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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 27, No. 2, August 1962

THE OXIDIZED COMPLEX OF NICKEL WITH 4-CARBOXY-1,2-CYCLOHEXANEDIONEDIOXIME IN ALKALINE MEDIA

The reaction of oxygen with a nickel(II) complex of 4-carboxy-1,2-cyclohexanedionedioxime in alkaline media was studied spectrophotometrically, polarographically, and by spectrophotometric titrations with tin(II) chloride. Magnetic susceptibility measurements were also performed. The rate of formation of the oxidized complex was found to be first order at 25° and 50°. The average values obtained for the rate constant k'_1 are $(2.71 \pm 0.23) \times 10^{-2}\ h^{-1}$ (25°), spectrophotometrically; $(5.99 \pm 0.83) \times 10^{-2}\ h^{-1}$ (50°), polarographically; $(4.98 \pm 0.90) \times 10^{-2}\ h^{-1}$ (50°), titrimetrically; $(2.87 \pm 0.29) \times 10^{-2}\ h^{-1}$ (50°), curve fitting. The value obtained for the rate constant k'_2 is $(1.59 \pm 0.16) \times 10^{-2}\ h^{-1}$ (50°), curve fitting. The effect of reducing agents on the formation of the oxidized complex was studied. It was found that tin(II) chloride, hydrazine sulfate, and hydroxylammonium chloride prevented the formation of the oxidized complex. A reaction mechanism for the formation and decomposition of the oxidized complex is proposed.

C. V. Banks and J. P. LaPlante, *Anal. Chim. Acta*, 27 (1962) 101–112

ANALYSIS OF BRASS BY ANION-EXCHANGE CHROMATOGRAPHY

A method is described for the determination of each constituent in alloys of nickel, copper, lead, iron, zinc, tin, manganese and aluminum. The essential feature of the method is the separation of the constituents by anion-exchange chromatography. The separation requires only 3.5 h. The accuracy and precision are good.

W. H. Gerdes and Wm. Rieman III, *Anal. Chim. Acta*, 27 (1962) 113–118

THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING METALS AND METALLOIDS

The determination of carbon and hydrogen in organometallic compounds is described. Cobaltocobaltic oxide is used as the catalytic tube filling in a rapid procedure. Compounds containing Na, K, Cu, Be, Mg, Ca, Zn, Cd, Hg, Al, B, Ga, Ti, Pb, Nb, P, As, Bi, Mo, U, Se, Te, Mn, Fe Co, Ni were examined; interferences were overcome where necessary and tungstic oxide proved a valuable auxiliary reagent.

Y. A. Gawargious and A. M. G. Macdonald, *Anal. Chim. Acta*, 27 (1962) 119–130

SPECTROPHOTOMETRIC ERRORS ASSOCIATED WITH CELLS OF CIRCULAR CROSS SECTION

It is shown that the use of spectrophotometric cells having circular cross sections leads to errors that depend on the absorbance, on the ratio of beam width to cell diameter, and on the distance between the center of the beam and the diameter of the cell, but that the nature and magnitude of these errors render them essentially undetectable in practical analytical work.

L. Meites, *Anal. Chim. Acta*, 27 (1962) 131–135

ABSORPTIOMETRIC DETERMINATION OF BISMUTH WITH THORIN

A simple, precise absorptiometric method for bismuth based upon its reaction with Thorin is described. The effect of foreign elements was established.

H. A. MOTTOLA, *Anal. Chim. Acta*, 27 (1962) 136–143

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN NIOBIUM WITH DITHIOL

A new procedure for the determination of molybdenum and tungsten in niobium has been developed. The method involves the formation of the intensely colored complex of molybdenum with toluene-3,4-dithiol in an aqueous medium and its extraction into carbon tetrachloride followed by the reduction of tungsten and the formation and extraction of its complex. The recommended reagent is stable for at least 90 days. Both the molybdenum and the tungsten dithiol complexes are formed quantitatively within 5 min. Interlaboratory evaluation of the method reveals within-laboratory and between-laboratory relative standard deviations of about 1.5% and 2.9% respectively.

E. W. HOBART AND E. P. HURLEY, *Anal. Chim. Acta*, 27 (1962) 144–152

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH 2-THENOYLTRIFLUOROACETONE

The rapid extraction and simultaneous spectrophotometric determination of mg amounts of cobalt(II) by means of 2-thenoyltrifluoroacetone is described. The yellow cobalt(II)-TTA chelate solution in acetone–benzene obeys Beer's law at 430 mμ over the range 12 to 51 μg of cobalt(II) per ml. At pH 5.1–6.8 a single extraction with 0.15 *M* TTA in acetone is satisfactory. The system is stable for 96 h. Silver, zirconium, strontium, thorium, zinc, lead(II) and mercury(II) do not interfere.

A. K. DE AND S. K. MAJUMDAR, *Anal. Chim. Acta*, 27 (1962) 153–157.

DETERMINATION OF TOTAL SULPHUR IN SOIL AND PLANT MATERIAL

A rapid and accurate method for the determination of the total sulphur content of soil or plant material is described. The sample is heated with sodium bicarbonate and silver oxide at 550° for 3 h, and the sulphur content of the whole residue is reduced to hydrogen sulphide and determined as methylene blue. The results compare favourably with those of other methods. In routine use, at least 30 analyses may be completed in a day.

A. STEINBERGS, O. IISMAA, J. R. FRENEY AND N. J. BARROW, *Anal. Chim. Acta*, 27 (1962) 158–164.

ANALYTICAL APPLICATIONS OF THE DETERMINATION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART III. DETERMINATION OF HYDROGEN PEROXIDE, PEROXYDISULPHATE AND THEIR MIXTURES

Hydrogen peroxide can be determined by reaction with excess of alkaline hexacyanoferrate(III), the excess being titrated with ascorbic acid. Peroxydisulphate is determined by reaction with hexacyanoferrate(II) in acidic medium, the hexacyanoferrate(III) formed being titrated with ascorbic acid. To determine hydrogen peroxide and peroxydisulphate in the presence of each other, two titrations are needed; the results are readily calculated.

L. Erdey, G. Svehla and L. Koltai, *Anal. Chim. Acta*, 27 (1962) 164–168

ANALYTICAL APPLICATION OF CARBON DIOXIDE DISTILLATION

A DISTILLATION AND TITRATION METHOD FOR DETERMINATION OF CARBON DIOXIDE FORMED FROM ORGANIC MATERIALS BY WET OXIDATION

(in German)

Organic materials in aqueous solutions are determined by the carbon dioxide formed by complete oxidation. This is distilled in a special apparatus into barium hydroxide solution covered with pentane and the excess of alkali titrated. 0.06–6 mg of organic carbon can be determined.

L. Maros, Frau M. Pintér-Szakács and E. Schulek, *Anal. Chim. Acta*, 27 (1962) 169–175

DETERMINATION OF FORMATES BY OXIDATION WITH IODINE

A selective determination of formates based on oxidation with iodine at 100° in presence of potassium hydrogen tartrate, and final titration with thiosulphate solution, is described. The error is below 0.5% for 25–90 mg of formic acid. Few other organic acids interfere.

R. M. Verma and S. Bose, *Anal. Chim. Acta*, 27 (1962) 176–178

AMPEROMETRIC TITRATION OF COPPER WITH TETRAETHYLENEPENTAMINE

Tetraethylenepentamine is a very selective titrant for the determination of copper in acidic medium. With amperometric end-point detection as little as 0.1 mg copper in a volume of 25 ml can be determined with an accuracy of ± 1%. When the titration is performed in acetic acid/ammonium acetate buffer of pH 4.1, only mercury causes significant interference.

E. Jacobsen and K. Schrøder, *Anal. Chim Acta*, 27 (1962) 179–182

EXTRACTION OF CAESIUM WITH TETRAIODOBISMUTHITE IN NITROBENZENE

(in French)

Caesium can be extracted from aqueous solutions with a solution of tetraiodobismuthite in nitrobenzene. The optimum conditions for the extraction have been studied. Caesium can be separated from most important fission products.

M. Kyrš and S. Podešva, *Anal. Chim. Acta*, 27 (1962) 183–187

THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART II. EXTRACTION BEHAVIOUR AND SPECTRA OF THE REAGENTS

Extraction experiments in the carbon tetrachloride-water system for diphenylcarbazone above pH 7.5 give a value of $(2.9 \pm 0.3) \cdot 10^{-9}$ for the dissociation constant. At lower pH values the partition coefficients were found to be 7.5 for carbon tetrachloride-water and 39 for toluene-water in 0.1–1 *M* $NaClO_4$. The solubility of the carbazone in water is $3.8 \cdot 10^{-4}$ *M* in acid perchlorate medium.

Spectra of diphenylcarbazone in water, toluene and carbon tetrachloride, of the anion in water and of diphenylformazane in toluene are compared. In the infra-red spectrum the $C = O$ band was present in the carbazone, but not in the sodium salt.

S. Balt and E. van Dalen, *Anal. Chim. Acta*, 27 (1962) 188–193

A GENERAL FORMULA FOR THE CALCULATION OF pH OF ACIDS AND BASES

(Short Communication)

A. Claeys, *Anal. Chim. Acta*, 27 (1962) 193

ON THE PREFERENTIAL FORMATION OF PLATINUM OXIDES AT THE GRAIN BOUNDARIES OF PLATINUM ELECTRODES

(Short Communication)

D. M. Mohilner, W. J. Argersinger Jr. and R N. Adams

Anal. Chim. Acta, 27 (1962) 194–197

STUDIES ON ADSORPTION INDICATORS

PART IV. SULPHONEFLUORESCEIN AND ITS HALOGENATED DERIVATIVES AS ADSORPTION INDICATORS

(Short Communication)

K. N. Tandon and R. C. Mehrotra, *Anal. Chim. acta*, 27 (1962) 198–199

THE OXIDIZED COMPLEX OF NICKEL WITH 4-CARBOXY-1,2-CYCLOHEXANEDIONEDIOXIME IN ALKALINE MEDIA*

CHARLES V. BANKS AND J. P. LAPLANTE**

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(Received December 10th, 1961)

INTRODUCTION

Although the reaction between an oxidizing agent and bis(*vic*-dioximato-N,N')-nickel(II) in alkaline media has been used for the determination of nickel for many years, no detailed study of the reaction kinetics has been reported.

Several investigations[1-4] have been performed since FEIGL[5] studied the reaction of oxidizing agents with bis(2,3-butanedionedioximato-N,N')nickel(II) in alkaline media, but the conclusions of these investigators have differed substantially. Even after it was realized[6,7] that two complexes were formed, controversy still existed as to the *vic*-dioxime to nickel ratio, and the oxidation state of the nickel. The red color obtained from the reaction has been attributed to a *vic*-dioxime complex of nickel(IV) in which the ratio of ligand to metal was 2 : 1[5], 3 : 1[1-4,8], and 4 : 1[7,9]; to a complex of nickel(III) in which the ratio of ligand to metal was 3 : 1[10-13]; and to complexes of an unknown oxidation product of the *vic*-dioxime with nickel(II) in which the ratio of ligand to metal was 1 : 1[14], 2 : 1[15,16], 3 : 1[17,18], and 4 : 1[18].

The oxidizing agents that have been used are bromine[15,19-35], iodine-potassium iodide[10,29,36-43], sodium hypochlorite[44,46], sodium hypobromite[15,45], ammonium peroxydisulfate[1,16,46-48], potassium peroxydisulfate[1,6,49,50], lead dioxide[29], and atmospheric oxygen[51,52].

An exhaustive study of the reaction was performed by OKÁČ AND ŠIMEK[3,4]. They studied the oxidation of bis(2,3-butanedionedioximato-N,N')nickel(II) photometrically, potentiometrically, and by means of paper chromatography. The oxidizing agents used were hydrogen peroxide, potassium ferricyanide, lead dioxide, potassium peroxydisulfate, and atmospheric oxygen. The reduction of $[Ni(IV)D_3]^{2-}$ with sodium stannate, hydrazine, hydroxylamine, and cobalt(II) salts was also studied. The following mechanism for the oxidation of bis(2,3-butanedionedioximato-N,N')nickel(II) was proposed,

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* Contribution No. 1055 from the Ames Laboratory of the U.S. Atomic Energy Commission: Paper No. XXVII in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series was No. XXVI, *Anal. Chim. Acta*, 27 (1962) 80. Abstracted from dissertation submitted by J. P. LAPLANTE to graduate faculty of Iowa State University in partial fulfilment of requirements for the degree of Doctor of Philosophy, 1960.

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$$2[\mathrm{Ni(DH)_2}] + 6\mathrm{OH^-} = [\mathrm{DNi(OH)_2NiD}]^{2-} + 2\mathrm{D}^{2-} + 4\mathrm{H_2O},$$

$$[\mathrm{DNi(OH)_2NiD}]^{2-} + 4\mathrm{D}^{2-} = 2[\mathrm{NiD_3}]^{4-} + 2\mathrm{OH^-},$$

$$[\mathrm{NiD_3}]^{4-} = [\mathrm{NiD_3}]^{2-} + 2e.$$

The present investigation was undertaken to study the kinetics of the oxidation of the nickel(II) complexes of 4-carboxynioxime in alkaline media.

EXPERIMENTAL

Apparatus and materials

A Cary Recording Spectrophotometer, Model 14, was used to obtain all of the spectrophotometric data. Matched silica cells were used for the measurements in the ultraviolet, visible, and infrared. When required, silica slugs were used to give cell paths of 0.005, 0.02, 0.05, and 0.2 cm.

Magnetic susceptibility measurements were made on a Gouy type apparatus. This apparatus and its operation have been described by VANDER HAAR[53]. The pH titrations were made using a Beckman, Model G, pH meter equipped with a Type E glass electrode.

Nickel(II) chloride stock solutions were prepared from special low-cobalt $\mathrm{NiCl_2 \cdot 6H_2O}$ obtained from the Baker Chemical Company. The solutions were prepared using deionized distilled water and were standardized by the heptoxime method[54].

The 4-carboxy-1,2-cyclohexanedionedioxime was prepared in this Laboratory by the procedure of BANKS *et al.*[55]. 4-Carboxylcyclohexenfuroxane was also prepared in this Laboratory by the procedure of BANKS AND RICHARD[56].

The potassium hydroxide was of certified reagent-grade quality and was obtained from Fisher Scientific Company. All other chemicals were of reagent-grade quality.

All computations were made on a Magnetic Drum Data-Processing Machine, Type 650, manufactured by International Business Machines Corporation.

The stock solutions were prepared by the following procedure. A weighed amount of 4-carboxynioxime was transferred to a 50-ml class A volumetric flask, an aliquot of standard nickel(II) chloride solution, 28 g of potassium hydroxide, and approximately 40 ml of distilled deionized water were added. The flask was placed in the cold water bath and shaken until the potassium hydroxide had dissolved. The solution was allowed to come to room temperature and then diluted to volume with distilled deionized water. It was transferred to a polyethylene bottle, with provisions for passing a gas continuously into it, and the bottle was then placed in a constant temperature bath. The temperatures used in this study were 25° and 50°. The solutions that were studied spectrophotometrically were prepared by removing 3-ml aliquants of the stock solution at various time intervals, diluting to a volume of 25 ml with 8.923 *M* potassium hydroxide and scanning immediately. The reference was air. All absorbancies were corrected for the absorbancy due to potassium hydroxide solutions.

Determination of the ratio of ligand to metal

Job's method was used to establish the ratio of 4-carboxynioxime to nickel in the oxidized complex at 25°. A series of solutions was prepared by the procedure cited previously. Oxygen was bubbled continuously through the stock solutions. The description of the solutions used is given in Table I. It was found that the maximum falls at a mole fraction corresponding to a ratio of 4-carboxynioxime to nickel of approximately 3 : 1. Similar results were obtained from mole ratio studies.

The mole ratio method was used to determine the ratio of 4-carboxynioxime to nickel at 50°. The solutions were prepared by the procedure cited above. The description of the solutions used is given in Table II. It was found that there is one break, corresponding to a ratio of 4-carboxynioxime to nickel of 3 : 1 for the various time intervals.

TABLE I

DESCRIPTION OF SOLUTIONS USED TO DETERMINE THE RATIO OF *vic*-DIOXIME TO NICKEL BY JOB'S METHOD

Solution no.	$[D^{3-}]_t \times 10^3$	$[Ni^{2+}]_t \times 10^3$
1	7.414	0.0
2	6.673	0.741
3	5.931	1.483
4	5.709	1.706
5	5.486	1.928
6	5.264	2.150
7	5.190	2.224
8	4.968	2.446
9	4.746	2.669
10	4.522	2.892
11	4.449	2.966
12	4.226	3.188
13	3.707	3.707

TABLE II

DESCRIPTION OF SOLUTIONS USED TO DETERMINE THE RATIO OF *vic*-DIOXIME TO NICKEL BY THE MOLE RATIO METHOD

Solution no.	$[D^{3-}]_t \times 10^3$	$[Ni^{2+}]_t \times 10^3$	$[D^{3-}]_t/[Ni^{2+}]_t$
1	1.446	1.446	1.00
2	2.892	1.446	2.00
3	4.338	1.446	3.00
4	5.856	1.446	4.05
5	8.821	1.446	6.10

Magnetic susceptibility studies

The magnetic susceptibility determinations were made at 20° only because of the rapid attack of potassium hydroxide on the sample tube and instrumental limitations. The solutions were prepared by the procedure cited above. The concentration of 4-carboxynioxime was varied from $4.727 \cdot 10^{-2}$ M to $2.0 \cdot 10^{-1}$ M, while the concentrations of nickel(II) chloride ($4.634 \cdot 10^{-2}$ M) and potassium hydroxide (8.923 M) were held constant. Measurements were made at 24-h intervals. The results are shown in Fig. 1. It will be seen that the number of unpaired electrons found decreases with increasing time. This decrease in the number of unpaired electrons may be due to the oxidation of nickel(II) to the nickel(IV) state in which the nickel in the complex, *tris*(4-carboxynioximato-N,N')nickel(IV) may have $3d^24s4p^3$ bonding or to the oxidation of the *tris*(4-carboxynioximato-N,N')nickel(II) to some oxidized state, followed by the decomposition of this complex to give NiD^- and oxidized 4-carboxynioxime.

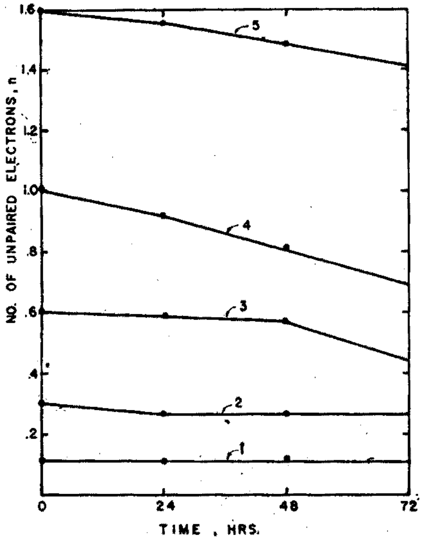


Fig. 1. The change in the number of unpaired electrons obtained from a rate study of a solution treated with oxygen at 25°. Curve 1, $4.727 \cdot 10^{-2}$ *M*, $4.634 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 2, $6.250 \cdot 10^{-2}$ *M*, $4.634 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 3, $7.499 \cdot 10^{-2}$ *M*, $4.634 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 4, $1.000 \cdot 10^{-1}$ *M*, $4.634 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 5, $2.000 \cdot 10^{-1}$ *M*, $4.634 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp.

Rate studies

The solutions used were prepared by the procedure cited previously. The tempera-

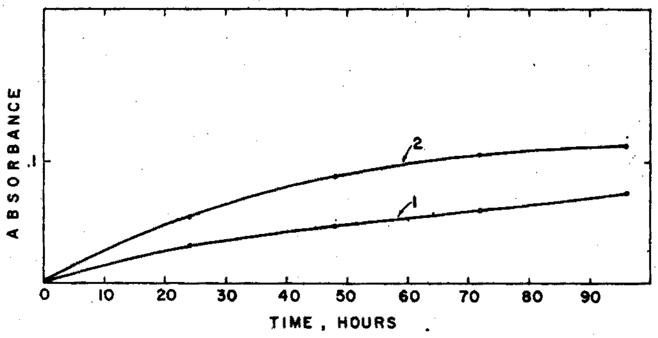


Fig. 2. A plot of the rate data obtained from solutions treated with oxygen at 25°. Curve 1, $5.632 \cdot 10^{-2}$ *M*, $3.615 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 2, $7.136 \cdot 10^{-2}$ *M*, $2.132 \cdot 10^{-2}$ *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp.

tures used in the rate studies were 25° and 50°. The samples were removed from the stock solutions at various time intervals and the measurements were made.

The rate of formation of the oxidized complex at 25° was determined spectrophoto-

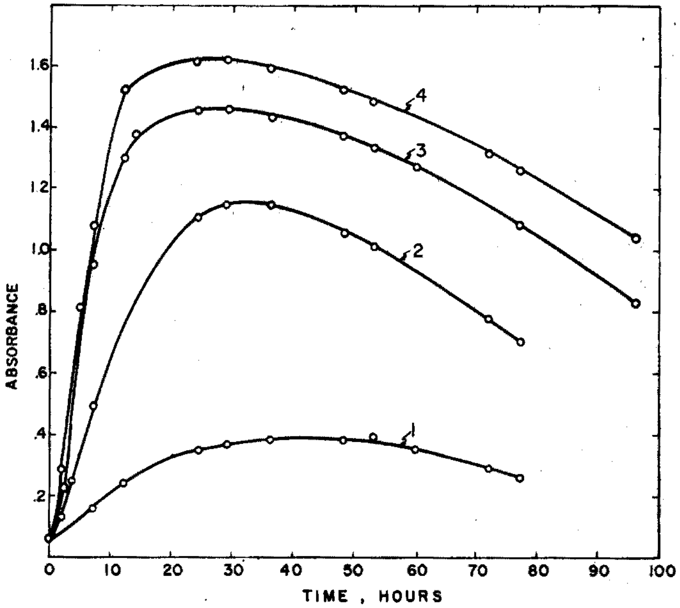


Fig. 3. A plot of the rate data obtained from solutions treated with oxygen at 50°. Curve 1, $1.446 \cdot 10^{-3}$ M, $1.446 \cdot 10^{-3}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 2, $2.924 \cdot 10^{-3}$ M, $1.446 \cdot 10^{-3}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 3, $5.862 \cdot 10^{-3}$ M, $1.446 \cdot 10^{-3}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 4, $2.924 \cdot 10^{-3}$ M, $0.732 \cdot 10^{-3}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp.

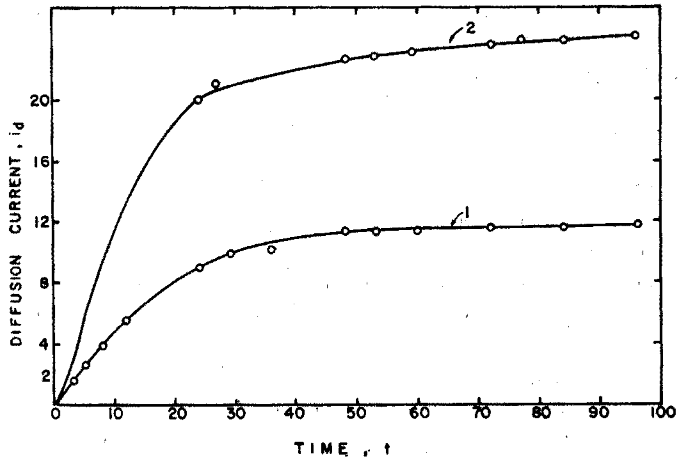


Fig. 4. A plot of the rate data obtained from solutions treated with oxygen at 50°. Curve 1, $1.954 \cdot 10^{-3}$ M, $4.820 \cdot 10^{-4}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 2, $3.908 \cdot 10^{-3}$ M, $4.820 \cdot 10^{-4}$ M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp.

metrically at 490 mμ. Rate data for the experiments in which the concentrations of 4-carboxynioxime and nickel(II) were varied are plotted in Fig. 2. Similar results were obtained at 740 mμ.

The rate of formation of the oxidized complex at 50° was determined spectrophotometrically, polarographically, and by the reduction of the oxidized complex with tin(II) chloride. Rate data for the spectrophotometric studies at 490 mμ in which the concentration of 4-carboxynioxime and nickel(II) chloride were varied are shown in Fig. 3. Similar results were obtained at 740 mμ.

Rate data were obtained from the polarographic wave with a half-wave potential of —1.06 volts *vs.* the saturated calomel electrode by measuring the increase of the diffusion current. The 4-carboxynioxime-nickel(II) complex exhibits a polarographic wave with a half-wave potential of —1.51 volts *vs.* the saturated calomel electrode. Rate data for the experiments at various concentrations of 4-carboxynioxime and nickel(II) chloride are shown in Fig. 4.

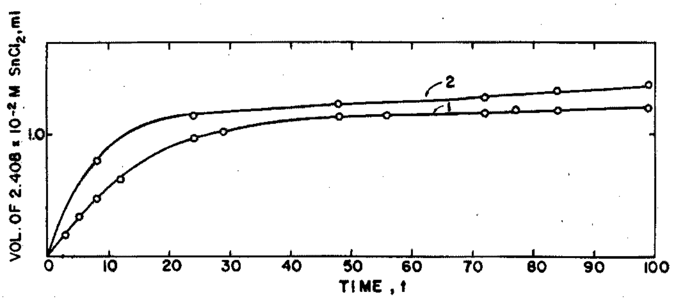


Fig. 5. A plot of the rate data obtained from solutions treated with oxygen at 50°. Curve 1, 1.954 · 10^{-3} *M*, 4.820 · 10^{-4} *M*, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp. Curve 2, 9.770·10^{-4} *M*, 4.820·10^{-4} *M* and 8.923 *M* in 4-carboxynioxime, nickel (II) chloride, and potassium hydroxide, resp.

The rate of formation of the oxidized complex was followed by spectrophotometric titrations with tin(II) chloride. The wave length used was 490 mμ. Rate data for the experiments are shown in Fig. 5.

The general rate equation is

$$\frac{d[\mathrm{NiD_3}^{5-}]}{dt} = k'_1[\mathrm{D}^{3-}]^m[\mathrm{NiD}_x{}^{2-3x}]^n - k'_2[\mathrm{NiD_3}^{5-}]^p \tag{1}$$

where x may equal 0, 1, 2, or 3, and the sum of m and n is the order of the formation and p, the order of the decomposition of $\mathrm{NiD_3}^{5-}$. The partial pressure of oxygen was assumed to be constant and was included in k'_1 and k'_2. To determine m and n, the ratio of the reactants was varied. The concentrations of nickel(II) chloride and potassium hydroxide were held constant and the concentration of 4-carboxynioxime was doubled. The curves are shown in Fig. 3. The ratio of the slopes of curves 1 to 2 and 2 to 3 for short intervals is equal to 2^m. It was found that m is equal to one. To determine n, a study was made varying the concentration of nickel while holding the concentrations of 4-carboxynioxime and potassium hydroxide constant. The ratio of the slopes for short intervals of the curves 2 and 4 is equal to the ratio of the concentrations of nickel. Therefore, the value of n is one. The same values for m and n were obtained from Fig. 2. To determine p, a plot of log A versus t of the data shown in

Fig. 3 was made. A straight line was obtained for the last portion of the curve, indicating that the decomposition of $\mathrm{NiD_3^{5-}}$ is first order with respect to the starting material. Therefore, p is equal to one. There seems to be no direct way to determine the value of x. But, the magnetic susceptibility measurements indicate that either $\mathrm{NiD_2^{4-}}$, $\mathrm{NiD_3^{7-}}$, or both are present in solution and only 7% of the total nickel is present as $\mathrm{NiD^-}$ at the beginning of the study of Curve 1, Fig. 3. Thus the rate-determining step is

$$\mathrm{NiD_2^{4-} + D^{3-} = NiD_3^{7-}} \tag{2}$$

Therefore, equation 1 may be written

$$\frac{d[\mathrm{NiD_3^{5-}}]}{dt} = k'_1[\mathrm{D^{3-}}][\mathrm{NiD_2^{4-}}] - k'_2[\mathrm{NiD_3^{5-}}] \tag{3}$$

The values of k'_1 and k'_2 are $(2.87 \pm 0.29) \times 10^{-2}\,\mathrm{h^{-1}}$ (50°) and $(1.59 \pm 0.16) \times 10^{-2}\,\mathrm{h^{-1}}$ (50°), respectively. These values were obtained from the data shown in Fig. 3 by a curve-fitting procedure. The values of k'_1 obtained from the data shown in Figs. 2, 4, and 5 were calculated from the following equation

$$k'_1 = \frac{2.303}{t} \log \frac{a}{a - x} \tag{4}$$

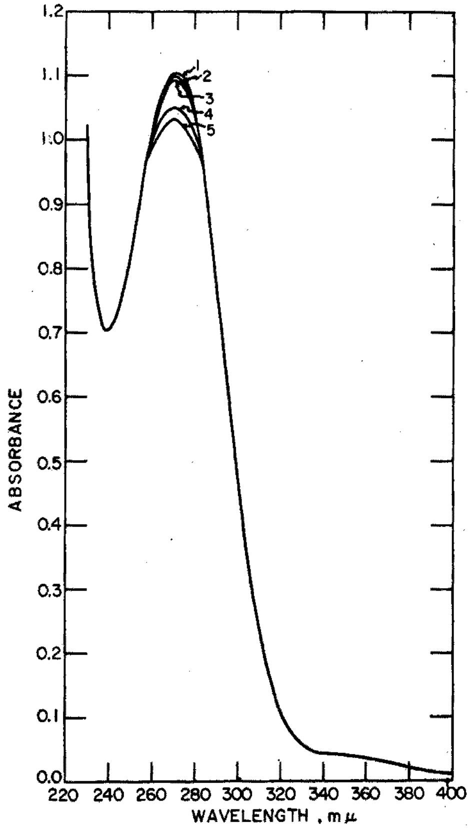


Fig. 6. Absorption spectra obtained from a rate study of a solution treated with oxygen at 25°. Curve 1, 0.0 h; Curve 2, 12.0 h; Curve 3, 60 h; Curve 4, 84 h; Curve 5, 96 h.

where *a* is the initial concentration of reactant, and *x* is the amount reacting in time *t*. The values calculated for k'_1 from the above data are [2.21 ± 0.15 (Curve 1, Fig. 2) and 3.21 ± 0.44 (Curve 2, Fig. 2)] $\times 10^{-2}$ h^{-1} (25°) spectrophotometrically; [6.10 ± 0.70 (Curve 1, Fig. 4) and 5.88 ± 0.97 (Curve 2, Fig. 4)] $\times 10^{-2}$ h^{-1} (50°), polarographically; and [4.71 ± 1.00 (Curve 1, Fig. 5) and 5.25 ± 0.82 (Curve 2, Fig. 5)] $\times 10^{-2}$ h^{-1} (50°), titrimetrically, respectively. The rate studies indicate that there was an exchange of two electrons in the reduction of the oxidized complex.

Several attempts were made to isolate and identify the products of the oxidation. A small amount of an acidic substance was obtained from ether extractions of the neutralized solution. The substance decomposed very rapidly upon contact with air. No reaction was observed with nickel(II) chloride at any pH. After reducing a small quantity with zinc in acetic acid, a red color was obtained when a drop of nickel(II) chloride (0.2317 *M*) was added and the solution made slightly alkaline. This indicates that the compound obtained upon reduction may be the *vic*-dioxime. Two nitro tests were performed. Positive results were obtained with the ferrous hydroxide test reported by HEARON AND GUSTAVSON[57] and the lithium aluminum hydride test reported by NYSTROM AND BROWN[58] and KRYNITZKY, *et al.*[59]. 4-Carboxycyclohexenfuroxane gave a negative nitro test. These results indicate that the oxidation product was a nitro compound and not a furoxane.

A study of the decomposition of 4-carboxynioxime in the presence of oxygen at 25° and 50° was made. The solutions were prepared by the procedure cited above and the concentrations of 4-carboxynioxime and potassium hydroxide were $1.00 \cdot 10^{-4}$, $8.896 \cdot 10^{-3}$, and 8.923 *M*, respectively. The spectra obtained are shown in Fig. 6.

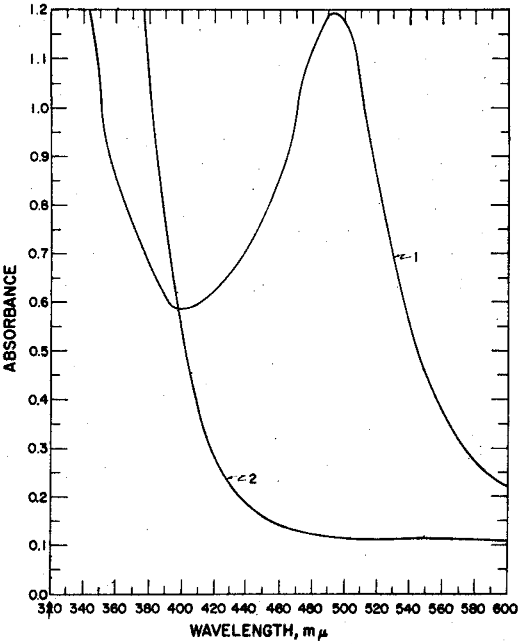


Fig. 7. Absorption spectra obtained from a solution treated with oxygen for 72 h before and after the addition of $SnCl_2$. Curve 1, no $SnCl_2$. Curve 2, an excess of $SnCl_2$.

There was no change in the absorption spectrum from 400 to 900 mµ at 50°. It is seen that there is a slight decrease in the absorption maximum at 273 mµ.

Reduction of the oxidized complex

The reduction of the oxidized species was studied spectrophotometrically. The reducing agents used were tin(II) chloride, hydrazine sulfate, and hydroxylammonium chloride. An excess of the reducing agent was added to a solution that oxygen had been bubbled through for 72 h at 50°. The concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were $5.863 \cdot 10^{-3}$, $2.169 \cdot 10^{-3}$, and 8.923 *M*, respectively. The results are shown in Figs. 7 and 8. The absorption maxima at 490 and 740 mµ disappeared and no maximum was observed at 393 mµ. The solutions became turbid after 20 min. If a slight excess of the *vic*-dioxime was added, the precipitate disappeared and the original yellow color of the nickel(II) complex was obtained with absorption maximum at 393 mµ. This indicates that no *vic*-dioxime-nickel complexes were present after the addition of the reducing agents.

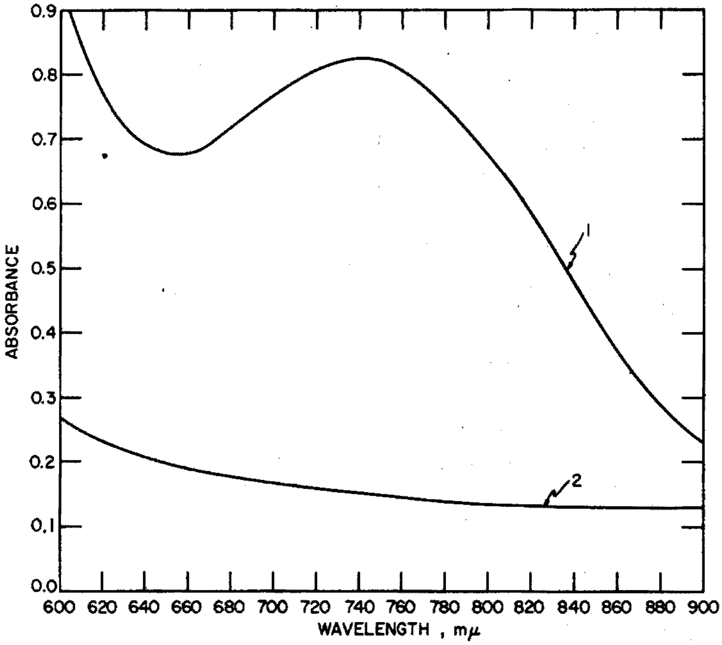


Fig. 8. Absorption spectra obtained from a solution treated with oxygen for 72 h before and after the addition of $SnCl_2$. Curve 1, no $SnCl_2$ present. Curve 2, an excess of $SnCl_2$ present.

The effect of tin(II) and tin(IV) on the nickel(II) complexes of 4-carboxynioxime was studied. They were added 15 min after the preparation of the solutions in which the concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were $1.603 \cdot 10^{-3}$, $1.446 \cdot 10^{-3}$, and 8.923 *M* respectively. There was no change in the absorption spectrum, indicating that the nickel(II) complexes were not destroyed. From a similar study, it was also found that hydroxylammonium chloride and hydrazine sulfate do not destroy the nickel(II) complexes.

DISCUSSION

The rate data indicate that the rate-determining step in the formation of the oxidized complex is either

$$NiD_2^{4-} + D^{3-} = NiD_3^{7-} \tag{5}$$

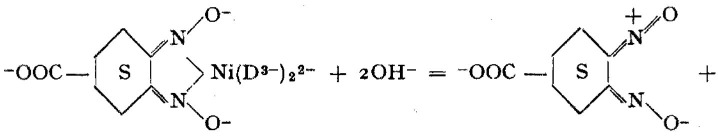
or

$$NiD_2(OH)_2^{6-} + D^{3-} = NiD_3^{7-} + 2OH^- \tag{6}$$

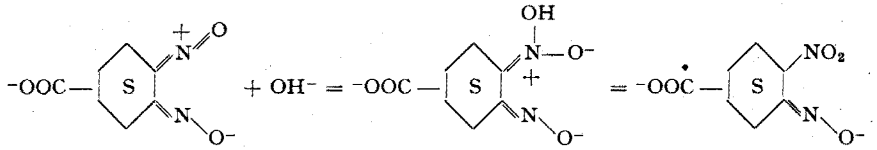
The oxidation of NiD_3^{7-} and the decomposition of NiD_3^{5-} may be described in the following manner

$$NiD_3^{7-} + \tfrac{1}{2}O_2 + H_2O = NiD_3^{5-} + 2OH^- \tag{7}$$

If we assume that nickel(IV) is present in NiD_3^{5-}, then the decomposition of NiD_3^{5-} may occur by the following mechanism



(8)



(9)

Consideration of all the evidence concerning the complexes of 4-carboxynioxime and nickel, leads to the following probable course of reaction

$$Ni(OH)_2 + D^{3-} = NiD(OH)_2^{3-} \tag{10}$$

$$NiD(OH)_2^{3-} + D^{3-} = NiD_2(OH)_2^{6-} \tag{11}$$

or,

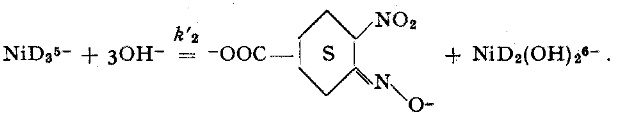
$$2NiD(OH)_2^{3-} = [DNi(O)_2NiD]^{6-} + 2H_2O \tag{12}$$

$$[DNi(O)_2NiD]^{6-} + D^{3-} + 2H_2O = NiD_2(OH)_2^{6-} + NiD(OH)_2^{3-} \tag{13}$$

then,

$$NiD_2(OH)_2^{6-} + D^{3-} \overset{k'_1}{=} NiD_3^{7-} + 2OH^- \tag{14}$$

$$NiD_3^{7-} + \tfrac{1}{2}O_2 + H_2O = NiD_3^{5-} + 2OH^- \tag{15}$$



(16)

The proposed mechanism is consistent with:

(a) The fact that the 1 : 1 complex ion is dependent on the hydroxide concentration.

(b) The magnetic susceptibility data reported in this work and by previous workers[20,21,60–65].

(c) The formation of a substance containing a nitro group.
(e) The fact that previous workers[1,6,24,37,66] have not isolated furoxanes or their derivatives from the oxidation of the complexes of the *vic*-dioximes and nickel (II).
(f) The hypothesis by various workers[1,6,24,47,49,66–70] that the ligand is oxidized.

The following interpretation of the magnetic susceptibility data by the valency bond theory is proposed. The diamagnetic NiD^-, $NiD(OH)_2^{3-}$, or $[DNi(O)_2NiD]^{6-}$ is a square planar complex ion with $3d4s4p^2$ hybrid bonding orbitals. The paramagnetic NiD_2^{4-} is a tetrahedral complex ion with $4s4p^3$ hybrid bonding orbitals. The paramagnetic $NiD_2(OH)_2^{6-}$ and NiD_3^{7-} are octahedral complex ions with $4s4p^34d^2$ hybrid bonding orbitals. The diamagnetic NiD_3^{5-} is an octahedral complex ion with $3d^24s4p^3$ hybrid bonding orbitals.

SUMMARY

The reaction of oxygen with a nickel(II) complex of 4-carboxy-1,2-cyclohexanedionedioxime in alkaline media was studied spectrophotometrically, polarographically, and by spectrophotometric titrations with tin(II) chloride. Magnetic susceptibility measurements were also performed. The rate of formation of the oxidized complex was found to be first order at 25° and 50°. The average values obtained for the rate constant k'_1 are $(2.71 \pm 0.23) \times 10^{-2}\,h^{-1}$ (25°), spectrophotometrically; $(5.99 \pm 0.83) \times 10^{-2}\,h^{-1}$ (50°), polarographically; $(4.98 \pm 0.90) \times 10^{-2}\,h^{-1}$ (50°), titrimetrically; $(2.87 \pm 0.29) \times 10^{-2}\,h^{-1}$ (50°), curve fitting. The value obtained for the rate constant k'_2 is $(1.59 \pm 0.16) \times 10^{-2}\,h^{-1}$ (50°), curve fitting. The effect of reducing agents on the formation of the oxidized complex was studied. It was found that tin(II) chloride, hydrazine sulfate, and hydroxylammonium chloride prevented the formation of the oxidized complex. A reaction mechanism for the formation and decomposition of the oxidized complex is proposed.

RÉSUMÉ

La réaction de l'oxygène sur le complexe nickel(II)-4-carboxy-1,2-cyclohexanedionedioxime en milieu alcalin a été étudiée spectrophotométriquement, polarographiquement et par titrages spectrophotométriques au moyen de chlorure d'étain(II). On a pu constater que le chlorure d'étain(II), le sulfate d'hydrazine et le chlorhydrate d'hydroxylamine empêchent la formation du complexe oxydé. Un mécanisme de réaction de formation et de décomposition de ce complexe oxydé est proposé.

ZUSAMMENFASSUNG

Die Reaktion des Sauerstoffs mit dem Nickel-(II) Komplex des 1,2-Cyclohexandion-dioxims in alkalischer Lösung wurde unter Anwendung von Spektrophotometrie, Polarographie und spektrophotometrische Titration mit Zinn-(II)-chlorid untersucht. Es wurde festgestellt, dass Zinn-(II)-chlorid, Hydrazinsulfat und Hydroxylamin die Oxydation des Komplexes verhindern. Der Reaktionsmechanismus für die Bildung und Zersetzung des oxydierten Komplexes wird diskutiert.

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ANALYSIS OF BRASS BY ANION-EXCHANGE CHROMATOGRAPHY

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Kraus[1-2] and his co-workers have shown that most metals can be very efficiently separated from each other by elution through a column of anion-exchange resin with an eluent containing a complexing anion. Hydrochloric acid[1] is the eluent that has been most thoroughly studied in this respect. Most of Kraus' work was done with very small quantities of metals and involved radioactive tracers. There are very few investigators who, like Wilkins[3], have applied anion-exchange chromatography to the macroanalysis of alloys or other samples containing metals. The purpose of this paper is to describe a method for the analysis of brass or bronze by anion-exchange chromatography.

PRELIMINARY WORK

Small quantities of nickel, copper, lead, iron(III), zinc and tin(IV) were eluted individually through columns of Dowex 1-X8, 200 to 400 mesh, with hydrochloric acid of various concentrations. From the elution graphs, values of C were calculated by the equation

$$U^* = CV + V \tag{1}$$

U^* is the volume of eluate collected from the addition of the sample to the peak of the elution curve. C, the distribution ratio, is the amount of metal in the resin of any plate divided by the amount in the interstitial volume of the same plate at equilibrium. V, the interstitial volume, was taken as 38% of the bed volume[4].

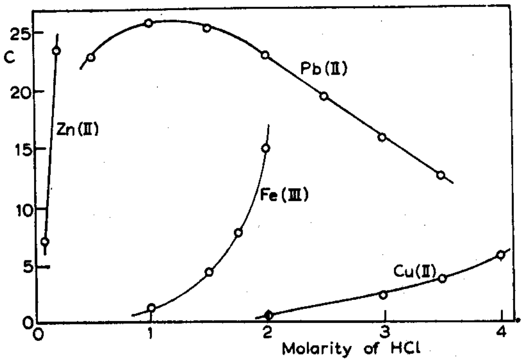

Fig. 1. Plot of distribution ratio, C, *versus* concentration of HCl for several metals.

The results, except for nickel and tin(IV), are given in Fig. 1. For nickel, $C = 0$ throughout the entire range of concentration of hydrochloric acid. Tin(IV) behaves very peculiarly. It is not absorbed at all by Dowex 1-X8 from solutions of less than 0.35 *M* hydrochloric acid. On the other hand, if it is once absorbed by the resin from a more concentrated solution of hydrochloric acid, subsequent elution with more dilute hydrochloric acid fails to remove the tin satisfactorily, the elution graph being very low and long. Unsatisfactory results were also obtained with hot hydrochloric acid and with hydrochloric acid containing a reducing agent.

Preliminary elutions of mixtures of the six cations through a column, 6.9 cm × 3.8 cm², were performed. It was found that 185 ml of 3.4 *M* hydrochloric acid eluted nickel, copper and lead in this order, each metal being quantitatively separated from the others. Then 30 ml of 0.5 *M* hydrochloric acid eluted the iron quantitatively. However, a satisfactory separation of zinc and tin could not be achieved with hydrochloric acid because of the peculiar behavior of tin, mentioned above.

For this reason, elutions of zinc and tin(IV) with oxalic acid were studied. It was found that the distribution ratio of zinc in 0.50 *M* oxalic acid was 6.4 whereas that of tin(IV) was very much greater. It was also found that tin(IV) was rapidly removed from the resin by 1.0 *M* nitric acid.

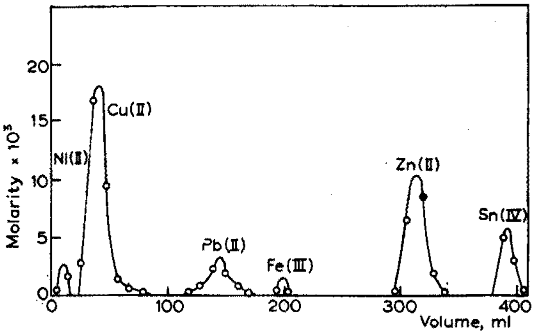

Fig. 2. Elution graph.

The elution shown in Fig. 2 was then performed. The column contained 6.9 cm × 3.8 cm² of Dowex 1-X8, 200 to 400 mesh. The eluents were 185 ml of 3.4 *M* hydrochloric acid, 30 ml of 0.50 *M* hydrochloric acid, 100 ml of 0.50 *M* oxalic acid and 100 ml of 1.0 *M* nitric acid. The entire elution required only 3.5 h. Fig. 2 indicates that the separations were excellent.

RECOMMENDED PROCEDURE

Transfer a weighed portion of the alloy (usually about 600 mg) containing not over 430 mg of copper to a 25-ml borosilicate volumetric flask. Add 7 ml of concentrated hydrochloric acid. Add cautiously 36% hydrogen peroxide in small increments. When the sample is dissolved, destroy the excess peroxide by heating on a steam bath. After cooling the flask, dilute the contents to the mark.

Pass 100 ml of 3.4 *M* hydrochloric acid through the column. Drain the liquid almost to the top of the resin. Pipet accurately 1 ml of the sample solutions to the top of the resin bed. Let this drain into the resin. Rinse the inner walls of the chromatographic tube with about 1 ml of 3.4 *M* hydrochloric acid and let this drain almost to the top of the resin. Repeat the rinsing and draining twice more. Now elute at 0.4 cm per min or 1.5 ml per min with the sequence of eluents given above. Collect fractions in graduated cylinders as follows: 25 ml for the nickel, 80 ml for the copper, 80 ml for the lead, 30 ml for the iron, 60 ml containing no metal(to be rejected), 70 ml for the zinc, 20 ml containing no metal and 50 ml for the tin.

Determine the nickel by a spectrophotometric method with dimethylglyoxime[5] as follows. Transfer the first fraction to a 100-ml volumetric flask. Add 2 ml of 0.5 *N* potassium bromate-bromide solution. After mixing add 6 *M* ammonia until the brown color of bromine disappears and three drops in excess. Developed the color by the addition of 0.5 ml of 1% dimethylglyoxime in ethanol. Dilute to the mark. Measure the absorbance of this solution in a 10-cm cell at 520 mμ against a blank containing all the reagents except nickel. Use a standard curve to correlate the nickel content with the absorbance.

Determine copper by titration with EDTA[6]. Transfer the second fraction to a 250-ml beaker and evaporate to dryness. Dissolve the residue in several drops of 1 *M* hydrochloric acid, and transfer it to a 100-ml volumetric flask. After dilution to the mark, transfer 10.00 ml to a 250-ml Erlenmeyer flask containing 25 ml of water. Add 6 *M* ammonia dropwise until the dark-blue color of the complex appears. Add a quantity of a 1:100 mixture of murexide and sodium chloride sufficient to yield a brilliant yellow color. Titrate with 0.01 *M* EDTA previously standardized with pure copper, using a 5-ml buret with 0.01-ml graduations. Use as a comparison solution for the end-point a solution containing no copper.

Determine lead by titration with EDTA[7]. Evaporate the third fraction to dryness in a 250-ml beaker. Dissolve the residue in 5 ml of a buffer consisting of 1 *M* ammonium chloride and 1 *M* ammonia, containing also several crystals of tartaric acid and potassium cyanide. Add enough 1:100 mixture of eriochrome black T and sodium chloride to produce a distinct purple color. Titrate with 0.01 *M* standard EDTA to a blue color. High results are occasionally obtained by this method, presumably owing to traces of lead in the hydrochloric acid used as eluent. Therefore a blank correction must be applied. This is done as follows: run a blank elution exactly like the main elution except that no sample is taken. Collect and titrate the third fraction of eluate as above.

Determine iron by the spectrophotometric method with nitroso R salt[8]. Evaporate the fourth fraction to dryness, and dissolve the residue in water. Transfer it to a 25-ml volumetric flask. Add 0.5 ml of 20% hydroxylamine sulfate and a drop of 0.05% metanil yellow indicator. Add 6 *M* ammonia to a pinkish-yellow color. To develop the color, add 1 ml of 0.5% nitroso R salt and 2 ml of 33% sodium acetate. After dilution to the mark and mixing, measure the absorbance at 660 mμ against a reagent blank. As in the case of lead, it is necessary to apply a blank correction for the iron in the eluent.

Determine zinc by titration with EDTA[9]. Transfer the sixth fraction to a 250-ml flask. Add 5 ml of the same buffer used in the determination of lead. Add sufficient mixture of eriochrome black T and sodium chloride to yield a wine-red color. Titrate with 0.01 *M* EDTA to a blue color.

Determine tin by the spectrophotometric method with dithiol[10]. Transfer the eighth fraction to a 250-ml beaker. Add several ml of concentrated sulfuric acid and evapo-

TABLE I

ANALYSIS OF STANDARD SAMPLES

	Sheet brass, no. 37E			*Phosphorus bronze, no. 63C*			*Alloy, no. 157A*			*Ounce metal, no. 124C*		
	N.B.S. (%)	*Found* (%)	*Std. devn.*	*N.B.S.* (%)	*Found* (%)	*Std. devn.*	*N.B.S.* (%)	*Found* (%)	*Std. devn.*	*N.B.S.* (%)	*Found* (%)	*Std. devn.*
Ni	0.53	0.528	0.008	0.32	0.319	0.013	11.82	11.92	0.21	0.60	0.600	0.009
Cu	69.61	69.64	0.20	80.48	80.56	0.33	58.61	58.60	0.24	84.22	84.24	0.14
Pb	1.00	1.07	0.053	9.35	9.46	0.14	0.034	[a]		4.74	4.80	0.13
Fe							0.174	0.178	0.018	0.107	0.110	0.002
Zn	27.85	27.76	0.33	0.093	0.119	0.026	29.09	29.02	0.09	4.93	4.94	0.14
Sn	1.00	0.99	0.017	9.03	8.91	0.085	0.02	[a]		5.13	5.08	0.10
Mn							0.174	0.183	0.010			

[a] Quantity too small to be determined by the recommended procedure.

rate to dense fumes. If more than 1.0 mg of tin is present, take an appropriate aliquot. Transfer the solution or aliquot thereof to a 50-ml volumetric flask. Add 10 ml of 5.4 M sulfuric acid and 5 drops of thioglycolic acid. Dilute to about 40 ml and add 2 ml of 2% sodium lauryl sulfate. To develop the color, add 1.0 ml of 0.30% dithiol. After cooling, dilute to the mark. Measure the absorbance at 530 mμ against a reagent blank. Use a standard curve to convert the absorbance to the quantity of tin.

Manganese and aluminum

Since these metals are found in some samples of brass or bronze the procedure was extended to permit their determination. Both of these metals are eluted in the first fraction with the nickel. Manganese can be determined in an aliquot of this fraction without interference from nickel or aluminum by the spectrophotometric method as permanganate after removal of the chloride by evaporation with 10 ml of concentrated sulfuric acid. Details of the procedure may be found elsewhere[11,12]. Similarly, aluminum can be determined by spectrophotometry with aluminon[11,13] without interference by nickel or manganese.

The spectrophotometric determination of nickel in a third aliquot is not subject to interference by aluminum. However, manganese interferes unless the ratio of manganese to nickel is very small. Where necessary, a second aliquot of the sample solution was eluted through a column, 5.0 cm × 3.8 cm^2, of Dowex 1-X8 with 12 M hydrochloric acid. Nickel and lead are the only metals not retained by the resin under these conditions. Lead does not interfere in the spectrophotometric determination of nickel.

RESULTS AND DISCUSSION

Four samples from the National Bureau of Standards were analyzed in triplicate by the recommended procedure. The results (Table I) indicate that the accuracy and precision of the recommended method are good. Much time is saved in comparison with classical methods because the separation requires only 3.5 h. The necessity of running elution blanks for the determination of lead and iron is an annoyance. This could possibly be avoided by preparing 3.4 M hydrochloric acid freed from these metals by passage through a large bed of Dowex 1-X8. Time did not permit the investigation of this point.

Different batches of Dowex 1-X8 differ appreciably from one another. Another batch of this resin may require a slightly different elution procedure in order to give a quantitative separation. For example, the different behavior of 2 batches of Dowex 1-X10 has been reported for the separation of the halides[14]. A few preliminary elutions with a new batch of Dowex 1-X8 will indicate if a modification of the elution procedure is necessary.

SUMMARY

A method is described for the determination of each constituent in alloys of nickel, copper, lead, iron, zinc, tin, manganese and aluminum. The essential feature of the method is the separation of the constituents by anion-exchange chromatography. The separation requires only 3.5 h. The accuracy and precision are good.

RÉSUMÉ

Une méthode est décrite pour le dosage de chacun des constituants des alliages de nickel, cuivro, plomb, fer, zinc, étain, magnanèse et aluminium; elle est basée sur une séparation par chromategraphie, (échangeur d'anions). La méthode est rapide et les résultats obtenus sont bons.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Nickel, Kupfer, Blei, Eisen, Zink, Zinn, Mangan und Aluminium in Legierungen. Sie beruht auf der Trennung der Metalle mit Hilfe der Anionen-Austauscher Chromatographie. Methoden zur Bestimmung der einzelnen Metalle in den Eluaten werden angegeben.

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THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING METALS AND METALLOIDS

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INTRODUCTION

Increasing interest is constantly shown in organometallic compounds at the present time, both in industrial and academic circles, but little information is available in the literature on the determination of carbon and hydrogen in such compounds; such data as exist pertain mainly to the slow classical procedures[1]. A programme was therefore initiated to develop rapid methods for the analysis of these compounds.

Previous experience had shown that the rapid "empty tube" method of BELCHER AND INGRAM[2] was unsuitable for many organometallic compounds, because undecomposed material was swept into the main combustion chamber under the very rapid flow conditions; when the compound then decomposed completely, the metallic residues caused deterioration of the combustion tube and sometimes errors in subsequent analyses. An examination was therefore made of other fast procedures in which a short straight combustion tube is used with an active combustion catalyst; the cobalto-cobaltic oxide method of VEČEŘA[3] was finally chosen on the basis of its superior performance in the analysis of general non-metallic materials[4]. In this method, the tube filling consists of a 4–5 cm layer of pelleted cobalto-cobaltic oxide and a 7-cm roll of silver gauze maintained at 600° in a 35-cm long combustion tube of conventional design. Combustion and sweeping are complete in 10 min. Apart from speed, the advantages of this procedure for the analysis of organometallic compounds are that the catalyst requires no conditioning and can therefore be replaced with little break in the sequence of operations should it become poisoned, and that the combustion tubes are cheap so that their possible deterioration in contact with hot metallic residues is of relatively minor importance.

In the study reported here, as many samples containing as many different metals as could be obtained were analysed. Altogether, the behaviour of 26 different metals or metalloids was examined, including at least one element from each group in the Periodic Table. For some elements only a few samples were available, hence only inferences on general behaviour could be made; for others, a representative collection of samples allowed definite conclusions to be drawn. It is possible to give only a representative selection of all the results obtained, on account of the space involved.

In the determination of carbon and hydrogen in organometallic compounds, difficulties may arise from the formation of metal carbonates and, less probably, hydroxides; carbides may also be formed, though little evidence was found for this in the present study. Other troubles can be caused by poisoning of the catalytic filling or by retention of carbon dioxide or water by metallic compounds which sublime to cooler parts of the combustion system. Experience has shown that the likelihood of interference by carbonate formation can be predicted with reasonable certainty from literature data on the decomposition temperatures of metal carbonates. Data on the volatility of oxides are however much less reliable, even allowing for the difference in conditions. Important data[5,6] of this type are listed in Table I.

TABLE I

DISSOCIATION AND VOLATILIZATION TEMPERATURES OF SOME METAL SALTS[5,6]

Metal	*Dissociation temp.*		*Volatilization temp. of oxide*
	of carbonate	*of hydroxide*	
Beryllium	25	200	Very high
Magnesium	540	350	very high
Calcium	900	547	very high
Strontium	1289	778	very high
Barium	1360	998	very high
Zinc	350	39	1720, 1200
Cadmium	350	39	1930
Bismuth	417	—	1010

In the following sections, the behaviour of the various elements studied is described according to their order in the Periodic Table. Silicon-containing materials were difficult to analyze by the cobalto-cobaltic oxide method and their analysis will be discussed at a later date. For all the other elements examined, either the straightforward method or a slight modification proved satisfactory. Data were also obtained on the possibility of determining the metals by weighing the residues in the boat. A reagent which proved of great utility throughout this study — tungstic oxide — should be mentioned here; this oxide was first suggested by Belcher, Fildes and Nutten[7] as a combustion aid in the analysis of phosphorus-containing compounds, and was later applied in the same way by Kissa[8] for compounds containing alkali or alkaline earth metals. The present work confirmed its usefulness for these purposes and showed that it also had unexpected retentive properties for certain metals. The reagent has the advantages over classical sample boat additives such as vanadium pentoxide or potassium dichromate, that it does not spatter and attack the combustion tube, and it is readily removed from the boat after a determination[7].

EXPERIMENTAL

Procedure

The apparatus, the preparation of the cobalto-cobaltic oxide catalyst and the procedure were exactly as described previously[4]. With an oxygen flow rate of 12 ml/min and the platinum sample boat about 3 cm from the entrance of the combustion furnace, the "first combustion" was done with a low Bunsen flame during 3 min, and the "second combustion" with a strong flame during 3 min; the sweeping out period was 4 min after which the Pregl absorption tubes were detached and weighed in the conventional way. When tungstic oxide was used as a sample boat additive, the boat had to be heated strongly for at least 2 min during the "second combustion". Any modifications necessary for particular elements are described below.

Additional reagents

Magnesium oxide pellets: see[9]. Tungstic oxide: ignite analytical reagent grade tungstic acid or tungstic oxide over a Meker burner for 1 h with occasional stirring. Cool and store in a small desiccator over phosphorus pentoxide[7]. Other reagents used were of analytical purity and were rigorously dried before use.

RESULTS AND DISCUSSION

Sodium and potassium

The difficulties encountered in the analysis of substances containing alkali metals are well-known; the formation of thermally stable carbonate causes low carbon

TABLE II

ANALYSIS OF VARIOUS ORGANO-METALLIC MATERIALS

Compound	*% C theor.*	*% C found*	*% H theor.*	*% H found*	*% metal theor.*
Sodium α-methoxyphenylacetate	61.01	61.30	5.40	5.59	6.49
Copper acetylacetonate	45.88	46.05	5.39	5.46	24.27
Beryllium acetylacetonate	57.95	58.10	6.81	6.77	4.35
Zinc dibenzyldithiocarbamate[a]	59.04	59.13	4.62	4.79	10.71
Zinc benzoate[a]	54.66	54.73	3.28	3.42	21.25
Zinc β-chloropropionate[a]	25.70	25.90	2.87	2.85	23.31
Cadmium oxinate	53.95	53.88	3.02	3.01	28.05
Phenyl mercury acetate[b]	28.53	28.44	2.39	2.38	59.37
Perfluorodiphenylmercury[b,c]	26.95	26.79	0.00	0.16	37.52
Aluminium oxinate	70.58	70.62	3.95	4.00	5.87
$(CH_2O)_2BC_6H_4B(OH_2C)_2$[a]	55.13	55.08	5.55	5.57	9.93
$C_6H_5.B.(CH_2O)_2.C.(CH_2Cl)_2$[a]	51.02	51.09	5.06	5.07	4.18
$(C_6H_5)_3\ B.C_5H_5N$[a]	85.99	85.83	6.28	6.44	3.37
Methyl-β-D-glucopyranoside-4,6-phenylborate[a]	55.94	55.86	5.78	5.85	3.88
Gallium oxinate[a]	64.57	64.43	3.61	3.80	13.88
Bis-cyclopentadienyl titanium dichloride	48.23	48.40	4.05	4.12	19.24
$(C_2H_5)_2\ AlCl_2.Ti(OH)_2$	20.19	20.27	5.08	5.15	Al 11.33 Ti 20.13
Lead oxinate	43.63	43.70	2.44	2.46	41.82
o-Arsanilic acid[b]	33.20	33.30	3.71	3.72	34.51
3-Nitro-4-chlorophenylarsonic acid[b]	25.60	25.62	1.79	1.78	26.62
Triphenylmethylarsonium iodide[b]	50.92	50.90	4.05	4.14	16.72
Bismuth oxinate monohydrate	49.17	49.27	3.06	3.01	31.69
Molybdenum carbonyl[a]	27.29	27.34	0.00	0.03	36.34
Methylethylfulvene molybdenum carbonyl[a]	48.01	47.92	4.03	3.90	31.96
$K_4Mo(CN)_8.2H_2O$[a]	19.35	19.50	0.81	0.89	Mo 19.32 K 31.50
Uranyl β-chloroproprionate	14.85	14.90	1.66	1.86	49.07
Uranyl acetylacetonate	24.70	24.64	3.32	3.28	48.95
Cyclo-tri-selenium bis-benzoylacetone	43.11	43.32	2.89	2.94	42.51
Tellurium acetylacetonate	26.60	26.77	2.68	2.64	56.54
Acetyl ferrocene[b]	63.19	63.35	5.30	5.38	24.49
Trans-4-phenyl-cyclohexylferrocene carboxylate[b]	71.14	71.11	6.23	6.34	14.38
Ferric dipyridyl iodide pentahydrate[b]	41.49	41.52	3.95	3.83	6.43
Nickel ethylenediamine-bis-acetylacetonate	51.29	51.25	6.46	5.53	20.89
Nickel-di-isopropyldithiophosphate[a]	29.70	29.63	5.82	5.74	12.09

[a] WO_3 added to the sample boat.
[b] See text.
[c] MgO added to the sample.

recoveries. To overcome this, an oxidizing agent, *e.g.* tungstic oxide[8], potassium dichromate[1], vanadium pentoxide[1] or potassium persulphate[10], or some other reagent, *e.g.* powdered silica[11] or sodium bisulphate[12], is added to the sample in the boat. Tungstic oxide is the preferred reagent because it does not attack the combustion tube or exhaust the tube filling. Excellent results were obtained for sodium and potassium compounds with a cover of tungstic oxide; no samples containing the other alkali metals were available but the same treatment should be successful.

Copper, silver, gold

No troubles have been reported in the analysis of compounds containing copper, silver or gold, and none would be expected, for these metals are components of classical tube fillings. Analysis of copper dianisidine tetraacetate and of copper acetylacetonate (Table II) showed that good carbon and hydrogen results could be obtained without any modification of the usual method. However, the copper did not remain quantitatively in the boat and so could not be determined. The small amounts of copper oxide on the combustion tube and in the catalytic filling did not affect later analyses. No compounds containing silver or gold were obtainable; probably these metals would remain in the boat as in slow methods[1] but if any did reach the catalytic filling, they would tend to enhance[13] rather than diminish its activity.

Beryllium and magnesium

The dissociation temperatures of these metal carbonates (Table I) are well below the working temperature of the procedure, hence no difficulties would be expected, particularly with magnesium whose oxide can be used as a combustion catalyst[9]. Results for magnesium oxinate were excellent, but the amount of magnesium calculated from the residue in the boat was consistently 0.5% high, possibly because of the hygroscopicity of the oxide even during rapid transference to a weighing piggie.

Beryllium acetylacetonate was easily analysed without modification of the general method (Table II); precisely the same results were obtained with or without tungstic oxide added to the sample boat. Beryllium oxide did not remain in the boat. On the other hand, two chelates of expected empirical formula $C_6H_5O_3NBe$ and $C_7H_7O_3NBe$, gave results about 1% low for carbon with correct hydrogen values, and the percentage of beryllium calculated from the residue was about 1% high. This would indicate carbonate formation, but the residue gave no reaction for carbonate and boat additives made little difference to the results, which were essentially the same as those found by a conventional slow method of decomposition. Accordingly it was assumed that the samples were impure.

Calcium, strontium, barium

No pure samples were available, but tungstic oxide as a boat additive should be successful[8].

Zinc

Zinc-containing compounds have been analysed for carbon and hydrogen by the classical Pregl method with cerium dioxide and platinum gauze added to the normal filling[14]. It has also been noted that zinc oxide volatilizes from the sample boat, so that zinc cannot be determined by weighing the residue[1]. Zinc carbonate decomposes at a moderate temperature, and the volatilization temperature of the oxide is high (Table I) so that no interference would be expected. However, when a series of zinc-containing compounds was analysed, the first results were satisfactory but by the end of the third run, about 15% of the carbon was retained in the combustion tube; hydrogen results were correct throughout. Tests showed that zinc oxide, which volatilized particularly during the "second combustion", had spread to every part of the tube filling. Low results were due partly to deactivation of the catalytic filling and partly to retention of carbon dioxide by zinc oxide on the cooler parts of the tube.

Addition of tungstic oxide to the sample completely prevented volatilization of zinc oxide, and excellent results were obtained for a series of different compounds (Table II). After about 12 determinations the tube filling was removed sectionally and extracts were tested for zinc with completely negative results; tests on the boat filling after an analysis were positive. It seems likely that zinc tungstate was formed. The presence of halogens or sulphur in the compound did not affect the behaviour of the zinc.

Cadmium

Excellent results were obtained for cadmium oxinate without modification of the general procedure. There was no evidence for volatilization of cadmium oxide and cadmium could be determined by weighing the boat residue as CdO (% Cd found, 28.09; theor. 28.05).

Mercury

Mercury interferes by distillation through the system leading to high hydrogen results. In slow procedures 1 or 2 determinations can be done successfully before mercury appears in the water absorption tube and the tube filling becomes poisoned; some gold wire in the beak end of the tube prevents mercury from reaching the absorption system in later determinations[15]. In macro analysis, mercury is said to be retained quantitatively in silverized asbestos placed in front of the sample boat[16]. Silver and lead salts have also been used in micro and semimicro methods[17]; in some cases the mercury could be determined by weighing the silver or gold absorbent.

Tests were made with silverized asbestos, silver and gold wire. Silverized asbestos was placed in a narrow silica tube inserted into the main combustion tube from the sidearm up to the furnace entrance; this tube contained the sample boat, a short layer of cobalto-cobaltic oxide and a 2-cm layer of silverized asbestos, the order being a modernized version of the original specification[16]. However, with phenyl mercury acetate as standard sample, only two correct analyses were achieved before mercury appeared in the water absorption tube; even this mercury was held by the silver gauze at the beak end of the combustion tube rather than by the silverized asbestos. When extra silver was placed in the beak end, without any other modification of the general method, mercury again broke through after 1–2 determinations. Gold wire proved more satisfactory and 5–6 determinations were possible before the breakthrough point was reached. The gold wire (100 cm of 0.5 mm diameter; gold wool would be more efficient) was tightly coiled through the exit tube and a 1-cm layer of coiled wire was placed in the beak end separated from the silver gauze by a plug of silica wool in order to keep it relatively cool. The gold could be partially regenerated in the tube by heating in the oxygen stream, which distilled the mercury into a suitable collector. Excellent results were obtained in this way (Table II).

Aluminium

Aluminium compounds are said to be analyzed without difficulty, the metal being determined simultaneously by weighing the oxide[1]. However, it is necessary[18] to carry out the combustion of aluminium phenyl derivatives in moist oxygen to obtain correct carbon values. No other information was available in the literature.

Analysis of aluminium oxinate proved to be simple and exact by the general method; aluminium oxide could not be weighed because the sample distilled while undecomposed, but aluminium oxide along the combustion zone did not interfere in later analyses. Another compound gave consistently 1% low carbon values; addition of 6 different wet and dry boat additives made no difference to the results, which agreed well with those obtained by a "slow" procedure, and it was eventually assumed that the sample was impure. Formation of aluminium carbide seems a possible source of error, but this would certainly have been prevented by the moist additives. Accordingly, the general procedure can be recommended.

Boron

According to Roth[1] it is advisable to mix boron-containing samples with vanadium pentoxide to prevent enclosure of carbon particles in beads of boric oxide. For classical procedures, temperatures of 1,000–1,100° have been recommended for the sample burner[19] while some compounds may require a temperature of 1,300° (induction heating) for complete decomposition by the rapid empty-tube technique[20].

In the present study, only 1 of 8 compounds examined gave incorrect results by the general cobalto-cobaltic procedure, and this compound, the only one that did not contain oxygen, gave excellent results when it was mixed with tungstic oxide. Without the additive, a dark glassy bead was formed; the other samples volatilized completely from the boat before decomposing and so there was no opportunity for bead formation. Typical results are given in Table II. As a general recommendation, the sample should be mixed with tungstic oxide. Other possible additives had no advantage. Any boron oxides that reached the catalytic filling had no effect on later results.

Gallium

With gallium oxinate, low (0.6%) results were obtained for carbon unless tungstic oxide was added. The samples partly volatilized undecomposed so that the metal could not be determined. No samples containing other metals in group II could be obtained. It would probably be necessary to add tungstic oxide to achieve complete combustion in all cases; gallium carbonate is not mentioned in the literature[5,6] but was apparently formed.

Titanium

No difficulties were found with these compounds. The boat residue was of indefinite composition, hence titanium could not be determined. A compound containing titanium and aluminium also gave no trouble, the unexpected results being confirmed by infra-red analysis (Table II).

Lead

Lead compounds proved simple to analyse, as was expected, for lead oxides are contained in most classical tube fillings. Analysis of lead aryl derivatives is straightforward[21]. The only sample available in the present work was lead oxinate, which gave excellent results for carbon and hydrogen; weighing the residue as PbO[1] gave slightly low recoveries for lead, presumably because of some volatilization of the sample before decomposition.

Tin

No samples were available but it may be useful to summarize the information available in the literature. According to Roth[1] tin compounds offer no difficulties and tin can usually be weighed as SnO_2 in the boat, although it may be necessary to add vanadium pentoxide to achieve complete combustion. An additional layer of red lead (Pb_3O_4) in a platinum gauze cylinder has, however, been suggested[22]. With a relatively simple copper oxide filling at 750°, a layer of silver vanadate impregnated on pumice is necessary to prevent occlusion of carbon in stannic oxide when aryl tin halides are burned under fairly rapid conditions[21]. Present experience suggests that addition of tungstic oxide to the sample might be successful.

Vanadium, niobium and tantalum

Analysis of vanadium-containing materials should be straightforward, for vanadium pentoxide is the classical boat additive to achieve complete combustion of refractory compounds. The analysis of niobium compounds was of interest and no information was available in the literature. In order to obtain a standard compound for testing, an attempt was made to prepare niobium oxinate by the method of KOSTA AND DULAR[23], which is said to give a precipitate of definite composition, $NbO(C_9H_6ON)_3$. However, the carbon and hydrogen results obtained with and without various boat additives, and the niobium values obtained by weighing the residues agreed with the above formula only on the assumption of a hemihydrate. The longstanding problem of the composition of niobium oxinate does not appear to have been solved by the latest study of it. The results obtained, however, indicate that no modifications would be required for the analysis of niobium compounds.

Phosphorus

The difficulties encountered in the analysis of phosphorus-containing materials are well-known[1]. Many modifications of the classical procedures have been recommended; tungstic oxide both as a sample boat additive and placed at the furnace entrance in a porcelain boat[7] is now widely applied. This arrangement was tested in the present work with completely satisfactory results for a representative range of compounds. The use of tungstic oxide for phosphorus compounds was also shown to be satisfactory when applied to the rapid "empty-tube" method.

Arsenic

Arsenical materials behave similarly to phosphorus-containing compounds in that the oxides formed tend to pass into the tube filling and poison it. The platinum catalyst of the macro-Dennstedt method can be protected by placing a boat of red lead between the sample and the catalyst[16]; a platinum gauze cylinder filled with red lead is necessary to prevent interference when the conventional Pregl method is used[22]. Lead dioxide can protect the platinum catalyst in the micro-Friedrich method[24]. With silver vanadate as catalyst, an auxiliary packing containing lead, cerium and silver oxides with silver and lead chromate is satisfactory for arsenic or antimony compounds[25].

In the present work it was found that *o*-arsanilic acid gave correct results for 2–3 determinations but later results became increasingly high owing to arsenic oxides reaching the absorption system. Tungstic oxide used in the same way as for phosphorus compounds, *i.e.* as a sample cover and in a boat at the furnace mouth, did not retain these oxides quantitatively. Magnesium oxide was then examined as an additional layer to the tube filling; retention of arsenic oxides seemed complete but results were low because of retention of carbon dioxide by magnesium oxide at 600°. Accordingly, the magnesium oxide layer was placed between the sample boat and the furnace mouth where it could be heated strongly with the Bunsen flame. Entirely satisfactory results were found in this way (Table II). The sample boat is placed about 5 cm from the furnace entrance, a 2-cm layer of magnesium oxide pellets between silica wool plugs being situated just outside the furnace mouth. This auxiliary filling is satisfactory for 8–10 determinations and can be easily replaced; the only conditioning required is strong heating in the oxygen steam to remove adsorbed water. After the sample boat has been introduced, the magnesium oxide layer is heated with a Bunsen flame which is then removed while the volatilization is done in the usual way. The time for total combustion is increased by a few minutes because of the greater distance between the furnace and the sample boat and because the magnesium layer must be heated strongly for about 2 min during the second combustion to ensure removal of carbon dioxide.

This procedure was chosen because it allows a simple extension of the VEČEŘA method to arsenical compounds. If the magnesium oxide were placed in the main furnace the temperature would have to be raised to about 800° to prevent retention of carbon dioxide. If many arsenicals had to be analysed, it would probably be preferable to use the straightforward magnesium oxide procedure as for fluorinated materials[9].

No samples containing antimony were available, but it seems likely that the measures taken to avoid interference from arsenic oxides would prove satisfactory also in the case of antimony oxides. The use of red lead[22] or the mixed additional filling[25] as described above for arsenicals has also been recommended for antimony-containing compounds.

Bismuth

The dissociation temperature of the carbonate is relatively low while the volatilization temperature of the oxide is high(Table I), hence no difficulties were expected. Bismuth oxinate gave excellent carbon and hydrogen values (Table II) but bismuth values were about 2% low calculated from the boat residue as Bi_2O_3. According to DUVAL[26] the residue of bismuth oxinate in thermogravimetry consists of bismuth trioxide with some bismuth. However, as a definite check that no bismuth had escaped from the boat, 20 mg of the oxinate was burned and the tube filling was removed in portions, extracted and tested for bismuth; the negative tests showed that all the bismuth had remained in the boat.

Chromium

No pure samples were available but no interference would be expected and in some cases the residue could probably be weighed as Cr_2O_3[1].

Molybdenum

ROTH[1] states that volatile molybdenum trioxide is formed in the conventional Pregl method but does not mention if carbon and hydrogen values can be obtained. The data available on the volatility of the trioxide as a weighing form are not in good agreement[26,27] but it appeared that a fair amount of volatilization could be expected at about 600°. However, excellent results were obtained for molybdenum carbonyl and it was proved with this compound and by ignition of large samples of molybdenum trioxide that no molybdenum reached the cobalto-cobaltic oxide filling or the absorption system. However, later analyses gave low results for carbon, owing to a slight sublimation of molybdenum trioxide (as far as the first silica wool plug holding the cobalt oxide pellets in position) which probably occluded carbon particles; carbonate or carbide formation seems to be ruled out[6]. When the accumulated deposit on the wool plug was removed, correct results were again obtained. Tungstic oxide proved valuable in preventing to a very great extent the volatilization of molybdenum trioxide from the sample boat. No suitable reagent could be found which completely prevented the volatilization, hence it is recommended that tungstic oxide be added and also that the first silica wool plug be renewed every 5–6 determinations. Excellent results were obtained on a series of compounds in this way (Table II).

No tungsten-containing compounds were available but clearly no difficulties should arise.

Uranium

A series of compounds proved straightforward to analyse, excellent results being obtained (Table II). In some cases, uranium could be determined by weighing the residue as U_3O_8.

Selenium

Such compounds have been analysed satisfactorily by addition of extra silver and platinum layers to the conventional Pregl filling[28]. With a platinum catalyst as the sole filling, the selenium dioxide can be collected in an empty quartz tube placed between the combustion tube and the water absorption tube[29]. Selenium dioxide is said[6] to sublime readily at 315°.

Satisfactory results were obtained for the only sample available (Table II) without modification of the general method. It was proved that the selenium dioxide was retained by the silver gauze placed at the beak end of the tube; the capacity of the 7-cm length of silver gauze seemed to be quite high. No selenium dioxide appeared in the cobalt oxide or in the absorption system.

Tellurium

No reference to such analyses could be found in the literature. Tellurium dioxide is said[6] to behave like selenium dioxide though its volatilization temperature is higher. On the other hand, DUVAL[26] found that tellurium dioxide could be heated to 1000° without loss in weight. In the present study, tellurium acetylacetonate was analysed easily (Table II) but tellurium dioxide was not retained quantitatively in the sample boat. Qualitative tests showed that most of the tellurium dioxide that escaped from the boat was retained at the beginning of the silver layer, with traces spread through the cobalt oxide filling. There was no evidence that the dioxide could proceed beyond the silver gauze; presumably silver tellurate is formed similarly to silver selenate[5], and on prolonged heating, all the tellurium would be found in the silver gauze.

In the cases of selenium and tellurium, exhaustive tests were made on the few samples available and the rather unexpected behaviour of the dioxides should prove to be general for all such compounds.

Manganese

As was expected, for manganese oxides are now widely used as tube fillings in carbon and hydrogen analyses, no difficulties were found in the analysis of a series of compounds containing manganese. Manganese reaching the catalytic layer did not affect later results. Even when manganese remained quantitatively in the boat, it could not be determined by weighing the residue, because mixed oxides were formed[1].

Rhenium

No samples were available but the literature data[5,6] suggests that such compounds would behave similarly to those containing selenium.

Iron

According to Roth[1], iron can be determined by weighing the boat residue as Fe_2O_3. However, some iron compounds may require layers of ceric oxide and platinum in addition to the usual Pregl filling[14]. In the present work, good results were obtained by the general procedure but red ferric oxide spread along the combustion tube and into the catalytic layer, completely masking the tube. Some compounds decomposed in the sample boat, but others, *e.g.* ferrocenes and acetylacetonates, reached the catalytic layer partially undecomposed. Strong heating of the ferric oxide along the volatilization zone led to rapid deterioration of the silica combustion tube, hence it was necessary to find a reagent which would retain the iron in the boat. Tungstic oxide, sodium fluoride, alumina, magnesium oxide, silica, manganese dioxide and cobaltic oxide were tested with little success; in all cases, ferrocenes escaped undecomposed, though cobaltic oxide was more efficient than the other reagents tested. Accordingly, a silica insert tube was made which fitted inside the combustion tube from the sidearm to the mouth of the furnace, and which could be removed with a hook. This tube held a 2-cm layer of cobalto-cobaltic oxide pellets kept in position by silica wool plugs; the sample boat was placed inside the tube immediately against this layer and the analysis was carried out by the usual timing. Satisfactory results were obtained for a series of compounds but only in the case of the dipyridyl compound (Table II) could iron be determined by weighing the boat residue. Otherwise, all the iron was retained in the specially inserted layer of cobalt oxide, which could be used for several determinations. Apparently, this layer decomposed the samples at a very low temperature and so prevented further progress of iron along the tube; the later strong heating of the second combustion served only to remove any carbon dioxide and water retained.

Cobalt

Several compounds were analysed by the general method with completely satisfactory results; the percentages of cobalt calculated from the weight of the residues on the basis of CoO formation were only slightly low.

Nickel

Again, analysis of a series of compounds caused no trouble. Nickel could not be determined by weighing the boat residue[1]; nickel reaching the catalytic layer did not affect later results.

CONCLUSIONS

For a surprisingly large number of metals, the cobalto-cobaltic procedure can be applied without modification. The principal difficulties are found in carbonate formation and in the occlusion of carbon particles by oxides. Tungstic oxide is valuable in preventing both these types of interference, as well as in retaining certain metals, *e.g.* zinc and molybdenum, volatile oxides of which otherwise interfere.

In most cases it has been possible to derive definite information on the general behaviour of each metal or metalloid with regard to the determination of carbon and hydrogen. However, the situation for the simultaneous determination of the metals by weighing the residual oxide in the sample boat is less happy, for the amount of volatilization of undecomposed sample from the boat is much greater in this rapid method than in the slow Pregl methods; it is seldom possible to predict accurately whether or not the metal can be determined.

ACKNOWLEDGEMENTS

We are heavily indebted to the many people who have assisted in this investigation by providing samples. PROF. G. WILKINSON of the Imperial College of Science, and the Mond Nickel Company have helped greatly in this respect. One of us (Y.A.G.) thanks the National Research Council of the U.A.R. for the financial support which made this work possible.

SUMMARY

The determination of carbon and hydrogen in organometallic compounds is described. Cobalto-cobaltic oxide is used as the catalytic tube filling in a rapid procedure. Compounds containing Na, K, Cu, Be, Mg, Ca, Zn, Cd, Hg, Al, B, Ga, Ti, Pb, Nb, P, As, Bi, Mo, U, Se, Te, Mn, Fe, Co, Ni were examined; interferences were overcome where necessary and tungstic oxide proved a valuable auxiliary reagent.

RÉSUMÉ

Une méthode est décrite pour le dosage du carbone et de l'hydrogène dans des composés organo-métalliques, en utilisant l'oxyde Co_3O_4 comme catalyseur. Des composés renfermant divers éléments (Na, K, Cu, Be, Mg, Ca, Zn, Cd, Hg, Al, B, Ga, Ti, Pb, Nb, P, As, Bi, Mo, U, Se, Te, Mn, Fe, Co, Ni) ont été examinés.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Kohlenwasserstoff Bestimmung von metallorganischen Verbindungen bei Verwendung von Co_3O_4 als Verbrennungskatalysator. Der störende Einfluss der einzelnen Metalle, soweit vorhanden, und dess en Ausschaltung wird beschrieben. Als Zusatz zur metallhaltigen Substanz wird Wolframoxyd empfohlen. Folgende anorganischen Komponenten wurden berücksichtigt: Na, K, Cu, Be, Mg, Ca, Zn, Cd, Hg, Al, B, Ga, Ti, Pb, Nb, P, As, Bi, Mo, U, Se, Te, Mn, Fe, Co, Ni.

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SPECTROPHOTOMETRIC ERRORS ASSOCIATED WITH CELLS OF CIRCULAR CROSS SECTION

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INTRODUCTION

Vessels, such as test tubes and beakers, that have circular cross sections are often employed as absorption cells in rapid routine spectrophotometric analysis and in photometric titrations. As in other cases in which the sample is inhomogeneously distributed in the light path, deviations from Beer's law may be expected to arise from the use of such cells. This communication presents a mathematical treatment of these deviations.

THEORY

As is illustrated by Fig. 1, a parallel beam of uniform intensity P_0 is considered to be incident on an infinitesimally thick layer of solution contained in a circular cell of unit radius. Despite the fact that it cannot be exactly true in any such cell, and may be grossly in error if the thickness of the cell wall varies across the width of the beam,

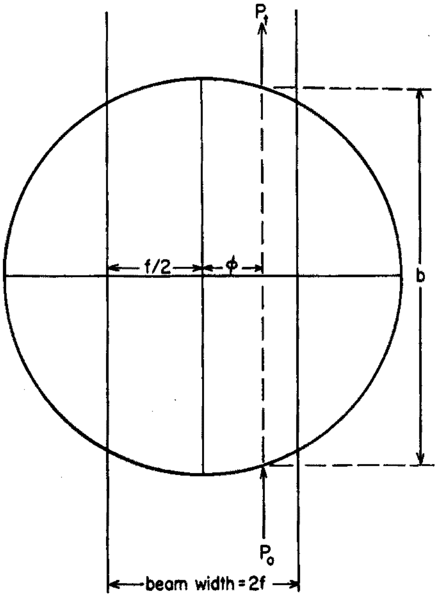

Fig. 1. Absorption in a cell of circular cross section, illustrating the definitions of b, ϕ, f, P_0 and P_t.

the simplifying assumption is made that the beam remains parallel during and after passage through the solution. It is further assumed (neglecting, for example, possible chemical sources of error as well as any variation of refractive index with the concentration, c, of the absorbing species) that Beer's law in the form

$$P_t = P_0 \mathrm{e}^{-kcb} \tag{1}$$

is obeyed in each element of solution. Here P_t represents the intensity of the beam after passing through the element of thickness b, and k represents the absorptivity of the species in question. Finally, it is assumed that the entire width of the beam is incident on the detector, so that the response of the latter is proportional to P_t.

For the element of solution indicated by the dashed line in Fig. 1,

$$b = 2\sqrt{1 - \phi^2} \tag{2}$$

where ϕ is the distance of the ray from the diameter of the cell. The mean intensity of the transmitted beam depends on the beam width; taking the beam width as equal to $2f$ (so that f may be regarded as the ratio of beam width to cell diameter), and assuming that the cell is exactly centered in the beam, the transmittance is given by

$$T = \frac{P_t}{P_0} = \frac{\int_{-f}^{+f} \mathrm{e}^{-2kc\sqrt{1-\phi^2}}\,\mathrm{d}\phi}{\int_{-f}^{+f} \mathrm{d}\phi} = \frac{1}{f}\int_0^f \mathrm{e}^{-2kc\sqrt{1-\phi^2}}\,\mathrm{d}\phi \tag{3}$$

The results described below were obtained by introducing the subsidiary variable $\theta = \sin^{-1} f$, expanding and integrating the exponential, and evaluating T numerically for various values of the parameters f and kc so chosen as to cover the range of analytical interest. The number of terms retained in each expansion was sufficient to yield a value of T correct to 5 significant figures. The values of f employed varied in 0.05-unit steps from 0.05 to 0.5; those of kc varied in 0.2-unit steps from 0.2 to 1.6.

RESULTS

It was found to be revealing to express the results in the form of the ratio T/T^*, where T^* is the transmittance that would be observed with the same solution in a cell of square cross section 2 units on each edge. Thus $T^* = \mathrm{e}^{-2kc}$, whence $kc = 1.6$ corresponds to an absorbance of about 1.4. A representative sample of the values of this ratio is shown in Fig. 2.

Empirically it is found that these values conform closely to the equation

$$(T/T^*) - 1 = \gamma(kc)f^2 \tag{4}$$

Although the value of γ is not strictly constant (it is 0.350 at $f = 0.1$, decreases to 0.330 at $f = 0.15$, and then rises slowly to 0.353 at $f = 0.4$ and thereafter more rapidly to 0.397 at $f = 0.5$), over the range $0.1 \leqslant f \leqslant 0.4$ it may be taken as 0.342 (± 0.008) without introducing an error as large as 0.3% in any absorbance value. If one writes

$$T^* = 10^{-2\varepsilon c} \tag{5}$$

where, obviously, $\varepsilon = 0.434k$, then the absorbance measured with the circular cell is given by

$$A = -\log T = 2\varepsilon c - \log(1 + 0.788\varepsilon c f^2) \qquad (6)$$

If f does not exceed 0.4 and the measured absorbance does not exceed 1.4, one may employ the approximation

$$\log(1 + 0.788\varepsilon c f^2) = 0.342\varepsilon c f^2 \qquad (7)$$

whence

$$A/A^* = 1 - 0.171 f^2 \qquad (8)$$

Since A^* ($= -\log T^*$) is assumed proportional to concentration, it follows that, within the limitations of the approximation expressed by eqn. (7), the absorbance values obtained in cells having circular cross sections should also be proportional to concentration. A sensitive test of this prediction is shown in Fig. 3 for several values of f. It is evident that the apparent absorptivity decreases as f increases, as is explicitly indicated by eqn. (8); this is obviously because the volume of solution traversed by the beam is smaller in the cylindrical cell. For any value of f up to the physically somewhat extreme value of 0.5, however, the deviations from a linear relationship between absorbance and concentration are negligible up to rather high absorbance values. Pronounced deviations from such a linear relationship are not unusual with such instruments as the Bausch and Lomb Spectronic 20 "Colorimeter", but this analysis shows that they must be attributed to causes (*e.g.*, stray light) other than the use of cylindrical cells.

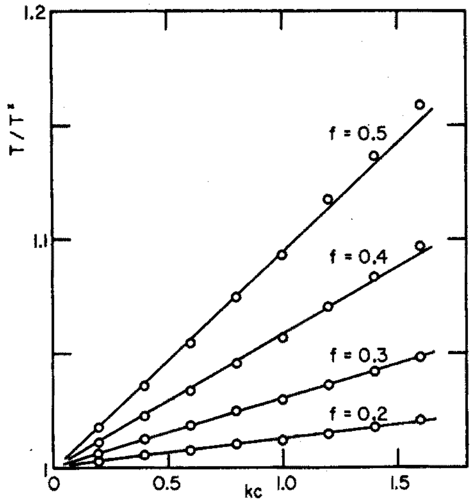

Fig. 2. Plots of T/T^* *vs.* kc for various values of f, illustrating the approximation expressed by eqn. (4).

It is generally assumed that the placement of a cylindrical cell with respect to the light beam is critical: *i.e.*, that the absorbance will be appreciably affected by even a small displacement of the cell toward one side of the beam. In evaluating this effect, it is convenient to define a parameter $\triangle$ as the ratio of the distance between the center of the beam and the diameter of the cell to the length of the cell diameter. If the total width of the beam is f, as defined above, displacing the cell $\triangle$ units to one side will cause the edges of the beam to fall at $(f/2 - \triangle)$ unit on one side of the cell diameter and at $(f/2 + \triangle)$ unit on the other side. Values of the absorbance corresponding to $f = 0.5$ and to values of $\triangle$ varying from 0 (where the beam is exactly centered) to 0.25 (where one edge of the beam passes through the center of the cell) are shown in

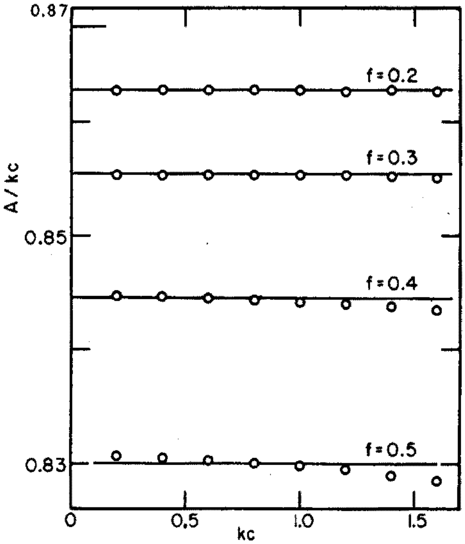

Fig. 3. Plots of A/kc *vs.* kc for various values of f, showing the apparent adherence to Beer's law that should characterize absorbance–concentration data obtained with cells having circular cross sections. The short horizontal line corresponds to the limiting value (= 0.8686) of A/kc as f approaches 0. The long horizontal line drawn for each value of f represents the value of A/kc that would be obtained in a cell of rectangular cross section in which the volume of solution traversed by the beam was the same as in the circular cell at that value of f.

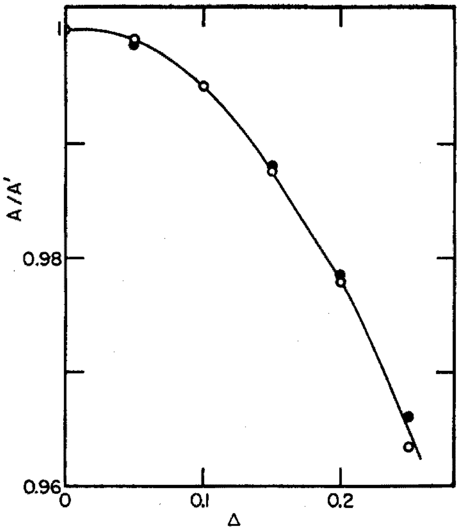

Fig. 4. Plots of A/A_c *vs.* $\triangle$ for $f = 0.5$ and $kc = 0.6$ (solid circles, $A_c = 0.516$) or 1.2 (open circles, $A_c = 1.031$), where A_c is the measured absorbance when the center of the beam coincides with the cell diameter.

Fig. 4 for absorbances close to 0.5 and 1.0. The effect is nearly, though not quite exactly, independent of the absorbance. For a cell of unit diameter, a sideways displacement of 0.05 unit lowers the absorbance only 0.1%; even if $\triangle = 0.25$, which is improbably large in practice, the decrease of A amounts to only a few per cent. Though it has sometimes been inferred in the literature that, for example, great care must be taken to avoid moving a beaker in which a photometric titration is being carried out for fear of changing the optical path length, it appears that the error caused by doing so would be quite negligible if the cell walls were of perfectly uniform thickness. A much more important source of error would be the change in beam direction caused by variations in wall thickness if the cell were rotated or displaced sideways in the beam.

SUMMARY

It is shown that the use of spectrophotometric cells having circular cross sections leads to errors that depend on the absorbance, on the ratio of beam width to cell diameter, and on the distance between the center of the beam and the diameter of the cell, but that the nature and magnitude of these errors render them essentially undetectable in practical analytical work.

RÉSUMÉ

Un calcul d'erreur a été effectué avec l'utilisation de cuves rondes, lors de déterminations spectrophotométriques. Les résultats dépendent de plusieurs facteurs, mais l'ordre de grandeur de cette erreur est très faible; elle est pratiquement négligeable pour les méthodes d'analyse usuelles.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die Verwendung von runden Küvetten bei der Spektrophotometrie zu fehlerhaften Ergebnissen führt. Diese sind abhängig von der Adsorption, dem Verhältnis Strahlenbreite zu Küvettendurchmesser und der Entfernung des Strahlzentrums von Diameter der Küvette. Die Grössenordnung dieser Fehler ist jedoch so klein, dass sie bei praktischen Arbeiten ohne Einfluss sind.

ABSORPTIOMETRIC DETERMINATION OF BISMUTH WITH THORIN

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The organic reagent 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid, also known as 1-(2-arsono-benzeneazo)-2-naphthol-3,6-disulfonic acid, Thoron and, more widely, as Thorin, has been used for the direct colorimetric determination of microgram quantities of thorium[1], plutonium[2], zirconium[3], uranium[4], beryllium[5] and neptunium[6]. An indirect method has been developed for fluoride[7].

RADY AND ERDEY[8] have used Thorin as an indicator in the EDTA titration of bismuth in nitric acid solution (pH 1–3). VANOSSI[9] has mentioned that in aqueous perchloric or nitric acid medium a few micrograms of bismuth give a sensitive color reaction with this reagent. However, an absorptiometric method for bismuth does not appear to have been reported in the literature. In the present work conditions for such a determination are discussed, including the effect of many foreign species.

EXPERIMENTAL

A Spectronic 20 spectrophotometer with cylindrical cells was used for absorptiometric determinations.

A stock solution 0.05% in bismuth was prepared from A.R. grade $Bi(NO_3)_3 \cdot 5H_2O$ in 0.1 *M* perchloric acid. Its bismuth content was gravimetrically determined[10] by weighing as oxide. Immediately before use this solution was diluted to 0.01 or 0.001% with water.

Thorin (Baker Analyzed Reagent) was used without further purification as a 0.1% aqueous solution.

A.R. quality reagents were used through the work. Less common element solutions were prepared from "Spec-pure" (Johnson Matthey & Co, London) metals, oxides or salts.

PROCEDURE

(*A*) For samples containing between 30–500 μg of bismuth. Transfer the nearly neutral or slightly acidic bismuth solution to a 25-ml volumetric flask. Add the necessary volume of perchloric acid to provide a final acidity of 0.02–0.04 *M* and 2 ml of 0.1% Thorin solution, make up to volume with distilled water and measure the absorbance at *ca.* 535 mμ against a reagent blank solution as reference. Prepare a standard curve from known amounts of bismuth following the same procedure. The sensitivity of this procedure is 0.022 μg Bi/cm^2 for log I_0/I equal to 0.001.

(*B*) For samples containing between 5–30 μg of bismuth. Proceed as in (*A*) but make the final solution up to a volume of 10 ml. The sensitivity is 0.011 μg Bi/cm^2 for log $I_0/I = 0.001$.

Effect of variables on color development

The immediately developed color intensity remains constant with time (the same absorbance values were obtained after more than 40 h of standing at room temperature under normal light conditions). Organic solvents such as carbon tetrachloride, chloroform, alcohols, acetates and ketones do not extract the coloured compound.

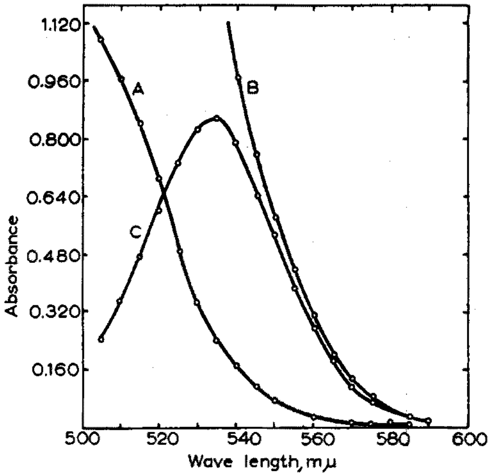

Fig. 1. Absorbance curves of: A, Thorin ($1.5 \cdot 10^{-4}$ *M*) with water as reference; B, Thorin ($1.5 \cdot 10^{-4}$*M*)-bismuth ($1.0 \cdot 10^{-4}$ *M*), with water as reference; C, Thorin ($1.5 \cdot 10^{-4}$ *M*)-bismuth ($1.0 \cdot 10^{-4}$ *M*), with reagent blank as reference. Acid concentration: 0.02 *M* in $HClO_4$.

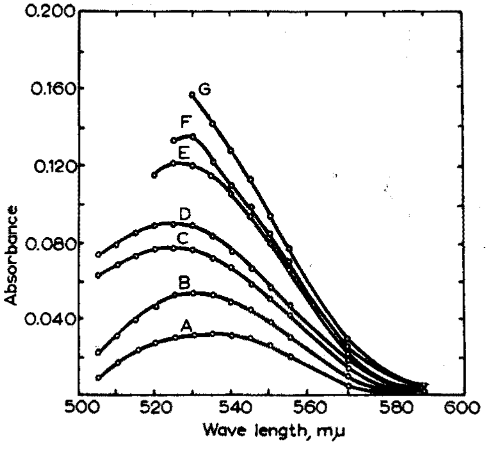

Fig. 2. Absorbance curves of Thorin-bismuth compound at varying Thorin concentrations. A, $3.75 \cdot 10^{-5}$ *M*; B, $7.5 \cdot 10^{-5}$ *M*; C, $1.13 \cdot 10^{-4}$ *M*; D, $1.5 \cdot 10^{-4}$ *M*; E, $2.3 \cdot 10^{-4}$ *M*; F, $3.75 \cdot 10^{-4}$ *M*; G, $4.5 \cdot 10^{-4}$ *M*. Bismuth concentration: $0.2 \cdot 10^{-4}$ *M*; perchloric acid concentration: $5.0 \cdot 10^{-3}$ *M*. Reagent blank as reference. (Curves E, F and G could not be extended toward lower wavelengths because of impossibility of setting reagent blank at 100% T.)

The absorption spectra of Thorin and the bismuth-Thorin compound are shown in Fig. 1. When the reagent blank is used as reference solution the bismuth-Thorin compound shows an absorption maximum at about 535 mμ. If water is used as reference, the absorption maximum appears at about 505 mμ. Since hydrochloric or sulfuric acid cannot be used for acidification, perchloric acid was chosen to provide the necessary acidity. Nitric acid free from nitrogen oxides may be used instead.

The effect of Thorin concentration on the absorption spectra and on the absorbance of the bismuth-Thorin compound at 530, 535 and 540 mμ is shown in Figs. 2 and 3

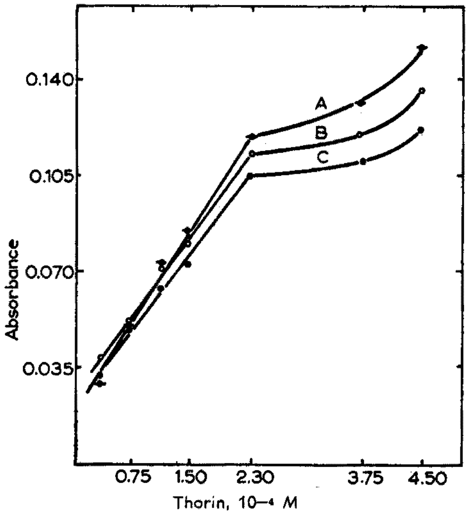

Fig. 3. Effect of Thorin concentration ($5.0 \cdot 10^{-3}$ M perchloric acid, $0.2 \cdot 10^{-4}$ M Bi). A, 540 mμ; B, 535 mμ; C, 530 mμ. Reagent blanks as references.

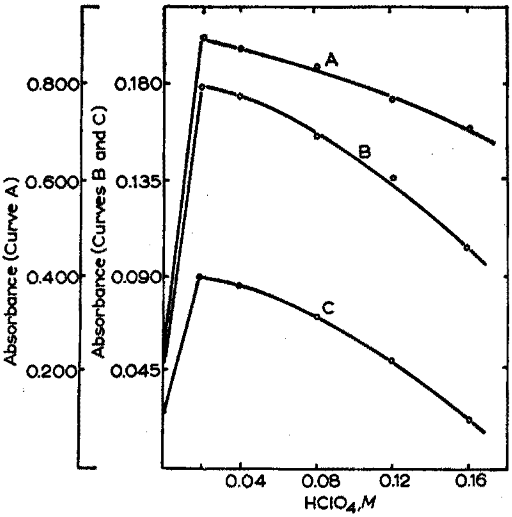

Fig. 4. Effect of perchloric acid concentration ($1.5 \cdot 10^{-4}$ M Thorin). A, $1.0 \cdot 10^{-4}$ M Bi; B, $0.2 \cdot 10^{-4}$ M Bi; C, $0.1 \cdot 10^{-4}$ M Bi). Absorbance measured at 535 mμ. Reagent blank as reference.

respectively. Absorbances were measured against the respective reagent blanks. Taking into account the reproducibility, sensitivity and the limitations of the instrument used, a concentration near $1.5 \cdot 10^{-4}$ *M* in Thorin seems to be the most suitable.

In Fig. 4 the effect of perchloric acid concentration on the bismuth-Thorin absorbance at 535 mµ is shown. A perchloric acid concentration of 0.02–0.04 *M* appears the most suitable for photometric purposes. Increasing amounts of acid decrease the absorbance of the colored compound.

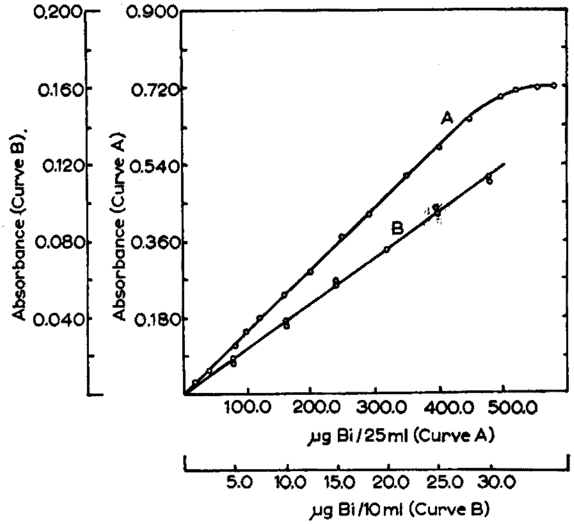

Fig. 5. Typical standard curve for determination of bismuth with Thorin ($1.5 \cdot 10^{-4}$ *M*) in 0.02 *M* perchloric acid, 535 mµ.

As shown in Fig. 5, curve A, the absorbance is proportional to the bismuth concentration at 535 mµ from approximately 20 µg/25 ml to 400 µg Bi/25 ml (1 to 16 p.p.m.). A RINGBOM plot[11] of the data in Fig. 5, curve A, shows that the concentration range for the highest accuracy lies between 4.0 and 16.0 p.p.m. The error of the average is not likely to exceed a few per cent. The average of 10 determinations in pure solution gave errors of ± 10% for 5 µg Bi/10 ml; ± 5% for 15 µg/10 ml; ± 1% for 20 µg/25 ml; ± 0.3% for 100 µg/25 ml and ± 0.05% for 500 µg in 25 ml.

The slope of the calibration curve (Fig. 5, curve A) changes at *ca.* 20 p.p.m. (500 µg/25 ml), yielding a clear break when the molar ratio Bi:Thorin is 2:3.

Behavior of other elements

Table I summarizes the interference data. The concentration of bismuth used was 0.0, 20.0 and 100.0 µg/25 ml (0.0, 0.8 and 4 p.p.m.) ($1.5 \cdot 10^{-4}$ *M* Thorin and 0.02 *M* perchloric acid).

The alkali metals, manganese(II), rhenium(VII), nickel, zinc, cadmium, thallium(I) and germanium do not interfere in amounts as large as 10 mg/25 ml, even if the sample is previously fumed to dryness with perchloric acid. The alkaline earth elements do not interfere up to 1 mg/25 ml. Magnesium can be tolerated to a level of 5 mg/25 ml.

The common tri- and quadri-valent elements give serious interference and a few tenths, hundredths or, in some cases, thousandths of a milligram only may be present.

Some bivalent or monovalent elements (*e.g.*, cobalt, copper, mercury, lead and silver) interfere above the mg-level. Palladium(II) may be present only in µg-quantities.

Anions have a general bleaching effect on the color of the bismuth-Thorin compound. Osmium and rhodium if present as chloride complexes, germanium (as

TABLE I

DETERMINATION OF BISMUTH WITH THORIN IN 0.02 *M* $HClO_4$ MEDIUM. EFFECT OF DIVERSE FOREIGN SUBSTANCES

Foreign element	*Amount added (mg)*	*Bi taken, µg*			*Bi found, µg*		
		I	*II*	*III*	*I*	*II*	*III*
Be	1	0.0	20.0	100.0	2.2	21.0	102.0
Ca	2	0.0	20.0	100.0	0.0	20.0	100.0
	10	0.0	—	100.0	9.0	—	111.1
Sr	10	0.0	—	100.0	9.2	—	113.5
	2	0.0	20.0	100.0	0.0	20.0	100.1
Ba	2	0.0	20.0	100.0	5.0	24.5	106.1
Sc	0.5	0.0	—	100.0	98.6	—	100.0
	0.005	0.0	20.0	100.0	4.2	22.0	102.0
Y	0.01	0.0	20.0	100.0	4.0	23.4	103.0
Ti[a]	0.07	0.0	—	100.0	20.7	—	68.5
	0.004	0.0	20.0	100.0	0.1	20.2	100.0
Zr (as $ZrOCl_2$)	0.1	0.0	—	100.0	20.0	—	115.5
	0.01	0.0	20.0	100.0	2.0	21.5	101.4
Hf	0.11	0.0	—	100.0	14.3	—	92.5
	0.06	0.0	20.0	100.0	0.0	21.0	100.0
V (as $NaVO_3$)	1	0.0	20.0	100.0	0.0	0.0	52.0
	0.4	—	20.0	100.0	—	19.2	100.0
V (as Na_3VO_4)	1	0.0	—	100.0	0.0	—	44.7
	0.3	—	20.0	100.0	—	18.5	98.0
Nb[a] [1]	0.07	0.0	—	100.0	14.0	—	110.0
[a]	0.02	0.0	20.0	100.0	3.5	21.8	100.6
Ta[a] [1]	0.07	0.0	—	100.0	14.0	—	116.0
[a]	0.02	0.0	20.0	100.0	4.2	22.6	109.0
Cr (as $K_2Cr_2O_7$)	0.3	0.0	—	100.0	0.0[b]	—	99.2[c]
	0.02	0.0	20.0	100.0	0.0	20.0[d]	100.0[d]
Cr(III)	1.3	0.0	—	100.0	39.0[e]	—	139.0[e]
	0.13	0.0	20.0	100.0	5.0[d]	24.0[d]	105.0[d]
Mo (as $(NH_4)_2MoO_4$)	1	0.0	—	100.0	0.0	—	82.0
	0.2	0.0	20.0	100.0	0.0	19.0	99.5
W (as $NaWO_4$)	1	0.0	—	100.0	0.0	—	0.0
	0.001	—	20.0	100.0	—	19.5	99.8
Fe(III)	0.5	0.0	—	100.0	300.0	—	380.0
	0.005	0.0	20.0	100.0	2.0	21.0	100.8
Ru (as $RuCl_4$)	0.1	0.0	—	100.0	64.5	—	152.0
	0.01	0.0	20.0	100.0	0.3	20.2	100.4

TABLE I (continued)

Foreign element	*Amount added (mg)*	*Bi taken, μg*			*Bi found, μg*		
		I	*II*	*III*	*I*	*II*	*III*
Rh (as $RhCl_3$)	9	0.0	20.0	100.0	14.0	35.9	107.0
	1.5	0.0	20.0	100.0	1.0	21.0	100.0
Ir (as $(NH_4)_2IrCl_6$)	0.5	0.0	—	100.0	24.4	—	131.0
	0.05	0.0	20.0	100.0	2.0	22.0	101.0
Pd(II)	0.005	0.0	20.0	100.0	4.3	24.0	103.0
Pt(IV)	1	0.0	20.0	100.0	0.0	19.8	100.0
Cu(II)	1	0.0	—	100.0	7.0	—	105.0
	0.5	0.0	20.0	100.0	1.0	21.0	101.0
Al	1	0.0	—	100.0	7.5	—	107.5
	0.5	0.0	20.0	100.0	2.0	21.0	102.0
Ga	1	0.0	—	100.0	128.0	—	229.0
	0.005	0.0	20.0	100.0	2.0	21.0	100.0
In	1	0.0	—	100.0	60.0	—	158.0
	0.005	0.0	20.0	100.0	2.2	23.0	102.0
Sn(IV)f)	0.1	0.0	—	100.0	7.2	—	94.0
	0.03	0.0	20.0	100.0	1.0	19.0	99.0
Pb(II)	5	0.0	—	100.0	24.0	—	124.0
	1	0.0	20.0	100.0	2.0	21.0	101.0
As (as Na_3AsO_4)	5	0.0	—	100.0	0.0	—	20.0
	0.3	—	20.0	100.0	—	20.0	100.0
Sb(V)g)	0.1	0.0	—	100.0	0.0	—	23.0
	0.005	—	20.0	100.0	—	18.0	99.0
Se (as Na_2SeO_3)	10	0.0	—	100.0	0.0	—	10.7
	1	—	20.0	100.0	—	20.0	99.0
Se (as Na_2SeO_4)	10	0.0	20.0	100.0	0.0	20.0	100.0
Te (as K_2TeO_3)	3	0.0	20.0	100.0	0.0	19.0	99.2
Te (as Na_2TeO_4)	2	0.0	20.0	100.0	0.0	20.0	100.0
Ce(IV)	1	0.0	20.0	100.0	h)	h)	h)
Ce(III)	1	0.0	—	100.0	60.0i)	—	190.0i)
	0.001	0.0	20.0	100.0	2.0	22.0	101.0
La	0.01	0.0	20.0	100.0	2.3	21.0	102.0
Pr, 0.2; Nd, 0.2		0.0	20.0	100.0	20.0	34.0	116.0
Pr, 0.02, Nd, 0.02		0.0	20.0	100.0	0.1	20.1	100.0
Sm	0.2	0.0	—	100.0	9.2	—	111.0
	0.02	0.0	20.0	100.0	0.0	21.0	100.0
Eu, 0.2; Gd, 0.2; Tb, 0.2		0.0	20.0	100.0	9.0	27.5	109.0
Eu, 0.04; Gd, 0.04; Tb, 0.04		0.0	20.0	100.0	0.5	21.0	101.0
Dy	0.20	0.0	20.0	100.0	4.0	24.5	103.9
	0.04	0.0	20.0	100.0	0.0	20.5	100.0
Er	0.15	0.0	20.0	100.0	2.3	24.0	103.0
	0.08	0.0	20.0	100.0	0.5	21.0	100.0
Ho	0.8	0.0	20.0	100.0	6.0	25.7	106.0
	0.25	0.0	20.0	100.0	0.0	20.0	100.0
Tm, 0.2; Yb, 0.2		0.0	20.0	100.0	2.0	22.1	101.6
Lu	0.2	0.0	20.0	100.0	4.6	25.0	107.0
Th	0.1	0.0	—	100.0	173.0	—	273.0
	0.001	0.0	20.0	100.0	2.0	23.0	101.0
U (as UO_2^{++})	0.05	0.0	—	100.0	33.9	—	134.0

TABLE I (continued)

Foreign element	*Amount added (mg)*	*Bi taken, µg*			*Bi found, µg*		
		I	*II*	*III*	*I*	*II*	*III*
U (as UO_2^{++})	0.005	0.0	20.0	100.0	2.0	22.0	101.5
SiO_3^{2-}	10	0.0	20.0	100.0	0.0	19.4	100.0
g)	2	—	20.0	100.0	—	13.0	92.5
PO_4^{3-} j)	10	0.0	20.0	100.0	0.0	20.0	100.0
k)	10	—	—	100.0	—	—	20.0
	0.5	—	20.0	100.0	—	19.0	99.0
SO_4^{2-}	100	0.0	20.0	100.0	0.0	12.0	84.0
	10	—	20.0	100.0	—	20.0	100.0
F^-	10	0.0	—	100.0	0.0	—	0.0
	0.2	—	20.0	100.0	—	18.0	98.0
g)	10	—	20.0	100.0	—	20.0	102.0
Cl^-	100	0.0	20.0	100.0	0.0	13.0	90.0
	10	—	20.0	100.0	—	19.0	100.0
Br^-, 10 mg; I^-, 10 mg		0.0	20.0	100.0	0.0	0.0	2.0
Br^-, 1 mg; I^-, 1 mg		—	20.0	100.0	—	20.0	99.8
Br^-, 10 mg; I^-, 10 mg g)		—	20.0	100.0	—	19.5	100.0

The following foreign species do not interfere in amounts indicated: Li, Na, K, Rb, Cs, NH_4^+, Mn(II), Ni(II), Zn, Cd, Tl(I), Ge (as Na_2GeO_3), Re (as ReO_4^-), CO_3^-, BO_3^{3-}, 10 mg; Mg, 5 mg; Hg(II), 3 mg; Os (as $OsCl_6^{2-}$), 3 mg; Ag, 2 mg; Au, 1 mg; Co, 1 mg, and NO_3^-, 100 mg.

a) Oxalate–oxalic acid solution. Oxalate, which complexes bismuth, was destroyed by fuming with nitric-perchloric acid.

b) When Cr was 1 mg the absorbance of the reference solution decreased considerably.

c) Absorbance decreased with time.

d) Absorbance remained constant for 1 h.

e) Absorbance increased with time.

f) Tin chloride in hydrochloric acid solution fumed with perchloric acid.

g) Fumed with perchloric acid.

h) Cerium(IV) oxidizes Thorin, decolorizing the reagent blank.

i) A slight turbidity appeared after short periods of standing.

j) Immediately mixed solutions.

k) Absorbance measured after 24 h of standing.

GeO_3^-) and selenium (as SeO_4^{2-}) are exceptions. Nitrate and borate do not interfere.

On fuming with perchloric or perchloric-nitric acid to near dryness, the bleaching effect of anions on the color of the bismuth-Thorin compound may be compensated or even positive errors may appear. This may be due to de-complexing of the metal element which develops absorbing species with Thorin. If the fuming is not prolonged to near dryness and the acidic residue is neutralized with sodium hydroxide and the acidity adjusted before developing the color, interfering anions can be tolerated in higher amounts. The absorbance of the bismuth-Thorin compound is not affected by the neutralization and re-acidification process.

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SUMMARY

A simple, precise absorptiometric method for bismuth based upon its reaction with Thorin is described. The effect of foreign elements was established.

RÉSUMÉ

Une méthode absorptiométrique, simple et précise, est décrite pour le dosage du bismuth au moyen de thorin. L'influence d'ions étrangers a été examinée.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Wismut mit Hilfe von Thorin. Der störende Einfluss von Fremd-Ionen wird angegeben.

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN NIOBIUM WITH DITHIOL*

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INTRODUCTION

In recent years, niobium has demanded increasing attention because of its desirable physical properties at elevated temperatures. Its rapid rise to commercial significance has presented analytical chemists with the need to devise a variety of methods for the determination of various impurities in niobium in the shortest possible time. In cooperation with the American Society for Testing Materials, this laboratory undertook the development and evaluation of a spectrophotometric method for the determination of 50–1000 p.p.m. of molybdenum and tungsten in niobium. This report presents the results of that investigation.

SANDELL[1] provides a detailed review of the methods which have been applied to the determination of molybdenum and tungsten in various materials. Of the reagents which have been proposed for the production of colored complexes with molybdenum and tungsten, toluene-3,4-dithiol, commonly referred to as "dithiol", seems attractive in that it forms intensely colored extractable complexes with both elements of interest and is subject to relatively few interferences. Various workers have recommended the use of thiocyanate as a reagent for molybdenum or for tungsten[1-4]. Thiocyanate methods in general, however, suffer from a lack of selectivity, from poor stability, and from unpredictable interelement effects. Thus, it is commonly recognized that iron(II), though not extracted alone as a thiocyanate complex, causes an increase in the intensity of the molybdenum thiocyanate complex[3]. Similarly, it has been demonstrated in this laboratory that niobium increases the sensitivity of the tungsten thiocyanate complex even though appropriately masked. Also, it has been observed in this laboratory that even though extracted molybdenum and niobium thiocyanate complexes exhibit different absorption spectra, a simple solution of simultaneous equations does not yield correct results for mixtures of these two elements. For these reasons, thiocyanate was not considered to be a promising reagent for the determination of molybdenum or tungsten in niobium. Among the other reagents which have been proposed are: phenylfluorone[5], 8-hydroxyquinoline[6,7], hydroquinone[8], catechol[9], 9-methyl-2,3,7-trihydroxy-6-fluorone[10], thioglycolic acid[11] and chloranilic acid[12]. None of these reagents were seriously considered in this work because of lack of

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selectivity, sensitivity, stability or availability, as the case may be, when compared to dithiol.

The colored complexes of molybdenum and tungsten with dithiol were first reported 20 years ago by HAMENCE[13]. Following the studies of MILLER[14], a number of workers have developed photometric methods for molybdenum and tungsten in various materials. BAGSHAWE AND TRUMAN[15] showed that by proper control of conditions, the molybdenum complex could be formed and extracted prior to the tungsten complex. Unfortunately, these authors also recommended the use of dithiol dissolved in an organic solvent as the reagent, a practice which has been followed by several subsequent workers[16-18]. The undesirable nature of this practice has been demonstrated in the course of this study and will be commented on further. An alternative and much more satisfactory reagent consisting of an aqueous alkaline solution of dithiol, stabilized with thioglycolic acid, was proposed by PIPER AND BECKWITH[19]. This reagent, or minor variations of it, has been utilized in various procedures[20-24]. ALLEN AND HAMILTON[21] noted that iron increased the absorbance of dithiol solutions containing molybdenum and tungsten. It remained for GILBERT AND SANDELL[25] in their study of the molybdenum-dithiol complex to show that the effect of iron was to hasten the completion of the reaction of molybdenum and dithiol. In view of the variety of conditions used by the authors noted above, it was felt that an investigation of the use of dithiol as a spectrophotometric reagent for the determination of molybdenum and tungsten in niobium was warranted.

EXPERIMENTAL

Apparatus

A Beckman Model DU Spectrophotometer was used throughout this study.

Reagents

Molybdenum standard solution. 10 μg Mo/ml. Dissolve 1.00 g of molybdenum metal in 10 ml of sulfuric acid and a few drops of nitric acid. Fume to dispel oxides of nitrogen. Dilute to 1 l in a volumetric flask with water. Transfer a 10.0-ml aliquot of this solution to a second liter volumetric flask containing 500 ml of water and 10 ml of sulfuric acid. Dilute to volume with water.

Tungsten standard solution. 10 μg W/ml. Dissolve 0.1794 g of assayed sodium tungstate dihydrate in water and dilute to 1 l in a volumetric flask. Transfer a 50.0-ml aliquot to a 500-ml volumetric flask and dilute to volume with water.

Hydroxylamine hydrochloride. 10%. Dissolve 1.0 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 10 ml of water.

Titanous sulfate solution. 4 mg Ti/ml. Transfer 1.0 g of titanium sponge into a 250-ml "Pyrex" volumetric flask. Add 175 ml of water and 25 ml of sulfuric acid. Heat in a boiling water bath until the metal is dissolved. Cool and dilute to volume with water. Prepare fresh daily.

Dithiol reagent. 0.5%. Dissolve 20 g of sodium hydroxide in about 500 ml of water in a 1-l beaker. Cool to room temperature. Break a 5-g vial of toluene-3,4-dithiol (Eastman #4508) under the surface of the solution. Stir until dissolution is complete, warming to 35° if necessary. Add 10.0 ml of thioglycolic acid. Dilute to about 1 l with water and mix well. Store in 4 oz. polyethylene bottles in a refrigerator.

Recommended procedure

Weigh a 0.5-g sample of niobium turnings into a 125-ml Erlenmeyer flask. Add 10 ml of sulfuric acid and 3.0 g of ammonium bisulfate. Heat strongly to dissolve the sample. Cool and transfer to a 50-ml volumetric flask using 1:2 sulfuric acid to effect the transfer. Dilute to volume with 1:2 sulfuric acid. Transfer a 15.0-ml aliquot of the solution to a 125-ml Erlenmeyer flask. Evaporate to fumes of sulfur trioxide. Cool. Add 15 ml of 1:2 hydrochloric acid, 10 drops of hydrofluoric acid and 12 drops of hydroxylamine hydrochloride solution. Cool to room temperature. Transfer the solution to a 125-ml separatory funnel using a minimum quantity of water to effect the transfer. Add 10 ml of dithiol reagent and shake thoroughly. Shake occasionally for 15 min. Add 20 ml of carbon tetrachloride and shake for 2 min. Drain the organic layer into a dry 50-ml volumetric flask. Wash the aqueous phase twice with 10-ml portions of carbon tetrachloride, shaking for 1 min and adding the washings to the volumetric flask. Reserve the aqueous layer for tungsten determination. Dilute the combined extracts to volume with carbon tetrachloride. Transfer a suitable portion to a 1.00-cm absorption cell and determine its absorbance at 680 mμ using carbon tetrachloride in the reference cell.

Evaporate the aqueous layer, reserved above, to fumes of sulfur trioxide. Add 10 drops of nitric acid and fume again. Cool. Add 25 ml of titanous sulfate solution, 20 ml of hydrochloric acid, and 10 drops of hydrofluoric acid. Place in a hot water bath (80–90°) for 5 min. Add 10.0 ml of dithiol reagent and 10 drops of hydrofluoric acid. Continue heating for 15 min, swirling the flask occasionally. Add 10 drops of hydrofluoric acid and remove from the water bath. Cool and transfer the solution to a 125-ml separatory funnel using two 2–3-ml portions of carbon tetrachloride to complete the transfer. Add 7 ml of carbon tetrachloride and shake for 2 min. Transfer the organic layer to a dry 25-ml volumetric flask. Repeat the extraction twice using 5-ml portions of carbon tetrachloride and shaking for 1 min. Combine the extracts in the volumetric flask and dilute to volume with carbon tetrachloride. Transfer a suitable portion of the solution to a 1.00-cm absorption cell and determine its absorbance at 640 mμ using carbon tetrachloride in the reference cell. Determine reagent blanks by performing the entire procedure, omitting only the sample. Calibrate the method by carrying aliquots of the standard molybdenum and tungsten solutions through the appropriate sections of the procedure.

Choice of dithiol reagent

Dithiol has been used as a chromophoric reagent for molybdenum and tungsten in 2 forms — dissolved in an organic solvent[15–18] or dissolved in an aqueous alkaline solution and stabilized with thioglycolic acid[19–24]. Those procedures involving the use of an organic solution of dithiol include precautions for avoiding decomposition of the reagent and generally specify that it be prepared immediately before use. Such precautions are conspicuous by their absence from the procedures utilizing the alkaline aqueous reagent. It has been shown by GILBERT AND SANDELL[25], among others, that the reactions of dithiol with metal ions are relatively slow. The aqueous alkaline reagent has a distinct advantage in this regard in that the effective concentration of dithiol in the aqueous phase is much greater than it is when an organic solution of dithiol is used. For these reasons, the recommended procedure specifies the use of an aqueous alkaline solution of dithiol. The absorbances of the molybdenum- and tungsten-dithiol complexes were unaffected by varying the amount of dithiol reagent from 1 to 20 ml. However, it was noted that the reactions were visibly slower in experiments using the smaller amounts of reagent. Therefore, 10 ml is specified in the procedure to assure a sufficiently rapid reaction.

Acid concentrations

Solution conditions for the formation of the molybdenum and tungsten complexes of dithiol are similar to those of GREENBERG[16]. Both the complexes are formed in strongly acidic media, between 9.0 and 10.0 *N* in total acidity. Of this acid, 1.8 *N* is hydrochloric acid during the molybdenum reaction and 3.8 *N* is hydrochloric acid during the tungsten reaction. Variation of the total acidity from about 8 *N* to 11 *N* had no effect on the observed absorbances. The hydrochloric acid concentration was varied from 0.8 to 2.0 *N* in the case of molybdenum and from 3.3 to 4.5 *N* in the case of tungsten with no effect.

TABLE I

EFFECT OF HYDROCHLORIC ACID ON TUNGSTEN-DITHIOL REACTION

Acid concentrations	*Absorbance due to 50 μg W after:*		
	5 min	*10 min*	*20 min*
9 *N* H_2SO_4	0.161	0.234	0.274
5.4 *N* H_2SO_4 + 3.8 *N* HCl	0.278	0.279	0.279

Initially, a solution of titanous chloride in 8.0 *N* hydrochloric acid was used for the reduction of tungsten. When titanous sulfate was substituted for the chloride, to provide better control of acidity, sufficient sulfuric acid was added to maintain the total acidity in the range of 9.0–10.0 *N*. However, no hydrochloric acid was present. Low and variable absorbances for the tungsten complex were observed. The data shown in Table I reveal that hydrochloric acid speeds completion of the tungsten-dithiol reaction. In the recommended procedure, hydrochloric acid is added to the solution containing tungsten for this reason.

Time required for complex formation

Both the molybdenum- and tungsten-dithiol complexes are formed quantitatively within 5 min under the conditions specified in the recommended procedure, no further increase in absorbance being noted up to at least 40 min of reaction time. The procedure recommends a 15-min reaction time simply to allow a margin of safety.

Choice of extracting solvent

Carbon tetrachloride was chosen as the extracting solvent because of the convenience of a solvent heavier than water and because of its freedom from oxidizing impurities often encountered in oxygen-containing solvents. LAFFERTY AND BOLTON[20] state that carbon tetrachloride is as effective as other solvents and that the absorptivity of the molybdenum-dithiol complex is about 30% higher in this medium than in amyl acetate.

Dissolution of niobium

Niobium samples are readily dissolved by use of the sulfuric acid–ammonium bisulfate technique recommended by VAN SANTEN[18].

RESULTS AND DISCUSSION

After a procedure was established for the determination of molybdenum and tungsten in niobium, it was necessary to evaluate the critical factors of the method as well as the procedure as a whole. The following sections present the results of these evaluations.

Stability of reagent

Aqueous alkaline reagent solutions were prepared from various lots of dithiol and stored for times up to 3 months with no significant effect on observed absorptivities of the molybdenum and tungsten complexes. In the belief that zinc dithiol might provide a more stable source of dithiol for the reagent, its use was attempted. However, it could not be weighed accurately because of its rapid loss in weight when exposed to the room atmosphere. The solution of dithiol obtained from zinc dithiol exhibited an oily layer of decomposition products which had to be removed by filtration. In spite of the difficulties encountered in preparing a reagent solution from zinc dithiol, the observed absorptivities were quite comparable to those obtained when the normal reagent was used. Data demonstrating the lack of influence of reagent storage and condition are presented in Table II.

TABLE II

REPRODUCIBILITY OF ABSORPTIVITIES WITH VARIOUS CONDITIONS OF REAGENT

Source of dithiol	*Days stored*	*Molar absorptivities*	
		Mo	*W*
Fresh dithiol	0	—	24,900
	3 (refrigerated)	24,300	24,800
	3 (room temp.)		24,800
Zinc dithiol	0	24,100	24,800
Partially decomposed dithiol	0	24,400	
Fresh dithiol	6	24,000	24,900
	25	24,200	(tungsten data invalid due to HCl omission during this period)
	41	24,200	
	52	24,000	
	85	24,300	
Fresh dithiol	5	24,700	24,900
	10	24,500	24,800
	91	23,900	25,000
	Average	24,240	24,860
	Standard deviation	238	74

TABLE III

EFFECT OF HYDROXYLAMINE AND THIOGLYCOLIC ACID ON ABSORBANCE DUE TO 50 μg OF MOLYBDENUM AS THE DITHIOL COMPLEX

Solution	*Absorbance (not corrected for blank)*
No thioglycolic acid or hydroxylamine	0.266
Hydroxylamine added	0.260
Hydroxylamine and thioglycolic acid added	0.257

Oxidation states of the complexed metals

GILBERT AND SANDELL[25] provide conclusive evidence that molybdenum is in the hexavalent state in its blue-green dithiol complex utilized in this and in other spectrophotometric procedures. Additional verification of this fact is provided by the data of Table III which illustrate that hydroxylamine and thioglycolic acid, added to reduce interferences and to stabilize the reagent, do not contribute to the intensity of the molybdenum-dithiol color but, if anything, reduce it slightly.

Tungsten, on the other hand, must be reduced to form its blue dithiol complex. Thus, omission of the titanium(III) reducing agent led to a colorless extract. Reprocessing of the resulting aqueous phase with titanium(III) solution and additional dithiol led to the usual blue extract with its normal absorbance. A study of the tungsten-dithiol complex, similar to GILBERT AND SANDELL's study[25] of the molybdenum-dithiol complex would be most desirable.

Separation of molybdenum and tungsten

Molybdenum(VI) reacts with dithiol in cold solutions under the conditions specified in this procedure. It was found that the reaction proceeds at a finite rate but that it is essentially complete within 5 min. Tungsten, on the other hand, must be reduced to react with dithiol and, even then, requires heating so that the reaction will proceed at a practical rate. Thus, by treating a cold acid solution of molybdenum and tungsten with dithiol, the molybdenum complex is formed quantitatively and extracted leaving the tungsten in the aqueous phase for subsequent determination. The efficacy of this separation is demonstrated by the results in Table IV.

TABLE IV

DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN THE PRESENCE OF EACH OTHER

Experiment	*μg Mo added*	*μg Mo found*	*μg W added*	*μg W found*
1	50.0	50.0	50.0	49.8
2	100.0	99.8	20.0	20.3
3	20.0	20.1	100.0	99.4
4	100.0	99.0	50.0	49.8
5	50.0	49.6	100.0	99.4

Interferences

One mg quantities of iron, nickel, chromium, vanadium, aluminum and cobalt do not interfere with the determination of 50 μg of molybdenum and of tungsten. Large

TABLE V

RECOVERIES OF MOLYBDENUM AND TUNGSTEN ADDITIONS TO NIOBIUM

Amount of Nb g	*Mo*			*W*		
	µg added	*µg present*	*µg found*	*µg added*	*µg present*	*µg found*
0.1023	—	—	3.6	—	—	29.0
0.1022	50	53.6	53.7	—	29.0	29.6
0.1028	—	3.6	4.0	50	79.1	80.9
0.1030	20	23.7	24.2	100	129.2	127.4

TABLE VI

RESULTS OF INTERLABORATORY EVALUATION, (p.p.m.)

Lab	*Mo in UCM-1344*	*W in UCM-1344*	*Mo in Cb-6*	*W in Cb-6*
Lab A				
Average of 8	541.6	104.0	106.7	546.7
Relative standard deviation	0.26%	1.45%	1.85%	1.63%
Lab B				
Average of 8	549.0	103.1	108.0	531.6
Relative standard deviation	0.38%	1.64%	2.57%	1.02%
Lab C				
Average of 8	536.1	82.4	115.5	482.9
Relative standard deviation	2.01%	10.8%	8.15%	4.92%
Lab D				
Average of 8	558.6	111.9	103.6	533.1
Relative standard deviation	0.67%	1.47%	2.18%	1.06%
Lab E				
Average of 8	536.4	102.4	99.0	522.0
Relative standard deviation	1.79%	1.56%	1.52%	2.33%
Over-all average of 32 (Lab C omitted)	546.4	105.3	104.3	533.4
Within-lab relative standard deviation (Lab C omitted)	0.97%	1.59%	2.05%	1.63%
Between-labs relative standard deviation (Lab C omitted)	1.74%	4.35%	3.68%	1.74%

amounts of copper, however, interfere by consuming the reagent to form an insoluble precipitate. The copper interference was not investigated further in that its presence in niobium is unlikely.

Determination of molybdenum and tungsten in niobium

Since no standard materials were available, the procedure was evaluated by addition of known quantities of molybdenum and tungsten standard solutions to samples of niobium. Excellent recoveries were achieved as indicated by the results in Table V. Finally 2 samples of niobium, one containing about 500 p.p.m. of tungsten and 100 p.p.m. of molybdenum and the other containing about 100 p.p.m. of tungsten and 500 p.p.m. of molybdenum, were analyzed by 5 laboratories of the Molybdenum and Tungsten Subgroup of the Columbium Task Force of the ASTM. The results of these determinations are summarized in Table VI and indicate within-laboratory relative standard deviations of about 1.5% and between-laboratory relative standard deviations of about 2.9%.

CONCLUSIONS

The use of an aqueous alkaline solution of dithiol, stabilized with thioglycolic acid, is recommended for the determination of molybdenum and tungsten in niobium. This reagent is stable and practically unaffected by the condition of the dithiol from which it is prepared. The large effective concentration of dithiol in the aqueous solution of the metal ions brings the reaction to completion in much shorter times than are required when the unstable organic solutions of dithiol recommended by many workers are used. Results obtained by the procedure described in this report demonstrate a relative standard deviation, within laboratories, of about 1.5%. Between laboratories relative standard deviations of about 2.9% were obtained. Although this procedure is specifically designed for the determination of molybdenum and tungsten in niobium, it should be applicable, with minor modification, to various other materials.

ACKNOWLEDGEMENTS

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SUMMARY

A new procedure for the determination of molybdenum and tungsten in niobium has been developed. The method involves the formation of the intensely colored complex of molybdenum with toluene-3,4-dithiol in an aqueous medium and its extraction into carbon tetrachloride followed by the reduction of tungsten and the formation and extraction of its complex. The recommended reagent is stable for at least 90 days. Both the molybdenum and the tungsten dithiol complexes are formed quantitatively within 5 min. Interlaboratory evaluation of the method reveals within-laboratory and between-laboratory relative standard deviations of about 1.5% and 2.9% respectively.

RÉSUMÉ

Une nouvelle méthode a été mise au point pour le dosage du molybdène et du tungstène dans le niobium: Par formation du complexe très coloré du molybdène avec le toluène-3,4-dithiol et son extraction dans le tétrachlorure de carbone, puis réduction du tungstène, formation et extraction de son complexe.

ZUSAMMENFASSUNG

Beschreibung einer neuen spektrophotometrischen Methode zur Bestimmung von Molybdän und Wolfram in Niob. Sie beruht auf der Bildung eines stark gefärbten Komplexes des Molybdäns mit Toluol-3,4-dithiol und Extraktion mit Tetrachlorkohlenstoff. In der wässrigen Phase wird das Wolfram reduziert, in den Komplex übergeführt und ebenfalls mit Tetrachlorkohlenstoff extrahiert.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH 2-THENOYLTRIFLUOROACETONE

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2-Thenoyltrifluoroacetone, a well-known chelating agent, has been used in this laboratory for the extraction and colorimetric determination of metals, *e.g.* uranium (VI), cerium(IV), copper(II), iron(III) and chromium(III)[1,2]. It was also found that cobalt forms a chelate with this reagent which can be applied gravimetrically[3]. The extraction of cobalt(II) has now been studied.

Early work on the extraction of cobalt followed by spectrophotometric determination has been discussed by SANDELL[4]. Other methods involve extraction of the cobalt-1-(2-pyridylazo)-2-naphthol chelate in carbon tetrachloride or other organic solvents[5], or extraction with tributylphosphate in presence of hydrochloric acid[6]. Cobalt(II) can be separated from nickel using tributyl phosphate[7].

The present work has shown that the cobalt(II) complex with TTA can be extracted with a mixture of acetone and benzene and the resulting bright yellow extract can be measured spectrophotometrically. This provides the basis of a new method for the rapid extraction and simultaneous spectrophotometric determination of cobalt(II) at mg levels.

APPARATUS AND REAGENTS

A Unicam SP-600 spectrophotometer with 1-cm glass cells was used for the absorbance measurements. All the pH measurements were carried out with a Cambridge pH meter. The chemicals used were either chemically pure or reagent grade materials unless otherwise mentioned.

TTA (Columbia Organic Chemicals, S. Carolina, U.S.A.) solutions in acetone (about 0.15 M) were used.

A stock solution of cobalt(II) was prepared by dissolving about 11.1 g of cobaltous sulphate (E. Merck) in 500 ml of water. The solution was standardised gravimetrically with α-nitroso-β-naphthol[8] and as cobalt sulphate (anhydrous)[8]. Test solutions (0.6126 mg of cobalt per ml) were prepared by ten-fold dilution of the stock solution.

Buffer solutions of different pH were prepared by standard procedures: hydrochloric acid–potassium chloride (pH 1.7–2.8), acetic acid–ammonium acetate (pH 4–6) and ammonia–ammonium chloride (pH 8.0).

GENERAL PROCEDURE

An aliquot (2 ml) of the cobalt sulphate test solution was treated with 10 ml of buffer solution of pH 6.1 in a 250-ml separating funnel. For pH studies this buffer solution was omitted and buffers of different pH were added. For studies of the effect of diverse ions, 1 ml of cobalt sulphate test solution was used and the solution containing the ion was added before the addition of buffer solution of pH 6. The aqueous solution was then shaken for 5 min with 10 ml of 0.15 *M* TTA solution in acetone. Then 5 ml of acetone and 5 ml of benzene were added and shaken for a few min. The layers were allowed to settle for about 3 min. The aqueous layer was drained into a beaker and the coloured organic layer into a 25-ml volumetric flask. The bright yellow extract was diluted to 25 ml with acetone and the absorbance was measured at 430 mμ against a reagent blank. The aqueous layers were stored for pH measurements where necessary.

RESULTS AND DISCUSSION

Absorption curve

The absorption spectrum of a solution of a cobalt(II)-TTA complex (cobalt = $8.3 \cdot 10^{-4}$ *M*) extracted as above at pH 6.0 and measured against the solvent is shown in Fig. 1. The bright yellow cobalt(II)-TTA solution absorbs strongly at 410 mμ but the reagent also shows considerable absorption at this wavelength. The absorbance of the complex steadily decreases and becomes negligible beyond 600 mμ. The reagent itself shows insignificant absorbance from 420 mμ onwards. All absorbance measurements were therefore carried out at 430 mμ. The molar extinction coefficient at 430 mμ is 800.2 ± 16.6 (calculated on the basis of cobalt content). Because of the strong absorbance of the reagent, tests were not made below 410 mμ.

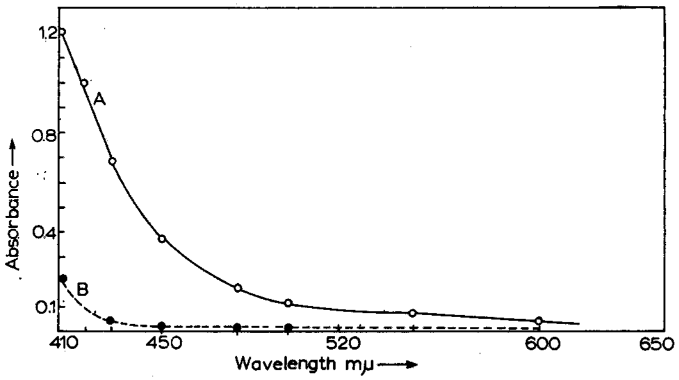

Fig. 1. A. Absorption spectrum of cobalt(II)-TTA complex in acetone-benzene *vs.* acetone-benzene (Co = $8.31 \cdot 10^{-4}$ *M*; TTA = 0.15 *M*; pH 6.0). B. Reagent *vs.* acetone-benzene (TTA = 0.15 *M*; pH = 6.0).

Ratio of acetone: benzene in solvent mixture

The cobalt(II)-TTA chelate is soluble in acetone alone and sparingly soluble in benzene. The addition of benzene in this procedure serves to extract the chelate from the aqueous phase in which acetone is miscible. It is therefore necessary to control the ratio of acetone to benzene in the extraction system for good layer separations. Acetone must be present in a large excess to ensure the solubility of the cobalt-TTA chelate and the amount of benzene must be kept to a minimum. The optimum acetone: benzene ratio is 15:5 (by volume) for a cobalt content of about 1.2 mg and 15:7 for about 0.5 mg of cobalt. With increased amounts of benzene, the organic layer becomes turbid on extraction as the solubility of the chelate is lowered.

Effect of pH

The solvent extraction behaviour of the cobalt(II)–TTA system was studied over the pH range 1.7 to 6.8. Fig. 2 shows the plot of percentage extraction of cobalt(II)–TTA chelate by acetone–benzene as function of pH. Extraction starts around pH 3.0, steadily increases and becomes 100% at pH 5.1. In the pH range 4.2 to 5 extraction is at least 80% complete. The pH region 5.1 to 6.8 can be used for quantitative extraction of cobalt by TTA. Above pH 6.8 it is difficult to keep cobalt(II) in solution owing to precipitation of the hydroxide.

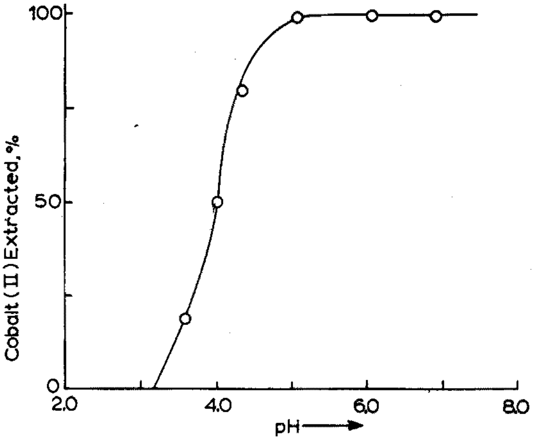

Fig. 2. Extraction of cobalt(II)–TTA complex with acetone–benzene as a function of pH.

Calibration curve

The absorbances of different amounts of cobalt(II) extracted at pH 6.1 were noted against a reagent blank at 430 mμ and at 450 mμ. The results in Table I show that the system obeys Beer's law at both wave lengths but 430 mμ is to be preferred because the absorbance readings are higher. At 430 mμ Beer's law is followed over a concentration range of 12 to 51 μg of cobalt per ml.

TABLE I

BEER'S LAW DATA

Cobalt(II) taken (mg)	*Absorbance*	
	430 mμ	*450 mμ*
0.31	0.15	0.07
0.61	0.31	0.14
0.92	0.48	0.21
1.25	0.65	0.32

Stability of colour

The absorbance of an acetone–benzene solution of cobalt–TTA complex (cobalt = 0.61 mg) prepared according to the general procedure, was measured at 430 mμ after intervals of 2, 24, 46, 96 and 120 h. The colour was quite stable up to 96 h.

Reagent concentration

The concentration of TTA was varied from 0.05 *M* to 0.50 *M*, other factors being kept constant. A satisfactory reagent concentration proved to be 0.15 *M*. Higher concentrations of reagent, *e.g.* 0.5 *M*, gave slightly higher readings, but were avoided because the slight improvement did not justify the waste of reagent.

Diverse ions

The ions (0.5 to 10 mg) shown in Table II were examined for interference. Up to 10 mg of silver, lead, mercury, thorium, zirconium, zinc and strontium could be tolerated but copper(II), iron(III), chromium(III), uranium(VI), nickel and manganese(II) interfered owing to their characteristic colours. Citrate and tartrate could be tolerated but EDTA interfered very seriously.

TABLE II

EFFECT OF DIVERSE IONS

(cobalt(II) = 0.61 mg)

Foreign ion	*Ion concentration in mg*	*Added as*	*Absorbance at 430 mμ*
None	—	—	0.330 ± 0.006
Ag^+	10	$AgNO_3$	0.325
Pb^{2+}	10	$Pb(NO_3)_2$	0.330
Hg^{2+}	10	$HgCl_2$	0.325
Cu^{2+}	2	$CuSO_4 \cdot 5H_2O$	colour
Fe^{3+}	0.5	$FeCl_3 \cdot 6H_2O$	colour
Cr^{3+}	0.5	$Cr_2(SO_4)_3 \cdot 12H_2O$	colour
Th^{4+}	5.96	$Th(NO_3)_4 \cdot 4H_2O$	0.330
Zr^{4+}	6.96	$ZrOCl_2$	0.325
Ni^{2+}	10	$NiSO_4 \cdot 7H_2O$	colour
Mn^{2+}	10	$MnSO_4 \cdot 4H_2O$	colour
Sr^{2+}	10	$Sr(NO_3)_2$	0.330
U^{6+}	0.5	$UO_2(NO_3)_2 \cdot 6H_2O$	colour
Citrate	10	Citric acid	0.320
Tartrate	10	Tartaric acid	0.330
EDTA	10	EDTA(disodium salt)	0.000

RECOMMENDED PROCEDURE

To an aqueous solution containing 0.3 to 1.2 mg of cobalt(II), add 10 ml of buffer solution pH 6 and extract with 10 ml of 0.15 *M* TTA in acetone solution in a separatory funnel for about 5 min. Add 5 ml of acetone and 5 ml of benzene and shake for 2–3 min. Allow the two layers to settle. Transfer the aqueous layer to a beaker and the organic layer to a 25-ml volumetric flask. Dilute the organic phase to 25 ml with acetone and measure the absorbance at 430 mμ against a reagent blank. Read the cobalt concentration from the calibration curve.

From eight such runs with 1.225 mg of cobalt(II) the absorbance found was 0.665 ± 0.016, so that the standard deviation was ± 2.4%. The method permits rapid extraction and simultaneous spectrophotometric determination in one operation requiring only 15–20 min. As little as 0.3 μg of cobalt per ml can be detected. Similar work with manganese(II) and nickel(II) is in progress.

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SUMMARY

The rapid extraction and simultaneous spectrophotometric determination of mg amounts of cobalt(II) by means of 2-thenoyltrifluoroacetone is described. The yellow cobalt(II)–TTA chelate solution in acetone–benzene obeys Beer's law at 430 mμ over the range 12 to 51 μg of cobalt(II) per ml. At pH 5.1–6.8 a single extraction with 0.15 *M* TTA in acetone is satisfactory. The system is stable for 96 h. Silver, zirconium, strontium, thorium, zinc, lead(II) and mercury(II) do not interfere.

RÉSUMÉ

Une méthode est décrite pour l'extraction et le dosage spectrophotométrique du cobalt, au moyen de 2-thénoyltrifluoroacétone. Il se forme un chélate jaune, avec maximum d'absorption à 430 mμ. L'argent, le zirconium, le strontium, le thorium, le zinc, le plomb et le mercure(II) ne gènent pas.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Extraktion und spektrophotometrischen Bestimmung von Kobalt mit Hilfe von 2-Thenoyltrifluoroaceton. Die Reaktion wird nich gestört durch Silber, Zirkonium, Strontium, Thorium, Zink, Blei und Quecksilber.

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DETERMINATION OF TOTAL SULPHUR IN SOIL AND PLANT MATERIAL

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INTRODUCTION

None of the published methods for the determination of total sulphur in soil has proved to be completely satisfactory in combining accuracy, sensitivity, speed and ease of manipulation. Methods based on the oxidation of sulphur to sulphate are tedious[1,2] and when sodium peroxide is used difficulties arise due to frothing and spitting. Such methods involve extraction steps and often considerable analytical skill is required to recover all the sulphate.

Methods based on reduction of the soil with metallic iron[3-5] or metallic magnesium[6,7] and estimation of the sulphide formed, avoid many of the difficulties associated with oxidation methods but are time-consuming. An additional difficulty encountered by the authors was that samples of iron obtained from various sources contained approximately 70 μg S/g, and as soils often contain less than 50 μg S/g it can be appreciated that methods employing iron (*e.g.* LITTLE[3], 4.5 g Fe per 0.5 g soil) containing this amount of sulphur lack precision because of the high blank.

In this paper modifications of a reduction method, and an oxidation method employing sodium bicarbonate are described and the results obtained by these two methods are compared with those given by a published oxidation method[8]. The bicarbonate method as applied to soil was extended to cover the determination of total sulphur in plant material, and the results obtained were compared with those derived by other published methods[9,10].

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent quality.

Reducing mixture. Boil 500 ml of hydriodic acid (sp. gr. 1.7), 250 ml of formic acid (90%), and 125 ml of hypophosphorous acid (50%) in a 1-l flask under reflux for 1 h. Pass nitrogen gas through the boiling solution to remove any hydrogen sulphide produced. This mixture was prepared as suggested by JOHNSON AND ARKLEY[11] except that a longer boiling period is recommended.

Zinc acetate–sodium acetate solution. Dissolve 50 g of zinc acetate and 12.5 g of sodium acetate in water and dilute to 1 l. Filter through Whatman No. 42 filter paper before use.

Ferric ammonium sulphate solution. Dissolve 25 g in 5 ml of concentrated sulphuric acid and 195 ml of water.

p-Aminodimethylaniline solution. Dissolve 2 g in 1500 ml of water. Add 400 ml of concentrated sulphuric acid, cool and adjust the volume to 2 l.

Nitrogen. Pass commercial nitrogen through a wash solution containing 5–10% mercuric chloride and 2% potassium permanganate to remove reduced sulphur compounds.

Water. All water used in the preparation of reagents and for washing of glassware must be free from copper and sulphur.

Magnesium metal. The powder, containing not more than 10 μg S per g.

Apparatus

Combustion vessels. Small porcelain crucibles (1.5 cm in diameter × 1.5 cm in height) obtained from Coors Porcelain Co., U.S.A., or transparent pyrex glass tubes, (4 cm in length × 1 cm in diameter) closed at one end.

Hydrogen sulphide generation and collection apparatus. Essentially as described by JOHNSON AND NISHITA[12].

Principle of the reduction method

The dry soil (0.5 g) was heated with magnesium (2.0 g) as described by SCHÖNIGER[7]. Hydrogen sulphide was evolved by the addition of hydrochloric acid in an apparatus similar to that used by LITTLE[3]. The apparatus was modified by the addition of an extra gas-washing tube, after the hydrogen sulphide collection tube, containing copper ions to collect the generated phosphine. The hydrogen sulphide evolved was determined as methylene blue as described by JOHNSON AND NISHITA[12].

Principle of the proposed bicarbonate method

The soil sample was mixed with sodium bicarbonate and a guard layer of the same reagent placed on top. The whole was heated in a muffle furnace to 550° and after cooling, the sulphate was determined by a reduction procedure involving digestion with hydriodic, hypophosphorous and formic acids. Hydrogen sulphide thus liberated was determined spectrophotometrically as methylene blue.

RESULTS

Reduction method

Results of many total sulphur analyses by the magnesium reduction method showed that consistent results can be obtained with 2 g of magnesium; for example, the results of 14 analyses for total sulphur on a lateritic red earth gave a mean total sulphur content of 284 p.p.m. with standard deviation of ± 1.6 p.p.m. S.

Variation of the total amount of magnesium used from 1.5–3 g while the weight of soil was kept constant at 0.5 g had little effect on the values obtained (see Table I). The use of less than 2 g of magnesium often resulted in explosions; these, however, were not dangerous because the glass had softened and did not shatter. Generally the results obtained by this reduction method were lower than those obtained by oxidation methods (see Table II).

TABLE I

EFFECT OF VARIATIONS IN THE AMOUNT OF MAGNESIUM ON THE TOTAL SULPHUR CONTENT OF SOIL BY THE REDUCTION METHOD

Amount of magnesium (g)	*Mean total sulphur content (p.p.m. S)*	*Standard deviation (p.p.m. S)*
1.5	286	1.7
2.0	284	1.6
3.0	279	2.3

TABLE II

COMPARISON OF RESULTS OBTAINED FOR TOTAL SULPHUR ANALYSES OF THREE SOILS BY THE REDUCTION, OXIDATION AND STEINBERGS' (1955) METHODS (p.p.m. S)

Soil	*Reduction method*	*Oxidation method*	*Steinbergs' method*
Yellow podzolic	73	74	94
Lateritic red earth	284	292	300
Grey-brown soil of heavy texture	424	450	450

Bicarbonate method

The proposed bicarbonate method gave reproducible results, and the magnitude of the variation from the mean total sulphur content was proportional to the total sulphur content of the soil. For the three soils listed in Table II with mean sulphur contents of 74, 292 and 450 p.p.m. S, the standard deviations from the means were ± 0.7, 1.9 and 2.4 p.p.m. S respectively when analysed by the proposed method. The results obtained by this method were slightly higher than those obtained by the reduction method described above, but generally were lower than the results yielded by STEINBERGS'[8] method for the three soils studied (see Table II). However, the recovery of sulphur added as methionine, cysteine, or S-methyl-cysteine was satisfactory (see Table III) and the mean recovery of added sulphur was 99.3% by the proposed method.

TABLE III

RECOVERY OF SULPHUR ADDED TO SOIL AS METHIONINE, CYSTEINE, AND S-METHYL-CYSTEINE BY THE PROPOSED OXIDATION METHOD (μg S)

Soil	*Sulphur added*	*Sulphur recovered*	*Standard deviation of mean*
Lateritic red earth	48.8 as methionine	51.0	1.2
Lateritic red earth	48.9 as cysteine	48.1	0.8
Lateritic red earth	52.4 as S-methyl-cysteine	52.8	0.9
Yellow podzolic	48.8 as methionine	45.6	1.0
Grey-brown soil of heavy texture	48.8 as methionine	48.4	0.4

To test the possibility that the lower results by the proposed bicarbonate method were due to incomplete oxidation of the soil sulphur, various oxidising agents were added to the mixture before combustion at 550°. When 0.1 g of sodium peroxide was added to a sample of the lateritic red earth the value obtained for the total sulphur content increased from 292 p.p.m. S (S.D. ± 1.9 p.p.m.) to 300 p.p.m. S (S.D. ± 1.4 p.p.m.). Addition of 0.01 g of silver oxide to this soil resulted in a value of 297 p.p.m. S (S.D. ± 0.2 p.p.m. S) which was not significantly different from the result obtained with sodium peroxide. Silver oxide had the advantage that it was easier to handle than sodium peroxide and its blank value was zero, whereas sodium peroxide had a variable and substantial blank value. Recoveries of sulphur added as methionine in the presence of sodium peroxide were unsatisfactory, the mean recovery for 28 samples being only 58.9%.

Increasing the temperature to 900°, in the absence of silver oxide or sodium peroxide, and using a silica tube in place of the glass tube or crucible, also resulted in a value of 300 p.p.m. S (S.D. ± 2.8 p.p.m.) for this lateritic red earth.

Addition of other reagents to this soil before combustion did not result in any increase in total sulphur above the figure of 300 p.p.m. S. As the results given above suggest that addition of an oxidising agent results in more complete oxidation of sulphur, several oxidising agents and catalysts were tested on a range of soils (see Table IV). The results support this suggestion. Other reagents such as ceric oxide, ammonium molybdate, and vanadium pentoxide were tested but their use did not result in any increase in the value obtained for the sulphur content. Variations in the amount of silver oxide used had no significant effect on the values obtained.

TABLE IV

EFFECT OF ADDITIONS OF VARIOUS CHEMICALS ON THE RESULTS OF TOTAL SULPHUR ANALYSES (p.p.m. S) BY THE PROPOSED BICARBONATE METHOD, COMPARED WITH RESULTS BY STEINBERGS' (1955) METHOD

(0.25 g $NaHCO_3$ mixed with the soil sample in all cases)

Soil	*No additions except 0.25 g* $NaHCO_3$	*Additional 0.25 g* $NaHCO_3$ *on surface of mixture as guard layer*	*0.1 ml of 30%* H_2O_2	*0.01 g of* $PtCl_4$	*0.01 g of* Ag_2O	*0.01 g of* Ag_2O *plus additional 0.25 g* $NaHCO_3$ *as guard layer*	*Steinbergs' (1955) method*
Peat	2,260	2,400	2,360	2,350	2,510	2,490	2,480
Calcareous sand	805	810	840	846	860	855	900
Alpine humus	405	400	454	420	445	445	440
Red podzolic	105	102	110	118	110	108	109
Red podzolic	76	68	78	85	85	82	78
Red podzolic	56	58	57	60	60	54	55

The results obtained showed that it was not necessary to use an extra 0.25 g sodium bicarbonate as a guard layer when 0.01 g silver oxide was added to the sample before combustion. It was also found that it was not necessary to neutralize the carbonate by the addition of hydrochloric acid before the addition of the reducing mixture for the reduction step.

The results of total sulphur analyses by the modified bicarbonate procedure (*i.e.* addition of 0.01 g of silver oxide plus 0.25 g sodium bicarbonate only to the soil sample, and combustion at 550°, followed by reduction) were compared with those obtained by STEINBERGS'[8] method for 69 different soils. The mean difference between the two methods was 4.8 p.p.m. S, which when tested against its standard error of 3.62 was not significant ($t = 1.32$).

It was found that the mean recovery of 48.8 μg of methionine sulphur added to the grey-brown soil of heavy texture in the presence of 500 p.p.m. barium was 48.8 (S.D. ± 0.7) μg S, and in the absence of added barium was 48.4 (S.D. ± 0.4) μg S. It was concluded, therefore, that the presence of barium ions does not affect the results obtained by the proposed bicarbonate method. The addition of 200 p.p.m. copper to the soil did not affect the value obtained for the total sulphur content of the lateritic red earth.

It can be seen from the results presented in Table V that this procedure can also be satisfactorily used for the determination of sulphur in plant material.

TABLE V

RESULTS OF ANALYSIS OF PLANT MATERIAL FOR TOTAL SULPHUR BY THE PROPOSED OXIDATION METHOD, COMPARED WITH RESULTS OBTAINED BY IISMAA'S (1959) AND STEINBERGS' (1953) METHODS

(% S)

	Coarsely ground material 30 mesh		*Finely ground material 150 mesh*		*Results by Iismaa's method*	*Results by Steinbergs' method*
	$NaHCO_3$ only	*$NaHCO_3$ plus 0.01 g Ag_2O*	*$NaHCO_3$ only*	*$NaHCO_3$ plus 0.01 g Ag_2O*		
Trifolium subterraneum var. Mt. Barker	0.21	0.21	0.20	0.23	0.21	0.20
Trifolium subterraneum	0.23	0.28	0.27	0.27	0.26	0.24
Trifolium subterraneum	0.23	0.23	0.25	0.27	0.25	0.25
Trifolium subterraneum	0.29	0.31	0.29	0.30	0.31	0.25
Trifolium subterraneum	0.27	0.29	0.27	0.29	0.28	0.26
Rye grass (stubble)	0.10	0.12	0.12	0.12	0.10	0.10
Rye grass (dried)	0.10	0.12	0.12	0.13	0.11	0.11
Rye grass (dried)	0.13	0.15	0.14	0.15	0.15	0.12
Rye grass (green)	0.27	0.32	0.28	0.31	0.29	0.30
Rye grass (green)	0.27	0.32	0.34	0.35	0.30	0.33
Rye grass (green)	0.33	0.36	0.33	0.37	0.35	0.38

The results obtained for total sulphur in plant material were not affected by the fineness of grinding or the presence of incompletely oxidised material. When silver oxide was present no black particles were formed in either the finely or coarsely-ground plant material. The results in Table V again demonstrate that the presence of an oxidising agent, other than oxygen, is necessary for complete oxidation of the sulphur. The results obtained by this oxidation method were in substantial agreement with the results obtained by either IISMAA'S[9] or STEINBERGS'[10] methods. High nitrate contents of plant material did not interfere with this determination of sulphur; additions of 2000 p.p.m. of nitrate nitrogen did not affect the results.

RECOMMENDED PROCEDURE FOR TOTAL SULPHUR DETERMINATION

Take 0.01–0.5 g of soil or plant material (depending on the sulphur content) ground to pass an 80 mesh sieve, and mix with 0.25 g of sodium bicarbonate and 0.01 g silver oxide or an appropriate mixture of both in a small porcelain crucible or glass tube. Place the container in a cold muffle furnace, raise the temperature to 550°, and heat for 3 h. Cool, and transfer to a 50-ml digestion flask (described by JOHNSON AND NISHITA[12]). If the glass tube is used it must be broken into the flask by using a hot rod and a drop of water. Add 2 ml of water and 4 ml of reducing mixture and determine the sulphur content as detailed by JOHNSON AND NISHITA[12].

If the sample contains more than 50 μg S, it is necessary to dilute the solution, before reading, with a solution containing the same concentration of zinc acetate, sodium acetate, *p*-aminodimethylaniline, ferric ammonium sulphate and sulphuric acid as described by JOHNSON AND NISHITA[12], or to take a smaller sample.

When the soil contains minerals rich in sulphur (*e.g.* gypsum) it is recommended that the sample be ground to pass a 150-mesh sieve and well mixed before sampling.

DISCUSSION

Because of the possibility of explosions during the heating of soil with magnesium, the generation of phosphine and the time taken for analysis (approximately 8 samples per working day), the reduction method is not recommended for routine analytical work. However, it is of value as a reference method for total sulphur in soil (see Table II).

The bicarbonate method proposed differs from BARDSLEY AND LANCASTER's[13] method for "soil sulphur" in that an oxidising agent is added to the mixture, and the whole of the ignited material is used for the final determination of sulphate; BARDSLEY AND LANCASTER extracted the ignited residue with a sodium dihydrogen phosphate reagent. The proposed method would determine all the sulphur present even when barium or appreciable amounts of calcium are present, but this would not be the case using BARDSLEY AND LANCASTER's method. The grey-brown soil of heavy texture contains much calcium (as gypsum and calcium carbonate) and even when extra barium ions were added, complete recovery of added methionine was obtained using the proposed method.

The proposed method is sufficiently rapid for routine work and has the advantage that large numbers of oxidations can be performed with little or no supervision — the number is limited only by the size of the muffle furnace used. The determination step is also rapid and with a bank of 6 units (JOHNSON AND NISHITA[12]), at least 30 determinations can be completed per day when the method is operated on a routine basis.

In both the methods described the sulphide produced by the reduction step was determined by a colorimetric method. This is particularly appropriate for soils with a low sulphur content. Alternatively, the sulphide may be absorbed in a sodium hydroxide solution and titrated with mercuric or cadmium ions using dithizone as an indicator[14]. This method may be more appropriate for soils with a high sulphur content, and it also has the advantage that complete transfer of the hydrogen sulphide can be continuously checked by a stoichiometric reaction instead of working with an arbitrary standard curve.

SUMMARY

A rapid and accurate method for the determination of the total sulphur content of soil or plant material is described. The sample is heated with sodium bicarbonate and silver oxide at 550° for 3 h, and the sulphur content of the whole residue is reduced to hydrogen sulphide and determined as methylene blue. The results compare favourably with those of other methods. In routine use, at least 30 analyses may be completed in a day.

RÉSUMÉ

Une méthode rapide et précise est décrite pour le dosage du soufre total dans des terrains et des végétaux. L'échantillon à analyser est chauffé avec du bicarbonate de sodium et de l'oxyde d'argent à 550°, pendant 3 h. Le soufre est ainsi réduit en hydrogène sulfuré et dosé comme bleu de méthylène.

ZUSAMMENFASSUNG

Beschreibung einer Schnellmethode zur Bestimmung des Gesamtschwefels in Böden und Pflanzenmaterial. Die Substanzprobe wird mit Natriumbicarbonat und Silberoxyd auf 550° erhitzt, der Schwefel zu Sulfid reduziert und als Methylenblau spektrophotometrisch bestimmt.

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ANALYTICAL APPLICATIONS OF THE DETERMINATION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART III. DETERMINATION OF HYDROGEN PEROXIDE, PEROXYDISULPHATE AND THEIR MIXTURES[1]

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The simple, rapid and accurate titrimetric determination of hexacyanoferrate(III) with ascorbic acid[2], and the favourable redox potential of the hexacyanoferrate(III)–(II) system, can be utilized for the determination of several oxidizing or reducing ions[1,3,4]. For the determination of reductants, an excess of hexacyanoferrate(III) is added, the excess being titrated with ascorbic acid. For oxidants, on the other hand, an excess of hexacyanoferrate(II) is required; the hexacyanoferrate(III) ions which are formed by the reaction are then titrated with ascorbic acid. In the present paper, methods based on this principle are described for the determination of hydrogen peroxide and peroxydisulphate separately and in their mixtures.

EXPERIMENTAL

Reagents

0.1 N Ascorbic acid solution[5] prepared from 8.9 g of recrystallized ascorbic acid dissolved in 1 l of glass-distilled water. For standardization, 20.00 ml of standard 0.1 *N* potassium iodate solution was acidified with 5 ml of 2 *N* hydrochloric acid, 1 g of potassium iodide was added and the liberated iodine was titrated with ascorbic acid to colorless. The solution must be standardized daily.

2.6-Dichlorophenolindophenol indicator: A filtered aqueous 0.1% solution; this is stable for 3 weeks. It is better to prepare a 1 :500 solid mixture of 2.6-dichlorophenolindophenol with pure, powdered sodium chloride. For a titration, 1 ml of 0.1% indicator solution or about 0.2 g of solid indicator mixture were used.

0.1 N Hydrogen peroxide solution: The concentration of commercial 30% hydrogen peroxide was determined by titration with permanganate, and an adequate amount was diluted to give a 0.1 *N* solution. The solution was standardized by titration with permanganate and by the iodometric method.

0.1 N Potassium peroxydisulphate solution: 13.52 g of analytically pure potassium peroxydisulphate was dissolved in water, diluted to 1 l, and standardized by iodometric titration. In our experience, a peroxide-free solution cannot be prepared from ammonium peroxydisulphate.

0.1 N Potassium hexacyanoferrate(III) solution: The solution was prepared from analytically pure (Merck p.a.) $K_3[Fe(CN)_6]$ reagent.

0.5 N Iron(II) chloride solution: 28 g of pure iron metal was completely dissolved in 120 ml of 1 : 1 hydrochloric acid, and diluted to 1 l. Before use, the solution was passed through a Jones reductor filled with cadmium, to ensure that all the iron was present in the bivalent form.

All other reagents used were of purissimum grade.

Determination of hydrogen peroxide

Hydrogen peroxide reduces hexacyanoferrate(III) in alkaline medium[6]:

$$2[Fe(CN)_6]^{3-} + H_2O_2 = 2[Fe(CN)_6]^{4-} + 2\,H^+ + O_2$$

VULTERYN AND ZYKA[7] have used the reaction potentiometrically, while ERDEY AND BUZÁS[8] have applied it with chemiluminescent indicators for the determination of hexacyanoferrate(III).

When hydrogen peroxide is added to an alkaline solution of potassium hexacyanoferrate(III), the reaction proceeds rapidly and stoichiometrically, and the excess of hexacyanoferrate(III) ions can be titrated with ascorbic acid. The reaction is so rapid that the auto-decomposition of hydrogen peroxide, which normally occurs in alkaline solutions, does not take place. The recommended procedure is as follows.

Procedure: To 25.00 ml of 0.1 *N* potassium hexacyanoferrate(III) solution, add 20 ml of 5 *N* sodium hydroxide. Add the sample solution containing 10–20 mg of hydrogen peroxide. Shake the mixture and allow to stand for 4–5 min. Then add 2,6-

dichlorophenolindophenol indicator. Neutralize cautiously with 1:1 hydrochloric acid, until the colour of the indicator turns from green to reddish brown (the solution is then slightly acidic). Neutralize the solution with 1 g of solid potassium hydrogen carbonate, and titrate the excess of hexacyanoferrate(III) with 0.1 *N* ascorbic acid solution. During the titration the colour of the solution changes gradually to blue; at the end-point, the solution becomes colorless with one drop of the titrant. 1 ml of 0.1 *N* solution is equivalent to 1.7008 mg of H_2O_2.

The results of some titrations of hydrogen peroxide are shown in Table I. The standard deviation of the method, calculated from the first 12 titrations, is ± 0.3%; the deviation of the mean of these determination is ± 0.1%. The mean and true values differ by 0.1%.

TABLE I

DETERMINATION OF HYDROGEN PEROXIDE OR PEROXYDISULPHATE

Amount taken (mg)	*Average amount found (mg)*	*Error (mg)*	
		maximum	*minimum*
Hydrogen peroxide			
20.72	20.69 (12 results)	+ 0.14	± 0.00
17.01	17.11 (3 results)	+ 0.15	+ 0.01
10.63	10.68 (3 results)	+ 0.23	+ 0.07
Peroxydisulphate			
186.74	186.85 (12 results)	+ 1.05	± 0.00
140.05	140.21 (3 results)	+ 0.29	+ 0.01
112.04	112.06 (3 results)	+ 0.15	+ 0.06
56.02	56.16 (3 results)	+ 0.17	+ 0.08
28.01	28.08 (3 results)	+ 0.14	+ 0.04

Determination of peroxydisulphate ions

Peroxydisulphate ions oxidize hexacyanoferrate(II) ions in acidic medium[9].

$$2[Fe(CN)_6]^{4-} + S_2O_8^{2-} = 2[Fe(CN)_6]^{3-} + 2\,SO_4^{2-}$$

The reaction proceeds slowly in the cold, but at 60° it is so rapid that it can be used even for direct titration[10]. In our experience, it is better to work in the cold. With 0.1 *N* solutions the reaction is complete within 20 min.

Thus, the peroxydisulphate solution is treated with an excess of potassium hexacyanoferrate(II) in acidic medium, and after 20 min, the hexacyanoferrate(III) ions formed in an amount equivalent to the peroxydisulphate, are titrated with ascorbic acid. The recommended procedure is as follows.

Procedure: To the alightly acidic solution containing 20–200 mg of $S_2O_8^{2-}$ add 2–3 g of pure potassium hexacyanoferrate(II) and shake until dissolution is complete. Let the mixture stand for 20 min. Then neutralize the solution with 2–4 g of solid potassium hydrogen carbonate, add dichlorophenolindophenol indicator and titrate with 0.1 *N* ascorbic acid to colorless. 1 ml of 0.1 *N* ascorbic acid is equivalent to 9.606 mg $S_2O_8^{2-}$.

The results of some persulphate determinations are shown in Table I. The standard deviation calculated from the first 12 results is ± 0.2%, the deviation of the mean being ± 0.05%. The difference between the mean and true values is 0.07%.

Determination of peroxydisulphate ions and hydrogen peroxide in presence of each other

When ascorbic acid is used as titrant, analyses of systems containing peroxydisulphate ions and hydrogen peroxide can be carried out fairly simply. Two titrations must be made. For the first titration, the sample solution is added to a mixture of potassium hexacyanoferrate(II) and a known excess of potassium hexacyanoferrate(III) in alkaline solution. The hydrogen peroxide reduces an equivalent amount of hexacyanoferrate(III) ions, while peroxydisulphate does not react. The solution is then acidified, when the peroxydisulphate oxidizes the hexacyanoferrate(II). After the reaction is complete, the hexacyanoferrate(III) can be titrated with ascorbic acid (A ml).

For the second titration, the sample solution is treated with an excess of iron(II) in acidic medium. Under the given experimental conditions, both peroxydisulphate and hydrogen peroxide oxidize iron(II) to iron(III), and the iron(III) formed can be titrated with ascorbic acid[11] (B ml).

Let X represent the volume of 0.1 N ascorbic acid equivalent to the amount of hydrogen peroxide in the solution, and Y the volume of 0.1 N ascorbic acid equivalent to peroxydisulphate. Let Z represent the volume of ascorbic acid equivalent to the hexacyanoferrate(III) originally added. The following equations are then valid for these titrations:

$$X + Y = B \qquad \text{and} \qquad Z - X + Y = A$$

thus

$$X = (B + Z - A)/2 \qquad \text{and} \qquad Y = (A + B - Z)/2$$

On a similar basis the two ions can be determined with permanganate solution[12].

Procedure: (*1*) To 25.00 ml of 0.1 N potassium hexacyanoferrate(III) add about 3 g of potassium hexacyanoferrate(II) and shake to dissolve. Make the solution alkaline with 20 ml of 5 N sodium hydroxide. Then add the sample solution containing

TABLE II

DETERMINATION OF HYDROGEN PEROXIDE AND PEROXYDISULPHATE IN PRESENCE OF EACH OTHER

Amount taken (mg)		*Average amount found (mg)*		*Maximum error (mg)*		*Minimum error (mg)*	
H_2O_2	$S_2O_8^{2-}$	H_2O_2	$S_2O_8^{2-}$	H_2O_2	$S_2O_8^{2-}$	H_2O_2	$S_2O_8^{2-}$
49.26	191.35	48.91	192.45	−0.41	+1.92	−0.24	+0.96
		(6 results)					
24.63	191.35	24.38	192.30	−0.33	+1.34	−0.19	+0.39
		(3 results)					
49.26	95.68	49.20	97.56	−0.16	+2.30	+0.01	+1.14
		(3 results)					

20–50 mg of H_2O_2 and 100–200 mg of $S_2O_8^{2-}$. After 4–5 min, acidify the solution slightly using phenolphthalein with 1 : 1 hydrochloric acid, and wait for 20 min. Then neutralize the solution with 2–4 g of potassium hydrogen carbonate, add indicator and titrate with 0.1 *N* ascorbic acid to colorless (*A* ml).

(2) To a similar aliquot of sample solution, add 20 ml of 2 *N* hydrochloric acid and 10 ml of iron(II) chloride solution, mix the solution, and titrate with 0.1 *N* ascorbic acid. Near the end of the titration (when the solution is almost colorless) heat the solution to 60°, add 2 ml of 0.5% potassium thiocyanate indicator, and titrate dropwise to colorless (*B* ml).

Typical results are shown in Table II; it can be seen that the accuracy of the determination is satisfactory.

SUMMARY

Hydrogen peroxide can be determined by reaction with excess of alkaline hexacyanoferrate(III), the excess being titrated with ascorbic acid. Peroxydisulphate is determined by reaction with hexacyanoferrate(II) in acidic medium, the hexacyanoferrate(III) formed being titrated with ascorbic acid. To determine hydrogen peroxide and peroxydisulphate in the presence of each other, two titrations are needed; the results are readily calculated.

RÉSUMÉ

Description d'une méthode pour le dosage du peroxyde d'hydrogène, au moyen de ferricyanure, avec titrage de l'excès par l'acide ascorbique et description d'une méthode pour le dosage du persulfate au moyen de ferrocyanure; le ferricyanure formé est titré par l'acide ascorbique. Une méthode est proposée pour le dosage du peroxyde d'hydrogène et du persulfate, l'un en présence de l'autre.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Wasserstoffperoxyd und Peroxydisulfat mit Hexacyanoferrat-(III) bezw.-(II) und Titration des überschüssigen Hexacyanoferrats-(III) bezw. des gebildeten Ferrats-(III) mit Ascorbinsäurelösung.

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DIE ANALYTISCHE ANWENDUNG DER KOHLENDIOXYDDESTILLATION

II. DESTILLATIONS- UND TITRATIONSMETHODE ZUR BESTIMMUNG DES SICH BEI DER TOTALEN OXYDATION VON ORGANISCHEN STOFFEN BILDENDEN KOHLENDIOXYDS

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Die Bestimmung organischer Substanzen in wässrigen Lösungen durch „nasse Verbrennung" ist besonders vom biologischen Gesichtspunkte aus von Bedeutung.

Zur Oxydation organischer Stoffe wird meist Bichromat-Schwefelsäure[1-3] und die mit Silber katalysierte verdünnte saure Persulfatlösung[4,5] verwendet. Grundlegende Probleme bei diesen Bestimmungen sind die richtige Wahl des Oxydationsmittels, die vollkommene Absorption und Bestimmung des Kohlendioxyds, sowie der Ausschluss der Luftkohlensäure. In unseren früheren Mitteilungen[6-8] beschrieben wir zur Isolierung und Bestimmung des Kohlendioxyds eine einfache Destillations- und

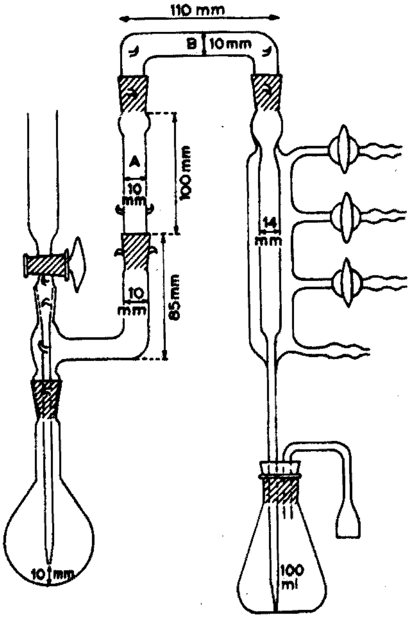

Abb. 1. Distillationsapparat.

Titrationsmethode. Dieses Verfahren ist auch zur Bestimmung des Gehalts von organischen Stoffen in wässrigen Lösungen über das Kohlendioxyd geeignet.

Die auf Abb. 1 gezeigte Vorrichtung ist eine modifizierte Apparatur zur „blasenfreien Destillation" des Kohlendioxyds. Die mit Schliffen versehenen Röhren „A" bzw. „B" können elektrisch beheizt werden. Die Röhre „A" ist mit geglühten Silberpermanganat[9], die Röhre „B" mit Kupfer beschickt. Das geglühte Silberpermanganat dient zur Oxydation des bei dem Aufschluss mit Bichromat-Schwefelsäure in kleinen Mengen gebildeten Kohlenmonoxyds. Von den zahlreichen ausprobierten Oxydationsmitteln hat sich hierzu das Zersetzungsprodukt des Silbermanganats als am besten geeignet erwiesen. Das mit glühendem Kupfer gefüllte Röhrchen hat die Aufgabe, den vom heissen Zersetzungprodukt des Silberpermanganats kontinuierlich abgegebenen, überschüssigen Sauerstoff sowie den bei den Oxydationsvorgängen im Kolben gebildeten Sauerstoff abzufangen. Die blasenfreie Destillation des sich bei der totalen Oxydation bildenden Kohlendioxyds wird ebenso durchgeführt, wie dies in unseren früheren Mitteilungen bereits beschrieben wurde. Durch Kochen der Schwefelsäurelösung im Destillationskolben wird die Luft und das Kohlendioxyd aus dem Apparat ausgetrieben. Nachdem aus dem Ausflussrohr des Kühlers einige Minuten hindurch ein lebhafter Wasserdampfstrom ausgetreten ist, wird das Kühlwasser (durch entsprechende Einstellung der Hähne am Kühler) auf die schwächste Kühlungsstufe eingestellt. Hierauf wird der Vorlagekolben, der mit Pentan überschichtete Bariumhydroxydlösung enthält, ohne Unterbrechung des Siedens am Ausflussrohr des Kühlers befestigt. Bei der Erhöhung des Niveaus des Kühlwassers im Kühlmantel steigt die Bariumhydroxydlösung im Kühlerrohr nach oben. Das Oxydationsmittel und die zu untersuchende Lösung werden nun durch den Hahntrichter in den Destillationskolben eingebracht. Das mit dem Wasserdampf ausgetriebene Kohlendioxyd gelangt im Kühler mit der Bariumhydroxydlösung in Berührung und wird dort absorbiert, ohne dass Kohlendioxydbläschen in den Vorlagekolben entweichen. Die karbonathaltige Bariumhydroxydlösung wird bei der Beendigung der Destillation durch Verminderung der Kühlung aus dem Kühlerrohr gedrückt, und das überschüssige Bariumhydroxyd wird nach Abnahme des Vorlagekolbens mit Säure titriert.

Wir führten unsere Untersuchungen mit einigen aus Kohlenstoff, Wasserstoff und Sauerstoff aufgebauten organischen Verbindungen durch. Als Oxydationsmittel

TABELLE I

Verbindung	*Gebildetes CO_2 in % der untersuchten Substanz nach der Oxydation mittels*		
	Bichromats in 50%iger Schwefelsäurelösung	*Bichromats in 50%iger Perchlorsäurelösung*	*Silberpersulfats in 2%iger Schwefelsäurelösung*
Methanol	100.0	—	100.0
Essigsäure	0.0	—	100.0
Butanol	—	—	99.9
Glukose	99.8	99.8	99.8
Phenol	98.0	—	100.0
Resorcin	99.0	—	100.0
Benzoesäure	30.0	90	99.8
Salicylsäure	100.0	—	100.0
Phthalsäure	99.7	—	100.0
Benzolsulfonsäure	2	85	100.0

wurde 50%iges schwefelsaures Bichromat, 50%iges perchlorsaures Bichromat und 2%-iges schwefelsaures Silberpersulfat verwendet. Anwendung von Schwefelsäure- bzw. Perchlorsäurekonzentrationen über 50% empfiehlt sich nicht, weil die höher konzentrierte Schwefelsäure schwach flüchtig ist, bzw. weil die konzentrierte Perchlorsäure gleichfalls an der Oxydation des organischen Stoffes teilnimmt und ihre flüchtigen Reduktionsprodukte in die Vorlage gelangen könnten. Als das wirksamste Oxydationsmittel erwies sich das Silberpersulfat. In Tabelle I sind die Ergebnisse der mit den drei verschiedenen Oxydationsmitteln durchgeführten Bestimmungen miteinander verglichen.

Die auf der blasenfreien Destillation beruhende Bestimmung des Kohlendioxyds kann sowohl im 0.1 wie auch im 0.01 *N*-Massstabe durchgeführt werden. Der Gehalt an organischen Stoffen lässt sich in Lösungen mit einem Kohlenstoffgehalt von 6.0 bis 0.06 mg mit einer Genauigkeit von ± 0.5–2% bestimmen.

In Tabelle II sind die Ergebnisse der totalen Oxydation verschiedener Glukosemengen zusammengestellt.

Nachstehend geben wir eine ausführliche Beschreibung des Verfahrens, wie es sich bei unseren zahlreichen Versuchen als am besten geeignet erwiesen hat.

TABELLE II

BESTIMMUNG DER GLUKOSE ÜBER DAS BEI DER OXYDATION MIT PERSULFAT GEBILDETE KOHLENDIOXYD

mg Glukose	*Verbrauch an $Ba(OH)_2$ Lösung (ml)*		*Gefunden Glukose*	
	Einzeln	*Mittel*	*mg*	*%*
12.22	*0.1 N* 8.12 8.14 8.11	8.12	12.19	99.8
6.09	*0.1 N* 4.04 4.05 4.07	4.05	6.08	99.9
2.44	*0.1 N* 1.62 1.62 1.60	1.62	2.43	99.6
1.479	*0.01 N* 9.90 9.87 9.85	9.87	1.482	100.2
0.737	*0.01 N* 4.90 4.88 4.93	4.90	0.736	99.8
0.294	*0.01 N* 1.96 1.95 1.95	1.95	0.286	99.3

BESCHREIBUNG DES VERFAHRENS

Reagenzien

0.1 bzw. 0.01 *N* Bariumhydroxydlösung (mit 5% Bariumchloridgehalt). Die Masslösungen werden in automatischen Büretten aufbewahrt; sie sind durch eine 0.5-cm hohe Pentanschicht von Luftzutritt geschützt.

4%-ige Kaliumpersulfatlösung. (Die Lösung wird zum Sieden erhitzt, eventuell durch ein Glasfilter filtriert, und in verschlossenen Schliffkolben aufbewahrt.)

Ausgekochtes destilliertes Wasser. (1- 1.5 l destilliertes Wasser werden in Gegenwart von 10–15 Körnchen Bimsstein 25–30 Min lebhaft gekocht, ohne Schütteln abgekühlt, und in Flaschen mit eingeschliffenem Glasstopfen aufbewahrt. Das ausgekochte destillierte Wasser muss jeweils frisch hergestellt werden.) Nach Vorschrift hergestelltes[9] Silberpermanganat wird in Portionen 2–3 g im Porzellantiegel über der Gasflamme 5–10 Min erhitzt. Nach dem Abkühlen wird die pulverförmige Substanz zu Pastillen gepresst, auf Partikel mit dem Durchmesser von 3–6 mm zerkleinert und auf einem Sieb entstäubt. Auf den Boden der senkrecht stehenden Röhre „A" gibt man zunächst einen Propfen von 0.5–1 cm Höhe aus Kupfer-, Silber- oder Eisendraht und füllt darauf die zerkleinerten Pastillen. Die horizontal stehende Röhre „B" wird mit analytisch reinem Kupferoxyd in Drahtform beschickt und beide Enden der Röhre mit Propfen aus Kupferdraht verschlossen. Um die Verbrennungsröhren werden Heizdrahtspiralen gewickelt. Die Temperatur wird mit Schiebewiderständen reguliert.

Der Destillationsapparat wird am Kühlerteil an einem Stativ befestigt und bei der Winkelröhre über dem Destillationskolben spannungsfrei mit einer Klemme gestützt. Die Schliffe werden ohne jede Schmierung mit starken Stahlfedern zusammengehalten. Zur Heizung des Destillationskolbens dient ein kleiner elektrischer Heizkörper. Dieser besteht aus einer Heizspirale, die auf einen Isolationskörper mit geringer Wärmekapazität befestigt ist; der Heizdraht steht mit dem Kolben in direktem Kontakt[6]. Der Heizkörper ist mit Hilfe einer Haltestange gleichfalls am Stativ fixiert. Der Vorlagekolben (100-Erlenmeyer Schliffkolben) wird am Ausflussrohr des Kühlers mit Hilfe eines doppelt durchbohrten Korken angeschlossen. In die zweite Bohrung des Korken wird der Stiel eines doppelt gebogenen Kelchtrichters geschoben (siehe Abbildung), dessen Öffnung mit einem mit verdünnter Lauge angefeuchteten Wattebausch verschlossen wird.

Die Vorbehandlung der zu analysierenden Lösung hängt ab von der Flüchtigkeit der organischen Substanz. Ist diese mit Wasserdampf nicht flüchtig, so wird die mit Schwefelsäure angesäuerte Lösung im Destillationskolben ausgekocht und durch den Hahntrichter nur die Persulfatlösung nachträglich in den Kolben einlaufen gelassen. Beim Vorhandensein einer flüchtigen Komponente wird die Lösung vom Kohlendioxyd dadurch befreit, dass man durch die mit Schwefelsäure angesäuerte Lösung während 10–15 Min einen lebhaften Strom kohlensäure freier Luft saugt. Hierzu wird der, die Lösung enthaltende Kolben mit einem doppelt durchbohrten Korken verschlossen, der eine bis zum Boden des Kolbens reichende und eine kurze Glasröhre trägt. Zur Entfernung der Luftkohlensäure wird eine Natronkalkrohr vorgeschaltet. Bei der Durchführung der Bestimmung wird dann die so vorbereitete Lösung durch den Hahntrichter in den Destillationskolben eingebracht. Bei der nassen Verbrennung fester Stoffe kann eine mit ausgekochtem destilliertem Wasser hergestellte Stamm-lösung direkt verwendet werden. Bei der Durchführung unserer Modellversuche gingen wir in jedem Falle nach diesem Verfahren vor.

Vor der eigentlichen Bestimmung wird zunächst das Kupferoxyd in der an den Kühler angeschlossenen Röhre B mit Wasserstoff reduziert. Hierbei lässt man das Kühlerende in destilliertes Wasser eintauchen. Nach der Reduktion werden die Röhre „A" und die Winkelröhre angeschlossen. Man füllt nun durch Ansaugen das Auslaufrohr des Hahntrichters mit ausgekochtem destilliertem Wasser. In den 100-ml fassenden Destillationskolben des Apparats werden 0.1–0.2 g Silbersulfat (kristallin) sowie 3–5 ml 10%-ige Schwefelsäure gegeben und das Lösungsvolumen mit destilliertem Wasser auf 30–50 ml ergänzt. Nach Zugabe von einigen Körnchen Bimsstein (Ø 2–3 mm) wird der Destillationskolben mit Federn am Aufsatz befestigt und die Heizung eingeschaltet. (Das Kühlwasser wird noch nicht eingeschaltet, der Kühlmantel ist leer!). Gleichzeitig schaltet man die Heizung der Oxydationsröhre ein. Der Schiebewiderstand wird so eingestellt, dass die Heizspirale dunkelrot glüht. Nachdem ein lebhafter Wasserdampfstrom aus dem Ausflussrohr des Kühlers austritt, wird auch die Heizung der Röhre „B" eingeschaltet. Man lässt 5 ml Pentan und 15.00 ml Bariumhydroxydlösung in den Vorlagekolben (100 ml-ige Erlenmeyer-Schliffkolben) fliessen. (Bei Bestimmungen im 0.01 *N* Massstabe wird das einem Volumen vom 50 ml entsprechende Niveau am Vorlagekolben vorher markiert.) Die an der Kolbenwand haftende Bariumhydroxydlösung wird mit 5 ml ausgekochtem destilliertem Wasser unter die Pentanschicht gespült.

Man schaltet nun – ohne das Kochen zu unterbrechen – die erste Kühlstufe ein (der untere Hahn wird geöffnet, die beiden oberen Hähne werden geschlossen und das Kühlwasser wird eingeschaltet). Der Vorlagekolben wird mit Hilfe des doppelt durchbohrten Korken am Ausflussrohr des Kühlers befestigt, und zwar so, dass das Rohrende knapp über den Boden des Kolbens endet. Man öffnet nun den mittleren Hahn des Kühlers und verschliesst den unteren. Mit der Erhöhung des Niveaus des Kühlwassers im Kühlmantel steigt die Bariumhydroxydlösung im Kühlerrohr nach oben. Nun werden 3–5 ml Persulfatlösung in den Hahntrichter gegossen, die man dann durch vorsichtiges Öffnen und Schliessen des Hahnes in kleinen Anteilen (0.30–0.5 ml) in die lebhaft siedende Lösung einlaufen lässt. Man pipettiert unverzüglich auch die zu untersuchende Lösung in den Hahntrichter und lässt auch diese in kleinen Anteilen in den Destillationskolben einlaufen. Während dieser Operation wird das Niveau der Bariumhydroxydlösung im Kühler dauernd beobachtet. Während der Zugabe der einzelnen Anteile der Lösungen steigt dieses Niveau um einige mm nach oben und sinkt dann wieder zurück. Beim Einsetzen der Kohlendioxydentwicklung sinkt das Niveau des Bariumhydroxyds; man schaltet dann die dritte Kühlstufe ein (der obere Hahn wird geöffnet und der mittlere verschlossen) und erreicht dadurch eine erneute Erhöhung des Bariumhydroxyd-Niveaus. Je nach der Menge der organischen Substanz lässt man nun weitere Persulfatmengen in den Kolben einlaufen. Die Kapazität des Kühlers sowie der Kupferfüllung sind auf einen Kohlenstoffgehalt von maximal 3–6 mg bemessen, dies entspricht einem Volumen von 5–10 ml 0.1 *N* Bariumhydroxydlösung. Das Persulfat soll in einem 100–200% betragenden Überschuss angewandt werden.

Sofern das plötzlich freiwerdende Kohlendioxyd das Bariumhydroxyd im Kühler stark nach unten drückt, wird der Heizstrom mit Hilfe des Schiebewiderstandes reduziert. Mit der allmählichen Absorption des Kohlendioxyds steigt das Niveau der

Bariumhydroxydlösung im Kühler wieder nach oben. Während der Destillation steigt und sinkt die Bariumhydroxydlösung im Kühler dauernd; dies beschleunigt die Vermischung des kohlensäurehaltigen Wassers mit der Bariumhydroxydlösung. Die mit der Oxydation zusammenhängende Destillation beansprucht 25–30 Min. Während dieser Zeit lässt man durch den Hahntrichter ausgekochtes destilliertes Wasser in kleinen Anteilen in den Kolben einlaufen, um damit die zu untersuchende Lösung einzuspülen und das verdampfte Wasser zu ersetzen. Gegen Ende der Destillation wird der Kolbeninhalt wieder zum lebhaften Sieden gebracht. Zur Beendigung der Destillation reduziert man die Kühlung, ohne das Sieden zu unterbrechen. Der untere Hahn des Kühlers wird geöffnet, wobei das Niveau des Kühlwassers in Kühlmantel bis zur Höhe des unteren Hahnes sinkt. (Zum Übergang von einer stärkeren Kühlstufe auf eine schwächere, verfahre man wie folgt: An die bei den unteren Abflussstutzen des Kühlers werden Gummischläuche mit Innendurchmesser 5–7 mm mit grossem Gefälle angeschlossen. An den oberen Abflussstutzen schliesst man einen etwas weiteren Gummischlauch – Innendurchmesser 10–12 mm – an. Das Ende dieses letzteren Gummischlauches wird beim Umstellen auf ein höheres Niveau so eingestellt, dass der freie Rücklauf des Wassers gewährleistet ist. Die Strömungsgeschwindigkeit des Kühlwassers wird so eingestellt, dass der Übergang von einer stärkeren Kühlstufe auf eine geringere beim Öffnen der entsprechenden Hähne von selbst vor sich geht.)

Man lässt nun den Vorlagekolben samt Korken nach unten gleiten, so dass das Kühlerende über den Flüssigkeitsspiegel zu stehen kommt. Die Destillation wird noch 1–2 Min fortgesetzt und dadurch die Innenwand des Kühlerrohres ausgespült. Der Vorlagekolben wird hierauf abgenommen und sein Inhalt in Gegenwart von 5–10 Tropfen 0.3%-ige alkoholische Thymolblau als Indikator mit 0.1 bzw. 0.01 *N* Salzsäure titriert. Beim Arbeiten im 0.01 *N* Massstabe wird das Flüssigkeitsvolumen im Vorlagekolben vor der Rücktitration des Bariumhydroxyd-Überschusses mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Bei der Titration soll die Masslösung unter lebhaftem Rühren tropfenweise zugegeben werden. In der Nähe des Endpunktes (beim Verblassen der blauen Farbe) wird der Kolben verschlossen und die Lösung energisch durchgeschüttelt. Diese Operation wird während der Titration (bis zum Erscheinen der grünen Farbe) einige Male wiederholt.

Beim Arbeiten im 0.01 *N* Massstabe (bei der Bestimmung von 0.6–0.06 mg organisch gebundenen Kohlenstoff) müssen täglich Blind-Destillationen und- Titrationen durchgeführt werden. Im 0.1 *N* Massstabe genügt bei Verwendung der gleichen Reagenzien, eine einzige Blind-Probe. Mit reinen Reagenzien beträgt der Fehler bei der Titration nicht mehr als 0.05 ml 0.1 *N* Salzsäure. Bei Bestimmungen im 0.1 *N* Massstabe führen wir täglich blinde Titrationen durch, d.h. wir titrieren parallel mit den Bestimmungen jeweils 15.00 ml, mit 5 ml Pentan überschichtete Bariumhydroxydlösung in Gegenwart von 5–10 Tropfen Thymolblau-Indikatorlösung mit 0.1 *N* Salzsäure. Der Gehalt an organischen Stoffen ergibt sich aus der Differenz der Titrationen.

1 ml 0.1 *N* Salzsäure entspricht 0.605 mg organischem Kohlenstoff.

ZUSAMMENFASSUNG

Zur Feststellung des Gehalts wässriger Lösungen an organischen Substanzen wird die Menge des bei der totalen Oxydation gebildeten Kohlendioxyds bestimmt. Das Kohlendioxyd wird mit Hilfe der sogenannten „blasenfreien Destillation" in mit Pentan überschichteter Bariumhydroxydlösung aufgefangen und der Überschuss der Base titriert. Es kann nach dieser Methode 6–0.06 mg organisch gebundener Kohlenstoff im 0.1 bzw. 0.01 *N* Massstabe bestimmt werden.

SUMMARY

Organic materials in aqueous solution are determined by the carbon dioxide formed by complete oxidation. This is distilled in a special apparatus into barium hydroxide solution covered with pentane and the excess of alkali titrated. 0.06–6 mg of organic carbon can be determined.

RÉSUMÉ

Une méthode par oxydation est proposée pour le dosage de substances organiques, en solution aqueuse. L'anhydride carbonique, distillé dans un dispositif spécial, est recueilli dans une solution d'hydroxyde de baryum, recouverte d'une couche de pentane. On titre l'excès d'alcali par l'acide chlorhydrique.

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DETERMINATION OF FORMATES BY OXIDATION WITH IODINE

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INTRODUCTION

Several oxidants have been used for oxidising formic acid quantitatively. A method has been described[1] in which the hot alkaline solution is titrated with standard potassium permanganate solution; the detection of the end-point is difficult owing to formation of manganese dioxide. This trouble is avoided in Stamm's method[2], which is, however, seldom used.

Various methods involving mercuric chloride as oxidant have been proposed. AUERBACH AND PLÜDDEMANN[3] added excess of mercuric chloride solution and titrated the excess with iodide solution. A gravimetric procedure[4] involves weighing the calomel formed during oxidation. FUCHS[5], OLDEMAN[6] and BOSE[7] determined neutral formate solutions by oxidation with mercuric chloride and titration of the acid produced during oxidation; the carbon dioxide liberated in the reaction interferes. VERMA AND BOSE[8] titrated the calomel produced with standard potassium iodate solution. Bromine has also been used[1,9] as the oxidant for formic acid.

The use of iodine as oxidant has been tested for the first time in the present work and excellent results have been obtained. The method is based on the reaction:

$$HCOONa + I_2 = NaI + HI + CO_2$$

This may be applied for the determination of formates in two ways: determination of the hydriodic acid produced, or determination of the amount of iodine consumed. The former method has been examined by VERMA AND BOSE[10] while the latter forms the basis of the procedure described here.

According to DHAR[11] the hydrogen ions formed during the oxidation of formate by iodine tend to retard the rate of the reaction. To avoid this, different substances were added as buffer, but sodium acetate, sodium carbonate, sodium bicarbonate, sodium tartrate, sodium potassium tartrate, potassium tartrate and potassium citrate reacted with iodine, causing severe interference. The addition of potassium hydrogen tartrate carried the formate-iodine reaction to completion without interference even at 100°. The proposed method consists of heating a neutral formate solution with a known excess of iodine solution for 40 min in presence of 1 g of potassium hydrogen tartrate; the residual iodine is finally titrated with thiosulphate solution.

EXPERIMENTAL

Standard solutions of sodium formate were prepared by dissolving different amounts of the salt in distilled water, after drying at 100° for 1 h.

RECOMMENDED PROCEDURE

Pipette 5–20 ml of a neutral formate solution containing 25–90 mg of formic acid into a 250-ml flask, and add 1 g of solid potassium hydrogen tartrate and a measured excess of standard iodine solution. (For X ml of 0.1 *M* formate, 2 X ml of 0.2 *N* iodine solution proved suitable.) Attach a 100-cm water condenser by a ground glass joint to the flask and place the flask in an electric water bath at 25°. Cover the upper end of the condenser with an inverted 10-ml beaker. Switch on the bath, heat to boiling during 15–20 min and then heat for a further 25 min. Remove the flask from the bath and cool. Wash the condenser thoroughly with 5% potassium iodide solution to transfer any iodine particles to the flask. Titrate the residual iodine with standard 0.1 *N* thiosulphate solution using starch indicator. Carry out a blank determination in a similar manner.

RESULTS

Determination of amounts of sodium formate varying from 23–92 mg showed that the accuracy of the method is 0.5% or better. The effects of increases in the amounts of water and iodine and of changes in the time of heating and pH were studied. The following tests were made.

(*a*) 10 ml of 0.1 *M* sodium formate, 1 g of potassium hydrogen tartrate and 20 ml of 0.2 *N* iodine solution were taken, different amounts of water were added and formate was determined as described above. The addition of 10–50 ml of water did not affect the results.

(*b*) With the other conditions constant as in the above experiments the amount of 0.2 *N* iodine added was increased stepwise. Addition of 15–40 ml of 0.2 *N* iodine solution gave the correct results. The amount theoretically required is 10 ml hence even a four-fold excess did not affect the results.

(*c*) The period of heating was increased from 40–120 min without effect on the results. Heating for 30 min gave lower values.

(*d*) In several different procedures, *e.g.* determination of iodide after oxidation to iodate with bromine water, iodine must be titrated in presence of formic acid. Tests were therefore made to check the conditions under which iodine does not react with formic acid. The results obtained by titrating 10 ml of 0.2 *N* iodine in presence of 10 ml of 0.1 *M* sodium formate at different pH values and time intervals, are shown in Table I; the temperature was kept constant at 25°. Iodine and formate did not react significantly below pH 1.5 in under 30 min; an equimolecular mixture of formic acid (0.1 *N*) and iodine (0.2 *N*) reacted less than 0.5% in 15 min at 25°.

TABLE I

EFFECT OF pH AND TIME ON THE IODINE-FORMIC ACID REACTION

Initial pH	*% of formate decomposed*				
	15 min	*30 min*	*60 min*	*120 min*	*17 h*
7	2.0	4.0	6.5	11.0	41.0
3.56	2.0	3.0	5.5	10.0	39.0
2.1	1.25	2.5	5.5	8.0	30.0
1.85	0.75	2.0	3.5	5.2	25.5
1.54	0.0	0.25	1.0	2.0	10.5
1.24	0.0	0.0	0.0	0.0	2.25
0.85	0.0	0.0	0.0	0.0	0.75
0.64	0.0	0.0	0.0	0.0	0.0

INTERFERENCES

The interferences caused by salts of organic acids and various organic compounds were studied. In the tests, the effect of 0.2 g of the organic compound was examined with 10 ml 0.1 *M* sodium formate (68.0 mg) under the recommended conditions. No interference was found with methanol, ethanol, potassium citrate, the calcium salts of butyric, lactic and gluconic acids, the sodium salts of acetic, benzoic, boric and tartaric acids, or with benzaldehyde or glucose. In further tests, the sodium salts of phthalic, malic, maleic, fumaric, phenylacetic, aminoacetic and adipic acids (0.2 g of the acid) were shown not to interfere. Sodium oxalate and sodium salicylate caused errors of + 14.2 and + 28.2% respectively. Other interferences were sodium malonate, formaldehyde, acetaldehyde and salicylaldehyde; with malonate and acetaldehyde all the iodine was consumed.

DISCUSSION

Previous methods for the determination of formate by oxidation with mercuric chloride or other reagents have not been applicable in the presence of many organic salts. In the proposed method, the potassium hydrogen tartrate buffer removes the hydrogen ion formed during the oxidation and prevents interference from many organic salts which otherwise react with iodine at high temperatures; the pH of the solution on addition of the buffer is 3.56.

Apart from its improved selectivity, the proposed method has the advantages that the conditions are not critical, and that accurate results are readily achieved.

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SUMMARY

A selective determination of formates based on oxidation with iodine at 100° in presence of potassium hydrogen tartrate, and final titration with thiosulphate solution, is described. The error is below 0.5% for 25–90 mg of formic acid. Few other organic acids interfere.

RÉSUMÉ

Une méthode sélective est décrite pour le dosage des formiates, basée sur l'oxydation par l'iode à 100°, en présence d'hydrogénotartrate de potassium et titrage final au moyen de thiosulfate.

ZUSAMMENFASSUNG

Beschreibung einer selektiven Methode zur Bestimmung von Formiaten durch Oxydation mit Jod bei 100° in Gegenwart von saurem Kaliumtartrat und Titration des überschüssigen Jods mit Thiosulfatlösung.

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AMPEROMETRIC TITRATION OF COPPER WITH TETRAETHYLENEPENTAMINE

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INTRODUCTION

Ethylenepolyamines form stable complexes with certain metal ions and have consequently been recommended as titrants for cadmium, copper, zinc, lead, nickel and mercury ions. REILLEY AND SHELDON titrated these metal ions singly and in two-component mixtures with triethylenetetramine using metallochromic indicators[1] and by potentiometric end-point detection[2]. More recently REILLEY AND VAVOULIS introduced tetraethylenepentamine as a titrant in the potentiometric determination of mercury, copper, nickel, cadmium or zinc ions in presence of the alkaline earths, rare earths, aluminum, bismuth and lead[3]. Preliminary experiments with the dropping mercury electrode indicated that the titration also may be performed using amperometric end-point detection. This type of titration is advantageous because much smaller amounts of the metals can be determined than by the potentiometric method. In the present work the best conditions for the amperometric titration of copper and possible interferences from other metal ions have been investigated.

EXPERIMENTAL

Apparatus

A Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany) was used for recording polarograms and for the amperometric titrations. An external saturated calomel electrode (S.C.E.) served as reference electrode and was connected by means of a conventional agar bridge. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis.

Reagents

Triethylenetetramine (trien) was obtained as the disulphate from J. T. Baker Co., Philipsburg, N.Y. and standardized by complexometric titration[1]. Technical grade tetraethylenepentamine (tetren), obtained from Fluka AG., Switzerland, was purified and standardized as described by REILLEY[3]. The molarity was also checked by amperometric titration of a copper solution following the procedure given below. Pentaethylenehexamine (penten) was obtained as a mixture of amines designated "polyamine H Special" from Carbide and Carbon Chemicals, New York, and was purified and standardized as described by JONASSEN *et al.*[4] The remaining chemicals were of reagent grade and used without further purification. A 0.1 *M* stock solution of copper(II) was prepared by dissolving cupric chloride in redistilled water, and standardized by complexometric titration with EDTA. Less concentrated copper solutions were prepared by appropriate dilution of the stock solution. A 0.5 *M* acetic acid/ammonium acetate buffer of pH 4.1 was used as supporting electrolyte for the amperometric titrations. The buffer was prepared by mixing appropriate amounts of acetic acid and ammonia. Triton X-100, obtained from Rohm and Haas Co., Philadelphia, was found to be effective as maximum suppressor.

Preliminary tests

Current-voltage curves of copper, cadmium, lead and zinc in 0.5 *M* ammonia buffer showed that the half-wave potentials of the metal ions were shifted to more negative values upon addition of trien, tetren or penten to the supporting electrolyte. The diffusion current of the metal-ammonia complexes decreased linearly with the amount of reagent added. The diffusion current of simple copper ions decreased linearly upon addition of polyamines also in acidic medium,whereas the polarograms of cadmium, lead, and zinc in presence and in absence of polyamines, were identical, indicating a complete dissociation of these complexes in acid medium.

These preliminary experiments indicate that copper, lead, cadmium and zinc may be determined singly in alkaline solutions by amperometric titration with polyamines, and that copper may be titrated in acidic medium without interference from the other metal ions.

In order to find the best medium for the titration of copper in presence of other metals, polarograms of copper alone and in presence of trien, tetren and penten respectively, were recorded from supporting electrolytes of different pH. In solutions of pH below 4 the waves of the simple copper ions and of the copper polyamine complex were poorly separated and copper could not be determined accurately by titration at these low pH values. Titrations of copper in less acidic solutions showed that a large excess of nickel and zinc interfered when the pH of the supporting electrolyte exceeded 4.5. The best results for the amperometric titration of copper in presence of other metal ions was obtained from acetic acid/ammonium acetate buffer of pH 4.1. At this pH value, mercury is the only metal other than copper, that forms stable complexes with the ethylenepolyamines.

The copper complexes formed with tetren and penten are more stable than the corresponding trien complex and the sharpest end-point on the titration graph is obtained when tetren or penten is used as titrant. Tetren is more easily purified than penten, and the latter was not found to have any advantage over tetren as titrant. Consequently, tetren was preferred as reagent in the amperometric titration of copper. The technical grade tetren is contaminated with lower polyamines and, in order to obtain a sharp end-point, tetren should be purified as described by REILLEY[3].

The reaction between copper and tetren is very rapid and equilibrium conditions are obtained about 1 min after the addition of reagent. Based on the present results the following procedure is suggested.

Procedure

Transfer the sample solution to the cell, add 25 ml of acetic acid/ammonium acetate buffer of pH 4.1 and 1 ml of 0.1% Triton X-100, and deaerate the solution with oxygen-free nitrogen. Titrate with a tetren solution using an applied potential of —0.10 V *vs.* S.C.E., passing nitrogen through the cell for about 1 min after addition of reagent. Plot the titration results graphically (after correction for dilution) and determine the equivalence point from the L-shaped graph. Standardize the reagent by repeating this titration with known quantities of copper.

The results of some titrations of various amounts of copper following the above procedure are reported in Table I. As seen from the table, 0.1–1.5 mg copper can be determined with an accuracy of ± 1%.

TABLE I

TITRATION OF COPPER IN 0.5 *M* ACETATE BUFFER pH 4.1 WITH TETREN AT —0.10 V *vs.* S.C.E.

Copper taken, mg	*Added species, mg*	*Copper found, mg*	*Error %*
1.571		1.578	+ 0.4
0.571		0.572	+ 0.2
0.571		0.567	— 0.7
0.358		0.360	+ 0.6
0.358		0.359	+ 0.3
0.316		0.316	0
0.157		0.156	— 0.6
0.079		0.081	+ 2.5
0.157	30 Pb^{2+} 30 Cd^{2+} 30 Tl^{+} 15 Co^{2+} 15 Ni^{2+} 15 Zn^{2+}	0.158	+ 0.6
0.476	14 Fe^{2+} 14 Mn^{2+} 14 Cr^{3+}	0.475	— 0.2
0.476	30 MoO_4^{2-} 30 VO_4^{-} 30 CrO_4^{2-} Hydrazine sulphate	0.474	— 0.4
0.571	30 Mg^{2+} 30 Ca^{2+} 60 Sr^{2+} 60 Ba^{2+}	0.570	— 0.2
0.571	25 Al^{3+} 50 Bi^{3+} 50 Sn^{4+}	0.566	— 0.9

Interfering ions

In the titration of copper at pH 4.1 it was found that the results are not affected by: Cd^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Tl^{+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Sn^{4+} and MoO_4^{2-} in amounts 100 times greater than the amount of copper. Large excesses of anions such as nitrate, chloride, sulphate, etc., do not interfere in the titration. Cyanide interferes in the titration. The interferences from vanadate, chromate and iron(III) which give a cathodic wave at —0.10 V, can be avoided by addition of hydrazine sulphate which converts these metal ions to the reduced state. A large excess of hydrazine sulphate should be avoided, because the cathodic wave of the simple copper ions is shifted to more negative values. Tin(II) gives an anodic wave at —0.10 V and should be oxidized to the tetravalent state. Mercury, which is the only metal in addition to copper which forms a stable complex with tetren at pH 4, will interfere with the titration. Silver and platinum(IV) do not form complexes with tetren in acetic acid buffer, but the simple metal ions are reduced at a more positive potential than copper, hence large amounts interfere in the titration; amounts less than or equal to the amount of copper do not interfere.

In Table 1 the results of a few titrations of copper in presence of other metals are reported.

SUMMARY

Tetraethylenepentamine is a very selective titrant for the determination of copper in acidic medium. With amperometric end-point detection as little as 0.1 mg copper in a volume of 25 ml can be determined with an accuracy of ± 1%. When the titration is performed in acetic acid/ammonium acetate buffer of pH 4.1, only mercury causes significant interference.

RÉSUMÉ

Une méthode est décrite pour le dosage ampérométrique du cuivre au moyen de tétraéthylènepentamine. Au pH 4.1, seul le mercure peut gêner.

ZUSAMMENFASSUNG

Beschreibung einer amperometrischen Methode zur Bestimmung von Kupfer mit Tetraäthylenpentamin. Bei pH 4.1 wird die Reaktion nur von Quecksilber beeinflusst.

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EXTRACTION DU CÉSIUM, SOUS FORME DE TÉTRAIODOBISMUTHITE, PAR LE NITROBENZÈNE

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L'extraction du césium en phase aqueuse par les solvants organiques peut être d'une importance considérable. Si le coefficient de partage est suffisamment grand, ce procédé permet un enrichissement préliminaire du césium dans des solutions peu radioactives (retombée radioactive, etc.). D'autre part, si la sélectivité est suffisante, cette méthode peut être employée pour la séparation du césium d'avec d'autres produits de fission.

Nous avons examiné le comportement du tétraiodobismuthite et de son dérivé avec le césium et effectué des recherches pour déterminer les coefficients de partage entre l'eau et d'autres solvants organiques. En se basant sur les résultats obtenus, nous proposons une méthode d'extraction du césium par une solution de tétraiodobismuthite dans le nitrobenzène, non décrite jusqu'à présent.

PARTIE EXPÉRIMENTALE ET RÉSULTATS

Mode opératoire

Nous avons utilisé des produits chimiquement purs pour analyse, de l'eau tridistillée et des solvants organiques (voir tableau I) rectifiés. La solution aqueuse de tétraiodobismuthite a été préparée de la façon suivante: 1 g de protoxyde de bismuth, 10 ml d'une solution saturée d'iodure de sodium, 12 ml d'acide acétique glacial et de l'eau

TABLEAU I

EXTRACTION DU TÉTRAIODOBISMUTHITE DE CÉSIUM PAR LES SOLVANTS ORGANIQUES

	Constante diélectrique	q_{Cs}
Nitrobenzène	36.1	0.55
Méthylcyclohexanone	12–14	0.51
Méthylisobuthylcétone	13.1	0.47
Acétylacétone	23.8	0.30
Nitrotoluène	—	0.22
Ether acétylacétique	15.9	0.20
Cyclohexanone	18.2	0.057
Acétate d'éthyle	6.4	0.033
Aniline	7.0	0.033
Alcool amylique	15.8	0.022
Chloroforme	4.8	0.01
Ether éthylique	4.3	0.01
Benzène	2.2	0.01
Hexane	4.0	0.01

distillée de façon à obtenir un volume de 200 ml; mélanger pendant 4 heures. Après 20 heures de repos, la solution est filtrée et additionnée de 0.5 ml d'acide acétique.

Les radioisotopes utilisés sont les suivants: ^{137}Cs, ^{86}Rb, ^{89}Sr, ^{91}Y, ^{95}Zr, (^{95}Nb), ^{106}Ru, ^{137}Cs sans entraîneur avec pureté radiochimique de 99.5%, ^{89}Rb sous forme de carbonate avec activité spécifique de 50 mC/g. Les autres isotopes ont été employés avec entraîneur inactif sous forme de nitrate, en vérifiant chaque fois que l'échange isotopique soit complètement effectué.

Les deux phases de deux ml chacune ont été agitées chaque fois pendant une demi-heure au moyen d'un agitateur de verre, afin d'obtenir l'équilibre. Bien que les deux phases se séparent très vite (moins d'une minute), les solutions ont été encore centrifugées avant la prise des échantillons. La radioactivité a été mesurée de la façon habituelle[1]. Du rapport des radioactivités (de la phase organique et de la phase aqueuse) on a pu en tirer le coefficient de partage. La concentration en acide dans la phase aqueuse, à l'équilibre, a été déterminée par titrage.

Choix du solvant organique

Des traces de ^{137}Cs ont été ajoutées à la solution aqueuse de tétraiodobismuthite; 2 ml de cette solution ont été mis en équilibre avec un même volume de solvant. Le coefficient de partage a ensuite été déterminé; les résultats sont indiqués dans le tableau I.

Il est évident que la capacité d'extraction du césium augmente avec la constante diélectrique du solvant choisi. L'explication de ce phénomène et la bonne extractibilité du césium par le nitrobenzène a déjà été donnée[2].

Préparation de la solution d'extraction

Pour éviter une hydrolyse du sel de bismuth, on préfère utiliser une solution de nitrobenzène contenant le complexe de bismuth iodé. On prépare cette solution d'extraction à partir de protoxyde de bismuth et d'iodure de sodium. Ce n'est qu'après addition d'acide acétique à 70% que le complexe rouge bien connu se forme et peut s'extraire dans le nitrobenzène. Un acide acétique plus dilué ne dissolverait pas complètement le protoxyde de bismuth et un acide acétique plus concentré ne formerait qu'une phase avec le nitrobenzène. On pourrait utiliser également les acides sulfurique, nitrique et chlorhydrique, mais une partie de bismuth se sépare sous forme de triiodure (12.4 mg Bi_2O_3 pour 1 ml d'acide normal). Parfois cependant, il serait préférable d'utiliser des acides minéraux car l'acide acétique se dissout partiellement dans le nitrobenzène et se réextrait après traitement de la solution de nitrobenzène à l'eau[3]. Si l'on change les proportions du protoxyde de bismuth et de l'iodure de sodium, le volume de l'acide acétique utilisé (70%) doit toujours représenter les 40% du volume de nitrobenzène.

D'autre part, les essais sur la distribution du césium ont montré que la solution aqueuse doit contenir une certaine concentration d'iodure pour éviter la formation d'un dépôt de triiodure de bismuth. On a toujours ajouté l'iodure de sodium à la phase aqueuse, à une concentration de 0.025 *M*.

Lors des études détaillées de l'influence de la préparation de la solution d'extraction sur la séparation des traces de césium, nous avons pu faire les conclusions suivantes:

(1) Les coefficients de partage se trouvent compris entre 3 et 12 et dépendent générale-

ment peu de la quantité des deux composants utilisés pour la préparation de la solution d'extraction.

(2) L'augmentation du rapport moléculaire I : Bi, au-dessus de 4 : 1, conduit à une diminution du coefficient de partage.

(3) Le rapport moléculaire I : Bi = 4 et la proportion de 5.6 mg Bi_2O_3 pour 1 ml de nitrobenzène ont fourni les coefficients de partage les plus élevés. La solution d'extraction utilisée correspondant approximativement à $2 \cdot 10^{-2}$ *M* $HBiI_4$ et à l'acide acétique 2 *M*, est stable pendant plusieurs mois.

Coefficient de partage en fonction de la composition de la phase aqueuse

D'après nos essais préliminaires, l'extraction doit se faire en milieux relativement fortement acides, ce qui n'est pas possible de réaliser lors de l'extraction avec le dipicrylaminate[1,4] et le tétraphénylborate[5,6]. C'est pourquoi nous avons suivi l'influence de la concentration de l'acide sur la phase aqueuse en équilibre. Les résultats obtenus sont indiqués dans le tableau II, ainsi que l'influence de l'iodure de sodium.

TABLEAU II

COEFFICIENTS DE PARTAGE q_{Cs} EN FONCTION DE LA COMPOSITION DE LA PHASE AQUEUSE

Iodure de sodium[a] *(mole/l)*	*Acide acétique*[b] *1.5 N*	*Acide acétique*[b] *4.4 N*	*Acide nitrique*[b] *0.7 N*	*1.4 N*
		q_{Cs}		
0.05	12.0	8.6		
0.07	10.2	7.1		
0.09	8.5	5.8	3.6	2.6
0.11	7.2	4.6		
0.13	6.1	3.3		
0.15	4.8			
1.0	0.32			

[a] Solution aqueuse initiale
[b] Phase aqueuse d'équilibre

Il est évident que pour une augmentation de la concentration d'iodure de sodium, le coefficient de partage q_{Cs} diminue. La concentration en sodium ne joue pas de rôle, l'influence de la concentration en sulfate de sodium jusqu'à 0.5 *N* étant pratiquement nulle. Ce sont en effet les ions iodures qui interviennent; ceux-ci formant des ions BiI_6^{3-} (éventuellement BiI_5^{2-}) dont l'existence dans des solutions d'iodure libre à une concentration supérieure à 0.01 *M* a déjà été constatée[7]. Des essais ont montré que la limite inférieure de la concentration en iodure de sodium (formation du dépôt de triiodure de bismuth) correspond approximativement, suivant les conditions expérimentales d'essai, à une concentration en NaI de $1 \cdot 10^{-2}$ *M* et augmente pour une concentration plus élevée en acide.

Nous avons examiné ensuite l'influence du rubidium sur l'extraction du césium.

Séparation du césium d'avec quelques produits de fission de longue période et d'avec le rubidium

Les essais ont été effectués avec des échantillons dont la composition répondait à celle des solutions aqueuses, obtenues après la séparation de l'uranium.

La composition de la solution utilisée et les coefficients de partage obtenus sont les suivants: H^+, 0.4 N; NO_3^-, 1.3 N; Cl^-, 0.3 N; Al^{3+}, 0.3 M; Fe^{3+}, 0.1 M; Na^+, 0.25 N; I^-, 0.25 N; Cs, 20 mg/l, $q_{Cs} = 13$; Sr^{2+}, 6.7 mg/l, $q_{Sr} = 2 \cdot 10^{-3}$; Y^{3+}, 54 mg/l, $q_Y = 8 \cdot 10^{-3}$; Zr^{4+}, 21 mg/l, $q_{Zr} = 3 \cdot 10^{-3}$; Ru (nitrate de nitrosyle) 10 mg Ru/l, $q_{Ru} = 5 \cdot 10^{-3}$.

On voit que la séparation de ces produits de fission est relativement bonne.

D'autre part, il nous a semblé intéressant d'examiner la séparation du césium et du rubidium par extraction de leurs tétraiodobismuthites. Les coefficients de partage q_{Cs} et q_{Rb} obtenus sont donnés dans le tableau III. On constate que le facteur de séparation est indépendant de leur quantité relative, ce qui permet d'appliquer une simple séparation par extraction graduelle. Notons encore que $\sqrt{q_{Cs} \cdot q_{Rb}} \simeq 1$.

TABLEAU III

Concentration initiale en iodure de sodium, 0.06 M

Concentration initiale en rubidium (mole)	*Concentration initiale en césium (mole)*	q_{Cs}	q_{Cs}/q_{Rb}
$3.8 \cdot 10^{-2}$	Traces	1.34	4.2
$1.9 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	1.49	4.0
Traces	$1.2 \cdot 10^{-2}$	3.55	4.7

Réextraction du césium en phase aqueuse

Dans ce cas, on peut utiliser des solutions aqueuses d'iodure en forte concentration; mais nous avons examiné encore la possibilité suivante:

La solution d'extraction de nitrobenzène est diluée dans un rapport 1:1 (en volume) par un solvant choisi; on vérifie le coefficient de partage q_{Cs} entre le solvant et la solution aqueuse renfermant NaI 0.25 M et HNO_3 0.2 N. On détermine ensuite les valeurs de q_{Cs} en fonction du solvant nitrobenzène 10.2; éther éthylique 0.10; acétate d'éthyle 0.78; méthylisobutylcétone 0.23; alcool isoamylique 0.078. Les résultats obtenus montrent que l'éther ou l'alcool isoamylique sont les plus avantageux. Il serait même possible de régénérer la solution d'extraction en chassant le solvant le plus volatil.

Extraction du césium à l'aide de la solution de tétraiodobismuthite et de nitrobenzène en présence de réducteurs et d'oxydants

Au cours des essais d'extraction du tétraiodobismuthite de césium, de l'iode élémentaire peut se former. Nous avons voulu examiner son influence sur les résultats obtenus, le polyiodure de césium étant soluble dans le nitrobenzène[8].

Pour cela, nous avons fait barbotter un courant d'anhydride sulfureux dans la phase aqueuse avant extraction, pour réduire l'iode éventuellement libéré. Le coefficient de partage q_{Cs} n'a pratiquement pas changé. Ces résultats permettent de conclure que l'iode qui peut se dégager éventuellement est sans influence. Par contre, en présence de fer(III) dans la phase aqueuse, le coefficient de partage q_{Cs} augmente considérablement à la suite du dégagement d'iode, suivant la réaction:

$$2\,I^- + 2\,Fe^{3+} = I_2 + 2\,Fe^{2+}$$

CONCLUSIONS

La méthode d'extraction proposée permet de concentrer le césium des solutions aqueuses diluées et de le séparer des produits de fission de longue période les plus importants. La séparation quantitative du rubidium n'est pas possible avec une seule extraction, mais le facteur de séparation établi permet une séparation par extraction graduelle. Le principal avantage de la méthode est la possibilité d'extraction du césium même en solutions acides.

RÉSUMÉ

Une extraction du césium en solution aqueuse est décrite au moyen d'une solution nitrobenzènique de tétraiodobismuthite. L'influence des conditions d'extraction sur l'efficacité du procédé a été étudiée. Les coefficients de partage obtenus varient de 3 à 12. Par ce procédé, il est possible de séparer le césium d'avec les produits de fission importants.

SUMMARY

Caesium can be extracted from aqueous solutions with a solution of tetraiodobismuthite in nitrobenzene. The optimum conditions for the extraction have been studied. Caesium can be separated from most important fission products.

ZUSAMMENFASSUNG

Cäsium kann aus wässriger Lösung mit Tetrajodowismutit in Nitrobenzol extrahiert werden. Die Bedingungen für eine optimale Extraktion werden angegeben. Anwendung der Methode zur Abtrennung des Cäsiums aus Spaltprodukten.

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THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART II*. EXTRACTION BEHAVIOUR AND SPECTRA OF THE REAGENTS

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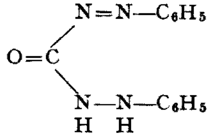
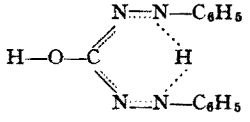
Although diphenylcarbazide and diphenylcarbazone have been used in analytical chemistry for many years, very little is known about the composition and stability constants of the colored complexes they can form with certain cations and about the behaviour of diphenylcarbazone as an acid. Cazeneuve[1] and Bamberger[2,3] reported that diphenylcarbazone can split off only one proton to form the mono-sodium or -potassium salt, which would prove diphenylcarbazone to be a monobasic acid, while the carbazide did not form the corresponding salt.

The sodium salt of diphenylcarbazone is strongly colored; Bamberger[2] takes this fact to indicate that diphenylcarbazone is present in the enolic form in this compound.

From the ultraviolet spectrum Grammaticakis[4] concluded that in alcoholic solution both reagents resemble azo compounds and differ from formazanes, so that in the tautomeric equilibrium between the ketonic(I) and enolic form(II) of the carbazone, postulated by many authors[5], the first component is in excess:



(I)



(II)

In 1937 Krumholz and Krumholz[6] found that the commonly used diphenylcarbazone, the oxidation product of the carbazide, was a mixture of both substances. They succeeded in separating the carbazone from the carbazide.

We have established by titration with base that diphenylcarbazone behaves as a monobasic acid. Furthermore, from spectrophotometric measurement of the partition of the carbazone between carbon tetrachloride and water at various pH values the dissociation constant of the acid could be evaluated: $2.9 \cdot 10^{-9}$. Irving *et al.*[7] and Sandell[8] used this method to determine the corresponding constant of dithizone. The solubilities and spectra of diphenylcarbazone in carbon tetrachloride and toluene were also studied.

All the constants given in this paper are expressed in concentrations instead of activities; only the hydrogen ion concentration is given as an activity (from pH measurement). All experiments were performed at room temperature (21–23°).

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* Part I: *Anal. Chim. Acta*, 25 (1961) 507.

EXPERIMENTAL

Commercial diphenylcarbazone (pro analyse) was purified according to KRUMHOLZ[6]. Diphenylcarbazide (pro analyse) was recrystallized from alcohol.

The solvents, carbon tetrachloride and water, and the other chemicals used were all of analytical purity. Sodium perchlorate solutions were made by neutralization of perchloric acid with sodium hydroxide. Toluene was made methylthiophene-free by refluxing with a sodium-potassium alloy[9].

Separatory funnels were equipped with teflon stoppers and stopcocks. The pH was measured with a Philips PR 9400 pH-meter. Extinction measurements were made on a Unicam SP 500 spectrophotometer in 1 cm quartz cuvettes. Infra-red spectra were recorded on the Perkin-Elmer Infracord for the carbazone itself and the sodium salt in KBr discs.

RESULTS

Solutions of diphenylcarbazone in carbon tetrachloride (10^{-3} – 10^{-5} M) and in toluene ($5 \cdot 10^{-3}$–10^{-5} M) obey Beer's law. Fig. 1 gives the spectra of the carbazone. Table I

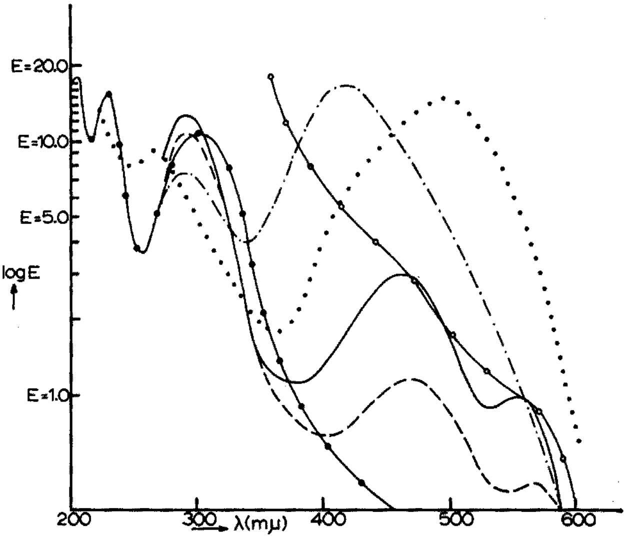

Fig. 1. Spectra of diphenylcarbazone and diphenylformazane. —— 10^{-3} M diphenylcarbazone in carbon tetrachloride. – – – 10^{-3} M diphenylcarbazone in toluene. .... 10^{-3} M diphenylcarbazone anion in water, pH = 10.5. –•–•–•– 10^{-3} M diphenylcarbazone in water, pH = 1.0 (converted). –○–○–○– 10^{-2} M diphenylcarbazone in water, pH = 1.0 (converted from a saturated solution, 4-cm cuvettes). —·—·— 10^{-3} M N,N′-diphenylformazane in toluene.

TABLE I

ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS OF DIPHENYLCARBAZONE

Carbon tetrachloride		*Toluene*	
λ_{max}	ε	λ_{max}	ε
288 mμ	$(12.5 \pm 0.5) \cdot 10^3$ cm^{-1} mole^{-1} l	289 mμ	$(10.8 \pm 0.1) \cdot 10^3$ cm^{-1} mole^{-1} l
465 mμ	$(3.04 \pm 0.05) \cdot 10^3$ cm^{-1} mole^{-1} l	467 mμ	$(1.21 \pm 0.05) \cdot 10^3$ cm^{-1} mole^{-1} l
555 mμ	$(0.91 \pm 0.06) \cdot 10^3$ cm^{-1} mole^{-1} l	565 mμ	$(0.47 \pm 0.02) \cdot 10^3$ cm^{-1} mole^{-1} l

gives the wavelengths of maximum absorption for both solvents as well as the molar extinction coefficients. Care was taken to keep the solutions in the dark because irradiation alters the spectrum.

With the data given above, the saturation concentrations were measured spectrophotometrically and were found to be $2.75 \cdot 10^{-3}$ *M* in carbon tetrachloride and $1.0 \cdot 10^{-2}$ *M* in toluene.

To evaluate the partition quotient for undissociated diphenylcarbazone between water and the two solvents, 225 ml of water was shaken with 15 ml of the organic phase containing the carbazone in varying concentrations. In all extraction experiments the solvents of both phases were mutually saturated beforehand.

The extinction was measured before (E) and after (E') the shaking. Equilibrium was attained after 5 min of shaking. $p_{\text{org.}}$ = (diphenylcarbazone)$_{\text{org.}}$/(diphenylcarbazone)$_{\text{water}}$ was calculated from $p = E'/(E-E') \times 225/15$. Table II gives p_{CCl_4} for various pH values and compositions of the aqueous phase. The pH was kept low to prevent complex formation with traces of metal ions and acid dissociation of the carbazone. For toluene, the partition coefficient proved to be independent of ionic strength in a perchlorate medium (0.1–1 *M*). The value 39 ± 2 was found.

TABLE II

PARTITION OF DIPHENYLCARBAZONE BETWEEN CCl_4 AND WATER

pH	*Solutes in the aqueous phase*	p_{CCl_4}
0.77	only $HClO_4$	7.4
0.95	only $HClO_4$	7.3
1.08	$HClO_4$ + $NaClO_4$, 0.1 *M in toto*	6.7
1.10	$HClO_4$ + $NaClO_4$, 0.1 *M in toto*	7.4
1.12	$HClO_4$ + $NaClO_4$, 0.1 *M in toto*	7.2
1.51	$HClO_4$ + $NaClO_4$, 0.1 *M in toto*	8.4
2.90	$HClO_4$ + $NaClO_4$, 0.1 *M in toto*	8.4
0.97	$HClO_4$ + $NaClO_4$, 1.1 *M in toto*	7.9
1.28	$HClO_4$ + $NaClO_4$, 1.1 *M in toto*	7.1
0.81	H_2SO_4 only	10.5
0.82	H_2SO_4 only	9.5
0.79	H_2SO_4 + Na_2SO_4, 1.1 *M in toto*	21.2
0.77	H_2SO_4 + Na_2SO_4, 1.1 *M in toto*	19.8

100 ml of a 10^{-3} *M* solution of diphenylcarbazone in an alcohol-water mixture (20:80 v/v) was titrated with $1.3 \cdot 10^{-2}$ *N* barium hydroxide. The curve did not show any steep rise; the only equivalence point occurred at pH 9.6, when one equivalent of base was consumed, hence the carbazone behaves as a monobasic acid. Diphenylcarbazide did not consume any base.

The sodium diphenylcarbazonate was isolated by partial evaporation of the basic solution prepared by dissolving the carbazone in water at pH 10.5; 10^{-4} *M* potassium cyanide was added to complex traces of metals. After filtration, washing with a little water and drying, the salt was treated with sulphuric acid to yield sodium sulphate. Weighing the sulphate confirmed the sodium diphenylcarbazonate as the monosodium salt.

The infra-red spectrum of the sodium salt did not contain the C=O band, whereas for diphenylcarbazone itself this band was found at 5.85 μ, lying in the region of the amide compounds (5.80–6.15 μ).

To evaluate
$$K_{diss.} = \frac{(H^+)(HD^-)}{(H_2D)}$$

(H_2D = diphenylcarbazone, HD^- = anion), equal volumes of solutions of diphenylcarbazone in carbon tetrachloride were shaken with aqueous phases of various pH values greater than 7.5. It proved to be necessary, even for water of AnalaR quality to add potassium cyanide (up to 10^{-4} M) to prevent complex formation of the reagent with traces of metal ions at these pH values. The ionic strength of the water phase was kept constant at 0.1 N $NaClO_4$. The system attained equilibrium within 1 min. From extinction measurements on the carbon tetrachloride phase before (E) and after (E') shaking, $K_{diss.}$ was calculated:

$$\frac{E'}{E-E'} = \frac{p_{CCl_4}(H^+)}{(H^+) + K_{diss.}}$$

(H^+) was measured after the equilibration. The water used was made oxygen-free by bubbling nitrogen through the solution. pH measurements were also made in a nitrogen atmosphere. Fig. 2 gives the percentage of carbazone in the organic phase as a function of the pH. From these values we calculated $K_{diss.}$ to be $(2.9 \pm 0.3) \cdot 10^{-9}$. In a previous short communication[10] erroneously the value $(2.2 \pm 0.2) \cdot 10^{-8}$ was mentioned.

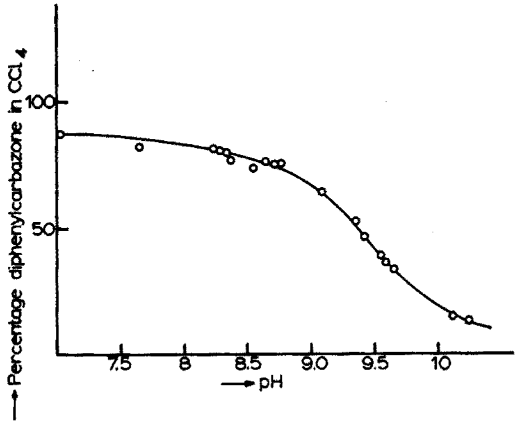

Fig. 2. Partition of diphenylcarbazone between carbon tetrachloride and water ($V_{CCl_4} = V_{water}$) in the pH range 7.0–10.5.

The concentration of a saturated solution of the carbazone in water (pH = 1.00 with perchloric acid) was determined by extraction of the reagent with toluene; it proved to be $3.8 \cdot 10^{-4}$ M.

DISCUSSION

Comparison of the spectra of diphenylcarbazone in water and diphenylformazane in toluene leads to the same conclusion as GRAMMATICAKIS has drawn for the alcoholic solutions. The carbazone in aqueous solution does not resemble the formazane in toluene solution. Solutions of diphenylcarbazone in carbon tetrachloride and toluene, however, give a different spectrum: the visible spectrum shows two absorption bands, a strong one at 450–470 mμ, and a weaker one at 550–570 mμ. In the spectrum of the aqueous solution these two maxima have weakened to 2 shoulders on the 300 mμ band.

In toluene or carbon tetrachloride solutions diphenylcarbazone seems to resemble the formazane more than it does in aqueous or alcoholic solution. This may indicate that a considerable part of the carbazone is present in the enolic form (II) in carbon tetrachloride and toluene. In this case the absorption at 550–570 mμ that is missing in the anion and in the formazane, is probably due to the ketonic form (I). Concordant with this conclusion is the absence of the C=O band in the infra-red spectrum of the solid sodium diphenylcarbazonate, an indication that the enolic form is the only form present in the solid salt. BAMBERGER[3] has already proposed, and given evidence for, this structure for the sodium salt.

In this case $K_{\text{diss.}} = 2.9 \cdot 10^{-9}$ is not the true dissociation constant, because it is reasonable to assume that (I) will rearrange into (II) before forming the anion. If K_{enol} is the enolisation constant for (I) $\rightleftarrows$ (II), then

$$K_{\text{diss.enol}} = \frac{K_{\text{enol}}}{K_{\text{enol}} + 1} K_{\text{diss.}}$$

The partition of diphenylcarbazone between carbon tetrachloride and water is strongly influenced by sulphate anions (Table II). The increase in the partition coefficient indicates a decrease in the solubility of the carbazone in sulphate solutions. Perchlorates have no influence; in this case, p_{CCl_4} is constant at 7.5 ± 0.5.

From the data given, the solubility of diphenylcarbazone in water appears to be $3.7 \cdot 10^{-4}$ (from p_{CCl_4}) or $2.7 \cdot 10^{-4}$ mole/l (from p_{toluene}) in 0.1–1 M $NaClO_4$. Direct measurement gives $3.8 \cdot 10^{-4}$ mole/l, so for the toluene-water system the value found is too low, which indicates that p_{toluene} will decrease at carbazone concentrations of about 10^{-2} M.

ACKNOWLEDGEMENT

Some of the experiments described were performed by Mr. TJ. HOMSMA AND Mr. J. KLEINE DETERS.

SUMMARY

Extraction experiments in the carbon tetrachloride-water system for diphenylcarbazone above pH 7.5 give a value of $(2.9 \pm 0.3) \cdot 10^{-9}$ for the dissociation constant. At lower pH values the partition coefficients were found to be 7.5 for carbon tetrachloride-water and 39 for toluene-water in 0.1–1 M $NaClO_4$. The solubility of the carbazone in water is $3.8 \cdot 10^{-4}$ M in acid perchlorate medium.

Spectra of diphenylcarbazone in water, toluene and carbon tetrachloride, of the anion in water and of diphenylformazane in toluene are compared. In the infra-red spectrum the C=O band was present in the carbazone, but not in the sodium salt.

RÉSUMÉ

Les auteurs ont effectué une étude sur la diphénylcarbazone: extraction dans les systèmes tétrachlorure de carbone-eau et toluène-eau; solubilité dans l'eau; mesures spectrophotométriques.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von Diphenylcarbazon im System Tetrachlorkohlenstoff-Wasser und Toluol-Wasser mit Angabe der Verteilungskoeffizienten, Löslichkeit in Wasser und Absorptionsspektren.

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Short Communications

A general formula for the calculation of pH of acids and bases

All the methods proposed for the calculation of the pH of aqueous solutions of acids and bases are characterised by different difficulties. They refer only to the case of a strong or a weak acid and there is a real need for a formula for the pH-calculation of a fairly strong acid or base. Moreover, different calculations have to be used for different acidity or basicity constants and original concentration, while in many cases the influence of the water is not taken into account.

After a complete calculation in which the problem of the formation of protons was solved separately from that of the influence of the water, it is possible to propose a new general formula for the pH-calculation of all acids (with acidity constant K) at all concentrations (original normality N); the proton activity $[H^+]$ of the aqueous solution is given by

$$[H^+] = \frac{\sqrt{KN}}{2}\left(\frac{\sqrt{K+4N}-\sqrt{K}}{\sqrt{4N}}\right) + \frac{1}{2}\sqrt{KN\left(\frac{\sqrt{K+4N}-\sqrt{K}}{\sqrt{4N}}\right)^2 + 4\cdot 10^{-14}}$$

The same formula is used for the calculation of the $[OH^-]$ activity of an aqueous solution of a base, replacing K by K' (basicity constant) and N by N' (original normality of the base).

The origin of this formula will fully be discussed in a further communication.

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On the preferential formation of platinum oxides at the grain boundaries of platinum electrodes

A recent inquiry into the role of platinum surface oxides in electrode kinetics indicated that the platinum oxide tended to concentrate on the grain boundaries. This was based on a study of photomicrographs of platinum electrode surface wich had been subjected to chemical and electrical reduction and oxidation[1]. More recently the photomicrographic evidence of preferential grain boundary attack has been used to supplement certain conclusions regarding the oxidation of both platinum and gold surfaces[2,3]. While we do not argue that grain boundary attack may or may not occur during oxidation of platinum surfaces, we do contend that evidence of such a surface reaction has not yet been obtained by ordinary visual photomicrography.

In the previous study two photomicrographs of the surface of a non-electropolished platinum foil electrode were taken at a magnification of 600 ×. The first of these photomicrographs showed the surface of the electrode after it had been immersed in a solution of argentic oxide in 6 M nitric acid. The second showed the surface after it had been subjected to cathodic reduction at controlled potential in 1 M sulfuric acid. It was stated that the only noticeable difference between the surfaces of an oxidized and reduced electrode was that the grain boundaries appeared to be darkened in the case of the oxidized electrode. These results were taken to indicate that PtO and PtO_2 form principally at the grain boundaries.

It is necessary, however, to call attention to the fact that there are hardly any grain boundaries to be seen on these photomicrographs. There are, perhaps, the remnants of three grain boundaries near the top of each photomicrograph; the other marks on the surface are evidently scratches and pits produced during the rolling of the foil and in subsequent handling. The differences between the appearance of these remnants is no more than the differences between the scratches and pits. Such differences could easily be due to the focusing of the microscope.

In view of the uncertain nature of this evidence an investigation was carried out on the question of the formation of platinum oxide in the grain boundaries using an electropolished platinum microelectrode which had been prepared in this laboratory in connection with another problem in electrode kinetics[4]. On this electrode there was no uncertainty about the identification of the grain boundaries.

EXPERIMENTAL

The electrode was made from a platinum wire of high purity whose diameter before electropolishing was about one mm and whose length one inch. One end of this wire was threaded and screwed into the end of a brass rod. The brass rod served as a handle to avoid having to touch the wire and also provided electrical contact for electropolishing and polarization experiments. The electropolishing bath was a fused eutectic mixture of KCl-NaCl (50 mol per cent KCl)[5] contained in a platinum crucible. After electropolishing the platinum wire was sealed directly to a thin walled capillary which had been carefully slipped over the electropolished area under the microscope. This capillary was then sealed to a 6 mm glass tube.

The microscope used in these studies was a standard metallographic microscope manufactured by Cooke, Troughton and Sons, Leeds, England. A traveling stage combined with a rotatable chuck made it possible to locate repeatedly any given microscopic portion of the electrode surface.

Illumination was provided by an external xenon arc light with a green metallographic filter. A Leitz metallographic camera was used for the photographs and a Leitz stage micrometer for the determination of the magnification.

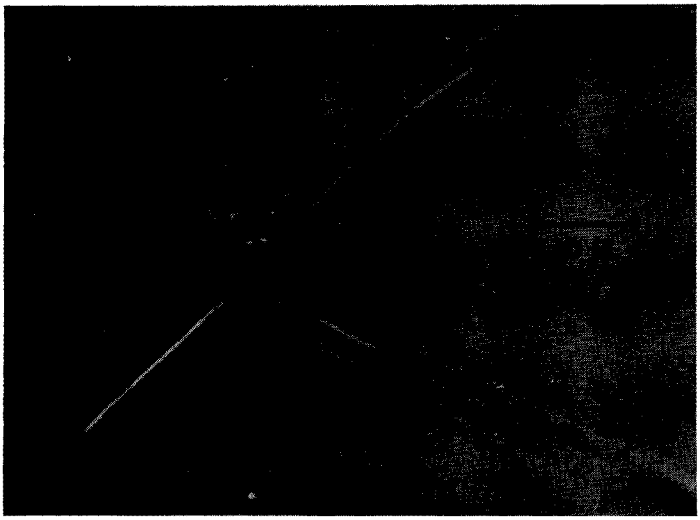

Fig. 1. Electropolished platinum electrode after cathodic reduction.

The electrode was first reduced at controlled potential for 10 min at −0.100 V *vs.* S.C.E. in 1 *M* sulfuric acid. Fig. 1 is a photomicrograph of a section of the surface of the electrode after this treatment. Next the electrode was immersed in a saturated solution of potassium dichromate in concentrated sulfuric acid for a period of 12 h. Fig. 2 is a photomicrograph of the electrode surface after this treatment.

It is well known that this treatment oxidizes a platinum electrode, yet there is no essential difference between the reduced and oxidized surfaces of the electropolished electrode. In fact, it was noticed that by very slightly changing the focus on the microscope it was possible, at will, to cause any grain boundary or section thereof to appear dark or bright.

Next, the oxide was stripped off the electrode by controlled potential reduction at −0.1 V *vs.* S.C.E. for 10 min and then a controlled potential polarization curve was run from zero to 2 V *vs.* S.C.E. A plateau with a very slight maximum occurred on this polarization curve between 0.820 and 1.20 V *vs.*S.C.E. Scanning in the cathodic direction from 2 V *vs.* S.C.E. produced a typical strip-off pattern at about 0.46 V.

The measured area under the anodic oxide formation pattern corresponded to

1.98×10^{-4} microequivalents. The area under the cathodic strip-off pattern corresponded to 2.38×10^{-4} microequivalents. Assuming that these quantities of electricity were due to the formation and stripping off of PtO and taking the area of the electrode to be 4.7 mm², one finds that these quantities of electricity correspond to uniform layers of PtO of thickness 3.0 and 3.6 Å respectively. Since the strip-off pattern would include any additional platinum oxide formed between 1.20 and 2.00

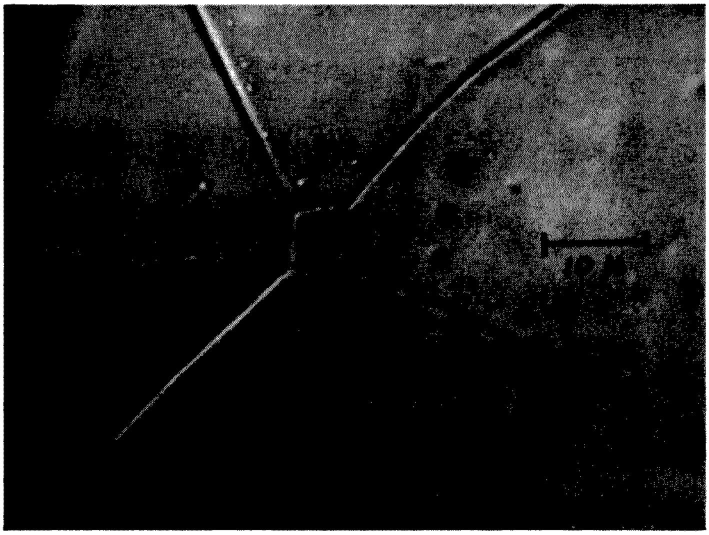

Fig. 2. Electropolished platinum electrode after 12 h in a saturated solution of $K_2Cr_2O_7$ in concentrated H_2SO_4.

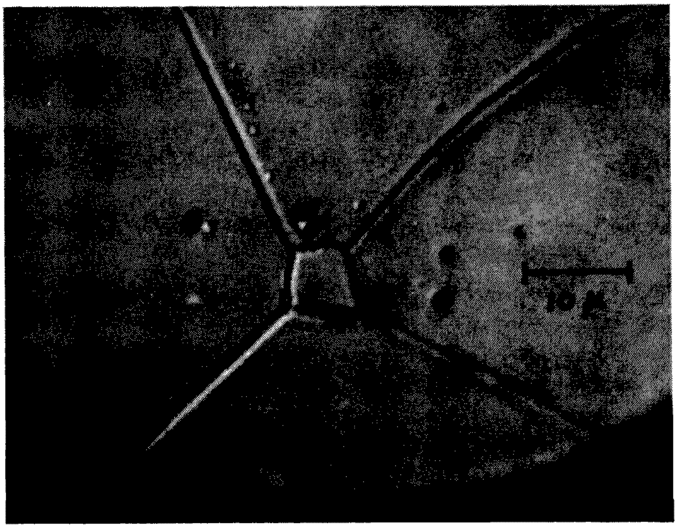

Fig. 3. Electropolished platinum electrode after electrochemical oxidation at 2 V *vs.* S.C.E.

volts *vs.* S.C.E., it was not surprising that the amount of oxide corresponding to the cathodic strip-off pattern was slightly greater than that corresponding to the anodic formation plateau. A monolayer of PtO would be expected to have a thickness of about 3 Å. A rough estimate shows that if all of this oxide were confined to the grain boundaries, the thickness of the layer would still be only about 200 Å; so thin a layer is hardly detectable with an ordinary metallographic microscope.

After the strip-off pattern was obtained, the potential of the electrode was again scanned to 2.00 V *vs.* S.C.E. This polarization curve was identical with the first anodic scan. The electrolysis was continued at 2.00 V for several minutes and then the electrode was removed from the cell and a photomicrograph of the electrochemically oxidized surface was taken. This photomicrograph is shown in Fig. 3. Again there was no essential difference between the appearence of the grain boundaries of the oxidized and the reduced electrode. The magnification in these photomicrographs is 1350 ×, more than twice that used in the previous study.

In light of the foregoing experiments the evidence previously cited in favor of the assumption that platinum oxides are preferentially formed at the grain boundaries of a platinum electrode appears to be doubtful. It might also be noted that the recent study of gold by LAITINEN AND CHAO[3] which employed electron microscopy of shadow-casted replicas was hardly more conclusive. Thus, these workers reported a reduced gold electrode kept at 0.65 V and an oxidized electrode, kept at 1.65 V for 20 min before the replica was made, appeared quite similar. A gold electrode strongly oxidized at 2.15 V for 3 min had so thick an oxide layer that the boundary lines were obscured[3]. In the absence of further evidence to the contrary, it would seem to be preferable to hold to the simpler assumption that platinum oxide forms in an essentially random manner on the surface of a platinum electrode.

The authors take pleasure in acknowledging the helpful cooperation of PROFESSOR DAVIS in lending the original negatives of his photomicrographic studies. They also wish to express their appreciation to PROF. KENNETH E. ROSE, of the Department of Mining and Metallurgical Engineering, for making available the photomicrographic equipment and for valuable advice on its use. Part of this work was supported by General Research Grant 3389 from the University of Kansas and by the Atomic Energy Commission through contract AT(11–1)-686.

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Studies on adsorption indicators

Part IV. Sulphonefluorescein and its halogenated derivatives as adsorption indicators

Fluorescein[1] and several of its halogenated derivatives are well known adsorption indicators for argentometric titrations. In the present work the behaviour of sulphonefluorescein and its halogenated derivatives for this purpose were studied. It was expected that sulphonefluorescein (resorcinolsulphonphthalein), being a stronger acid than fluorescein, would be a better indicator, and this was confirmed for titrations of chloride, thiocyanate, bromide and iodide. Titrations are possible in weakly alkaline, neutral or slightly acidic media (pH > 5).

Fajans[2] arranged halogen-substituted dyes in the order of their suitability for the titrations of chloride, bromide and iodide with silver solution. Fluorescein can be used only above pH 7, dichloro-R-fluorescein[3] above pH 4 and eosin[4] above pH 1; this was explained on the basis that the introduction of the halogen into the resorcinol nucleus increased the dissociation constant of the dye acid, the effect increasing with the atomic weight of the halogen introduced. The stronger the dye acid, the less does the formation of undissociated acid interfere with the adsorption of the dye anion at a given pH.

A similar behaviour is observed with halogen-substituted sulphonefluorescein dyes. Dichloro-R-sulphonefluorescein is a better indicator than sulphonefluorescein and is comparable to dichloro-R-fluorescein in its applicability; halides and thiocyanate can be titrated with silver solution above pH 4. Dibromo-R-sulphonefluorescein is unsuitable for chloride titrations in neutral media but is applicable in the pH range 2–3.5; thiocyanate, bromide and iodide can be titrated in the pH range 2–8. Diiodo-R-sulphonefluorescein cannot be used in neutral or weakly acidic solutions; like erythrosin, it is very strongly adsorbed from the very start of the titration.

Reagents

All the inorganic salts used were of analytical reagent grade. Pure sulphonefluorescein was prepared from *o*-sulphobenzoic acid and from saccharin[5]. The dibromo and diiodo derivatives were then prepared from sulphonefluorescein[5]. Dichloro-R-sulphonefluorescein was prepared as follows: 3.68 g of pure sulphonefluorescein was dissolved in 25 ml of 0.5 N sodium hydroxide and 40 ml of 0.5 N sodium hydroxide previously saturated with chlorine gas in the cold was added; 40 ml of 1 N hydrochloric acid was then added dropwise with constant stirring during 30 min. The mixture was stored overnight and then filtered on a Buchner funnel. The product was twice dissolved in sodium bicarbonate solution and reprecipitated with hydrochloric acid; it was finally washed with water and dried at 110°. (Yield 4.05 g; Cl found 16.4%; Cl theoretical 16.2%).

Since sulphonefluorescein is only slightly soluble in water or in ethanol, the indicator solution was prepared by dissolving 0.1 g of the dye in a few ml of dilute ammonium hydroxide, evaporating to dryness on a water bath and dissolving the residue in 100 ml of water. Solutions (0.1%) of the dihalo derivatives were prepared similarly. Two drops of indicator solution were added for each 10 ml of 0.1 N halide or thiocyanate solution.

With sulphonefluorescein the end-point of the titration of halide or thiocyanate is indicated by a very sharp and reversible change from a yellow suspension to a pink precipitate within the pH range 5–8. An accuracy of ± 0.5% is attainable in titrations of 0.01 N chloride, 0.005 N bromide or thiocyanate, and 0.001 N iodide.

With dichloro-R-sulphonefluorescein, the colour change is the same as that obtained with the parent compound but the pH range is wider (4–8), and 0.001 N chloride solutions can be titrated accurately.

Dibromo-R-sulphonefluorescein, like eosin[4], is suitable for titrations of bromide, iodide and thiocyanate even in 0.01 N nitric acid media. At the end-point, which is reversible, the colour changes sharply from an orange yellow on the suspension to deep pink on the precipitate. Solutions varying from 0.1 to 0.0005 N can be titrated. Chloride cannot be titrated in neutral medium but a sharp colour change is obtained in the pH range 2–3.5.

Diiodo-R-sulphonefluorescein is unsatisfactory in neutral or slightly acidic solution but sharp end-points are obtained in 0.5–2.0 N nitric acid media, the colour changing from orange to reddish violet on the coagulated precipitate. For 10 ml of sample solution, 10 ml of 1–4 N nitric acid and 2 drops of indicator are added before the titration. Chloride and thiocyanate can be titrated at dilutions of 0.02 N, bromide at 0.01 N and iodide at 0.002 N.

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Book Reviews

Submicrogram Experimentation. Microchemical Journal Symposium Series Vol. I, edited by N. D. CHERONIS, Interscience Publishers Inc., New York—London, 1961, viii + 351 pp., \$12.75 (paper \$10.75).

Submicrogram Experimentation contains the Proceedings of a Symposium held in Arlington, Virginia in May, 1960. The field covered is wide, virtually the only point of unification being that the substances sought or determined are present in very small amounts. Of the 21 papers presented, over half deal with biochemical aspects; this ratio seems justified, for as is pointed out with some asperity in a discussion, submicrogram amounts of substances were being identified and estimated in clinical laboratories long before the so-called *pure* analytical chemists began to consider such procedures as other than laboratory curiosities. In the papers which deal with biochemical analyses, the reader may be fascinated by the development of microbiological assays, instructed by discussions on X-ray spectroscopy, ultra-violet and infra-red methods and the possibilities of the electron microscope, somewhat comforted by the results of a new assay for carcinogenicity in cigarette smoke, and perhaps amused by what are grandiosely called olfactory sensing methods.

Gas chromatography is discussed with reference to general detector systems, as well as in connexion with microcoulometry as a highly sensitive means of quantitation. The determination of pesticide residues is considered from the latter point of view and also in terms of enzymatic procedures. A general description of instrumental techniques for the determination of traces in high-purity materials is followed by a paper on trace analysis in marine chemistry. Microscopic identification of single particles is dealt with and some methods applied in the study of the synthetic elements are described. The latter paper is invaluable because it is the only one which provides information on actual weighing in the micro- and submicrogram range.

There are also several more general papers, one of the most interesting being an excellent account of identifications in the submicrogram range. The discussions of each lecture are reported verbatim; they would have been more meaningful, though less amusing, had they been thoroughly edited.

In most of the methods discussed, the submicrogram quantity of substance present needs separation from very large amounts of other materials so that, properly speaking, the main topic is trace analysis. Only in a few cases has the worker been presented with a minute sample in which a substance must be detected and/or determined. The difficulties involved in trace analyses are immense, but they are at least of a chemical nature, whereas the problems encountered in dealing with very small samples are as much physical as chemical. The verge of visibility to the naked eye is about 10 μg and while microscopes can be used for smaller amounts, the purely mechanical difficulties of taking a sample through even one or two operations with any certainty must narrow the range of possible chemical procedures. Virtually the whole of this volume deals with instrumental methods.

Throughout the proceedings, reference is made to nomenclature in the submicrogram range. Undoubtedly, problems are involved in obtaining widespread adherence to the recommendations made by the IUPAC Commission on Microchemical Techniques. These recommendations include the term milligram analysis for the designation of methods involving milligram samples, microgram methods for methods involving microgram samples, and so on. The anomaly of milligram samples being used in micro methods and microgram samples in sub- or ultra-micro methods is thus avoided. Further down the scale the terminology is nanogram (10^{-9} g) and picogram (10^{-12} g) analysis. It remains to be defined if this classification is to be based on the weight of sample taken or on the amount of substance actually determined or detected. The bottom of the above-mentioned range is now in sight experimentally and already various suggestions have been made to extend the range to even smaller quantities. Thus it has been proposed to designate 10^{-15} g as one "Emich" and to work from there with the usual prefices, milli, micro, etc., down to atomic quantities. There are of course, excellent precedents for naming units after well-known scientists, but in all previous cases, the unit so named has involved some new concept in science. It seems fundamentally wrong to attempt to introduce an entirely new name for a concept that is basically ancient and it can only lead to endless confusion. An extension of the existing gram nomenclature would be greatly preferable. A possible system might be quintogram or quinogram (qg) for 10^{-15} g, trillogram (tg) for 10^{-18} g and vintogram (vg) for 10^{-21} g. By this time, the molecular range has been reached and it would be more meaningful to discuss concentrations in terms of molecules (as is in fact done in one of the papers in these proceedings). Moreover, the introduction of additional prefices allows a simple extension to designate 10^{-15} liter, 10^{-15} molar, etc. should the need for such terms arise. The mind boggles before the possibilities of a proper name system supposing that one should require to state that 1×10^{-18} g of X dissolved in 10^{-15} l of Y gives a 10^{-17} molar solution. An additional argument in favour of a prefix system would be that the above-mentioned prefices follow alphabetical order in the lower ranges, so that memorization would be much simplified.

This is, of course, a digression, but the fascinating point about these proceedings is that serious discussion of such minute quantities is seen to be entirely probable. Normal chemical work is now firmly established in the microgram range, and this collection of papers shows that the nanogram range is already being explored, while the boundaries of the picogram range have been reached. This text will be of endless fascination to anyone interested in the analysis of very small quantities of any type of substance.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 27 (1962) 200–201

Photometric Titrations, by J. B. HEADRIDGE, Pergamon Press, Oxford, 1961, x + 131 pp., 45s.

This slim volume, No. 4 in the Pergamon International Series of Monographs on Analytical Chemistry, gives a comprehensive account of the literature up to mid-1960 on photometric detection of the end-point in titrimetry. The author is to be congratulated on having the wisdom to realise and to stress that photometric titrations have a particular place in the armoury of weapons at the disposal of the analytical chemist and that they should not be used indiscriminately. These methods permit determinations to be made where other techniques fail or are inferior in accuracy, and should be reserved for this purpose.

The major part of the book deals with particular applications of the technique, and the theoretical section is short and less satisfying. It might have been pointed out for instance that when an indicator is used in an acid-base titration, and the concentration of either the acidic or basic form of the indicator is measured photometrically, the photometer is being used indirectly for the determination of pH, and can in fact replace a pH meter in titrations to a given hydrogen ion concentration such as the mannitol method for boric acid (an application that escapes mention in the text).

There is an occasional looseness in the writing; for one reader at least, the phrase "tightness of the complex" conjured up visions of a particle pursuing a straight path through a solution instead of the usual random one. In general, however, the book is well done. As is usual nowadays, the price seems high for the size of the book, and not best calculated to induce purchase for personal use. It is nonetheless strongly recommended as a reference work that is not likely to find a rival for some time to come.

R. A. CHALMERS (Aberdeen)

Anal. Chim. Acta, 27 (1962) 201–202

Kern- und Radiochemie. Grundlagen, praktische Methoden und technische Anwendung, von R. LINDNER, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961, 369 S., 140 Abb., DM 49,80.

Aus Vorlesungen, die der Autor für Studierende der Fachrichtungen Chemie, technische Physik, Elektrizitätslehre und Mechanik gehalten hat, ist dies Buch entstanden. Dementsprechend wendet es sich in erster Linie an den Studenten, dem eine Einführung in das umfangreiche Gebiet auf begrenztem Raum gegeben wird, daneben aber auch an den Praktiker, der dem behandelten Gebiet noch fernstehend, sich rasch einen Überblick verschaffen will. Es wird praktisch das gesamte durch den Titel des Buches charakterisierte Gebiet abgehandelt und es dürfte kaum eine Frage geben, die von jemandem, der anfängt, sich in die Materie einzuarbeiten, gestellt werden könnte, die nicht angeschnitten wäre. Der Text ist leicht zu lesen und für jeden Naturwissenschaftler ohne weiteres verständlich, wozu auch der klare, übersichtliche Drucksatz und die zahlreichen fast ausnahmslos recht instruktiven Abbildungen mit beitragen. Bei dem Umfang des Buches und dem Benutzerkreis, an den es sich wendet, wird man nicht erwarten dürfen, durchweg erschöpfende Auskunft zu finden. So wird der mehr chemische Teil dem Chemiker meist nicht wesentlich mehr bringen, als dass er auf die Dinge aufmerksam macht, die in dem jeweiligen Zusammenhang Bedeutung besitzen. Eine auf 10 Seiten gegebene Zusammenstellung der über die einzelnen Teilgebiete erschienenen Bücher und die Zeitschriften, in denen vorweigend Probleme der Radio- und Kernchemie behandelt werden, lässt aber leicht den Eingang zu weiterem Studium finden.

H. BODE (Hannover)

Anal. Chim. Acta, 27 (1962) 202

Radiochemistry USSR (A Quarterly Journal), Scientific translation editor, A. G. MADDOCK, Pergamon Press, Oxford, 1961, £20 per annum.

The Russian journal "Radiokhimiia" first appeared in 1959 and now translations of certain of the papers are being published by Pergamon Press in a new Journal "Radiochemistry USSR". In this first issue, which corresponds to Volume 1 of "Radiokhimiia", there are 22 full translations, 37 abstracts and a list of the papers to be published in full in English in the second issue. Dr. Maddock is acting as translation editor; in his foreword, he points out that the papers for complete translation will be chosen from those considered to be of greatest intrinsic importance, those for which adequate abstracts cannot be made, and those dealing with subjects at present not well-known outside the Russian literature. There can be no-one in this field of chemistry better qualified than Maddock to be responsible for a selection of this type.

"Radiochemistry USSR" is printed in Poland and is well produced. There are typographical errors and examples of literal translation of phrases, but they do not really reduce the usefulness of the Journal. It will be valuable to chemists of many types, and it is likely that their only regret will be the inevitable high price.

J. C. BEVINGTON (Birmingham)

Anal. Chim. Acta, 27 (1962) 203

Monographies de Chimie Organique. Tome IV. *Microanalyse Organique Elémentaire*, par ROGER LÉVY; *Détermination des Masses Moléculaires et des Degrés de Polymérisation*, par P. PIGANIOL, H. JEAN, G. VALLET et C. WIPPLER, Masson et Cie, Paris, 1961, Pages viii + 428 avec 124 figures. Broché 72 NF; cartonné toile 82 NF.

Ce livre constitue le tome IV de la série "Monographies de Chimie Organique", publiée en complément du "Traité de Chimie Organique" terminé en 1955. Le but de ces deux ouvrages est de fournir une bonne documentation en chimie organique et dans les domaines qui lui sont proches.

La première partie, "Microanalyse Organique Elémentaire Qualitative et Quantitative" par Roger Lévy, a 226 pages, avec un chapitre de 21 pages sur l'analyse qualitative, le reste se rapportant à l'analyse quantitative: prise d'essai; carbone et hydrogène; oxygène; azote, halogènes et soufre; phosphore, arsenic, antimoine; métalloïdes et métaux; dosages élémentaires simultanés. Cet ouvrage comprend des méthodes entièrement nouvelles, des méthodes ultramicroanalytiques et instrumentales (par dilution isotopique, par spectrométrie de masse, etc.).

Les exposés, clairs et intéressants, sont souvent donnés dans un esprit critique, les auteurs ne se contentant pas de décrire les possibilités offertes par les différentes méthodes, mais également les difficultés souvent rencontrées, sans cependant y apporter tous les détails d'un livre d'enseignement.

Il est regrettable qu'on ait laissé de côté les méthodes biologiques; en effet pour le dosage colorimétrique du phosphore, par exemple, des travaux importants ont été effectués dans ce domaine. C'est d'ailleurs la seule remarque que nous puissions faire; cette excellente publication occupera certainement une place importante dans chaque bibliothèque scientifique.

Anal. Chim. Acta, 27 (1962) 203–204

La deuxième partie du livre traite de la détermination des poids moléculaires. Elle est divisée en deux sections: "La Mesure des Masses Moléculaires" (37 pages, par P. Piganiol et H. Jean) et "Substances Macromoléculaires" (125 p. par G. Vallet et C. Wippler).

La première section traite des méthodes basées sur les propriétés d'association des molécules, applicables aux petites molécules et aux molécules homologues polymères, avec degré de polymérisation moderé. Parmi les méthodes mentionnées, les plus importantes, la cryoscopie, l'ébullioscopie et la tonométrie sont données en détail. L'osmométrie est traitée dans la deuxième section.

Les "Substances macromoléculaires" font l'objet de 11 chapitres (terminologie) conception de polymolécularité, fractionnement et thermodynamique des solutions macromoléculaires). Un chapitre est consacré à la configuration et aux effets d'interaction des molécules en chaînes. La théorie de la diffusion de la lumière est bien décrite, mais la partie expérimentale peu développée. Le calibrage absolu n'est malheureusement pas traité. Une grande place est réservée aux méthodes de détermination des constantes de diffusion, de rotation et aux moments dipoles des molécules rigides et en chaînes. Les théories hydrostatiques concernant différents modèles de molécules sont traitées conjointement avec la viscosité. Les deux derniers chapitres sont consacrés à la diffusion de translation et à l'ultracentrifugation, cette dernière essentiellement du point de vue théorique. Il est regrettable que les références bibliographiques soient en nombre si limité, cela pouvant nuire à l'actualité de l'ouvrage.

En conclusion, nous pouvons féliciter les auteurs et nous sommes persuadés que tout chemiste organicien appréciera cette intéressante introduction aux méthodes de mesures en chimie macromoléculaire.

WOLFGANG J. KIRSTEN
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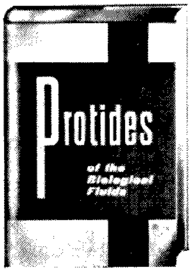
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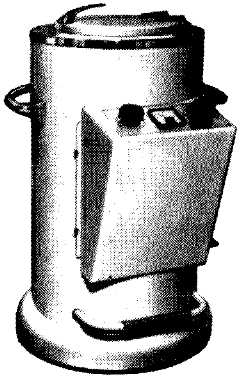

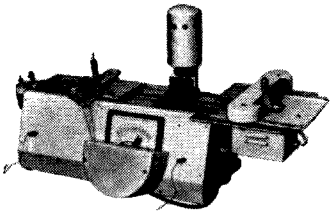

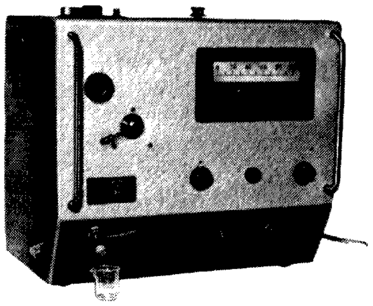

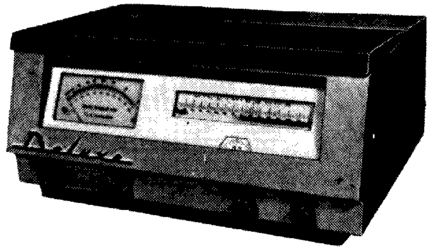

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