-Dihydroxy-3,4-dimethoxybenzophenone[8]	470	0.50	685	0.29
5	2,5-Dihydroxy-4-methoxybenzophenone[9]	470	0.59	685	0.27
6	3′,4′,7-Trihydroxyflavanone	380	1.02	530	1.00
7	2′,5′-Dihydroxy-3,4′,5,6,7-pentamethoxyflavone[10]	450	0.31	690	0.28
8	*cis*-1-(4-Hydroxy-2,3-dimethoxy-benzyl)-2-(2′-methoxyphenyl)-ethylene[11]	460	0.58	665	0.37

As for xanthones, the curves of 1,5-dihydroxy-6-(3′,3′-dimethylallyl)-xanthone (guanandin) (Fig. 18, curve A) and of 1,5-dihydroxy-8-(3′,3′-dimethylallyl)-xanthone (isoguanandin) (Fig. 18, curve B) contain, besides the maxima indicative of the presence of a 1-hydroxyl with an unsubstituted *p*-position, relatively intense maxima at 445 nm. As expected, with 1-hydroxy-(2′,2′-dimethylchromane-6′,5′,5,6)-xanthone (cycloguanandin) (Fig. 18, curve C) only the high wavelength maximum is observed.

Combinations of the outlined techniques make the location of hydroxyls in most mono- and dihydroxyxanthones feasible, even in presence of additional oxygenation by methoxyl groups. With caution, spectra of more highly hydroxylated xanthones can also be interpreted. Since these spectra may be measured rapidly with recording equipment on milligram or microgram quantities of sample, they constitute an attractive auxiliary tool for the structural investigation of xanthones.

EXPERIMENTAL

The foregoing discussion is based on an examination of ultraviolet and Gibbs test spectra of the following xanthones. Only substituents are quoted. The numbering system is based on xanthene-9-one as the basic skeleton[12]. The compounds were either synthesized or were natural products obtained during work on the constituents of Brazilian Guttiferae species[13,14]. 1-OH; 2-OH; 3-OH; 4-OH; 1,2-diOH; 1-OH-2-OMe; 1-OMe-2-OH; 1,3-diOH; 1-OH-3-OMe; 1,4-diOH; 1-OH-4-OMe; 1,7-diOH; 1-OH-7-OMe; 1,8-diOH; 2,3-diOH; 1-OMe-2,3-diOH; 1,2-diOMe-3-OH; 1-OH-3,4-diOMe; 1,4-diOH-3-OMe; 1,5-diOH-3-OMe; 1-OH-3,5-diOMe; 1,3-diOMe-5-OH; 1-OH-3,7-diOMe; 1,5,6-triOH; 1-OH-5,6-diOMe; 1,7,8-triOH; 1-OH-7,8-diOMe; 2-OMe-3,4-diOH; 2,4-diOMe-3-OH; 2,3-diOMe-4-OH; 2,3-O_2CH_2-4-OH; 1-OH-(4′,5′-dihydro-6′,6′-dimethylpyrano-2′,3′,5,6); 1,5-diOH-6-(3′,3′-dimethylallyl); 1,5-diOH-8-(3′,3′-dimethylallyl); 1,5-diOH-(6′,6′-dimethylpyrano-2′,3′,3,2); 1,7-diOH-(6′,6′-dimethylpyrano-2′,3′,3,2); 1,5,6-triOH-(6′,6′-dimethylpyrano-2′,3′, 3,2).

Spectra were taken with a Beckman DU spectrophotometer. Additives were introduced in equal amounts into the cell containing the solution and the cell containing the blank. Solutions were prepared containing 1 mg of compound in 100 ml of 95% ethanol. Three aliquots of these solutions were used. The first one served for the successive determination of three spectra: (*1*) without any addition, (*2*) after addition of 2 drops of 20% aqueous sodium hydroxide, and (*3*) after acidification of the alkaline solution by 2 drops of concentrated hydrochloric acid. The second one served for the successive determination of two spectra: (*1*) after addition of excess of sodium acetate trihydrate, and (*2*) after addition also of boric acid. The third one served to determine the spectrum after addition of excess of aluminum chloride hexahydrate.

Gibbs test. Solution A: The compound (1 mg) was dissolved in pyridine (6 ml) and borate buffer pH 9.2 (14 ml) was added. Solution B: To pyridine (6 ml) borate buffer was added (14 ml). The spectrum (350–750 nm) of solution A was determined with solution B as blank. Solution C: 2,6-Dichlorobenzoquinone chlorimide (1 mg) was dissolved in 10 ml of solution A. Solution D: 2,6-Dichlorobenzoquinone chlorimide (1 mg) was dissolved in 10 ml of solution B. Ten minutes after preparation of these solutions, the spectrum (350–750 nm) of solution C was determined, against solution D as a blank. The Gibbs test curve was constructed by subtracting the values obtained for solution A from the values obtained for solution C.

SUMMARY

Ultraviolet spectral shifts in presence of certain additives may be used to determine the hydroxylation pattern of xanthones. Thus, 3-hydroxyxanthones are characterized by an intense band around 355 nm which appears in presence of sodium hydroxide. *o*- and *p*-Dihydroxyxanthones decompose in presence of this reagent, the reaction rate depending on the position of the substituents. While the spectra of 1- and 2-hydroxyxanthones do not suffer modification in presence of sodium acetate, 3- and 4-hydroxy groups produce typical shifts which are dependent on the presence of additional oxygen functions. The spectra of 1-hydroxy-, as well as of *o*-dihydroxyxanthones, are affected by the addition of aluminum chloride. 1- and 4-Hydroxy groups with unsubstituted *p*-positions may be detected and distinguished through the visible spectrum (350–750 nm) of the reaction product of the xanthone with 2,6-dichlorobenzoquinone chloroimide (Gibbs test). Relatively acidic hydroxyls give rise to two maxima in this region. Two maxima, even if of different relative intensity, are also obtained with *o*- and *p*-dihydroxy-, as well as with *o*- and *p*-hydroxyallylxanthones.

RÉSUMÉ

Une étude est effectuée pour déterminer les positions des groupes hydroxyles dans des échantillons de xanthones par spectroscopie dans l'ultraviolet. Ainsi les hydroxy-3-xanthones sont caractérisées par une bande intense à 355 nm apparaissant en présence d'hydroxyde de sodium. Les *o*- et *p*-dihydroxyxanthones se décomposent en présence de ce réactif, la vitesse de réaction dépend de la position des substituants. Les spectres des hydroxy-1 et 2-xanthones ne sont pas modifiés en présence d'acétate de sodium contrairement aux 3- et 4-hydroxydérivés. Les spectres des hydroxy-1 et *o*-dihydroxyxanthones sont affectés par addition de chlorure d'aluminium. Les groupes hydroxy-4 para non substitués peuvent être décelés et caractérisés dans le spectre visible (350–750 nm) du produit de réaction de la xanthone avec le dichloro-2,6-benzoquinone chloroimide (test de Gibbs). Les hydroxyles relativement acides donnent deux maxima dans cette région. Deux maxima, même d'intensité relative différente, sont obtenus avec des *o*- et *p*-dihydroxy, de même qu'avec des *o*- et *p*-hydroxyallylxanthones.

ZUSAMMENFASSUNG

Um die Lage der Hydroxylgruppen bei Xanthonen zu bestimmen, werden die Verschiebungen ultravioletter Spektren in Gegenwart von bestimmten Zugaben benutzt. So wird das 3-Hydroxyxanthon durch eine intensive Bande bei 355 nm charakterisiert, welche in Gegenwart von Natriumhydroxyd auftritt. *o*- und *p*-Dihydroxyxanthon zersetzen sich in Gegenwart dieses Reagenzes. Die Reaktionsgeschwindigkeit ist von der Lage der Substituenten abhängig. Während die Spektren von 1- und 2-Hydroxyxanthon sich in Gegenwart von Natriumacetat nicht verändern, ergeben die 3- und 4-Hydroxy-Gruppen typische Verschiebungen, welche von der Gegenwart zusätzlicher Sauerstofffunktionen abhängig sind. Die Spektren von 1-Hydroxyxanthon ebenso wie die von *o*-Dihydroxyxanthon werden durch die Zugabe von Aluminiumchlorid beeinflusst. 1- und 4-Hydroxy-Gruppen mit unsubstituierten *p*-Stellungen können nachgewiesen und unterschieden werden durch die sichtbaren Spektren (350–750 nm) der Reaktionsprodukte von Xanthonen mit 2,6-Dichlorobenzochinonchloroimid (Gibbscher Test). Relativ saure Hydroxyle ergeben zwei Maxima in diesem Bereich. Diese ergeben sich auch, aber mit unterschiedlicher Intensität, mit *o*- und *p*-Dihydroxy- ebenso wie mit *o*- und *p*-Hydroxyallylxanthonen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

Determination of iron in copper–aluminum alloys by atomic absorption spectroscopy. Usable resonance lines of iron

Atomic absorption spectroscopy has been applied to the analysis of iron in many substances including ferrous and non-ferrous alloys[1–5], rocks and minerals[6–9], water and effluents[10,11], blood and blood serum[12–14] and agricultural materials[15,16]. This paper has a two-fold purpose: (*1*) to present a method for the analysis of trace amounts of iron in copper–aluminum alloys, and (*2*) to present the iron lines of high to medium sensitivity in atomic absorption spectrophotometric determinations. Optimum operating conditions for the determination of iron were also found.

Apparatus

All investigations were carried out with a Jarrell-Ash atomic-absorption spectrophotometer, model 82–546, equipped with a Tri-Flame burner (10-cm slit) with an air–acetylene flame in a single-pass system. The source was a Westinghouse iron hollow-cathode lamp, No. 22810, and the detector a R-106 photomultiplier coupled with an A.C. amplifier and a Sargent Model TR recorder. Standard iron solutions were prepared by dilutions of a 1000-p.p.m. stock solution made by dissolving iron wire in hydrochloric acid. Solutions of the alloys were prepared by carefully dissolving them in hot, concentrated nitric acid with a small amount of hydrochloric acid added. The hydrochloric acid and excess of nitric acid were slowly fumed off since chloride interferes at higher concentrations[17].

Determination of optimum operating conditions

Since the absorption was found to vary directly with both hollow-cathode current and photomultiplier voltage, these were maintained so as to obtain the highest signal-to-noise ratio, *i.e.*, a low photomultiplier voltage (650 V) and a hollow-cathode current (28 mA) near the recommended maximum. The optimum flow rates of air and acetylene were found in the usual manner and were 9.0 and 2.4 l/min, respectively. A vertical flame profile was then taken to find the region of highest absorption; the optimal burner height was found to be 6 mm. The slit was maintained at 25μ so as to give good resolution, reasonable intensity and to allow all lines to be calibrated without altering the setting.

Results and discussion

The sensitivities of the lines investigated range from 0.01 to 1.79 p.p.m. per 1% absorption and, together with the analytical range of each line, are listed in Table I. The analytical range is defined herein as the range of concentrations from p.p.m./3% absorption (three times the sensitivity) to the concentration at which a plot of absorption *versus* concentration deviates from linearity. The absorptions of solutions containing 20 p.p.m. Fe + 1000 p.p.m. Cu and 20 p.p.m. Fe + 1000 p.p.m. Al were compared at all the lines listed in Table I. When twice the standard deviation was taken as the statistical criterion, no significant interference was found at any line under the optimal

TABLE I

SENSITIVITIES AND ANALYTICAL RANGE OF THIRTY-ONE IRON LINES

Line (Å)	*Analytical range (p.p.m.)*	*Sensitivity (p.p.m./1% absorption)*
2166	3.9–50	1.3
2472	1.2–50	0.40
2479	1.1–25	0.36
2483	0.03–4	0.01
2488	0.06–5	0.02
2491	0.18–10	0.06
2501	1.9–50	0.63
2510	2.3–50	0.76
2518	0.09–8	0.03
2524	0.45–50	0.15
2526	3.2–50	1.07
2545	2.4–100	0.80
2719	0.08–3	0.04
2737	4.8–70	1.61
2936	1.4–50	0.47
2947	1.9–50	0.64
2966	0.21–20	0.07
2973	0.84–50	0.28
2983	0.69–50	0.23
2994	0.72–40	0.24
3001	1.4–50	0.48
3020	0.09–10	0.03
3025	5.1–250	1.70
3037	2.1–50	0.70
3047	0.87–50	0.29
3059	1.1–50	0.36
3581	1.7–50	0.55
3719	0.15–50	0.05
3734	5.4–250	1.79
3859	0.39–20	0.13
3878	3.2–50	1.05

[a] Relative sensitivity disagrees with literature [11,15]. However, studies show relative sensitivity to be a function of slit width.

TABLE II

ANALYSIS OF COPPER–ALUMINUM ALLOYS

Alloy	*Atomic absorption results (% Fe)*	*MRC results (% Fe)*	*Difference (%) (with respect to MRC results)*
A	0.0698	0.085	17.9
B	0.0606	0.060	1.00
C	0.0180	0.020	10.0
D	0.0391	0.041	4.64
E	0.077	0.080	3.75
		0.084[a]	8.34
F	0.026	0.050	48.0
		0.038[a]	31.6

[a] Independent wet chemical analysis.

conditions specified above. Slight differences in the amount of interferences may be obtained owing to line width since a fixed slit was used for all lines.

The iron contents of several copper–aluminum alloys were determined with the 2483 Å line. The results obtained in these analyses along with the results submitted by the Materials Research Corporation are presented in Table II. For alloys E and F, wet chemical analysis by means of a spectrophotometric determination with 2-benzoylpyridine-2-pyridylhydrazone was obtained independently of the above two sources[18] and is also presented in Table II. Alloy F was found to be a non-homogeneous solid solution causing the large discrepancies between the 3 results since samples were taken from various places on the block.

In conclusion, it has been shown that copper and aluminum do not appreciably interfere with iron absorption at any of the 31 lines studied and therefore iron can be determined at the lines in the presence of these two elements. Further, the choice of a line for analysis depends on the concentration of iron in the material to be analyzed.

The authors wish to thank Dr. WILLIAM SAVAGE for the alloy samples and JOHN E. GOING for performing independent analysis of the alloys.

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(Received February 23rd, 1968)

The turbidimetric determination of sulfate without the use of additives

Nearly all of the numerous methods described in the literature for the turbidimetric or nephelometric determination of sulfate involve the addition of various compounds to the turbid dispersion, ostensibly for stabilization of the dispersion. The most recent publication, in which no additives were used, seems to be that by HIBBARD in 1924[1]; he used a solution of barium chloride as the precipitating agent, but the accuracy was poor (±18.7% error). OWE[2] seems to have been the first to use additives. HOCHSEGANG has reviewed this determination as well as nephelometry and turbidimetry in general[3].

In the present note, an accurate turbidimetric determination of sulfate without additives is described and compared with the standard method[4]. The simplicity of the described method and the stability of barium sulfate dispersions formed without the use of additives refute the traditional necessity of additives.

Apparatus

Absorbance measurements were made with a Beckman DB spectrophotometer using 1-cm matched silica cells.

Preparation of standard curves

Pipet 25 ml of standard sulfate solution (prepared from A.R. potassium sulfate in deionized water), containing 10–100 p.p.m. of sulfate, into a 50-ml mixing cylinder. Add a scoop (*ca.* 0.25 g) of barium chloride dihydrate (20–30 mesh), stopper the cylinder and shake for about 30 sec. After a minimum of 20 min, and not longer than 2 h, mix the contents again by inverting the cylinder several times. Transfer the turbid solution to a 1-cm cell and measure the absorbance at 480 nm. Use deionized water to set the instrument at 100% transmittance.

The procedure previously used in this laboratory in the past was similar to the standard method[4]. To a measured volume (or weight) of sample, add 15 ml of salt-acid solution (73.1 g of sodium chloride and 20.7 ml of concentrated hydrochloric acid per liter), 25 ml of alcohol–glycerin solution (334 ml of glycerin, 666 ml of isopropanol and 1 l of deionized water) and make up to 75 ml in a 100-ml mixing cylinder with deionized water. Add 1 scoop of 20–30 mesh barium chloride dihydrate, invert the cylinder 12 times, let stand exactly 2 min and read the absorbance in a 1-cm cell at 630 nm.

Results and discussion

Figure 1 shows working curves for the proposed and standard methods. The proposed method yields a straight line for the range 10–100 p.p.m. whereas the method employing additives exhibits curvature. The line for the present method fits the equation: p.p.m. sulfate = absorbance $\cdot$ 102.5 + 3. The accuracy of the method was checked with standard solutions of potassium sulfate and also by comparison with gravimetric analysis of some phosphate rock samples (Table I). For the precision, eight determinations on a 50-p.p.m. standard showed an average deviation of 1.0%.

The stability of turbidities produced from 3 different concentrations of sulfate was studied by both methods. The suspensions were poured into a 1-cm cell and the %T recorded *vs.* time (Fig. 2); the 480-nm wavelength was used for both methods for the sake of comparison. In each case, a minimum in %T is apparent. However, the time required to reach a minimum for the additive method varies from 10 to 50 min, whereas for the proposed method a minimum appears in about 20 min in each case *i.e.* the time required to form the maximum number of barium sulfate particles is nearly constant. It should be noted that at no time do all 3 concentrations exhibit a minimum simultaneously when the standard method is used; this may explain the curvature of the working curve. The minimum in the 80-p.p.m. curve does not last very long, but this posed no problem provided that the suspension was left in the mixing cylinder and reshaken just before the absorbance was measured. For example, a suspension of 100 p.p.m. of sulfate showed a percentage transmittance

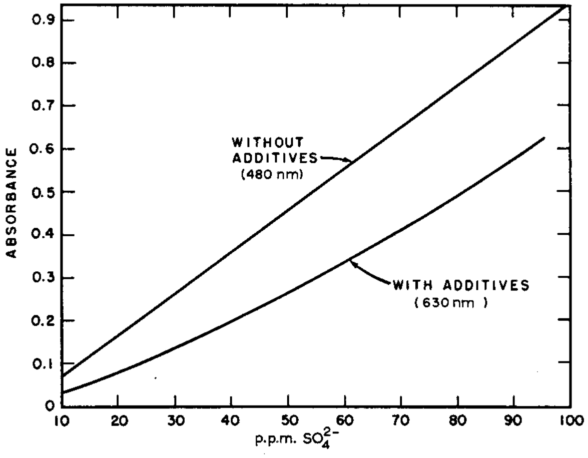

Fig. 1. Standard curves.

TABLE I

ACCURACY DATA FOR DETERMINATION OF SULFATE

Synthetic standards

p.p.m. Present	*p.p.m. Found*	*%E*
15.0	15.1	0.7
25.0	24.6	1.6
40.0	38.7	3.2
50.0	49.4	1.2
72.0	70.7	1.8
90.0	87.5	2.8 Av. 1.9%

Phosphate rock samples

% SO_4 Gravimetric	*% SO_4 Turbidimetric*	*% Difference*
2.24	2.19	4.2
2.49	2.71	8.8
3.68	3.86	4.9
6.05	5.85	3.3
12.80	11.92	6.9 Av. 5.6%

of 11.2 after 20–30 min; the value changed only to 11.4 after 280 min, when the suspension was shaken before the measurement. This stability is convenient for routine work.

Figure 2 shows that additives serve little purpose, except possibly to decrease the solubility of barium sulfate and thus increase slightly the sensitivity of the method. If more sensitivity is required, longer cells can be used; 4-cm cells were used with the proposed method and a straight line was obtained for the range 5–25 p.p.m.

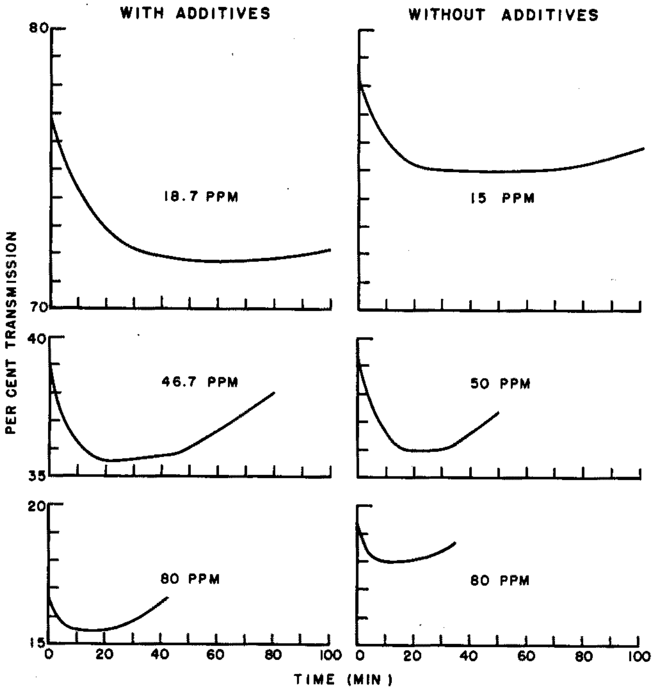

Fig. 2. Comparison of the stability of $BaSO_4$ turbidities.

The effect of temperature was not studied, all the tests being made at room temperature (22–26°). Obviously, high temperatures should be avoided.

The advantages of the proposed method are as follows: fewer manipulations and fewer reagents are required, it is not necessary to follow exactly an elaborate technique, and the timing of measurements is not critical.

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(Received December 21st, 1967)

Utilization of hyamine as a selective extraction agent in the spectrophotometric determination of cobalt

In recent years several long-chain aliphatic amines and quaternary ammonium compounds have been used to charge-neutralize the anionic cobalt–thiocyanate complex and thus enhance the percentage of cobalt extracted into organic solvents[1–8]. During the course of a systematic study of the effect of quaternary ammonium salts on the polarographic behaviour of various metal complexes, it was observed that Hyamine 1622 reacts with cobalt–thiocyanate to form a compound which is insoluble in water but extremely soluble and chemically stable in some organic solvents. The present investigation was undertaken to study the extraction behaviour of the complex and the possible application of hyamine as a selective extraction agent for the cobalt–thiocyanate complex ion.

Apparatus and reagents

Absorption curves were recorded with a Beckman DB spectrophotometer. Extinctions were determined in matched 1.000-cm glass cells with a Zeiss model PMQ II spectrophotometer. All pH measurements were made with a Beckman Zeromatic pH meter. The extractions were performed in ordinary separatory funnels and the organic phase transferred to 10-ml borosilicate glass tubes stoppered with polyethylene caps. Whenever the organic phase was not completely clear, it was centrifuged for 1–2 min before determination of the extinction. All measurements were performed at room temperature, 22±2°.

Stock solutions of cobalt were prepared by dissolving the appropriate amount of cobalt nitrate in distilled water, and standardized by titration with EDTA using murexide as indicator. Solutions of thiocyanate were prepared by dissolving potassium thiocyanate (dried at 120°) in distilled water. Hyamine 1622 (di-isobutylphenoxyethoxyethyldimethylbenzylammonium chloride monohydrate, M.W. 466.09; Rohm and Haas Co, Philadelphia, Pa., USA) is very pure and a stock solution was prepared by simply dissolving the product in water. The remaining chemicals were of reagent grade and used without purification.

Results

On addition of an aqueous solution of Hyamine 1622 to a slightly acidic solution of cobalt–thiocyanate, a blue precipitate is formed which is soluble in several organic solvents (benzene, nitrobenzene, cyclohexane and various halogenated hydrocarbons). The Hyamine reagent is very soluble in halogenated hydrocarbons but practically insoluble in, for instance, benzene[5]. However, the cobalt–thiocyanate–Hyamine complex appears to be most easily soluble in benzene and the complex is stable for several weeks in this solvent. Experiments showed that the complex is quantitatively transferred to a benzene phase in a single extraction whereas the solution must be treated twice with halogenated hydrocarbons in order to obtain complete extraction.

The absorption curve of the blue complex in benzene, measured against a blank of pure benzene, is given in Fig. 1. Maximum absorption is observed at 326 and 624 nm and a characteristic shoulder is obtained at 590 nm. The same absorption curve and maxima are also obtained when, for instance, chloroform is used as the organic phase.

The effect of thiocyanate on the extraction of cobalt was studied by varying the concentration of potassium thiocyanate while that of all other components was kept constant. The absorption of the benzene phase measured at 624 nm increases with increasing concentration of thiocyanate in the aqueous phase and reaches a limiting value when the molar concentration of thocyanate is about 150 times that of cobalt. A further increase in the concentration of thiocyanate has no effect on the extinction measured. The experiments were repeated using chloroform as the organic phase. In this case the excess of thiocyanate must be 200–250 times that of cobalt in order to obtain a limiting extinction.

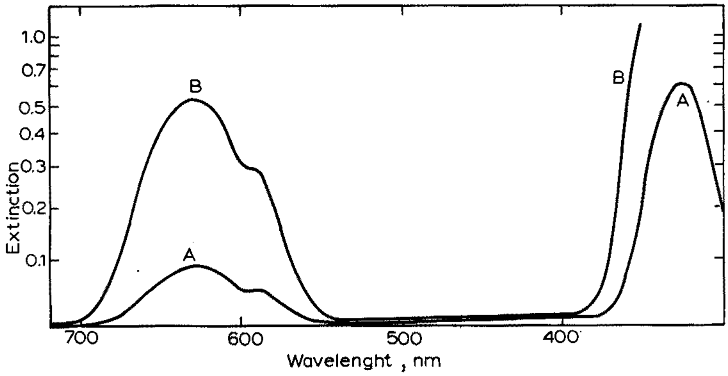

Fig. 1. Absorption curves of the cobalt–thiocyanate–hyamine complex in benzene. Concentration of cobalt: $5 \cdot 10^{-5}$ M (curve A) and $3 \cdot 10^{-4}$ M (curve B).

Solutions containing various amounts of cobalt were analysed following the procedure given below. The extinction plotted against the cobalt concentration showed a straight line in the concentration range 0.5 to $5 \cdot 10^{-4}$ M cobalt in benzene, indicating that Beer's law is obeyed. The molar extinction coefficient of the complex is 1780. Beer's law is obeyed also at 326 nm. The molar extinction coefficient at this maximum is 12000. As benzene gives a small absorption at this wavelength, the solutions were extracted twice with chloroform in these experiments. Because the interference from other metal ions is very serious at 326 nm, this more sensitive maximum is of little value in practical analysis and the extinction was measured only at 624 nm in the following experiments.

The extraction of the cobalt complex into benzene is complete in a single extraction and independent of pH in the range 1–8. At higher pH values the amount of cobalt extracted decreases rapidly and becomes zero at pH 11. A 0.1 M acetate buffer of pH 4.6 appeared to be the most suitable.

The effect of the hyamine concentration and the stoichiometry of the complex were investigated by the so-called limiting loading method[9]. The experiments were performed by varying either the hyamine or the cobalt(II) concentration while the concentrations of the other components were kept constant. Each solution was extracted with 10 ml of benzene and the extinction measured at 624 nm. The results (Fig. 2) indicate a limiting cobalt-to-hyamine ratio of 1:2 in the organic phase. At high hyamine concentrations (above 10^{-2} M), the extinction decreases, indicating that cobalt is not quantitatively extracted. Besides, the benzene phase becomes turbid and a clear solution is not obtained even after centrifugation for several minutes. When chloroform is used as the organic phase the turbidity is observed at even lower hyamine concentrations. This effect might be due to micelle formation of hyamine at high concentrations, but it was not further investigated. In order to avoid these effects it is important to keep the hyamine concentration below $5 \cdot 10^{-3}$ *M*.

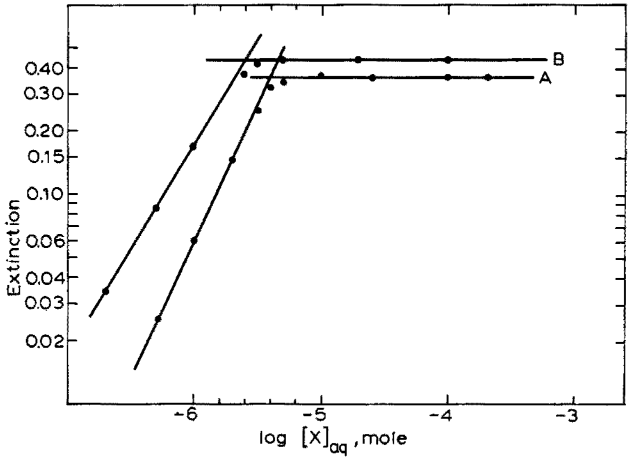

Fig. 2. Extraction isotherms for 0.1 *M* acetate buffered media extracted with 10 ml of benzene. (A) $2.0 \cdot 10^{-6}$ mole cobalt, $5 \cdot 10^{-3}$ mole thiocyanate and various amounts of hyamine (× = hyamine); limiting extinction obtained in the presence of more than $4.0 \cdot 10^{-6}$ mole hyamine. (B) $5.0 \cdot 10^{-6}$ mole hyamine, $5 \cdot 10^{-3}$ mole thiocyanate and various amounts of cobalt (× = Co^{2+}); limiting extinction obtained in the presence of more than $2.5 \cdot 10^{-6}$ mole cobalt.

The extraction of cobalt is not affected by the presence of even large excess of anions like chloride, phosphate, sulphate and perchlorate. However, the presence of citrate or very large amounts of acetate (above 0.5 *M*) causes a large negative error. Cations which do not form complexes with thiocyanate are not extracted and do not interfere. Chromium(III) reacts slowly with thiocyanate and only a small fraction (probably only the anionic chromium thiocyanate species) is extracted. The nickel complex is easily extracted but this complex as well as the chromium complex shows nearly no absorption at 624 nm. Iron(III) reacts with thiocyanate and hyamine, and the complex causes significant interference at 624 nm; however, iron(III) can be effectively masked by adding thiosulphate and phosphate to the aqueous solution and the extraction of iron avoided by separation of the organic phase as soon as possible after equilibration. A trace of iron–thiocyanate–hyamine complex extracted is easily backwashed by shaking the organic phase with an aqueous solution containing the same masking agents. The red copper(II) thiocyanate is reduced in the presence of thiosulphate, and the copper(I) thiocyanate formed is not extracted but a small amount of cobalt is coprecipitated. However, if the solution is extracted twice with benzene, a complete extraction of cobalt is obtained even in the presence of a large excess of copper.

On the basis of the above results the following procedure is suggested.

Procedure

The sample containing 0.03–0.3 mg cobalt is transferred to a separatory funnel and 5 ml of 0.5 M acetate buffer (pH 4.6), 5 ml of 1 M thiocyanate and 2 ml of an aqueous 1% solution of Hyamine 1622 are added. The total volume of the aqueous phase should be about 25 ml. The solution is extracted once with 10.00 ml of benzene and after shaking for 5–10 min, the organic phase is transferred to the cell and the extinction measured against a blank at 624 nm. If the benzene phase is not perfectly clear, it may be centrifuged for 1–2 min before the measurement.

If a large excess of iron, copper or nickel is present, 0.2 M thiosulphate and 0.2 M phosphate should be added to the aqueous solution, and the benzene phase backwashed with an aqueous solution containing 0.5 M thiocyanate, 0.25 M sodium thiosulphate and 0.25 M potassium phosphate.

Discussion

Cobalt is completely extracted only in the presence of a large excess of thiocyanate indicating that only the species $Co(SCN)_4^{2-}$ reacts with hyamine. As the mole ratio of cobalt to hyamine in the organic phase is 1:2, the reaction is probably:

$$Co(SCN)_4^{2-} + 2R_4N^+ \rightarrow (Co(SCN)_4(R_4N)_2)_{org}$$

where R_4N denotes Hyamine 1622.

Hyamine 1622 appears to be a very suitable reagent for the extraction of the cobalt–thiocyanate complex. The commercial product is very pure and gives no absorption in the visible region. Other long-chain amines and quaternary ammonium compounds tested, like Hyamine 2389 (Rohm and Haas) and various Arquads (Armour Hess Chemicals Ltd., Leeds), are all slightly coloured and hard to purify. The suggested method with Hyamine 1622 and benzene as the organic phase is simpler and faster than earlier methods[5,6] and there is less interference from large amounts of chromium, copper and nickel. Following the described procedure, cobalt may be determined in the presence of chromium, nickel, copper and iron at mole ratios of 600, 600, 450 and 250, respectively. However, the tricaprylmethylammonium-thiocyanate method[5] appears to be advantageous when the excess of iron exceeds 250 times that of cobalt.

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(Received March 6th, 1968)

The spectrographic analysis of plutonium for twenty-two trace impurities by the D.C. arc method

Plutonium, when used as a nuclear fuel, should be free not only of impurities of high neutron-capture cross-sections, but also from many other impurities which could affect its metallurgical properties. The plutonium is obtained after various separation and purification stages as nitrate, oxide or metal. A spectrographic method has been developed for determining 22 trace impurities in plutonium in these forms. Throughout, the aim was to achieve maximum sensitivity, minimise the health hazard and cover the maximum number of impurities in a single exposure on the large quartz spectrograph available. The single exposure kept the consumption of materials such as electrodes and photographic plates to the minimum.

The various methods[1-9] of spectrographic analysis of pure plutonium can be broadly classified as follows: (*1*) excitation of impurities separated from the plutonium sample, and (*2*) excitation of impurities employing a carrier distillation technique. The former method was preferred for this work in order to minimize the health hazard problems arising out of arcing large quantities (100 mg) of plutonium oxide. The bulk of the plutonium was therefore removed by anion exchange.

Preparation of standards

The dry mixed standards were prepared on a graphite base. Specpure compounds (Johnson Matthey, London and Spex Industries, Scotch Plains, N.J.) were used. The 22 impurities were classified into 5 different concentration groups. Calculated amounts of each of the impurities as the oxide or some other suitable form, were added to graphite to produce a high concentration standard. A "Wig-l-Bug" (Spex Industries, Scotch Plains, N.J.) was used to ensure homogeneous mixing. Standards of lower concentration were prepared by suitable dilution (not more than 2.5 times).

Internal standards

An aqueous stock solution (500 μg Sn/ml) of ammonium hexachlorostannate was prepared with 0.2 ml of concentrated hydrochloric acid to prevent hydrolysis. An aqueous stock solution (500 μg Pd/ml) of ammonium tetrachloropalladate was also prepared. The two internal standard solutions were added (0.01% each of Pd and Sn on the graphite basis) to graphite, dried and then used for the preparation of standards and dilutions thereof as described above.

For the samples, a solution containing 20 μg Pd/ml and 20 μg Sn/ml was prepared by mixing the two stock solutions, and was used as mentioned below.

Preparation of plutonium samples

Plutonium samples were prepared in a glove box under reduced pressure as follows. Dissolve the sample of plutonium oxide in a platinum dish in the minimum amount of concentrated nitric acid (twice-distilled from quartz). For complete dissolution, add a drop of hydrofluoric acid. Evaporate the solution (equivalent to 1 g Pu) under an infrared lamp to near dryness, and dilute to 20 ml with 7.2 *M* nitric acid. Add a few drops of hydrogen peroxide to keep plutonium in the tetravalent state, and remove excess of peroxide by heating as before. Pass the solution through a polythene ion-exchange column of 1 cm diameter, containing a 10-cm column (*ca.* 5 g) of Dowex 1-

X4 (50–100 mesh) in the nitrate form. Pass 10 column volumes of 7.2 *M* nitric acid through the column and collect the effluent (100 ml) containing impurities (with 400 μg Pu) in a quartz beaker. Add 500 μl of the internal standard solution containing tin and palladium to the effluent, and evaporate on 100 mg of pure graphite. Load the

TABLE I

PARAMETERS FOR SPECTROGRAPHIC EXCITATION AND PHOTOMETRIC ANALYSIS

Spectrograph	Hilger large quartz and glass spectrograph fully automatic E. 478–304
Slit width	0.015 mm
Slit illumination	The intermediate real image was formed 38 cm from the arc by means of a spherical lens (Hilger F. 958) 8 cm from the arc. This was refocussed on the collimating lens by keeping a spherical lens (Hilger F. 1025) 2 cm from the slit
Emulsion	Kodak B. 10
Wavelength range	2450–3500 Å
Excitation unit	Hilger and Watts BNF Source unit F.S. 131
Type of excitation	D.C. arc; 220 V, 10 A
Electrodes	Anode: 6.35-mm diameter U.C.P. graphite rod (grade UF 4S) with a cavity 3±0.5 mm deep and a wall thickness of 0.5 mm Cathode: 3.05-mm diameter U.C.P. graphite rod (grade UF 4S) tapered
Internal standards	Sn and Pd. For a charge of 10 mg of graphite per arcing, 1 μg each of Sn and Pd
Exposure	25 sec
Plate calibration	Rotating seven-step sector with a step ratio of 2:1 with iron arc at 3 A, exposure 15 sec
Processing	Kodak D-19b for 4 min at 20°; fixed in Kodak F-5 for 10 min
Densitometer	Hilger non-recording microphotometer L. 451

TABLE II

LINE PAIRS, CONCENTRATION RANGE AND REPRODUCIBILITY

Line pair[a]				*Concn. range (p.p.m.)*	*S.d. at 67% confidence level*
Impurity element		*Internal standard*			
Al(I)	3082.16Å	Pd(I)	3242.70Å	0.25–1	13
Ba(I)	3071.59	Pd(I)	3242.70	6.0–50	14
Ca(II)	3179.33	Pd(I)	3242.70	0.5–10	18
Cr(II)	2835.63	Pd(I)	3242.70	1.25–10	20
Cu(I)	3247.54	Pd(I)	3242.70	0.10–2.5	18
La(II)	3337.49	Pd(I)	3242.70	2.5–20	15
Mo	3132.59	Pd(I)	3242.70	0.5–10	14
Ni(I)	3050.82	Pd(I)	3242.70	0.60–5	14
Cb	3130.79	Pd(I)	3242.70	5.0–20	15
Ti(II)	3252.91	Pd(I)	3242.70	0.5–20	17
V(I)	3185.40	Pd(I)	3242.70	0.5–10	18
Zr(II)	3391.98	Pd(I)	3242.70	1.0–20	23
Sb(I)	2598.06	Sn(I)	2839.99	6.0–50	14
Bi(I)	3067.72	Sn(I)	2839.99	0.5–10	14
B(I)	2497.73	Sn(I)	2839.99	2.5–25	14
Cd(I)	3261.06	Sn(I)	2839.99	2.5–50	14
Fe(I)	2599.57	Sn(I)	2839.99	1.0–20	19
Pb(I)	2833.07	Sn(I)	2839.99	2.5–20	12
Mg	2779.83	Sn(I)	2839.99	0.5–20	18
Mn(II)	2605.69	Sn(I)	2839.99	0.5–5	13
In(I)	3256.09	Sn(I)	2839.99	0.5–10	17
Zn(I)	3345.02	Sn(I)	2839.99	5.0–20	22

[a] M.I.T. Wavelength Tables[10].

graphite powder (*ca.* 10 mg) in the graphite electrode. Add a drop of hydrofluoric acid to the powder in the electrode cavity and dry under the infrared lamp. Prepare standards for arcing in the same way. Similar procedures were adapted for nitrate and metal samples. The data for the measurement process are given in Table I.

Volatilization studies

The racking plate technique was used to study the volatilization of the various impurities and some selected internal standards. The impurities could be divided into two groups whose volatilities matched with the internal standard elements tin and palladium, respectively.

Results and discussion

Table II gives details of the line pairs and the range of determination with the standard deviations at the 67% confidence level. The standard deviations were calculated from at least 15 values of intensity ratios for each standard. The values were obtained from 3 or 4 photographic plates exposed independently by two persons at different times, thus giving a standard deviation inclusive of photometric, personal

TABLE III

DETECTION LIMITS OF THE DIFFERENT METHODS IN p.p.m. ON PLUTONIUM BASIS

Element	*Ref. 1*	*Ref. 2*	*Ref. 3*	*Present method*	*Ref. 4*	*Ref. 5*	*Ref. 6*[a]	*Refs. 6*[b]	*Ref. 7*
Al	20	10	0.5	0.2	2	300	300	100	1000
B	0.1	—	0.5	1.0	—	300	1200	1	1000
Ba	5	20	0.1	3.0	125	200	400	—	100
Bi	0.5	—	—	0.2	31	—	—	—	1000
Ca	—	2	1	0.2	2	200	100	10	1000
Cd	10	40	0.4	1.0	—	—	1200	1	1000
Cr	5	4	0.2	0.5	6	300	100	20	100
Cu	5	—	1.0	0.1	—	300	—	1	—
Fe	5	—	1.0	0.5	12	300	300	20	2500
In	—	40	—	0.2	—	—	—	—	500
La	—	20	0.02	0.5	—	—	1200	—	—
Mg	2	2	0.5	0.2	12	200	10	5	500
Mn	—	2	0.05	0.2	12	—	10	5	50
Mo	20	—	0.05	0.2	I.S.	—	400	—	—
Cb	—	—	—	0.5	—	—	—	—	—
Ni	2	40	0.2	0.1	31	1000	1000	5	250
Pb	1	40	0.5	1.0	—	300	—	10	1000
Sb	10	—	—	2.0	—	—	—	—	10000
Ti	50	—	0.05	0.2	6	200	—	—	500
V	20	—	0.1	0.2	—	—	—	—	100
Zn	50	—	—	0.5	125	1000	3000	150	5000
Zr	—	—	0.1	0.5	31	200	—	—	—
No. of impurities detected[c]	10	6	36	—	4	3	7	3	21

[a] Cu spark.
[b] Carrier distillation.
[c] Other than those compared here by the various methods.

and other likely errors in such analyses. The overall standard deviation of the method is 16% at the 67% confidence level.

The detection limits of the present method are compared with those of other methods in Table III. The detection limits obtained by the present method for the 22 elements are comparable with the limits obtained by FARIS[3], whose procedure consists of multiple exposures on 3 types of photographic emulsions and employs a grating spectrograph to cover 54 impurities. With regard to other methods[1,2,4–9], the detection limits of the present method are better. The standard deviation of 14% at the 67% confidence level for boron is inclusive of any uncertainty due to the evaporation and other losses of boron.

Enhancement of line intensities for zirconium and other elements

There is a marked increase in the line intensities of certain elements obtained when a drop of hydrofluoric acid is added to the charge in the electrode cavity before arcing. The effect is most pronounced for zirconium but is also noticeable for molybdenum and other elements. Table IV gives the line densities for such elements. The enhancement is probably due to the conversion of the impurity to its fluoride which is more volatile.

TABLE IV

LINE DENSITY VALUES SHOWING THE ENHANCEMENT CAUSED BY ADDITION OF HYDROFLUORIC ACID

Element	*Sn*[a]	*Pd*[a]	*Zr*	*Ti*	*Mo*	*La*	*V*
Without HF	0.50	1.05	0.67	1.2	0.55	0.68	1.0
With HF	0.51	1.10	1.35	1.5	0.75	0.86	1.15

[a] Internal standard.

Sincere thanks are due to SHRI N. SRINIVASAN, Head of the Fuel Reprocessing Division, Bhabha Atomic Research Centre, for his keen interest and encouragement.

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(Received January 20th, 1968)

The use of mass balance conditions in calculations involving ionic equilibria

Most books[1–4] containing elementary treatments involving chemical equilibria introduce principles such as the proton balance and the charge balance or the electroneutrality relation (condition) in conjunction with the conditions for mass (material) balance. Our experience is that the use of mass balance conditions for *all* components simplifies the algebraic treatment of chemical equilibria, especially in more complicated systems. The elaborate computer program "HALTAFALL", for instance, constructed by SILLÉN *et al.*[5], uses the mass balance condition only.

Three examples will illustrate the futility of replacing one mass balance condition by the electroneutrality relation.

Example 1. State the equations for the calculation of the concentrations of various species (*e.g.* the pH) in a mixture of a M acetic acid (HAc) and b M calcium acetate ($CaAc_2$).

Mass balances:

$$\text{Total H: } a = [H^+] + [HAc] - [OH^-] \tag{1}$$

$$\text{Total Ac: } a + 2b = [Ac^-] + [HAc] + [CaAc^+] \tag{2}$$

$$\text{Total Ca: } b = [Ca^{2+}] + [CaAc^+] \tag{3}$$

Electroneutrality:

$$[H^+] + 2[Ca^{2+}] + [CaAc^+] = [Ac^-] + [OH^-] \tag{4}$$

Equation (4) may also be obtained by doubling eqn. (3), adding eqn. (1) and subtracting eqn. (2) and is, thus, superfluous.

In order to solve the problem, expressions for the equilibrium stability constants (complex formation constants) are, of course, needed in addition to the conditions for the mass balance. These are: $[HAc] = K_1[H^+][Ac^-]$ and $[CaAc^+] = K_1[Ca^{2+}][Ac^-]$, where values for the K_1's may be selected from a compilation of stability constants[6].

Example 2. Calculate the pH of an a M thorium nitrate solution.

Mass balances:

$$\begin{aligned}&\text{Total Th: } a = [Th^{4+}] + [Th(OH)_2^{2+}] + 2[Th_2OH^{7+}] + 2[Th_2(OH)_2^{6+}] +\\&2[Th_2(OH)_3^{5+}] + 6[Th_6(OH)_{14}^{10+}] + 6[Th_6(OH)_{15}^{9+}]\end{aligned} \tag{5}$$

$$\begin{aligned}&\text{Total H: } 0 = [H^+] - [OH^-] - 2[Th(OH)_2^{2+}] - [Th_2OH^{7+}] - 2[Th_2(OH)_2^{6+}] -\\&3[Th_2(OH)_3^{5+}] - 14[Th_6(OH)_{14}^{10+}] - 15[Th_6(OH)_{15}^{9+}]\end{aligned} \tag{6}$$

$$\text{Total } NO_3\text{: } 4a = [NO_3^-] \tag{7}$$

Electroneutrality:

$$\begin{aligned}&[H^+] + 4[Th^{4+}] + 2[Th(OH)_2^{2+}] + 7[Th_2OH^{7+}] + 6[Th_2(OH)_2^{6+}] +\\&5[Th_2(OH)_3^{5+}] + 10[Th_6(OH)_{14}^{10+}] + 9[Th_6(OH)_{15}^{9+}] = [OH^-] + [NO_3^-]\end{aligned} \tag{8}$$

Equation (8) may also be obtained by multiplying eqn. (5) by four, adding eqn. (6) and subtracting eqn. (7). Additional equations are obtained from the stability constants $^*\beta_{nm} = [Th_m(OH)_n^{4m-n}][H^+]^n/[Th^{4+}]^m[H_2O]^n$. The mass balance condition for the nitrate component (eqn. (7)) is not needed since we have neglected all complexes with NO_3^-. Thus, by using the electroneutrality relation a superfluous quantity, namely $[NO_3^-]$, is introduced into the calculation of the pH.

Example 3. Calculate the solubility of calcium oxalate in *a M* sodium oxalate and *b M* hydrochloric acid.
Mass balances:

$$\text{Total Ca:}\quad S=[Ca^{2+}]+[CaC_2O_4]+[Ca(C_2O_4)_2^{2-}] \qquad (9)$$

$$\text{Total } C_2O_4\text{:}\quad S+a=[C_2O_4^{2-}]+[CaC_2O_4]+2[Ca(C_2O_4)_2^{2-}]+[HC_2O_4^-]+[H_2C_2O_4] \qquad (10)$$

$$\text{Total H:}\quad b=[H^+]-[OH^-]+[HC_2O_4^-]+2[H_2C_2O_4] \qquad (11)$$

$$\text{Total Na:}\quad 2a=[Na^+] \qquad (12)$$

$$\text{Total Cl:}\quad b=[Cl^-] \qquad (13)$$

The first three equations, together with the constants for the formation of the proton and calcium complexes with oxalate, are sufficient for the calculation of S. It should be noted that when $CaC_2O_4(H_2O)$ dissolves, one oxalate ion goes into the solution for every calcium ion. The electroneutrality relation may be derived from a combination of the 5 mass balance equations, but it does not provide an additional condition needed for the calculation. On the contrary, it introduces the quantities $[Na^+]$ and $[Cl^-]$, and these species do not form any complexes.

Our experience is that many students are inclined to believe that the electroneutrality relation furnishes an additional condition independent of the mass balance equations. The above three examples show that this is certainly not the case. Textbooks dealing with the treatment of chemical equilibria do not normally state clearly which mass balance equation is left out in favor of the charge balance or electroneutrality relation. It is very often the total proton mass balance which is omitted. It should also be stressed that in titration procedures (as well as in many other analytical procedures) it is the mass balance which is determined and not the electroneutrality.

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(Received March 22nd, 1968)

Adsorption of some elements in acetic acid medium on Dowex 1-X8

In neutron activation analysis of many materials, for instance biological ones, the high concentration of the alkali metals requires the removal of ^{24}Na and ^{42}K before the determination of other induced radioactivities. Recently, a procedure has been reported by GIRARDI AND SABBIONI[1] for the selective separation of sodium, based on its retention on hydrated antimony pentoxide.

In the present work, the adsorption of 14 elements on Dowex 1-X8 (100–200 mesh) from acetic acid concentrations varying from 6 to 17.5 *M* was examined. Up to now, little attention has been paid to this medium, although HORNE *et al.*[2] investigated the behaviour of zinc in 8 *M* acetic acid. The ions investigated in this work were: As(III), Au(III), Br$^-$, Co(II), Cs(I), Cu(II), Fe(III), Hg(II), K(I), Mn(II), Mo(IV), Na(I), Sc(III) and Zn(II). The K_D values (*i.e.* the amount of element per g of dry resin/amount per ml of solution) were determined by batch equilibration and (or) column experiments.

TABLE I

K_D VALUES

M HAc *Ion*	*8*	*10*	*12*	*14*	*16*	*16.5*	*17*	*17.5*
As(III)	—	—	—	—	1	5	30	> 100
Au(III)	$3.4 \cdot 10^5$	$3.1 \cdot 10^5$	$2.9 \cdot 10^5$	$2.7 \cdot 10^5$	$2.8 \cdot 10^5$	$3.0 \cdot 10^5$	$3.6 \cdot 10^5$	$4.4 \cdot 10^5$
Br$^-$	$3.0 \cdot 10^3$	$4.1 \cdot 10^3$	$5.7 \cdot 10^3$	$9.8 \cdot 10^3$	$28 \cdot 10^3$	$40 \cdot 10^3$	$58 \cdot 10^3$	$90 \cdot 10^3$
Co(II)	—	—	—	—	$1.3 \cdot 10^3$	$16 \cdot 10^3$	$230 \cdot 10^3$	$> 10^6$
Cs(I)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Cu(II)	—	—	—	6	$2 \cdot 10^3$	$20 \cdot 10^3$	$200 \cdot 10^3$	$> 10^6$
Fe(II)	—	—	—	—	9.5	24	64	170
Hg(II)	$3.8 \cdot 10^4$	$4.0 \cdot 10^4$	$4.4 \cdot 10^4$	$4.8 \cdot 10^4$	$5.4 \cdot 10^4$	$5.7 \cdot 10^4$	$6.0 \cdot 10^4$	$6.4 \cdot 10^4$
K(I)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Mn(II)	—	—	—	3.8	160	750	$30 \cdot 10^3$	$> 10^5$
Mo(VI)	$1.9 \cdot 10^4$	$2.4 \cdot 10^4$	$2.8 \cdot 10^4$	$3.2 \cdot 10^4$	$3.8 \cdot 10^4$	$4.0 \cdot 10^4$	$4.3 \cdot 10^4$	$4.6 \cdot 10^4$
Na(I)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Sc(III)	—	—	—	—	1	3.6	20	$> 10^3$
Zn(II)	3	52	10^3	$44 \cdot 10^3$	$> 10^5$	$> 10^5$	$> 10^5$	$> 10^5$

The results are presented in Table I. Since all the elements except the alkali metals are adsorbed from glacial acetic acid, this medium should be suitable for the separation of ^{24}Na as well as ^{42}K from all the other induced activities in biological material. The determination of the K_D values for other elements is in progress and will be reported in due course.

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(Received March 15th, 1968)

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Etude d'une méthode de séparation préalable en vue du dosage spectrophotométrique du nickel dans le cobalt de très haute pureté

La spectrophotométrie du complexe formé par le nickel avec le diéthyldithiocarbamate, constitue une méthode de dosage très sensible, qui permet de procéder sans difficulté majeure à la détermination d'une quantité de nickel de l'ordre de quelques microgrammes[1]. La présence d'un certain nombre d'ions métalliques et, en particulier, du cobalt, risque cependant de perturber gravement le dosage et, dans la majorité des cas, une séparation préalable du nickel est nécessaire. L'extraction par le chloroforme du complexe formé par le nickel avec la dimethylglyoxime constitue une méthode de séparation très souvent utilisée. Celle-ci n'est cependant applicable que lorsque la quantité de cobalt est inférieure à 100 mg. Dans notre cas, il s'agit de doser quelques p.p.m. de nickel dans du cobalt de très haute pureté obtenu par fusion de zone, et, afin d'avoir une précision satisfaisante, nous sommes contraints d'opérer sur une prise d'essai de l'ordre de 2 g.

L'élimination de la majeure partie du cobalt, avant extraction du nickel par le chloroforme est alors indispensable. Pour cela nous avons tenté, en nous inspirant de la méthode utilisée par SHARP ET WILKINSON pour purifier les sels de nickel[2], d'éliminer la plus grande partie du cobalt par extraction de son thiocyanate, à l'aide de la méthylisobutylcétone. Cette méthode de séparation préalable ne peut être mise en oeuvre dans notre cas, que si le taux d'extraction du cobalt est supérieur à 95%, pour une prise d'essai de 2 g, celui du nickel étant par contre nul.

Nous avons, dans un premier temps, étudié le comportement du nickel en traitant la solution avec les quantités de thiocyanate d'ammonium et de méthylisobutylcétone nécessaires pour extraire 2 g de cobalt. Le Tableau I, qui résume les différents résultats obtenus, montre que la totalité du nickel reste dans la phase aqueuse. Dans une deuxième série d'essais, nous avons étudié le rendement de l'extraction du cobalt en dosant la quantité de cobalt restant dans la phase aqueuse. Le Tableau II montre que dans tous les cas, le rendement de la séparation est supérieur à 98%.

TABLEAU I

COMPORTEMENT DU NICKEL DANS L'EXTRACTION DU COBALT

Ni introduit (μg)	*Ni trouvé en phase aqueuse (μg)*	*Ecart*
2.5	2.4	−0.1
2.5	2.3	−0.2
5.0	5.2	+0.2

TABLEAU II

RENDEMENT DE L'EXTRACTION DU COBALT

Quantité de Co initiale (g)	*Quantité de Co en phase aqueuse (g)*	*Rendement*
2.180	0.001	99.90
2.028	0.014	99.30
2.061	0.032	98.50

L'ensemble de ces résultats montre que la séparation préliminaire du cobalt, par extraction de son thiocyanate, est parfaitement applicable au dosage des traces de nickel dans du cobalt de très haute pureté.

Mode opératoire de la séparation préliminaire

A la solution (HCl 0.1 *N*) résultant de l'attaque de 2 g de l'échantillon, on ajoute 16 g de thiocyanate d'ammonium. Après dissolution complète, on transvase la solution dans une ampoule à décanter de 250 ml. On ajoute 100 ml d'un mélange de méthylisobutylcétone et d'alcool éthylique (80:20). Après agitation pendant 30 sec on laisse décanter. On recueille ensuite la phase aqueuse dans une seconde ampoule à décanter à laquelle on ajoute 50 ml de méthylisobutylcétone. On agite pendant 30 sec. Après décantation on transvase la phase aqueuse dans un bécher.

On procède ensuite au lavage des phases organiques. Dans la première ampoule à décanter on ajoute 20 ml d'une solution de thiocyanate d'ammonium obtenue en dissolvant 12.5 g dans 100 ml d'acide chlorhydrique 0.25 *N*. On agite 30 sec. On transvase la phase aqueuse dans la deuxième ampoule à décanter et on agite à nouveau 30 sec. Après décantation on joint la phase aqueuse à celle obtenue précédemment. Afin d'oxyder le thiocyanate éventuellement entraîné, on évapore la phase aqueuse à siccité. On ajoute ensuite goutte à goutte 20 ml d'acide nitrique concentré. Après cessation de l'effervescence on ajoute encore 30 ml d'acide nitrique concentré. On évapore à siccité et on reprend par 40 ml d'acide chlorhydrique 0.5 *N*. On est alors en mesure de poursuivre le dosage en procédant successivement à l'extraction de nickel et la spectrophotométrie du dithiocarbamate de nickel.

TABLEAU III

DOSAGE DE TRACES DE NICKEL DANS UNE SOLUTION CONNUE DE COBALT

Co (g)	*Ni introduit (μg)*	*Ni trouvé (μg)*	*Ecart*
2	2.5	2.6	+0.1
2	2.5	2.4	−0.1
2	5.0	4.75	−0.25
2	5.0	5.3	+0.3
2	5.0	5.1	+0.1
2	5.0	4.5	−0.5
2	10.0	10.0	0
2	10.0	9.9	−0.1

TABLEAU IV

DOSAGE DE NICKEL DANS COBALT DE TRÈS HAUTE PURETÉ

Echantillon	*Prise d'essai (g)*	*Ni trouvé (%)*
1	2.040	$67 \cdot 10^{-5}$
	2.498	$66 \cdot 10^{-5}$
	3.010	$66 \cdot 10^{-5}$
2	2.1547	$15 \cdot 10^{-5}$
	2.2752	$15 \cdot 10^{-5}$
	2.1505	$14 \cdot 10^{-5}$

Résultats

Afin de vérifier la validité de cette méthode, nous avons procédé au dosage de traces de nickel dans une solution connue de cobalt. Le Tableau III rend compte des résultats obtenus. Nous avons également dosé le nickel dans deux échantillons de cobalt de très haute pureté (Tableau IV).

L'ensemble des résultats obtenus montre bien l'intérêt que présente la séparation préalable de la plus grande partie du cobalt par extraction de son thiocyanate par la méthylisobutylcétone, qui permet de procéder, avec une précision très satisfaisante, au dosage spectrophotométrique de traces de nickel dans du cobalt de très haute pureté.

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(Reçu le 23 février, 1968)

Anal. Chim. Acta, 42 (1968) 341–343

Spectrophotometric determination of scandium with 3,5,7,4'-tetrahydroxyflavone

3,5,7,4'-Tetrahydroxyflavone (kaempferol) reacts with several metal ions to form coloured chelates, which can be used spectrophotometrically. Zirconium has been determined[1]. Physico-chemical studies on the chelates formed with UO_2^{2+}, Mo(VI), Fe(III), Th(IV), Ti(IV) and Ga(III) have been carried out[2]. In the present communication the spectrophotometric determination of scandium in the presence of yttrium and other rare earths is reported.

Not many sensitive and selective organic reagents for the spectrophotometric determination of scandium are known. Alizarin red S[3–5], anthrarufin-2,6-disulphonic acid[6] (disodium salt), xylenol orange[7] and 8-hydroxyquinoline[8] have been reported; among the flavones, morin[8] and quercetin[9] have been employed for this purpose. MACDONALD AND YOE[6] have expressed the need for a sensitive colorimetric reagent for scandium and/or yttrium. 3,5,7,4'-Tetrahydroxyflavone gives a deep yellow colour with scandium which can readily be utilized colorimetrically.

Experimental

Apparatus and reagents. A Perkin Elmer spectracord with 1-cm quartz cells was used for recording the absorption spectra and a Unicam spectrophotometer SP 600, for absorption measurements. pH measurements were carried out with a Metrohm pH meter, model E-350.

Kaempferol was prepared by the method of ROBINSON AND SINODA[10]. A stock solution was prepared by dissolving a suitable amount in 95% ethanol; subsequent dilutions were made with 95% ethanol. Stock solutions of scandium were prepared by dissolving scandium oxide (G.R., Merck) in hydrochloric acid. Solutions of yttrium, rare earths and other ions used in the study of interference were prepared from reagent-grade chemicals.

Absorption spectra and effect of pH. Absorption spectra of a series of solutions, containing a fixed amount of scandium and a large excess of the ligand (ten times) at different pH values, were recorded against the corresponding reagent blanks (Fig. 1). The curves showed an absorption maximum at 410–420 nm below pH 4; a wavelength of 415 nm was chosen for subsequent measurements. The absorption curves indicated the formation of only one complex up to pH 4.0. The maximum shifted to higher wavelengths above this pH value, probably because of the formation of hydroxo complexes. Though the absorption value increased with increase in pH, pH 3.0 was chosen for subsequent studies, since the absorption due to the yttrium and other rare earth chelates with the reagent was negligible at this pH. The use of buffers resulted in a decrease in sensitivity of the reaction, hence pH adjustments were made with the aid of a pH meter.

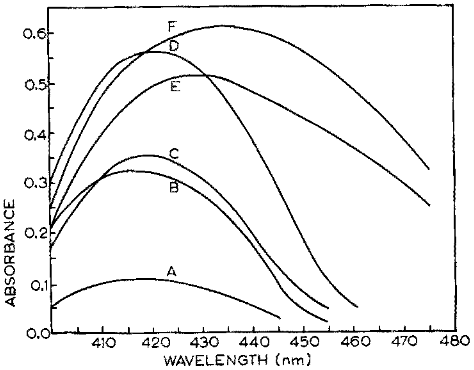

Fig. 1. Absorption spectra of the scandium–3,5,7,4′-tetrahydroxyflavone complex at pH values: (A) 2.0; (B) 2.5; (C) 3.0; (D) 3.5; (E) 4.0; (F) 4.5.

Stability, solubility and physico-chemical constants of the chelate

Maximum colour was attained almost immediately and was stable for *ca.* 24 h at room temperature. No change in absorption values was observed at temperatures slightly lower or higher than room temperature.

Since the scandium–tetrahydroxyflavone chelate is insoluble in water, the studies were made in 50% (v/v) ethanolic medium.

Beer's law, range and sensitivity. The absorption was linear from 0.4 to 1.8 p.p.m. of scandium (pH 3.0, $\lambda = 415$ nm). The sensitivity of the reaction, as calculated from Beer's law plot, was 0.0053 μg Sc/cm^2 for log $I_0/I = 0.001$. The molar extinction coefficient of the chelate was 8413. The optimum concentration range of scandium for accurate determinations, deduced from Ringbom's plot, was found to be 0.9–1.8 p.p.m. of scandium.

Composition of the chelate. The mole ratio method[11], the method of continuous variations[12] and slope ratio method[13] unequivocally pointed to the formation of a chelate containing one mole of reagent to one mole of scandium.

Instability constants. The apparent instability constant, K, calculated by using the conventional relationships: $\alpha = (E_m - E_s)/E_m$ and $K = \alpha^2 C/(1-\alpha)$, was found to be $1.42 \cdot 10^{-5}$ at room temperature and at pH 3.0, from the Job curve.

Determination of scandium

Recommended procedure. Solutions containing up to 1.8 p.p.m. of scandium and a *ca.* 5-fold excess of the reagent were prepared at pH 3.0 (pH adjusted with dilute hydrochloric acid or sodium hydroxide); the solutions were made up to 10 ml and contained 50%(v/v) of ethanol. The absorption was measured at 415 nm against the reagent blank.

Study of interferences. Since no appreciable colour formation occurred below pH 5.0 in the case of yttrium and other rare earths, the spectrophotometric determination of scandium with the tetrahydroxyflavone was possible in their presence. The tolerance limits (in brackets) for various rare earths with 1.44 p.p.m. of scandium were determined as given below: yttrium (6 p.p.m.), lanthanum (28 p.p.m.), samarium (15 p.p.m.), neodymium (12 p.p.m.), erbium (10 p.p.m.), praseodymium (10 p.p.m.), gadolinium (14 p.p.m.), ytterbium (15 p.p.m.).

Borate (150 p.p.m.), thiocyanate (20 p.p.m.) or iodide (100 p.p.m.) could also be tolerated. Bromide, nitrate, chloride and perchlorate ions did not interfere even when present in large excess (*ca.* 1000 p.p.m.). Uranyl, thorium, molybdenum, iron(III), titanium, zirconium, beryllium, aluminium, nickel, cobalt and vanadium interfered even in small quantities. Phosphate, sulphate, oxalate, tartrate and citrate were found to interfere seriously even in traces.

Discussion

3,5,7,4′-Tetrahydroxyflavone has the advantages over most spectrophotometric reagents for scandium that it is stable in solution and that scandium can be determined without recourse to prior separation from yttrium and rare earths when present in moderate quantities.

Two of the authors (B.S.G. and K.C.T.) are grateful to the Council of Scientific and Industrial Research, New Delhi (India) for the award of research fellowships.

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(Received December 23rd, 1967)

BOOK REVIEWS

Methods of Biochemical Analysis, Edited by DAVID GLICK, Vol. 15, Interscience Publishers–J. Wiley & Sons, Inc., New York, 1967, ix+531 pp., price 120 s.

The latest volume in this series contains seven articles. D. S. MCLAREN, W. W. C. READ, Z. L. AWDEH AND M. TCHLIAN consider the microdetermination of vitamin A and carotenoids in blood and tissue, describing in detail methods which require not more than 0.5-ml or 0.5-g samples and which have been found suitable in their laboratory. In a timely contribution, D. S. JACKSON AND E. G. CLEARY deal with the determination of collagen and elastin, proteins which are being increasingly studied in numerous physiological and clinical investigations. The determination of β-glucuronidases is the subject of W. H. FISHMAN'S review which deals with the preparation and use of a number of substrates for the assay of the enzymes in various biological materials. C. A. ANDERSEN gives an introduction to the electron-probe microanalyzer and its use in biochemistry. This instrument, which can be used to give an essentially complete chemical analysis of microstructures in histological tissue preparations *in situ* is shown to have considerable importance in chemical pathology, dental research, and histo- and cyto-chemistry. S. G. ANDERSON contributes a chapter on preparative zonal centrifugation and gives examples of the application of the technique to various types of biological material. C. H. WANG gives an account of radiorespirometry and shows how the study of respiratory $^{14}CO_2$ can be applied to the identification and estimation of metabolic pathways. Finally, J. D. WINEFORDNER, W. J. MCCARTHY AND P. A. ST. JOHN deal with phosphorimetry as an analytical approach in biochemistry and indicate how phosphorescence studies can be applied both quantitatively and qualitatively in biochemistry and pharmacy.

Once again, as readers have come to expect from this series, a high standard is maintained. Experimental details are given in full, the applications of each technique are indicated and extensive lists of relevant references are supplied.

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Handbuch der Analytischen Chemie, Herausgegeben von W. FRESENIUS UND G. JANDER, *Dritter Teil. Quantitative Bestimmungs- und Trennungsmethoden. Band VIIaβ. Elemente der Siebenten Hauptgruppe–Chlor, Brom und Jod,* Bearbeitet von A. OTTO GUEBELI, Springer-Verlag, Berlin, 1967, viii+614 S., Geheftet DM 163,—; Gebunden DM 168,—.

The present volume in this series describes methods for the determination of chlorine, bromine and iodine in all their various forms. From the size of the volume it can be seen that a considerable amount of material has been collected by the author. It is appreciated that the volumes in this series are not intended to be critical, and are concerned with bringing together extensive information scattered throughout the literature, but it would have been of great help for those seeking a particular method if the author had expressed some kind of preference.

There are some omissions; probably the most widely used method for the determination of trace chloride is the displacement method using mercuric thiocyanate as reagent, followed by measurement of the complex ferri-thiocyanate complex. This only receives a bare mention. Another very old method, which has interesting possibilities, is the determination of iodide by oxidation with periodate. The reviewer was unable to find any mention of this method; although a back-titration is involved, it provides a 24-fold amplification and is worth considering in certain circumstances.

This is probably the first time that an attempt has been made to bring together methods that have been used for the determination of periodate and iodate when in admixture, but the only reliable method, which is not a difference method, based on precipitation as zinc periodate is not mentioned.

Despite these minor shortcomings, this is a very valuable volume and it is likely to be consulted widely, for determinations of these three elements are among the commonest in analytical chemistry. The author is to be congratulated on his fortitude in amassing this vast collection of material which has hitherto been mainly dispersed throughout the literature.

R. BELCHER

Selected Readings in Chemical Kinetics, Edited by M. H. Back and K. J. Laidler, Pergamon Press, Oxford, 1967, viii + 175 pp., price 30 s.

This volume contains reprints of twelve papers which are thought to be important contributions to the field of general and gas-phase kinetics. The papers have been selected to give students the opportunity of reading the original contributions, so as to lead to a better understanding of modern aspects of the subject.

The selection starts with A. V. Harcourt and W. Esson's paper on kinetic laws, and S. Arrhenius' paper on sucrose inversion. Unimolecular and chain reactions are discussed separately, and papers on absolute reaction rates are also included. Informative notes and biographical sketches help to place the information in a proper perspective.

This is the first volume in a series entitled Selected Readings in Physical Chemistry. Publications of this type will certainly help to disseminate an understanding of the creative phases of concepts that are now taken for granted. The series will also be welcomed by those interested in the history of chemistry.

P. Zuman (Prague)

Anal. Chim. Acta, 42 (1968) 348

ERRATUM

E. Sawicki and R. A. Carnes, Fluorimetric determination of glycine and other amino acids with 2,4-butanedione, *Anal. Chim. Acta*, 41 (1968) 178–180.
The word 2,4-butanedione in the title should read 2,4-pentanedione.

Anal. Chim. Acta, 42 (1968) 348

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PRINTED IN THE NETHERLANDS