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THE ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM

*(Review)*W. T. ELWELL AND D. F. WOOD, *Anal. Chim. Acta*, 26 (1962) 1-31RADIOMETRIC TRACE ANALYSIS OF LEAD WITH
DIETHYLDITHIOCARBAMATE AND ^{204}Tl

Two methods for the determination of submicrogram amounts of lead are described. (A) Lead is selectively extracted with carbon tetrachloride from an alkaline solution containing excess diethyldithiocarbamate (DDC) and cyanide. Traces of DDC are back-extracted. The lead in the DDC complex is exchanged with ^{204}Tl and the amount of ^{204}Tl in the organic layer acts as a measure for the lead. The limit of sensitivity is $0.1 \mu\text{g}$; the standard deviation is 11% (for $0.1 \mu\text{g}$). Bismuth and thallium interfere; their influence can be accounted for with the help of EDTA, however. (B) Excess cyanide is added to the alkaline sample solution and lead is exchanged selectively with ^{204}Tl by shaking with a CHCl_3 solution containing $^{204}\text{Tl}(\text{DDC})_1$. As the process is not 100% effective (with a reasonable excess of the thallium complex) isotope dilution with ^{210}Pb is also carried out. The amount of ^{204}Tl in the aqueous layer acts as a measure for the exchanged lead. The limit of sensitivity is $0.05 \mu\text{g}$ and the standard deviation is 12% (for $0.05 \mu\text{g}$). Bismuth and thallium must be removed in advance, e.g. by anion exchange.

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 26 (1962) 32-45RADIOMETRIC TRACE ANALYSIS OF COBALT WITH
DIETHYLDITHIOCARBAMATE- ^{35}S , OR ^{203}Hg

Two radiometric methods for the determination of submicrogram amounts of cobalt are described. (A) Cobalt is extracted from an ammoniacal solution with a zinc-diethyldithiocarbamate- ^{35}S solution in chloroform. Excess reagent and interfering metals are removed with mercury(II) and cyanide. The ^{35}S in the final organic layer is a measure of the cobalt in this layer. (B) Cobalt is extracted from an ammoniacal solution with a fixed amount of zinc-DDC in chloroform. Excess reagent and complexes of foreign metals are removed by exchange with $^{203}\text{Hg}^{+2}$ and the ^{203}Hg in the chloroform (compared with a blank) acts as a measure of the cobalt. Method A is applicable to $0.1 \mu\text{g}$ of cobalt and method B to $0.8 \mu\text{g}$. As the efficiency of both processes is variable, isotope dilution with ^{60}Co is carried out. A 10-fold excess of foreign metals is permitted in method A and a 4-fold excess in method B; larger amounts are previously removed, e.g. by extraction with inactive zinc-DDC from sodium hydroxide media.

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 26 (1962) 46-57

POLAROGRAPHIC CHARACTERISTICS AND CONTROLLED-POTENTIAL ELECTRO-REDUCTION OF DIMETHYLGLYOXIME

Acidic solutions of dimethylglyoxime produce a well-defined polarographic wave corresponding to an 8-electron reduction to 2,3-diaminobutane. The effects of various experimental variables on the characteristics of the wave are described, and an equation is advanced for its rate-determining step. The reduction of dimethylglyoxime at a large mercury electrode at controlled potential induces the reduction of hydrogen ion, and the mechanism of this process is discussed on the basis of coulometric evidence. Acidic solutions of dimethylglyoxime slowly decompose, by a reaction whose rate law is given, yielding what is believed to be 2,3-dinitrosobutane as the principal product.

M. SPRITZER AND L. MEITES, *Anal. Chim. Acta*, 26 (1962) 58-65

HIGH PRECISION COMPARATIVE POLAROGRAPHY

A new cell assembly for use with the differential cathode ray polarograph is described together with full practical details of its use in comparative polarography. The difficulties of manipulating the cells and dropping mercury electrodes have been greatly reduced. Results obtained show that the coefficient of variation of a polarographic determination can be as low as 0.04%. Some general aspects of the technique are discussed.

H. I. SHALGOSKY AND J. WATLING, *Anal. Chim. Acta*, 26 (1962) 66-74

NEW METHOD FOR DETERMINING SMALL CONCENTRATIONS OF CHLORIDE ION

A new method has been devised for the determination of concentrations of chloride ion from approximately 10^{-6} to $2 \cdot 10^{-4}$ M. The test solution is equilibrated with solid silver chloride, the silver ion concentration is determined by potentiometric titration with iodide ion, and the chloride concentration is calculated by the solubility product principle. Chloride concentrations near 10^{-6} M can be determined with an accuracy of about $\pm 5\%$, and at 10^{-5} M the error is within $\pm 0.5\%$. Chloride concentrations above $2 \cdot 3 \cdot 10^{-4}$ M cannot be accurately determined because of the formation of AgCl_2^- .

D. G. PETERS AND J. J. LINGANE, *Anal. Chim. Acta*, 26 (1962) 75-80

SPOT TEST FOR THIOCYANATE BY A REDUCTIVE METHOD

A CONTRIBUTION TO THE CHEMISTRY OF SPECIFIC, SELECTIVE AND SENSITIVE REACTIONS

(in German)

In the reduction of thiocyanates in acidic or alkaline solution by Devarda alloy, respectively hydrogen sulfide or a mixture of methylamine and ammonia is formed. The identification of these reaction products in the vapor phase allows a fairly selective test for thiocyanates by means of spot test methods.

Limits of identification of 0.12 μg resp. 0.2 μg thiocyanate were obtained.

D. GOLDSTEIN, *Anal. Chim. Acta*, 26 (1962) 81-85

SOLVENT EXTRACTION STUDIES OF PHOSPHONIUM SALTS AND THEIR ANALYTICAL APPLICATIONS

II. DIFFERENTIATION OF *n*- AND ISOPROPYL HALIDES

A test is described for identification and differentiation of *n*-propyl and isopropyl halides. The halide is reacted with triphenylphosphine to form the phosphonium salt, and thiocyanate and copper or cobalt solutions are added. Extraction of the colored precipitate into a suitable solvent indicates *n*-propyl halide whereas isopropyl halides yield unextractable products. The test is applicable to solutions of each halide in the corresponding alcohol as well as to mixtures of both halides.

P. SENISE AND L. R. M. PITOMBO, *Anal. Chim. Acta*, 26 (1962) 85-88

SOLVENT EXTRACTION STUDIES OF PHOSPHONIUM SALTS AND THEIR ANALYTICAL APPLICATIONS

III. DETECTION OF GOLD. IDENTIFICATION OF GOLD AND MINOR CONSTITUENTS IN GOLD ALLOYS

Gold is very efficiently extracted with benzene or toluene after precipitation in acidic solution by excess thiocyanate and triphenylisopropyl phosphonium ions. An almost specific test for gold is thus possible and large amounts of gold can be separated from other elements. A scheme of separation is described for the identification of gold and other metal components in gold alloys, based on selective extraction of the triphenylisopropyl phosphonium salts of the corresponding thiocyanato complexes.

P. SENISE AND L. R. M. PITOMBO, *Anal. Chim. Acta*, 26 (1962) 89-93

ADSORPTION OF SOME METALS ON ANION-EXCHANGE RESINS
FROM POTASSIUM THIOCYANATE SOLUTIONS

The adsorption of a number of metals on Dowex-1 from potassium thiocyanate solutions has been studied. Distribution coefficients were measured as a function of thiocyanate concentration for zinc, cobalt, cadmium, scandium, and silver. Some separations of metals employing thiocyanate as the complexing agent are reported.

J. B. TURNER, R. H. PHILP AND R. A. DAY, JR., *Anal. Chim. Acta*, 26 (1962) 94-98

THE AGEING OF AMMONIUM MOLYBDATE REAGENT

(Short Communication)

H. BUCHWALD, *Anal. Chim. Acta*, 26 (1962) 99-100

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Review

THE ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM

W. T. ELWELL AND D. F. WOOD

Imperial Chemical Industries, Ltd., Metals Division, Kynoch Works, Birmingham (Great Britain)

(Received August 3rd, 1961)

INTRODUCTION

Niobium (columbium) and tantalum are nearly always closely associated in nature. Columbium was discovered by HATCHETT in 1801 and tantalum in the following year, by EKEBURG. Because of their similar chemical properties, these metals were later thought, by WOLLASTON, to be the same element and it was not until about the middle of the 19th century that ROSE confirmed the identity of these two closely related metals and re-named columbium as niobium.

Many of the minerals and ores containing niobium and tantalum are very complex and may contain, among other elements, varying amounts of titanium, zirconium, hafnium and, particularly, iron and manganese. The chief minerals are columbite and tantalite which are varieties of the same species, the former being rich in niobium, the latter in tantalum, but most other niobium/tantalum-bearing ores are richer in niobium.

Until comparatively recently, the analytical chemistry of niobium and tantalum was confined largely to the determination of these metals in minerals and ores and methods of analysis applied to these complex materials were almost exclusively based on the work of SCHOELLER and his co-workers, who devoted many years to studying the analytical chemistry of these two elements, following their discovery in 1922, of the use of tannin to precipitate niobium and tantalum from their complexes with oxalic and tartaric acids.

Within the last decade the industrial importance of niobium and tantalum has grown considerably. Because of its fairly low neutron capture cross-section, high strength to weight ratio at high temperatures, and compatibility with uranium fuel-elements, niobium is suitable as a cladding material in certain types of nuclear reactors and is used, for example, in the fast-breeder reactor at Dounreay. In addition, several niobium alloys, with excellent strength to weight ratio at temperatures between 1000° and 1400°, have been developed, and are now under active consideration for use in the jet-aircraft industry, particularly for gas-turbine blades.

Tantalum, because of its excellent corrosion resistance properties, and the fact that its very stable surface oxide film has a high dielectric constant, has found considerable uses in high-duty electrolytic capacitors, such as those used in radar assemblies. Tantalum is also used, to a small extent, in the chemical industry, but its high cost precludes its use on a large scale. The metal has a high strength to weight ratio, at temperatures above 1400°, and this property has been exploited in the manufacture

of nose-cones for space rockets, missiles and components of supersonic aircraft, where short-life high-temperature conditions prevail.

The analytical chemistry of these two metals has advanced concurrently with their rapid metallurgical development and increasing application during the last ten years. It is not surprising that a considerable amount of relevant analytical information has been published; it was, therefore, considered opportune to review the widespread information now available on this subject, so that the analyst may be better able to study the pros and cons and make a judicious selection for his particular needs.

GENERAL CHEMISTRY

Niobium and tantalum are transitional elements and thus capable of exhibiting valency changes of possible analytical interest. The stable valency of both metals is five, and, whilst lower, unstable valencies are known, present knowledge is incomplete. The lower valencies of tantalum are, generally, less stable than those of niobium and have not been produced in solution by simple reduction, whereas electrolytic reduction of solutions containing so-called niobic acid, gives a series of coloured solutions which are powerful reducing agents.

Serious difficulties are encountered in the analysis of materials containing niobium and tantalum, because their salts have a strong tendency to hydrolyse in solution, producing white precipitates of hydrated pentoxides. Hydrolysis can be prevented by forming complexes of the metals with tartaric, citric or oxalic acids, or by the formation of peroxy complexes in acid solution.

When heated in air, the metals form the corresponding pentoxides; niobium pentoxide becoming pale yellow (when hot) and tantalum pentoxide white.

DECOMPOSITION PROCEDURES

The ignited oxides are insoluble in mineral acids, but they may be decomposed by fusion with potassium hydrogen sulphate, carbonate or hydroxide. The product of fusion with potassium hydrogen sulphate is hydrolysed when extracted with water, but extraction with a solution of citric, tartaric or oxalic acid, etc., gives a clear solution. Extraction with sulphuric acid (1:3) containing hydrogen peroxide also prevents hydrolysis.

The melt obtained by fusion with potassium carbonate or hydroxide dissolves in water giving a solution of potassium niobate and tantalate. If sodium carbonate or hydroxide fusion is used, however, subsequent extraction with water gives an insoluble residue of sodium niobate and tantalate.

For decomposition of niobium and tantalum bearing minerals, hydrofluoric acid is often used, because, in this way, insoluble rare-earth, and alkaline-earth fluorides, are separated from soluble fluorides of niobium and tantalum. Some minerals respond readily to this preliminary treatment, although samarskite and many others do not. Some of the less soluble minerals can occasionally be decomposed by successive treatment with hydrofluoric acid, following evaporation almost to dryness. In some instances, a mixture of hydrofluoric and nitric acids is recommended. Fusion with potassium carbonate in a platinum vessel, or potassium hydroxide in a silver, gold or nickel container, is suitable for the decomposition of many minerals, including columbite and tantalite. A solvent used extensively for the decomposition of most minerals is a mixture of potassium hydrogen sulphate and sulphuric acid. Occasion-

ally a mixture of sulphur dichloride and chlorine is used; almost all niobium- and tantalum-bearing minerals are decomposed when heated in a current of the mixed vapours of these reagents; both metals volatilise as chlorides or oxychlorides, which are usually collected and then evaporated with sulphuric acid.

The metals niobium and tantalum are characterised by their extreme resistance to chemical attack; neither will dissolve in any mineral acid, with the exception of hydrofluoric acid and even then, they are attacked only very slowly. Fused alkalis are also slow to react with these metals. Both metals dissolve readily in a mixture of hydrofluoric and nitric acids and this method of solution is widely used; it is usually necessary to evaporate the solution to fumes with sulphuric acid, before proceeding with the analysis. Both metals, in the form of fine turnings, can be dissolved by heating with a mixture of either potassium or sodium hydrogen sulphate and concentrated sulphuric acid; niobium reacts more readily and the decomposition can be carried out in glass vessels (Pyrex). Another useful procedure for decomposing finely divided metallic samples is based on oxidation at about 800°, in oxygen, followed by fusion in alkali bisulphate or potassium carbonate.

SEPARATIONS

Miscellaneous separations

It is emphasised that in analytical separations involving niobium and tantalum, the presence of large amounts of other metals, particularly titanium and zirconium, may introduce serious difficulties, because of their marked influence on the otherwise normal chemical reactions of the two metals. These interferences are typified by the subsequent reactions when a bisulphate melt of a mixture of titanium, niobium and tantalum oxides is extracted with water; the presence of titanium causes some niobium and tantalum to pass into solution, depending on the amount of titanium present; on the other hand, an excess of niobium, or more particularly tantalum, causes some of the titanium to be precipitated.

Members of the hydrogen sulphide group, including copper, mercury, molybdenum and platinum, can be precipitated, and thereby separated, from niobium and tantalum, as sulphides from hydrochloric or sulphuric acid (0.1–0.2 *N*) containing tartaric acid (10–15%); a collector such as antimony (pentasulphide) is recommended where small amounts of sulphide-group metals are to be separated. Precipitation should be started from a cold, and finished from a hot solution^{1,2}. Elements, such as manganese, nickel, cobalt and zinc, can also be separated from small amounts of niobium and tantalum, by precipitation with hydrogen sulphide, from an ammoniacal tartrate solution, but substantial amounts of niobium and tantalum must first be separated by hydrolysis, *i.e.* by boiling the tartrate solution with a slight excess of hydrochloric acid¹.

Separation of silica is made by extraction of a bisulphate melt of the sample, with a solution of either tartaric or oxalic acid; niobium and tantalum dissolve and silica remains insoluble. Following the recovery and volatilisation of silica (conventionally), the final residue is fused in potassium hydrogen sulphate, extracted with a tartaric or oxalic acid solution, then transferred to the main filtrate for the recovery of small amounts of niobium and/or tantalum³.

Separation of niobium and tantalum from iron is made by passing hydrogen sulphide through a tartaric acid solution, until iron is reduced. Ammonium chloride and an excess of ammonium hydroxide are then added, and hydrogen sulphide is again

passed through the solution, after which it is allowed to stand for several hours until ferrous sulphide is deposited⁴. More recently a method based on chelation of ferric iron with amino or imino diacetic acid, followed by hydrolytic precipitation of niobium and tantalum in guanidine carbonate solution, at pH 12, has been recommended⁵.

Zirconium can readily be separated from niobium and tantalum by fusing the mixed oxides in potassium carbonate and extracting the cold melt with water⁶. Zirconium is precipitated and completely separated from niobium, but not entirely from tantalum. This method of separation is used in the authors' laboratories as a preliminary step in the determination of zirconium in niobium/zirconium alloys.

Separation from tungsten usually follows a carbonate fusion. To the aqueous extract is added an ammoniacal solution of magnesium sulphate/ammonium chloride, when niobium and tantalum are precipitated, and tungstate remains in solution⁷. Titanium and zirconium accompany the niobium and tantalum, although a preliminary separation of most of the titanium and zirconium can be made before the magnesium sulphate/ammonium chloride separation. In the presence of a large amount of tungsten, the process must be repeated and followed by precipitation with tannin. Another method occasionally used, is based on the insolubility of sodium niobate and tantalate and the solubility of sodium tungstate in solutions of high sodium-ion concentration⁷.

Separation of niobium and tantalum together, from titanium, by precipitation from oxalate solution with ammonium hydroxide and ammonium chloride, in the presence of ethylenediamine tetra-acetate (EDTA), has been reported⁸. Titanium forms a complex in the presence of EDTA and oxalate, and is not precipitated.

Hydrolytic precipitation

Although hydrolytic precipitation is sometimes used for the determination of tantalum and niobium, it is more often used as a method of separation from other elements. Hydrolysis (precipitation) of niobium and tantalum salts takes place when, (a) alkali solutions are decomposed by boiling with a slight excess of a mineral acid (usually hydrochloric acid), (b) the bisulphate melt is extracted with water, (c) solutions containing the tartaro-complexes are boiled with mineral acid, or (d) solutions of the oxalo-complexes are made ammoniacal⁹. Hydrolytic precipitation of niobic and tantallic acids can also be made from perchloric acid¹⁰ or hydrochloric acid/sulphurous acid media^{11,12}; these procedures have been incorporated into the analysis of alloyed steels to obtain a preliminary separation from iron. Precipitation of niobium and tantalum, in this way, may include impurities such as phosphorus, silicon, tin, titanium, tungsten and zirconium. Hydrolytic precipitation, from a tartrate solution, is used extensively in mineral analysis; a typical procedure involves fusion of the sample with potassium hydrogen sulphate, extraction with tartrate solution, removal of the acid sulphide group, and precipitation of the majority of niobium and tantalum by boiling the tartrate solution with hydrochloric acid. After filtration, iron and other sulphides are precipitated from an ammoniacal tartrate solution with hydrogen sulphide⁴; residual niobium and tantalum, etc., are recovered from the filtered solution by precipitation with tannin. An example of the use of hydrolysis (precipitation) by extraction of the bisulphate melt with water, is the separation of a large amount of niobium from chromium, a method used in the authors' laboratory in the analysis of niobium/chromium alloys.

MARIGNAC's classical procedure is one of the earliest methods for separating niobium from tantalum¹³. It is based on the difference in solubilities, in hydrofluoric acid, of potassium tantalum fluoride (K_2TaF_7) and potassium niobium oxyfluoride (K_2NbOF_5). This method is now obsolete, but the principle is still used as a means of extracting niobium and tantalum from ores.

Precipitating reagents

The satisfactory separation of niobium from tantalum is probably best achieved by the method of SCHELLER AND POWELL, based on fractional precipitation with tannin from a solution containing the oxalo-complexes of the metals¹⁴. The tannin precipitates are adsorption complexes produced by reciprocal flocculation of tannin with so-called niobic and tantalic acids. Both complexes are precipitated from hot, neutralised solutions of tartaric or oxalic acid, but in oxalate solution, almost quantitative separation of the two metals can be achieved, because of the relative instability of their respective oxalo-complexes. The tantalum precipitate (pale yellow) is obtained at a higher acidity than the niobium precipitate (vermilion-red). In the usual method of analysis, the melt obtained from fusion of the mixed oxides in potassium hydrogen sulphate is extracted with a hot solution of ammonium oxalate, and tantalum (yellow) or tantalum together with a small amount of niobium (orange), is precipitated from the boiling solution with tannin and ammonium chloride. After filtering and washing, the filtrate is treated with dilute ammonium hydroxide and tannin to give an orange-red precipitate. The pure yellow fraction is ignited and weighed as Ta_2O_5 ; the other precipitates are combined, ignited, fused and leached as before, and again precipitated with tannin. By repeating the procedure, an almost pure tantalum fraction is obtained; the niobium fraction is then precipitated from the combined filtrates with ammonium hydroxide and tannin. Both fractions normally contain some titanium. A study of the effect of oxalate concentration and pH on precipitation of the niobium and tantalum tannin complexes has been made by BHATTACHARYA¹⁵. Separation of niobium and tantalum with tannin in the presence of various organic compounds, including cinchonine, brucine, strychnine and antipyrine, has been studied by HAYASHI AND KATSURA¹⁶; a mixture of tannin and brucine is recommended as the best precipitating agent for tantalum and its separation from niobium. According to WIRTZ, in the "presence" of bromophenol-blue indicator, precipitation of tantalum is obtained with tannin, whereas niobium is hardly precipitated at all¹⁷. Precipitation with tannin from slightly acid oxalate solution, half-saturated with ammonium chloride, serves to separate niobium, tantalum and titanium from zirconium, hafnium, uranium, thorium, beryllium, aluminium and other metals^{6,18}. Tannin precipitation can also be used to separate niobium and tantalum from titanium¹⁹. This is effected by extracting the bisulphate melt of the mixed oxides with a solution of tannin in dilute sulphuric acid. Two extractions are usually necessary. This separation can also be made in dilute hydrochloric acid²⁰, or boric/hydrofluoric acid²¹. Another method of separation from titanium, though probably inferior to the tannin method, depends on the action of sodium salicylate on a solution of the oxalo-complexes of the three metals²². Soluble titanyl salicylate (orange) is formed while the oxalo-complexes of niobium and tantalum remain unaffected. Addition of calcium chloride precipitates niobium and tantalum as well as calcium oxalate. Titanium remains in solution and can be recovered by tannin precipitation.

Cupferron is also used for precipitating niobium and tantalum and provides a means of separating these metals from aluminium, chromium, and manganese²³. Cupferron precipitation is usually made from a dilute sulphuric acid solution containing the tartaro- or oxalo-complexes of the metals; the temperature of the solution is kept below 10° to minimise side-reactions. Titanium, zirconium, iron and several other metals also form precipitates with the reagent. According to MAJUMDAR AND CHOWDHURY²⁴, niobium can be separated from tantalum with cupferron. At pH 4.5 to 5.5 niobium is precipitated and tantalum remains in solution, provided the ratio Nb : Ta is not greater than 1 : 2.

Selenous acid precipitates niobium and tantalum completely, from a dilute hydrochloric acid solution containing tartaric acid; a double precipitation of these metals serves to separate them from titanium²⁵. Niobium can be separated from zirconium by this procedure, but the separation of tantalum from zirconium is unsatisfactory, because some tantalum remains in solution. A modification of this procedure has been used by GRIMALDI AND SCHNEFFE²⁶. Hydrogen peroxide is added during dissolution of the cooled melt of the mixed oxides, and precipitation is made at 100°. The precipitate is washed with ammonium nitrate solution instead of dilute hydrochloric acid. Under these conditions the specificity of the separation is improved. Tungsten and zirconium interfere.

Phenylarsonic acid precipitates niobium and tantalum from acidified tartrate or oxalate solutions; zirconium, titanium, hafnium and tin are also precipitated²⁷. In the analysis of rocks, these metals are precipitated with phenylarsonic acid from a boiling solution of dilute hydrochloric acid containing moderate amounts of tartaric and sulphuric acids. The solution is then digested on a water-bath and subsequently at room temperature, before filtering. According to FUCKE AND DAUBLANDER²⁸, phenylarsonic acid (or sodium hydrogen carbonate) can also be used to separate niobium from tantalum, by precipitation of the latter in sulphuric acid solution containing hydrogen peroxide. In the method of separation proposed by MAJUMDAR AND MUKHERJEE²⁹, tantalum phenylarsonate is selectively precipitated from a boiling dilute sulphuric acid solution containing ammonium oxalate; after adjusting the filtrate to pH 5.0, niobium phenylarsonate is precipitated. When the ratio of Ta₂O₅ : Nb₂O₅ is greater than 1 : 2, a double precipitation of tantalum is required. In the presence of EDTA, tantalum can be separated from most ions, but titanium, zirconium, lead, barium and strontium interfere.

N-Benzoyl-N-phenylhydroxylamine has also been used by MAJUMDAR AND MUKHERJEE, for separating niobium from tantalum³⁰. Tantalum is precipitated below pH 1.5, and niobium between pH 3.5 and 6.5. Effective separation at ratios of 1 : 100 can be achieved by double precipitation; titanium, zirconium, vanadate and molybdate interfere. The same authors have also published a method³¹ for separating niobium, tantalum, titanium, and zirconium. Niobium and tantalum are separated from the other metals by double precipitation with pyrogallol, from acid solution; tantalum is then separated from niobium by N-benzoyl-N-phenylhydroxylamine. Zirconium is determined in the filtrate with salicylhydroxamic acid in the presence of hydrogen peroxide, and titanium is precipitated with cupferron from the zirconium-free filtrate, after decomposing hydrogen peroxide. MOSHIER AND SCHWARBURG³² have also reported the use of N-benzoyl-N-phenylhydroxylamine for precipitating niobium and tantalum.

Salicylhydroxamic acid³³, cinnamohydroxamic acid³⁴ and N-cinnamoyl-N-phenylhydroxylamine³⁵ have also been used for the selective precipitation of niobium and tantalum, under carefully controlled pH conditions.

Other reagents include hexamethylenetetramine³⁶, used to precipitate both niobium and tantalum; morin and quercetin³⁷, which precipitate both metals from oxalo-sulphuric acid solution (morin has also been used to separate niobium from tantalum, by a procedure based on solution of the niobium-morin complex in sulphuric acid/acetone solution)³⁸; 8-hydroxyquinoline³⁹ which has been used to separate niobium from tantalum, titanium, tin and antimony, by precipitation of niobium from ammonium tartrate/ammonium chloride solution at pH 6; and sodium hypophosphite, which precipitates both metals in the presence of citric or tartaric acid (this reagent precipitates only tantalum in the presence of ammonium oxalate⁴⁰).

Sodiumdiethyl- and sodium tetramethylenedithiocarbamate have also been used to separate niobium from tantalum⁴¹. These reagents react with niobium in the pH range 2-6.

Recently the precipitation of niobium and tantalum, from homogeneous solution, with 3:3':4':5:7-pentahydroxyflavone has been reported⁴². The reagent 3:3':4':5:7-pentahydroxyflavanone (dihydroquercetin) does not precipitate niobium and tantalum in acid medium (6-9 N), but on boiling in the presence of air, the flavanone is converted to the pentahydroxyflavone which precipitates both metals. Zirconium and molybdenum do not interfere, but titanium must be absent. Tantalum is first precipitated together with a small amount of niobium, from sulphuric acid solution containing ammonium oxalate; niobium remaining in solution is then precipitated at a higher acidity.

CHLORINATION PROCEDURES

To overcome difficulties associated with various chemical separations used in the analysis of niobium and tantalum minerals, ATKINSON *et al.*⁴³, developed a procedure based on chlorination in an excess of octachloropropane at 300°. Ferric oxide must be removed to prevent catalytic decomposition of the chlorinating agent.

Separation of niobium from tantalum, in samples of ore, has been reported⁴⁴. The ore is first mixed with a base, such as calcium oxide, followed by chlorination at high temperature (below 1000°). A procedure in which niobium is selectively nitrided, prior to treatment with chlorine, bromine, or iodine, has also been described⁴⁵. In this method the nitride is converted selectively into a volatile halide, and then separated from tantalum by distillation and condensation.

TREADWELL and his collaborators have reported a chlorination procedure for separating titanium, as titanium tetrachloride, from the more volatile chlorides of niobium, tantalum, uranium and iron, by heating the sample at 500°, in a current of hydrochloric-acid gas, charged with carbon tetrachloride⁴⁶. The procedure has been applied to mineral analysis.

Niobium and tantalum have also been separated⁴⁷ by heating a mixture of the pentoxides with one of the aluminium halides (preferably aluminium iodide) in a closed tube at 200° to 400°. After removing gaseous products, the residues are sublimed. Niobium and tantalum halides can be separated by these procedures, because of their different volatilities. Temperatures of sublimation are: TaCl₅, 150°; NbOCl₃, 230°; NbBr₅, 220°; TaBr₅, 300° (all under vacuum); TaI₅, 540°; NbI₅ nonvolatile (at atmospheric pressure).

CHROMATOGRAPHIC AND ION-EXCHANGE PROCEDURES

Several chromatographic methods for separating niobium and tantalum from other elements, and from each other, were developed by WOOD⁴⁸, and by BURSTALL, SWAIN AND WILLIAMS^{49,50} between 1950 and 1952. These methods are based on elution of the ammonium fluoro-salts of the metals from a cellulose column, with ketone solutions containing various concentrations of hydrofluoric acid. Modifications to the original procedures have been made^{51,52}. Briefly, tantalum is selectively extracted from a hydrofluoric acid solution containing ammonium fluoride in a cellulose column, by elution with water saturated with methyl ethyl ketone. The column is washed with hydrofluoric acid (1%) to arrest the movement of titanium, zirconium, tin, etc., niobium is then extracted with a solution of hydrofluoric acid (12% w/v), saturated with methyl ethyl ketone. A similar procedure is described by BORNEMAN⁵³. Another column chromatographic method⁵⁴ is based on adsorption of niobium and tantalum from oxalate solution, on activated alumina, and subsequent elution at different pH values. BOGDANOVA has also described a procedure for separation of titanium from niobium and tantalum, based on elution with methyl ethyl ketone in dilute hydrochloric acid, from a cellulose column⁵⁵.

Methods of separating niobium and tantalum from each other, and from other elements, particularly titanium, by partition chromatography on filter paper strips, have been described by HUNT *et al.*^{56,57}, and are based on upward diffusion of the metal ions on the paper strip, with mixtures of methyl ethyl ketone (or methyl isobutyl ketone) and hydrofluoric acid. Both niobium and tantalum move in the solvent front when the hydrofluoric acid solution is about 4% v/v, but by reducing the acid concentration to about 2% v/v, only tantalum diffuses to any appreciable extent and niobium is retained near the original spot. A similar method, but involving descending chromatography with a mixture of dilute hydrofluoric acid and methyl isobutyl ketone, has been applied by SCOTT AND MAGEE⁵⁸. BRUNINX *et al.*⁵⁹ have shown that microscale separation of oxalo-complexes of niobium and tantalum is possible on Whatman No. 1 paper, by elution with a mixture of methyl ethyl ketone and strong hydrochloric acid. The separation can also be made using a cellulose column, on a semi-micro scale. These workers have also developed a procedure for separating micro-amounts (10–50 μg) of niobium and tantalum as oxalo-complexes by paper electrophoresis in a citric acid/potassium citrate buffer⁶⁰. A procedure described by SEKERSKII AND KOTLINSKAYA⁶¹ for chromatographic separation of niobium and zirconium is based on adsorption of both elements by tributyl phosphate, on a column of "siliconised" silica gel and subsequent elution with dilute nitric acid. The test solution, containing radioactive niobium and zirconium is introduced into the column, which is then washed with nitric acid (4.6 N) saturated with tributyl phosphate. Niobium separates first, then zirconium. The separation can be improved by adding dilute hydrogen peroxide to the nitric acid solution, before eluting niobium. ALEKSANDROVA AND CHMUTOV⁶² have reported a method for separating the oxalate complexes of niobium and tantalum in the presence of hydrochloric acid, on a column of activated carbon, saturated with phenylarsonic acid. Tantalum is retained and niobium passes into the eluate.

The behaviour of niobium, tantalum and several other metals on anion-exchange resin (Dowex-1), in various mixtures of hydrochloric and hydrofluoric acids, has been studied by KRAUS AND MOORE^{63,64}. Their work has shown that this principle can be

used to separate niobium from tantalum or zirconium, and niobium, tantalum and protoactinium from each other. HAGUE, BROWN AND BRIGHT have also published information on the behaviour of niobium, titanium, tungsten and molybdenum in various mixtures of hydrochloric and hydrofluoric acids on Dowex-I resin⁶⁵. A method for the separation of niobium, tantalum, titanium and zirconium has been developed by HAGUE AND MACHLAN, also using Dowex-I resin⁶⁶. In this method, a mixture of hydrochloric and hydrofluoric acids, containing the sample, is passed through a resin column and four separate eluates are obtained by successive elution with, (1) hydrochloric acid/hydrofluoric acid, (2) hydrochloric acid/hydrofluoric acid/ammonium chloride, (3) ammonium chloride/hydrofluoric acid and (4) ammonium chloride/ammonium fluoride adjusted to pH 5 to 6. The individual eluates contain titanium + zirconium; molybdenum + tin + iron; niobium; and tantalum. A procedure based on similar reactions is described by WILKINS⁶⁷ for the separation of niobium, tantalum, nickel, chromium, cobalt, iron, titanium, tungsten and molybdenum. According to CABELL AND MILNER⁶⁸, almost complete separation of less than 100 mg each of niobium and tantalum can be obtained by passing a solution of the metals, equilibrated with a hydrochloric acid and hydrofluoric acid mixture, through a column of De-Acidite FF resin, then eluting niobium rapidly with the equilibrated solution, followed by elution of tantalum with a solution of ammonium chloride and ammonium fluoride. Iron, titanium and tungsten contaminate the niobium fraction and tin the tantalum fraction.

Anion-exchange separation of niobium and zirconium can be made from an oxalic acid solution⁶⁹. Both metals are adsorbed on Dowex-I resin, from an oxalic acid solution, and can be preferentially eluted (zirconium first) with a hydrochloric acid/oxalic acid mixture. SANO AND SHICMI⁷⁰ have also separated niobium and zirconium by adsorbing both metals on Dowex-50W resin, from a hydrochloric acid solution containing hydrogen peroxide, then eluting zirconium with an oxalic acid solution. Niobium has also been eluted from Amberlite resin with oxalic acid solution, without affecting the bi- or trivalent metals⁷¹. A separation based on adsorption of niobium and titanium, from an oxalate solution, using the Russian anion-exchange resin EDEIOP (chloride form) has also been reported⁷²; by elution with a sodium chloride solution, about 95% of the niobium and 12% of the titanium originally present are obtained in the eluate. Residual titanium is removed from the resin by elution with hydrochloric acid; re-circulation of the niobium eluate serves to recover all but traces of titanium. According to HERRMANN⁷³, niobium and tantalum can be separated from a solution of mixed oxides in a mixture of hydrochloric/oxalic acids, by initial adsorption on Dowex-2 resin (chloride form), followed by elution with hydrochloric acid (*M*)/oxalic acid (0.5 *M*) mixture; pure niobium and tantalum fractions are obtained. This separation has also been effected by SPECKE AND HOSTE⁷⁴ using a column of Dowex-I resin; tantalum is eluted with a hydrochloric acid (2 *M*)/oxalic acid (0.01 *M*) mixture and niobium with hydrochloric acid (*M*)/oxalic acid (0.5 *M*) mixture. The procedure is particularly recommended for separation of trace amounts of niobium from tantalum and *vice versa*.

SOLVENT EXTRACTION PROCEDURES

Methods based on solvent extraction are relatively simple and rapid and, over the past few years, several investigations have been made into the solvent-extraction characteristics of niobium and tantalum.

The method of separation based on extraction of the yellow-orange complex formed between thiocyanate ions and trivalent niobium in acid solution, is well-known. ALIMARIN AND PODVAL'NAYA⁷⁵ have shown that this complex can be selectively extracted with a variety of organic solvents, including diethyl ether, ethyl and isoamyl acetates, cyclohexanol and methyl ethyl ketone. Diethyl ether appears to be the best. Other metals which are extracted under similar conditions, include iron, molybdenum, tungsten and uranium. TROITSKII⁷⁶ has more recently studied the process of extracting thiocyanate complexes of niobium, and recommends butyl alcohol, under specified conditions, as the best solvent for this purpose.

Niobium and tantalum can be separated from each other, and from many other metals, by extraction of their fluoride complexes from aqueous solution with various ketones. For the separation of tantalum from niobium, STEVENSON AND HICKS⁷⁷ recommend extraction of tantalum with diisopropyl ketone from hydrofluoric acid (0.4 *M*)/nitric acid (3.9 *M*), but for separating tantalum from other metals, particularly titanium, zirconium and tin, a solution of hydrofluoric acid (0.4 *M*)/sulphuric acid (6 *M*) is recommended. Niobium can be extracted by increasing the sulphuric and hydrofluoric acid concentrations. CHERNIKHOV *et al.*^{78,79} have reported that tantalum is best separated from titanium by extraction with cyclohexanone from a hydrofluoric acid (0.4 *M*)/sulphuric acid (2 *M*) solution, because, at the lower sulphuric acid concentration, transfer of titanium into the organic phase is minimised; retention of titanium in the aqueous phase is also promoted by addition of ammonium sulphate. In this procedure tantalum is re-extracted from the cyclohexanone with a solution of ammonium oxalate containing boric acid. Extraction of tantalum and niobium with cyclohexanone from sulphuric acid/ammonium sulphate/ammonium fluoride solution, has also been reported and it has been shown that niobium can be re-extracted from the organic phase with a mixture of sulphuric acid and ammonium sulphate, without tantalum being extracted⁸⁰. For separating niobium from nickel, iron and uranium, methyl ethyl ketone extraction from a solution containing ammonium fluoride, hydrofluoric acid and sulphuric acid has been used⁸¹. Methyl isobutyl ketone (hexone) has been used for separating macro amounts of niobium and tantalum from uranium and zirconium, by extraction from a hydrofluoric acid/sulphuric acid/ammonium fluoride solution. Both niobium and tantalum are re-extracted from the organic phase into aqueous hydrogen peroxide⁸². Extraction with hexone from hydrofluoric/sulphuric acid solution has also been used to separate tantalum from uranium and plutonium; in the presence of titanium and molybdenum a double extraction is made⁸³. Separation of tantalum from niobium has also been made by extraction with hexone from a hydrofluoric acid/hydrochloric acid mixture; tantalum is then precipitated with ammonium hydroxide in the organic solvent and, to minimise co-extraction of niobium, the acidified solution of the hydroxide precipitate is adjusted to hydrofluoric acid (0.9 *N*)/hydrochloric acid (2.9 *N*) and a second extraction is made⁸⁴. Niobium can be extracted with tri-*n*-butyl phosphate from a hydrofluoric/sulphuric acid solution, and recovered from the organic phase by shaking with ammonium hydroxide, which precipitates niobic acid⁸⁵. Tri-*n*-butyl phosphate can also be used to extract tantalum from a hydrofluoric acid solution. About 90% of the tantalum is extracted and niobium remains almost completely in the aqueous phase. The presence of hydrochloric or sulphuric acid increases the extraction of niobium; increase in temperature decreases the extraction of tantalum⁸⁶. Methods of separating niobium from proto-

actinium, by extraction with various solvents from a variety of acid solutions, have been investigated by MOORE⁸⁷. The best method of separation appears to be extraction of niobium with diisobutyl carbinol from a hydrofluoric acid/sulphuric acid solution. Niobium is re-extracted from the organic phase with water. MOORE has also shown that niobium can be separated from zirconium by extraction of the latter with thenoyl trifluoroacetone in xylene from a hydrochloric acid solution containing hydrogen peroxide⁸⁸.

Niobium and tantalum can be extracted from several other aqueous media (apart from fluoride solutions) with various organic solvents. SCADDEN AND BALLOU⁸⁹ have shown that niobium can be quantitatively extracted from a sulphuric acid/ammonium sulphate/oxalic acid solution, with dibutylphosphoric acid in *n*-butyl ether. Other metals quantitatively extracted under these conditions are zirconium, yttrium, holmium and indium; tin and tantalum are partially extracted.

Hydrochloric acid has also been used as a medium for solvent extraction of niobium and tantalum; it should be noted, however, that the low solubilities of niobic and tantallic acids in this medium, impose limitations on its use. HICKS AND GILBERT⁹⁰ have shown that extraction of niobium with diisopropyl ketone from a strong hydrochloric acid solution is almost quantitative. Quantitative extraction of niobium has been achieved from hydrochloric acid solution with a solution of methyldioctylamine in xylene⁹¹. Extraction of tantalum appears to be negligible and niobium can be recovered from the organic phase by extraction with nitric, sulphuric or dilute hydrochloric acid. Separation of niobium and tantalum has also been made by extraction of niobium with a chloroform/tribenzylamine solution from hydrochloric acid solution⁹². Tantalum is reported to be preferentially extracted by hydrochloric acid from a solution of the pentachlorides of niobium and tantalum in methyl isobutyl ketone/diisobutyl ketone⁹³. Recoveries of about 60% are obtained, but in the presence of a large amount of ferric chloride, the yield is increased to about 95%.

ALIMARIN AND GIBALO⁹⁴ have reported that the 8-hydroxyquinolate complex of niobium can be readily extracted with chloroform, dichloroethane, ethyl acetate, cyclohexanone, butyraldehyde, *n*-butanol or isoamyl alcohol, from a solution (pH 6–9) containing ammonium citrate or tartrate. The tungsten complex is not extracted with any of these solvents, and a quantitative separation of niobium and tungsten can be made with chloroform. The tantalum complex is not extracted with isoamyl alcohol and a separation of niobium and tantalum (in the ratio 1 : 1000) is possible. Extraction of the niobium–hydroxyquinolate complex with chloroform from citrate solution (pH 9.4) has also been reported⁹⁵; tantalum, tungsten, molybdenum, tin and vanadium remain in the aqueous phase. A preliminary hydrolytic precipitation of niobium and tantalum is recommended to avoid interference of other metals which form complexes with 8-hydroxyquinoline, under similar conditions.

Niobium, tantalum and titanium can be separated from each other, and from other metals, by extraction of their catechol complexes from ammonium oxalate solution at pH 3⁹⁶. Extraction with *n*-butanol removes tantalum and titanium, and leaves niobium in the aqueous phase. Titanium can be recovered from the *n*-butanol by extraction with dilute sulphuric acid. Separation of niobium and tantalum from titanium can also be achieved by extraction of titanium cupferrate from ammonium tartrate solution at pH 5, with isoamyl alcohol⁹⁷.

METHODS OF DETERMINATION

Gravimetric methods

Gravimetric methods for determining niobium and tantalum, irrespective of the procedure used for precipitation, are invariably aimed at obtaining the final product as the pentoxides. The most widely used procedures are based on an initial precipitation of the hydrated oxides, cupferrates or tannin complexes. Because of the difficulty encountered in separating small amounts of titanium, it is usually recommended to precipitate this metal along with niobium and tantalum and determine the titanium content of the final product by the peroxide method.

Methods based on hydrolytic precipitation have been applied to a variety of materials. As applied to the analysis of minerals and ores, precipitation is usually effected either by hydrolysis of the tartrate solution or by decomposition of alkali niobate or tantalate solutions with mineral acid, usually hydrochloric⁹⁸. The precipitate obtained is collected, washed with ammonium nitrate solution to remove alkali salts, ignited at 900° and weighed as (Nb,Ta)₂O₅. This method is also used in the analysis of ferro-niobium and ferro-tantalum⁹⁹. In the analysis of black-sand concentrates by this procedure, tungsten is separated by washing the final precipitate with warm dilute ammonium hydroxide¹⁰⁰. For the examination of steels, hydrolytic precipitation of niobium and tantalum can be made from perchloric, sulphuric or hydrochloric acid solution, containing sulphurous acid. A detailed description of the determination of niobium by hydrolysis with perchloric/sulphurous acid is given in A.S.T.M. methods for chemical analysis¹⁰¹. For determining niobium and tantalum in rustless steels, BAGSHAW AND ELWELL¹¹ recommend preliminary hydrolysis from a hydrochloric/sulphurous acid medium, followed by fusion of the recovered and calcined precipitate with potassium carbonate and precipitation of niobium (and tantalum) from an aqueous solution of the melt by the magnesia process (*i.e.* precipitation with a solution of magnesium sulphate containing ammonium chloride and ammonium hydroxide). A small amount of titanium invariably accompanies the final precipitate and must be allowed for. Results obtained in a co-operative examination by various laboratories, of some gravimetric methods available for determining niobium and tantalum in steels, containing nominally 1% niobium, have been reported by CRAVEN¹⁰² and indicate that the method of BAGSHAW AND ELWELL gives the most reliable and reproducible results. In the method recommended by JABOULAY¹⁰³ for the analysis of ferro-tantaloniobium alloys and steels, niobium and tantalum are first (hydrolytically) precipitated together. The precipitate is filtered and finally calcined, weighed and fused in potassium hydrogen sulphate. Tantalum is then precipitated from a sulphuric/hydrogen peroxide solution of the fused melt, and niobium is precipitated from the filtrate by boiling in a sulphuric/sulphurous acid solution. The precipitated niobic acid is washed with water, ignited and weighed. More recently, JABOULAY has described a method for determining tantalum in ferrous alloys, in which separation from niobium is effected by precipitating tantalum in hydrochloric/hydrogen peroxide solution¹⁰⁴. An alternative method for determining niobium, tantalum (and titanium) in ferro-tantaloniobium alloys involves precipitation with ammonium hydroxide¹⁰⁵. The sample is dissolved in nitric/hydrofluoric acid and, to the diluted solution, glycerol and boric acid are added followed by ammonium hydroxide and EDTA. The solution is boiled, filtered and the precipitate is ignited. Glycerol and EDTA are added to prevent co-precipitation of small amounts of iron,

tungsten and cobalt. Precipitation from a sulphuric/sulphurous acid solution is also used to determine the combined niobium and tantalum content of basic Bessemer slag¹⁰⁶. GOWARD *et al.*¹⁰⁷ have also applied hydrolytic precipitation from sulphuric/sulphurous acid medium to determine niobium in uranium–niobium alloys containing 8–12% niobium. A similar procedure has been used by KRIEGE AND GARDNER for determining tantalum in uranium-tantalum alloys¹⁰⁸.

Hydrolytic precipitation of niobium (and tungsten) from perchloric and hydrochloric acid solutions, and their subsequent separation by the magnesia process, has been studied by BYKOVSKAYA¹⁰⁹ in the development of methods for determining niobium and tungsten in iron-, nickel- and cobalt-base alloys. Results indicated that about 0.5% of the niobium and the same amount of tungsten remain unhydrolysed, when samples containing about 0.3 mg of tungsten and 0.1 mg of niobium are examined. In the magnesia separation, tungsten was only slightly occluded in the precipitate and 7–17% of the niobium remained in solution with the tungsten.

Cupferron precipitation has been used to determine niobium and tantalum in minerals, ferro-alloys and steels. This method does not permit separate determination of niobium and tantalum and, in this respect, is inferior to the tannin procedure. The procedure has been applied directly to the determination of niobium and tantalum in steel¹¹⁰, but it is recommended to make a preliminary separation from iron by hydrolytic precipitation from tartrate medium. The precipitated cupferrates are recovered and ignited to pentoxides. Titanium, if originally present, is obtained in the residue as titanium dioxide. In the analysis of ferro-alloys, an alternative separation of iron involves precipitation of iron with hydrogen sulphide, from an ammoniacal tartrate solution, prior to precipitation of niobium, tantalum and titanium with cupferron.

FUREY AND CUNNINGHAM¹¹¹ have applied the cupferron method for determining niobium and tantalum in tungsten carbides. Separation from tungsten is effected by precipitation of niobium and tantalum, with sodium hydroxide, followed by dissolution, hydrolysis, precipitation with cupferron and final ignition to pentoxides. According to BUDANOVA AND GAVRILOVA¹¹² niobium can be separated from tungsten by precipitation with cupferron in the presence of fluoride ions, and this procedure has been applied to the determination of niobium in steels. A procedure has been recommended by HAGUE AND MACHLAN¹¹³ for determining niobium and tantalum in titanium-base alloys. Titanium is first separated by passing a hydrochloric/hydrofluoric acid solution of the sample through a column of Dowex-1 resin and eluting with a solution of ammonium chloride/hydrochloric acid/hydrofluoric acid; this procedure removes titanium, iron, vanadium and tin. Niobium is then recovered from the column by elution with ammonium chloride/hydrofluoric acid solution and tantalum is finally eluted with an ammonium chloride/ammonium fluoride solution. Boric acid is added to the eluates containing niobium and tantalum to form a complex with fluoride ions and, after adding dilute hydrochloric acid, niobium and tantalum, in the separate solutions, are precipitated with cupferron and finally converted to oxides. KRIEGE AND GARDNER¹⁰⁸ have also used the cupferron method for the analysis of uranium–tantalum alloys. The sample is dissolved in hydrofluoric/nitric acid and the solution is fumed with sulphuric acid; the solution is then diluted, ferric iron is reduced with sulphurous acid and cupferron is added to precipitate tantalum. The precipitate is ignited and weighed as the pentoxide.

A gravimetric method, based on precipitation with tannin, is most extensively used for determining niobium and tantalum in minerals and ores. Conditions for quantitative precipitation and determination of these metals in ores, ferro-alloys and steels are given in detail by SCHOELLER AND POWELL¹¹⁴. Under specified conditions, this procedure can be used to determine niobium and tantalum, either together or separately. Details of the method as applied to the determination of niobium and tantalum in wolframite are given by CHERNIKHOV AND KARSAYEV'SKAYA¹¹⁵, and its application to the analysis of loparite ores and concentrates is described by BYKOVA¹¹⁶. BAILEY¹¹⁷ also describes application of the method to ore analysis, and recommends separation of niobium and tantalum by adding tannin to the solution at pH 5 (buffered with ammonium oxalate) to precipitate the yellow tantalum complex. After filtration, ammonium hydroxide is added to the filtrate to precipitate the red niobium-tannin complex. The tannin procedure has also been used to determine niobium and tantalum in minerals and ores, following chromatographic separation of their fluoride complexes from other elements, by elution with methyl ethyl ketone containing hydrofluoric acid from a cellulose column⁴⁸. A modified tannic acid procedure for determining niobium, tantalum and titanium together in minerals has been described, in which EDTA is added to mask many of the other elements usually present¹¹⁸. In this method, the three metals are quantitatively precipitated and separated from most of the associated elements, with tannin in oxalate solution containing EDTA at a pH of about 4.5. A single precipitation gives a good separation. This modified procedure has also been used by STONHILL¹¹⁹ as a preliminary step in the determination of niobium and tantalum in titanium dioxide pigments, titanium being separated subsequently on a cellulose column. Precipitation with tannin is particularly useful for determining niobium and tantalum in samples containing major amounts of titanium¹²⁰ and a procedure based on extraction of the bisulphate melt with a solution of tannin in dilute sulphuric acid has been successfully applied in the authors' laboratories to the analysis of titanium/niobium alloys and titanium/tantalum alloys, containing about 5% of niobium and tantalum respectively. For the determination of niobium in perovskite, PONOMAREV AND SHESKOL'SKAYA¹²¹ recommend the use of ascorbic acid to form a complex with titanium which is not precipitated by tannin in sulphuric/hydrochloric acid solution containing ammonium chloride. A small amount of titanium sometimes remains in the final oxide residue, but this may be determined by the peroxide method. Satisfactory results have been obtained using this method for samples containing 0.3 to about 1.0% of niobium.

For determining tantalum in carbide mixtures, SHCHERBAKOV AND STEGENDO¹²² first precipitate tantalum with 5:6-benzoquinoline from sulphuric acid solution and, after ignition and solution of the oxides, re-precipitate tantalum with ammonium hydroxide, before the final gravimetric determination.

Various other precipitants for niobium and tantalum, referred to under "Separations", can also be used for the gravimetric determination of these elements, but they have not been widely applied.

Volumetric methods

Niobium, but not tantalum, can be reduced from the pentavalent to the trivalent state, *e.g.* by zinc or preferably zinc amalgam, in acid solution, and then re-oxidised with standard potassium permanganate solution. Many attempts have been made

to apply this principle as a means of determining niobium in the presence of tantalum, but complete reduction of niobium is difficult to achieve, because of partial hydrolysis of niobium and tantalum, with the formation of a colloidal phase. To prevent this hydrolysis, and thus ensure complete reduction of niobium, the use of succinic acid¹²³ or a soluble fluoride¹²⁴, has been proposed. In applying these modified methods, SCHOELLER AND WATERHOUSE obtained low results¹²⁵. These workers also raised the objection that titanium, which is often present in materials containing niobium and tantalum, is also reduced under the same conditions. CUNNINGHAM¹²⁶ claimed to have obtained a stoichiometric reduction of niobium by adding succinic acid and an accurately measured amount of titania which, he states, forms stable complexes with niobium and tantalum and inhibits hydrolysis of their salts during reduction. These claims have been supported by BAGSHAWE, who has applied this modified procedure to the determination of niobium in the analysis of steels¹²⁷. The method has the disadvantage that the added titania is also reduced under similar conditions, and this must be taken into account. KNOWLES AND LUNDELL¹²⁸ have made a critical study of the volumetric procedure and concluded that, under very carefully controlled conditions, almost quantitative reduction can be achieved, without the addition of titania, for amounts of niobium pentoxide less than 300 mg. They stipulate that careful attention must be made to amalgamation of the zinc, length of the reductor, acidity, temperature of solution and concentration of niobium. Reduction is preferably made at $65^{\circ} \pm 5^{\circ}$ in sulphuric acid solution (20% v/v); reduced niobium is oxidised with an excess of ferric alum and the ferrous sulphate thereby produced is titrated with a standard potassium permanganate solution, with *o*-phenanthroline indicator. OKA AND MIYAMOTO¹²⁹ have also reported conditions for the stoichiometric reduction of niobium; a sulphuric acid solution (7 *N*) is recommended for reduction where the amount of niobium is less than 10 mg.

Methods involving electrolytic reduction of niobium, followed by titration with potassium permanganate solution, using a potentiometric end-point detection, have been reported by several authors^{130,131}. More recently TOMIČEK AND SPURNY have reported that reduction with zinc amalgam proved unsuccessful, but good results were obtained by electro-reduction of niobium(V) in sulphuric acid (26% v/v) using a mercury cathode cell¹³². Niobium(III) was oxidised with a ferric salt and the resulting ferrous sulphate was titrated with a standard ceric sulphate solution using *o*-phenanthroline indicator.

A method depending on reduction of niobium with zinc amalgam, oxidation of reduced niobium with ferric chloride and titration with a standard titanous chloride solution, using potassium thiocyanate indicator, has been described by SCHWARZ¹³³. The volumetric determination of niobium has been applied by KRAL¹³⁴ in the analysis of ores and concentrates but, although it is still occasionally used, the method has not been widely accepted as a reliable analytical method. A more satisfactory method of reduction would undoubtedly prove to be a useful contribution to the analytical chemistry of niobium and tantalum.

Colorimetric methods

The determination of relatively small amounts of niobium and tantalum by colorimetric procedures has received considerable attention during the last ten years. Although primarily intended for determining small amounts of these metals, many

of the methods can be extended to deal with alloying amounts of niobium and tantalum, *e.g.* by differential spectrophotometry. For determining niobium, a wide variety of colorimetric procedures have been applied in metallurgical analyses, but, of the colour reactions available for tantalum, only the pyrogallol reaction has been widely used.

One of the simplest methods for determining niobium is based on its reaction with hydrogen peroxide in sulphuric acid solution, when a yellow-coloured complex is formed. Tantalum does not produce a yellow coloured complex under these conditions, but titanium does. However, the intensity of the niobium-peroxy complex increases with increasing acid concentration, whereas that of the titanium complex decreases until, in concentrated sulphuric acid, the effect of titanium is sufficiently small to allow a correction to be applied. This method was used in 1939, by KLINGER AND KOCH¹³⁵ for determining niobium and titanium in steels and ferro-alloys; niobium was determined in concentrated sulphuric acid and titanium in dilute sulphuric acid solution. As an alternative method for determining titanium, KLINGER AND KOCH prefer to use chromotropic acid. The peroxide method has also been applied to the determination of niobium in tantalum¹³⁶, columbite¹³⁷, highly alloyed steels free from tungsten¹³⁸ and high-temperature alloys containing tungsten¹³⁹. In the latter application, absorption of the complex is measured at 420 m μ and correction factors are used for titanium and tungsten. A more recent application of this procedure is to uranium/niobium alloys¹⁴⁰; absorption is measured at 360 m μ and interference by uranium is avoided by using a reference solution of the sample. Phosphoric acid bleaches the peroxide colour produced by titanium and niobium. Because this effect is much greater with titanium, methods based on development of the niobium-peroxy complex in a mixture of concentrated sulphuric and phosphoric acids, have been recommended. A similar procedure has been used by THANHEISER¹⁴¹ for determining niobium in steels and ferro-alloys; a correction factor for titanium is applied, following its determination with chromotropic acid. TELEP AND BOLTZ¹⁴² have also determined niobium in phosphoric acid solution. They use a solution containing sulphuric acid (50% v/v) and phosphoric acid (10% v/v), and measure absorption of the complex at 342 m μ . This method is more sensitive than that using a sulphuric acid solution alone and measuring the absorption at 420 m μ ; the main interferences are titanium, iron, molybdenum, vanadium and tungsten. A sulphuric/phosphoric acid solution has also been used by PICKUP¹⁴³ in the analysis of niobium ores and concentrates; absorption measurements are made at 365 m μ , which is near the wavelength at which maximum absorption occurs. In this application, interferences by vanadium, chromium and cerium are avoided by adding hydrogen peroxide, before evaporation to fumes with sulphuric acid. Traces of platinum, which cause catalytic decomposition of the niobium-peroxy complex, are removed by precipitation with ammonium hydroxide and ammonium chloride. The simultaneous spectrophotometric determination of niobium and tantalum was made possible by the discovery of a tantalum-peroxy complex with an absorption peak at 285 m μ ¹⁴⁴. This complex is formed in concentrated sulphuric acid, under the same conditions as the niobium-peroxy complex, which has maximum absorption at 365 m μ . Titanium, tungsten, molybdenum and rhenium also form complexes with hydrogen peroxide, and absorb in the same region as the niobium and tantalum complexes. Ferric iron also absorbs strongly at 285 m μ , but the effect of small amounts of iron can be corrected by using a compensating solution containing an aliquot of the sample solution, *i.e.* omitting the hydrogen peroxide. The above

method has been satisfactorily applied to the determination of niobium and tantalum in mixtures of their oxides; the procedure is independent of the niobium: tantalum ratio. SCHAFFER AND SCHULTE¹⁴⁵ have examined the method in detail and recommend an optimum hydrogen peroxide concentration of 0.4%, at which the niobium complex reaches maximum colour intensity, and the titanium complex is only partially developed. A differential spectrophotometric method, based on formation of the niobium-peroxy complex in sulphuric/phosphoric acid has been described for application to high-purity niobium, and is suitable for amounts varying from about 92 to 100% niobium¹⁴⁶. Niobium in uranium/niobium alloys, has also been determined by a differential colorimetric method; absorption of the niobium-peroxy complex is measured in concentrated sulphuric acid at 360 m μ and a correction is applied for uranium which also absorbs at this wavelength¹⁴⁷.

The colorimetric method most widely used at present for determining niobium, is based on the reaction between niobium and thiocyanate ions in an acid solution containing stannous chloride; a yellow-coloured niobium-thiocyanate complex is formed. This method is more sensitive than the hydrogen peroxide method and is subject to less interference from iron and titanium. The analytical application of the reaction between trivalent niobium and thiocyanate was first reported by PENNINGTON in 1896 and later applied as a qualitative test. The reaction was first applied to the quantitative determination of niobium by ALIMARIN AND PODVAL'NAYA¹⁴⁸ in 1946. In this procedure, the niobium thiocyanate complex is developed in hydrochloric acid solution in the presence of tartaric acid and stannous chloride; the complex is extracted into ether. LAUW-ZECHA *et al.*¹⁴⁹ have made a detailed examination of this method and shown that the colour intensity depends on a variety of factors including the concentrations of acid, stannous chloride and thiocyanate. The presence of tartaric acid is necessary to prevent hydrolysis, particularly when tantalum is present; absorption of the complex in hydrochloric acid solution (4 M) is measured at 385 m μ . Vanadium, molybdenum, platinum and tungsten interfere due to the colour of their ions; iron, titanium and uranium, in large amounts, also interfere; fluoride, phosphate and oxalate inhibit the reaction. BUKHSH AND HUME¹⁵⁰ later reported that loss of niobium during extraction can be prevented if further thiocyanate is added before the second ether extraction. To inhibit polymerisation of thiocyanate, and stabilise the niobium complex, WARD AND MARRANZINO¹⁵¹ recommend addition of acetone to the ether extract. The same authors have also reported that interference from vanadium can be prevented if stannous chloride is omitted from the aqueous solution and the ether extract is shaken with stannous chloride in dilute hydrochloric acid, to remove ferric thiocyanate. By this modified procedure, 20 μ g of niobium can be satisfactorily determined in the presence of 1000 μ g of iron, titanium or uranium, 500 μ g of vanadium or 100 μ g of molybdenum or tungsten. The presence of tantalum, in amounts up to few times that of niobium, interferes. In applying the thiocyanate method to niobium-bearing rocks, FAYE¹⁵² has reported that fusion of the sample with potassium hydrogen sulphate leads to low results in the presence of uranium, and recommends dissolution in a mixture of hydrofluoric, hydrochloric and phosphoric acids. The solution is evaporated to a paste, extracted into tartaric acid solution and niobium is determined in an aliquot of the solution by the method of WARD AND MARRANZINO¹⁵¹. Determination of niobium in tantalum by ether-extraction of the thiocyanate complex has been described by HASTINGS AND McCLARITY¹⁵³; the effect of tantalum to inhibit colour

development is corrected for by preparing standards in the presence of tantalum. BERGSTRESSER¹⁵⁴ has also described an ether-extraction thiocyanate method for determining niobium in tantalum, in which niobium is separated by the ion-exchange procedure of CABELL AND MILNER⁶⁸ followed by co-precipitation of the eluted niobium with aluminium hydroxide, prior to colorimetric evaluation. An average error of 0.05 μg is obtained in the determination of 4–9 μg niobium, in amounts of tantalum up to 100 mg. Ethyl acetate extraction of the niobium–thiocyanate complex has been used¹⁵⁵ for determining niobium in stainless steel, following hydrolytic precipitation of niobium, tantalum and titanium. A modified procedure, also involving extraction with ethyl acetate has been described¹⁵⁶ for determining niobium in the p.p.m. range in rocks. Tungsten, molybdenum, vanadium and rhenium, which interfere, are first separated by fusing the sample in sodium hydroxide and leaching with water; iron and magnesium are used as carriers.

As an alternative to the ether-extraction procedure, niobium can be determined by carrying out the thiocyanate reaction in acid medium, modified by the addition of acetone, and measuring absorption of the complex directly in this solution. In this method¹⁵⁷, the concentration of acetone recommended is 20% v/v; absorption measurements are made at 385 $m\mu$, the wavelength of maximum absorption. The method has been applied to the analysis of low-grade ores and steels, by MILNER AND SMALES¹⁵⁸, following separation of niobium by precipitation with tannin and cinchonine. MARZYS¹⁵⁹ has also used this method for examining low-grade ores; in this latter procedure, absorption measurements are made at 405 $m\mu$. Corrections can be made for the effect of titanium and tungsten, but molybdenum, copper, vanadium and platinum must be separated. In the presence of uranium, chromium, nickel, thorium, copper, or a large amount of tantalum, the ether-extraction procedure is preferred. CROUTHAMEL *et al.*¹⁶⁰ have critically examined the thiocyanate procedure and give information on the effects of variations of colour developing media, temperature, miscible solvent and reagent concentration. They recommend the use of acetone (60% v/v) in ammonium thiocyanate (1.8 *M*) and hydrochloric acid (1.2 *M*) containing stannous chloride, to decolorise ferric iron. The high acetone concentration is used to minimise interference of other elements, and to reduce the hydrolysis of niobium salts. Factors influencing the formation and stability of the complex in the acetone method have also been studied by BACON AND MILNER¹⁶¹, who have applied the procedure to the determination of niobium in stainless steels, following precipitation of niobium (and titanium) with cupferron. NORWITZ *et al.*¹⁶² have applied the method of FREUND AND LEVITT¹⁵⁷ to the determination of niobium in titanium alloys, following separation of niobium from titanium by precipitation with tannin. In this procedure, absorption measurements were made at 420 $m\mu$, to minimise interference by tantalum. The method is designed for determining niobium in the range 0.05 to 10%. To avoid the time-consuming and uncertain separation of titanium, a method has been proposed by MUNDY¹⁶³ in which absorption measurements are made in acetone/acid medium, first at 400 $m\mu$, to give absorption mainly due to niobium, then at 360 $m\mu$, to give absorption due mainly to titanium. The ratio of absorbances due to niobium and titanium at 360 and 400 $m\mu$ respectively, was shown to be constant, and calculations enabled the fraction of the total absorption at 400 $m\mu$, contributed by each element, to be determined. The concentration of niobium in solution was then found from a standard calibration graph.

Pyrogallol (1 : 2 : 3-trihydroxybenzene) is the most widely used colorimetric reagent for determining tantalum; it is also used for determining niobium. Methods based on the use of this reagent, for determining both metals, were first reported by PLATONOV AND KRIVOSHLYKOV¹⁶⁴ in 1936 and further reports, by the same authors, appeared between 1937 and 1943¹⁶⁵⁻¹⁶⁸. Niobium gives a stable yellow coloration with pyrogallol, in the presence of sodium sulphite in alkaline solution, whereas tantalum gives the same colour in acid solution. In the normal course of analysis, the reaction is carried out, under specified conditions, on aliquots from a solution obtained by extraction of a bisulphate melt of the sample with an ammonium oxalate solution. Metals which positively interfere in the determination of both niobium and tantalum, include iron, molybdenum, tungsten, vanadium, uranium, chromium and particularly titanium. Niobium interferes to a small extent in the determination of tantalum, and *vice versa*. When the tantalum/pyrogallol reaction is applied in sulphuric acid/ammonium oxalate solution, as described by PLATONOV AND KRIVOSHLYKOV¹⁶⁴, maximum absorption occurs at about 400 $m\mu$ and there is serious interference from titanium. However, DINNIN¹⁶⁹ has shown that on replacing sulphuric acid by hydrochloric acid in increased concentration, maximum absorption of the tantalum-pyrogallol complex occurs at 325 $m\mu$, and interference by titanium (and niobium) is reduced. Interference by iron can be prevented by the addition of stannous chloride. The pyrogallol-hydrochloric acid method of DINNIN, has been modified by MARZYS¹⁷⁰, who recommends the use of tartaric acid as well as ammonium oxalate. In this medium, maximum absorption of the complex occurs at 365 $m\mu$ and, though interference by titanium is somewhat greater than in DINNIN's procedure, the effect of niobium is considerably reduced. GOTO AND KAKITA¹⁷¹ have reported that, in the determination of niobium and tantalum with pyrogallol; niobium can be determined in a solution of pH 4.6-6.8, and tantalum in sulphuric acid solution (3 *N*). The pyrogallol reaction has been applied by THANHEISER¹⁴¹ for determining tantalum in steel, ferro-alloys and slags. Titanium is determined independently using chromotropic acid and a correction is applied to compensate for its effect in the tantalum determination; niobium is determined by the peroxide method. In a method described by KRASIL-SHCHIKOV AND POPOVA¹⁷², tantalum is determined by the pyrogallol method in steel, following determination of niobium and tantalum as their combined oxides. The pyrogallol method has also been applied by VINOGRADOVA AND GUSHTYUK¹⁷³ to the determination of tantalum in loparite concentrates, after a preliminary separation of niobium and tantalum with tannin, and by NAZARENKO¹⁷⁴ for determining tantalum in ores. IKENBERRY *et al.*¹⁷⁵ have described application of the pyrogallol method to the analysis of stainless steels, in conjunction with the hydroquinone procedure for determining niobium and tungsten. The mixed oxides, obtained by repeated hydrolysis, are fused with sodium hydrogen sulphate and the melt is leached with ammonium oxalate solution. Tantalum is then determined in an aliquot of the solution, which has been acidified with dilute phosphoric acid. Tantalum has also been determined⁷⁸ with pyrogallol, in titanium dioxide, after a preliminary extraction of tantalum with cyclohexanone from hydrofluoric/sulphuric acid solution and re-extraction into ammonium oxalate solution. This method is also suitable for determining tantalum in niobium⁷⁹. For determining tantalum in titanium alloys, NORWITZ *et al.*¹⁷⁶ apply the pyrogallol reaction, following a preliminary separation of tantalum from titanium by a double tannin precipitation. DOBKINA AND PETROVA¹⁷⁷, have used a procedure similar to that

of MARZYS¹⁷⁰ in which the pyrogallol reaction is carried out in tartaric acid/ammonium oxalate/hydrochloric acid solution, for determining tantalum in titanium alloys following a preliminary separation with tannin. They have also applied the method, without preliminary separation, to the determination of tantalum in niobium pentoxide¹⁷⁸; corrections are made for niobium and titanium, following their determination by the thiocyanate and peroxide methods, respectively. THEODORE⁸⁴ also uses a tartaric acid medium for determining tantalum in niobium, with pyrogallol, following a preliminary extraction of tantalum with methyl isobutyl ketone from a hydrofluoric/hydrochloric acid solution. Both niobium and tantalum have been determined in steel with pyrogallol¹⁷⁹. According to EDER¹⁷⁹, the maximum colour of the niobium complex is developed at pH 6.8 to 7.5 and that of the tantalum complex at pH 2.0 to 2.5. A correction is applied for titanium, following its determination with hydrogen peroxide.

KIDMAN *et al.*¹⁸⁰ have also determined tantalum in steel by the pyrogallol method, following separation from titanium by double precipitation of tantalum from hydrochloric acid solution with phenylarsonic acid. The method was also applied to determine niobium independently in the same sample, by varying the pH at which the pyrogallol complex is formed. HUNT AND WELLS¹⁸¹ have also determined niobium and tantalum with pyrogallol, in ores and minerals, after chromatographic separation. Effects of pH, variation in reagent concentration and effects of various ions are reported. A direct procedure, using pyrogallol for determining niobium and tantalum in binary alloys and zirconium alloys, containing from 2 to 7% of either niobium or tantalum, has been described by WOOD AND SCHOLLES¹⁸²; a differential procedure is also given for samples containing from 7 to 20% of either metal. A correction is applied for amounts of iron greater than 0.5% and, in the presence of molybdenum, a preliminary ammonium hydroxide precipitation is made. Titanium, above about 0.01%, interferes.

A study of 22 polyphenols by KARYAKIN AND TELEZHNIKOVA¹⁸³, showed that, in addition to pyrogallol, the related compound gallic acid, and also catechol (1:2-dihydroxybenzene), formed yellow colours with solutions of niobium, tantalum and titanium. Niobium produces a yellow colour in alkaline solution, tantalum in acid solution and titanium in both acid and alkaline solution. The use of gallic acid for determining niobium and tantalum has also been reported¹⁸⁴. Catechol has been used for determining niobium and tantalum in ores¹⁸⁵. The procedure involves tannin precipitation, separation of niobium and tantalum by extraction of the catechol complexes and cupferron precipitation. Final determination is made by absorption measurements of the catechol complexes in aqueous solution. A more direct procedure has been described by PATROVSKY¹⁸⁶. In this method the catechol complexes are formed in the presence of EDTA and tartrate or oxalate, at about pH 2.5. The tantalum complex is yellow and has an absorption peak in the U.V. region, whereas the niobium complex is red with a maximum absorption at 470 m μ . Titanium, tungsten and iron, in three-fold excess, do not interfere.

According to PLATONOV and his collaborators¹⁸⁴, resorcinol (1:3-dihydroxybenzene) also forms coloured reaction products with niobium and tantalum in alkaline and acid solutions, but SHEMYAKIN AND PILIPENKO¹⁸⁷ state that niobium and tantalum do not give characteristic colour reactions with resorcinol in alkaline solutions, whereas ZVYAGINTSEV AND NAMORADZE¹⁸⁸ have reported that the reaction of resorcinol with niobium and tantalum is not quantitative. The other theoretically possible

dihydroxybenzene (hydroquinone or quinol) forms a coloured complex with niobium (and tungsten) in sulphuric acid solution, and this has been used for the quantitative determination of niobium and/or tungsten by BOGATSKI¹⁸⁹, HEYNE¹⁹⁰ and JOHNSON¹⁹¹. The hydroquinone method has also been used by IKENBERRY and his collaborators¹⁷⁵ to determine niobium (and tungsten) in stainless steels; more recently, WATERBURY AND BRICKER¹⁹² used a similar method to determine niobium in uranium and plutonium alloys, after extraction.

Both niobium and tantalum have been determined as the 8-hydroxyquinolates by SCOTT AND MAGEE⁵⁸, after separation by partition chromatography; the procedure has been applied to the determination of both metals in stainless steels. KASSNER *et al.*⁹⁵ have applied the 8-hydroxyquinolate method to the determination of niobium in steel, following separation by hydrolytic precipitation. The complex is extracted from citrate solution at pH 9.4 into chloroform; absorption of the extract is measured at 385 m μ . A procedure for determining niobium (and molybdenum) in uranium-base alloys by the colorimetric 8-hydroxyquinolate method has been described by MOTOJIMA AND HASHITANI¹⁹³. Extraction of uranium into the organic solvent is prevented by the use of a soluble fluoride.

A procedure based on the reduction of niobophosphomolybdate with stannous chloride to form "molybdenum blue" has been used to determine niobium. The method has been applied to steels by DAVYDOV *et al.*¹⁹⁴ who have shown that the colour of the complex is most intense in sulphuric acid solution of normality between 0.4 and 0.7; they claim that the colour is independent of the excess stannous chloride. NORWITZ AND CODELL¹⁹⁵ have described the application of the method to the determination of niobium in titanium alloys. The effects of a variation in concentration of reagents, and time allowed for reaction, were studied and several metals, including tungsten, vanadium, iron and tantalum were shown to cause serious interference. Absorption measurements are made at 715 m μ . The method has also been used to determine niobium in alloy steels¹⁹⁶; in carbide mixtures¹⁹⁷ and in iron and steel¹⁹⁸.

A method based on the formation of a niobium chloride complex in concentrated hydrochloric acid, with measurement of its optical density at 281 m μ , has been described¹⁹⁹; optical density increases with increase in acid concentration, and vanadium, chromium, lead, molybdenum and titanium interfere, but iron and copper do not, if they are reduced.

Another procedure, used for determining niobium in alloys of iron, chromium, cobalt or nickel, is based on absorption measurements of a potassium carbonate solution of niobium pentoxide, at 234.5 m μ ²⁰⁰. Niobium is first separated from other alloying constituents by acid hydrolysis, the recovered (ignited) precipitate is then fused in potassium carbonate and the melt extracted with water. Titanium, up to about 1.5%, does not significantly interfere.

Niobium has been determined colorimetrically with phenylfluorone²⁰¹, after separation from tantalum by extraction of the latter with methyl isobutyl ketone from a hydrochloric acid solution containing tartaric and sulphuric acids; absorption measurements are made at 502 m μ . Tantalum is recovered from the aqueous phase, into methyl isobutyl ketone, after adding hydrofluoric acid.

FLASCHKA AND LASSNER have shown that the yellow complex formed between niobium(V) and Tiron (disodium-1,2-dihydroxybenzene-3,5-disulphonate) is stable in acid and alkaline solution, and niobium can be determined with this reagent, prefer-

ably in acid solution²⁰². Interference from vanadium(V) can be prevented by reduction with ascorbic acid.

Anthracene chrome-violet (sodium-1-*o*-hydroxyphenylazo-2-naphthol-5-sulphonate) produces a red-violet coloured complex with niobium in hydrochloric acid (0.5 to 1.0 *N*) containing tartaric acid. BARSKAYA²⁰³ describes the application of this reaction to the determination of niobium in alloys containing nickel, iron or titanium. From 0.5 to 3.0% of niobium can be determined to within $\pm 0.02\%$.

Comparatively recently, several new colorimetric reagents for tantalum have been proposed, but as yet they have not been extensively applied. Arsenazo, (*o*-(1:8-dihydroxy-3:6-disulpho-2-naphthylazo)-benzenearsonic acid) has been used by NIKITINA for determining tantalum in titanium alloys²⁰⁴. The reaction is carried out in hydrochloric acid solution containing tartaric acid; the method enables up to 15% of tantalum to be determined, without preliminary separation of titanium.

The red complex formed between tantalum and phenylfluorone (2:3:7-trihydroxy-9-phenyl-6-fluorone) has been used by LUKE for determining tantalum²⁰⁵. Interference from other metals is circumvented by a preliminary extraction of tantalum with methyl isobutyl ketone from hydrofluoric/hydrochloric acid solution. The organic solvent is evaporated to dryness with perchloric and nitric acids and the residue is dissolved in dilute hydrofluoric acid. EDTA is added to form complexes with co-extracted metals, the solution is buffered to pH 4.5 with ammonium acetate/acetic acid and the coloured complex is then developed with phenylfluorone. Absorption measurements are made at 530 $m\mu$. The 9-(*p*-dimethylaminophenyl) derivative of 2:3:7-trihydroxy-6-fluorone has also been used²⁰⁶ for determining impurity amounts of tantalum in zirconium and niobium. In slightly acid solution this reagent produces a bright-red precipitate or colloidal solution with tantalum; the colloid can be stabilised with gelatin. Maximum absorption of the complex is at 500 $m\mu$, in dilute hydrochloric acid containing 0.4% of ammonium oxalate and a small amount of gelatin solution. As little as 3 μg of tantalum can be detected in 10 ml of solution and there is no interference from 400 μg niobium, 100 μg titanium, 500 μg zirconium, 150 μg tungsten, 100 μg molybdenum, or 1000 μg iron, if hydrogen peroxide is added.

Determination of tantalum in the presence of niobium has been made using quercetin (3,3', 4', 5,7-pentahydroxy-flavone)²⁰⁷. Tantalum forms a coloured complex with the reagent but niobium does not. The reaction is carried out in a dilute ammonium oxalate solution obtained by leaching a bisulphate melt of tantalum pentoxide with water. The reagent is added as a solution in a mixture of ethyl alcohol and hydrochloric acid. From 5 to 80 μg of tantalum in 10 ml can be determined in the presence of a five-fold excess of niobium. A similar colour reaction is obtained with 3-hydroxy-5:7:3':4'-tetramethoxyflavone.

A procedure based on development of a coloured complex when tantalum and methyl violet react, has been described for determining impurity amounts of tantalum in zirconium, hafnium and niobium²⁰⁸. A dilute hydrofluoric acid solution of the sample is extracted with benzene in the presence of methyl violet and the optical density of the organic extract is measured.

Polarographic methods

Note: All potentials are stated with reference to a standard calomel electrode.

(a) *Niobium.* Various supporting electrolytes have been reported for the polaro-

graphic determination of niobium. ZELTZER²⁰⁹ showed that niobic acid produces a fairly well-defined wave in nitric acid (*N*), at about -0.8 V, but observed no reduction wave with solutions of niobium pentoxide in hydrochloric acid nor in strong alkaline medium. The reduction wave for niobium(V) in nitric acid has been verified by STROMBERG AND REINUS²¹⁰ who found that the half-wave potential decreases from -0.84 V in nitric acid (0.06 *N*) to -0.76 V in nitric acid (0.9 *N*). The wave-height was shown to be directly proportional to the niobium concentration from 0.19 to 1.12 mmoles/l, and to increase with increase in nitric acid concentration. The addition of gelatin also affected wave-height. The same authors found no indication of a reduction wave for niobium(V) in either hydrochloric or sulphuric acid solutions, nor in solutions of tartaric, oxalic or salicylic acids.

The wave produced in nitric acid was originally attributed by ZELTZER, to be due to reduction of niobium(V) to the trivalent state but, because the wave-height was much greater than the expected value of a two-electron reduction, STROMBERG AND REINUS concluded that, after this initial reduction, niobium(III) is rapidly re-oxidised to the pentavalent state by hydrogen ions at the electrode surface, the net reaction being a catalytic reduction of hydrogen ions. COZZI AND VIVARELLI²¹¹ later showed that this wave is not diffusion controlled, but is the result of a kinetic reaction in which nitrate ions are reduced. DHAR²¹² has also reported that niobium gives a wave with characteristics of a catalytic reduction wave in the presence of nitric acid, but the wave is depressed by chloride, perchlorate or sulphate ions. He assumed that the wave was due to reduction of a nitroniobate complex.

VIVARELLI AND COZZI²¹³ have reported a procedure for the polarographic determination of niobium in the presence of tantalum, using a supporting electrolyte consisting of hydrochloric acid (10 *N*) containing ethylene glycol (20% v/v). The wave due to reduction of niobium(V) to niobium(IV) occurs at -0.395 V. The same authors showed that two waves were produced by reduction of niobium in concentrated hydrochloric acid; one at -0.455 V, the other at -0.695 V, the second being the less well-defined. The initial rise of the second wave introduced difficulty in measuring the height of the first wave, but this was eliminated by incorporating the ethylene glycol. Iron(III), copper(II), molybdenum(V) and titanium(IV) give waves in this solution; they precede the niobium wave, and several other metals also cause interference. In the analysis of minerals, a preliminary chemical separation of niobium and tantalum is made, and tantalum is calculated by difference from the weight of the mixed oxides. The procedure has also been applied to the determination of niobium in the presence of tungsten, molybdenum, titanium, tantalum and other components of stainless steels, after precipitation of niobic acid in perchloric acid solution, fusion of the precipitate in alkali carbonate and saturation of a solution of the melt with hydrochloric acid gas²¹⁴; niobium is then determined polarographically after adding ethylene glycol. BALCHIN AND WILLIAMS²¹⁵ have determined niobium polarographically in titanium ores and pigments, using concentrated hydrochloric acid as the supporting electrolyte. Niobium is first separated by extraction into methyl isobutyl ketone from hydrofluoric/sulphuric acid solution, then re-extracted into dilute hydrogen peroxide solution. After evaporation to fumes with sulphuric acid, concentrated hydrochloric acid is added and the solution is then polarographed. ELVING AND OLSEN²¹⁶ had previously reported a wave for niobium in this electrolyte.

A polarographic study of sulphuric acid solutions of niobium (and titanium) has

been made by KRYLOV *et al.*²¹⁷ and the polarographic determination of niobium and titanium in sulphuric acid (70% v/v) was shown to be possible. The half-wave potentials of titanium and niobium in this medium are -0.575 V and -1.05 V respectively. This method has been used as a basis for determining niobium and titanium in ores. Determination of niobium in sulphuric acid solutions (23 N, 15 N and 10 N) has also been made by means of oscillograph polarography²¹⁸. A sulphuric acid supporting electrolyte has recently been applied by STRICOS²¹⁹ for determining niobium in zirconium-base alloys.

Polarographic waves due to the reduction of niobium(V) to the tetravalent state, in oxalate and tartrate solutions, have been reported by ELSON²²⁰. These waves occur at -1.52 V in oxalic acid solution (0.1 M), and -1.93 V in tartaric acid solution (0.1 M), and suffer from interference by the hydrogen wave.

FERRETT AND MILNER²²¹ have shown that niobium produces two polarographic waves in EDTA solution (0.1 M) at pH 3.05, with half-wave potentials at -0.609 V and -1.05 V. The second wave coalesces with the hydrogen wave, but the wave at -0.609 V is proportional to niobium concentration from 500 to 5 $\mu\text{g}/\text{ml}$. FERRETT AND MILNER have also shown that polarographic waves for niobium are produced in malic, lactic, gluconic and citric acids²²². The complex formed in citric acid is the most stable (to hydrolysis) and a well-defined wave is obtained at -0.86 V in citric acid (2 M) of pH 1.0. This wave can be used as a basis for the determination of niobium at concentrations from 0.1 to at least 250 $\mu\text{g}/\text{ml}$. The niobium wave is well separated from that of uranium and both elements can be determined together; titanium, molybdenum, chromium and antimony interfere but iron, nickel, copper, manganese and tungsten do not.

According to MUKHINA AND TIKHONOVA²²³, niobium gives a polarographic wave at -0.28 V in hydrochloric acid (10 N) in the presence of citric acid; tungsten gives a wave at -0.42 V. With ratios of niobium to tungsten of between 1:1 and 1:5, both elements can be determined in the same solution. This method has been applied to the determination of niobium and tungsten in steels after separation of both elements by hydrolytic precipitation.

Orthophosphoric acid (6 M) containing sulphuric acid (14.5 M) has also been used as a supporting electrolyte for the simultaneous polarographic determination of niobium and tungsten in steels²²⁴.

KURBATOV²²⁵ has shown that niobium and titanium give well-defined polarographic waves at -0.52 V and -0.145 V respectively, in pyrophosphoric acid solution (sp.gr. 1.85). Direct proportionality of wave-height to niobium concentration was shown for solutions containing 0.9 to 25 mmoles/l.

A method has recently been described by BRINDLEY²²⁶ for determining niobium in highly alloyed steels. A preliminary hydrolytic separation of niobium is made from hydrochloric acid/sulphurous acid solution, the precipitate is ignited, fused in potassium hydroxide and the melt is extracted with dilute potassium hydroxide solution. EDTA is added, the pH is adjusted to 1.9 and niobium is determined polarographically by measuring the wave obtained at -0.65 V. Interference by molybdenum is prevented by preliminary extraction of its 8-hydroxyquinolate into benzene, immediately before the solution is polarographed.

(b) *Tantalum*. ZELTZER²⁰⁹ has shown that solutions of tantalum pentoxide in either hydrochloric acid or strong alkaline solution, do not produce a polarographic reduction wave. No polarographic wave was observed for tantalum from solutions of

oxalic, tartaric, citric, gluconic or lactic acid, by FERRETT AND MILNER²²².

To date, no characteristic waves have been reported for this element.

Other methods

Other methods which have been applied to the determination of niobium and tantalum, include emission spectrography, X-ray fluorescence, radio-isotope tracer and isotope dilution methods. It is not intended to discuss these physical methods in detail, but some references to their application are of interest.

A description of techniques employed in the spectrographic analysis of iron and manganese ores, with particular reference to the determination of niobium, zirconium and nickel has been given by INDICHENKO²²⁷. THORNE AND CHILDS²²⁸ have reported a method based on the iron-flux procedure, for determining niobium in low-grade minerals. In this method, working graphs are prepared from standards of known composition, prepared by adding niobium pentoxide to a flux consisting of an equal weight of titanium dioxide and ammonium sulphate; small pellets prepared from this mixture are subjected to arc excitation using copper supporting electrodes. The line pair used is Ti 4145.0-Nb 4100.9 Å, or if manganese is absent, Ti 4052.9-Nb 4058.9 Å. Small amounts of niobium in ores have also been determined spectrographically by NEDLER²²⁹, following preliminary separation of niobium by precipitation with tannin, using a stannous chloride collector. Ignited oxides are mixed with powdered quartz containing a thoria internal standard, then subjected to arc excitation. The lines Nb 3163.4-Th 3154.7 (for niobium contents 0.02 to 0.04%) or Nb 2972.8-Th 2942.8 Å (for niobium contents 0.08-1.0%) are used. Another method is described by BORODIN²³⁰ for the spectrographic determination of relatively large amounts (0.1-5%) of niobium in titanium and zirconium minerals. In this method, the sample is excited by a d.c. arc (10 A) to give complete volatilisation of 10-15 mg of sample in about 5 min. Standards are prepared by mixing niobium pentoxide with the minerals; the lines 2671.9 and 2716.6 Å are used for the analysis. A spectrographic method for determining niobium in rocks, after separation of niobium by precipitation with pyrogallol, on silica gel, has been reported by TARASEVICH AND SEMENENKO²³¹. A method suitable for determining Nb₂O₅ (2-20%) and TiO₂ (0.1-3%) in tantalum acid, has been reported by JORDAN AND PICARD²³². The oxides are compacted with graphite and subjected to excitation by a condensed low-voltage discharge. The lines used are Nb 3098.47 Å, Ta 3098.0 Å and Ti(II) 3017.19 Å. The determination of niobium and tantalum in tantalite-niobite ores has been reported by BOUDERGUES²³³. In this procedure, Nb₂O₅ (5-65%) is determined by intermittent arc-excitation, using Co₂O₃ as an internal standard, and lines Nb 2590.94 Å and Co 2582.24 Å. Using the same cobalt line, tantalum in the range 20-60% (Ta₂O₅), can be determined.

For the spectrographic analysis of steels, analysis lines and standardising tables have been given for niobium, tantalum and other metals, by GILLIS AND EECKHOUT²³⁴. Limits and suitable lines for more than twenty metals, including niobium and tantalum have been reported by SCHLISSMANN²³⁵, for application to the spectrographic analysis of iron and steels. A spectrographic method for the analysis of iron and steel has been described²³⁶; small samples (10 mg) are oxidised, mixed with graphite and subjected to arc-excitation in an a.c. arc discharge; up to about 1% of niobium can be determined in this way. A procedure suitable for the rapid routine determination of niobium in steels has been described by BELOHLAVEK²³⁷. NEULLY²³⁸ has reported

a method for determining niobium and tantalum in 18/8 (chromium/nickel) stainless steels, by means of a Feussner spark-source, and a medium dispersion spectrograph, following a preliminary chemical separation. Spectrographic determination of niobium (and manganese) in thin-sheet samples of stainless steel has been described²³⁹; excessive volatilisation of manganese and niobium is prevented by passing a stream of helium at 0° over the upper, unsparked side of the sample. NOMOKOVNA AND MOROZOVA²⁴⁰ and MOROSHKINA AND PROKOFIEV²⁴¹ have also reported spectrographic methods for determining niobium and tantalum; the latter procedure is particularly adaptable to the determination of micro amounts.

A method for determining tantalum in carbides of tungsten and tantalum has been reported by HAMPL AND DUFEK²⁴². TARASEVICH *et al.*²⁴³ have proposed a method for the simultaneous determination of niobium (0.004–0.3%) and tantalum (0.006–0.3%), in titanium, by arc-excitation of a mixture of the sample with graphite, using the line pairs Nb 2950.58–Ti 2958.28 and Ta 2714.67–Ti 2713.76 Å.

Other applications of spectrographic methods include the determination of both niobium and tantalum in the presence of titanium²⁴⁴, titanium and tungsten²⁴⁵, in cemented carbide mixtures²⁴⁶ and in bismuth matrices²⁴⁷. Methods for determining niobium in powdered tantalum^{248, 249}, uranium²⁵⁰ and tantalum pentoxide²⁵¹ and for determining tantalum in niobium pentoxide²⁵² and zirconium²⁵³ have also been reported.

X-Ray spectroscopic methods for determining niobium and/or tantalum have been reported^{254–257}. X-Ray fluorescence methods for application to ores and minerals have also been described^{258–261}.

A radio-isotope tracer technique has been applied by BOYD AND GALAN, to determine the efficiency of precipitation steps in the determination of niobium and tantalum in steel²⁶². A study of conditions for separating niobium–tantalum, niobium–zirconium and tantalum–zirconium mixtures by precipitation with ammonium benzene-seleninate at various levels of pH, and determination as benzene-seleninate by isotope dilution, has been made by ALIMARIN AND BILIMOVICH²⁶³. SAVOSTIN AND ALIMARIN²⁶⁴ have used the radioactive isotopes ¹⁸²Ta and ⁹⁵Nb, to show that adequate concentration of niobium and tantalum can be made to enable their determination in granite by precipitations with tannin and pyrogallol. Similarly, the coprecipitation of niobium and tantalum with silica, on treatment of the sample with perchloric acid has been shown to be quantitative by the use of radioactive isotopes²⁶⁵. Radiometric titration of niobium and tantalum in steel has also proved satisfactory, using a modified cupferron titration procedure²⁶⁵.

A method depending on the difference in intensity of β -radiations from niobium and tantalum and comparison of the intensity of the reflected β -radiations from test alloys, has been developed by GAIDADYMOV AND IL'INA²⁶⁶.

KOHN²⁶⁷ has reported a radioactive method for determining tantalum in ferro-niobium and niobium ores. The sample, and standards consisting of iron powder mixed with known amounts of tantalum, are irradiated in an atomic pile and set aside for about 7 days to reduce the activity of short-life radio-isotopes, resulting from impurities. The γ -activity is then measured and the tantalum content determined after allowing for slight activity of the iron powder.

A neutron-activation method for determining tantalum in rocks has been reported by MORRIS AND OLYA²⁶⁸. Tantalum is determined as ¹⁸²Ta by γ -scintillation counting. Carrier tantalum is added before separation by hydrolytic precipitation and extraction

with tributyl phosphate. A neutron-activation method for determining tantalum (and tungsten) in rocks and meteorites, has also been reported by ATKINS AND SMALES²⁶⁹. After irradiation and solution of the sample (and a standard, containing carriers), tantalum and tungsten are precipitated with tannin and cinchonine. Subsequently, tantalum is extracted into isopropyl ketone and finally converted to tri-2,2'-dipyridyl ferrous fluoro-tantalate for counting. Tungsten is recovered from the aqueous solution and counted as the 8-hydroxyquinolate. The activity is measured by either β - or γ -counting; limits of sensitivity are 10^{-10} g for tantalum and 10^{-11} g for tungsten.

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RADIOMETRIC TRACE ANALYSIS OF LEAD WITH DIETHYLDITHIOCARBAMATE AND $^{204}\text{Tl}^*$

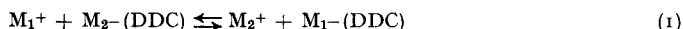
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INTRODUCTION

Preliminary radiometric experiments¹ on trace analysis of metals led to the choice of the system:



in which M_1 is the metal to be determined, M_2 is a radio-active metal and DDC stands for diethyldithiocarbamate. As the ions are soluble in water, and the DDC-complexes in a solvent which is immiscible with water, separations can easily be effected. Selectivity can be obtained by a proper choice of M_2 , the pH and masking agents.

The sequence of affinities of metals for DDC was elaborated by WICKBOLD², BODE AND TUSCHE³ and ECKERT⁴, and used in analysis by SEDIVEC AND VASAK⁵, PRIBIL⁶, MARTENS AND GITHENS⁷, KOVARIK AND VINS⁸ and DESZÖ AND FÜLÖP⁹. Spectrophotometry was the basis of all quantitative evaluations.

In our work radio-isotopes are used for this purpose. Selectivity for lead is obtained by carrying out the exchange at pH 14 in the presence of excess potassium cyanide. Only the DDC-complexes of bismuth(III), thallium(III), lead(II) and thallium(I) are stable under these conditions, the stability decreasing in this order. Thus with the radio-isotope ^{204}Tl two determinations of lead are possible, symbolized by both directions of eqn. (1). These two methods are described in parts A and B respectively.

EXPERIMENTAL METHOD A

Materials and methods

Acid ^{204}Tl solution. Dilute 2.4 mg (1 mC) of $^{204}\text{Tl}^+$ with 1 N nitric acid to 10 ml, add 0.5 ml of bromine water, boil for 30 min, cool, dilute with 1 N nitric acid to 100 ml, and standardise iodometrically (SANDELL¹⁰) after removal of nitrites.

Alkaline ^{204}Tl solution. Neutralize 8 ml of the above acid solution with sodium hydroxide, dilute to 25 ml, add potassium cyanide and sodium bicarbonate to give a 0.12% solution of each, and adjust to pH 13 and 30 ml with sodium hydroxide. Prepare daily (to avoid adsorption, etc.).

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^{210}Pb solution. 400 μg of lead and 4 μC ^{210}Pb (Ra-D in equilibrium with its decay products) per ml of 1 *N* nitric acid.

DDC- ^{35}S . Dissolve 100 mg (3 mC) of DDC- ^{35}S dihydrate* in 10 ml of 0.01 *N* sodium tartrate (AnalaR), add 300 mg of β -mercaptoethylamine hydrochloride and adjust to pH 11 with hydroxide. Store (under nitrogen) in a polyethylene vessel at 4°.

Ion-exchange water: resistivity at least 3 Megohms.

Cyanide-DDC solution (a). To 100 ml of 10% potassium cyanide in water, add 0.2 mole of sodium hydroxide and 20 mg of DDC dihydrate (all Merck p.a.**), purify with five 10-ml portions of carbon tetrachloride, store (in polyethylene at 4°) over carbon tetrachloride and purify occasionally by shaking (200 μg DDC/ml).

Cyanide-DDC solution (b). To 100 ml of 1% potassium cyanide in water, add 0.01 mole of sodium tartrate and 0.2 mg of DDC dihydrate. (pH 10.5). Purify and store as (a).

Cyanide-bicarbonate solution (a). 0.1% potassium cyanide containing sodium bicarbonate to give pH 10.

Cyanide-bicarbonate solution (b). Solution (a) adjusted to pH 13 with sodium hydroxide.

Tartrate. 0.1 *M* ammonium tartrate (AnalaR) in water.

Acid Tl-carrier. 1 mg $\text{Tl}(\text{NO}_3)_3$ per ml of 2 *N* nitric acid.

TL-(DDC) $_3$ -carrier. 0.5 mg Tl as $\text{Tl}(\text{DDC})_3$ per ml of carbon tetrachloride.

The hydrochloric acid (s.g. 1.18), nitric acid (s.g. 1.42), ammonia (s.g. 0.88), chloroform and carbon tetrachloride used were "AnalaR". The radionuclides involved are shown in Table I.

TABLE I

Nuclides	Half-life	β -radiation (MeV)	γ -radiation (MeV)	Measurement ^a	Remarks
^{204}Tl	3.9 years	0.76	—	1 ^b ;2	
$^{210}\text{Pb}^c$	20.4 years	0.018; 0.056	0.047	1	Ra - D
^{210}Bi	5 days	1.17	—	1 ^b ;2	Ra - E
^{210}Po	139 days	—	0.79	1	(5.3 MeV- α) Ra - F
^{35}S	87 days	0.15	—	3	

^a *Measurement 1*: A Philips well-type scintillation crystal for 1-ml samples (PW 4111/W) was combined with a scaler PW 4022-32-52 and a E.K.A.F. single channel analyzer. *Measurement 2*: A 20th-Century Electronics M6-GM tube for 10-ml samples, was desiccated between the electrodes to prevent leakage and combined with the Philips scaler. *Measurement 3*: A Philips end-window GM-tube (18506; window thickness 2 mg/cm²) was combined with the Philips scaler.

^b Bremsstrahlung

^c For the separation of ^{210}Pb from its decay-products, see below.

The extraction was carried out in a polyethylene pill-case (76 mm high; outer diameter 25 mm), covered with an efficient lid. Shaking was performed (in a vertical position) with a "Microid Flask Shaker" (Griffin and Tatlock) which made a vertical movement of about 0.5 cm. The arm of the shaker was connected to a

* From the Radiochemical Centre, Amersham (Great Britain).

** Potassium cyanide from Merck contains less than 10 p.p.m. Pb.

simple device for measuring its velocity. A ball-bearing was added to the spindle of the driving motor to give it a more constant velocity for a given position of the dial. To prevent spillage of a radio-active solution in case of an accident, the shaker was placed in a shallow polyethylene trough.

Scheme of method A

Lead diethyldithiocarbamate is extracted (with carbon tetrachloride) from an alkaline solution (pH 14), containing excess DDC, cyanide (to obtain selectivity) and tartrate (to prevent the precipitation of hydroxides and carbonates). The lead is then exchanged with $^{204}\text{Tl}^{+3}$ -ions. After an alkaline rinsing to remove residual traces of the aqueous layer, the ^{204}Tl -activity in the organic layer is measured.

Part of the DDC is coextracted and would react with the ^{204}Tl during the exchange procedure. As a large excess of DDC is required for the complete extraction of traces of lead, this coextraction of DDC would result in a considerable blank. Thus back-extractions of DDC are inserted.

Selective extraction of lead

3 ml of an alkaline solution (pH 14), containing 0.1 to 3.0 μg of labelled lead*, 5% potassium cyanide, 0.01 *M* tartrate and 300 μg of DDC, were shaken with 8 ml of carbon tetrachloride in the pill-case for 5 min. (A velocity of 800 to 1000 periods per min was optimal: insufficient extraction was obtained at lower velocities and emulsions occurred at higher ones). The pill-case was then centrifuged lightly to ensure complete separation of the phases.

Chloroform was slightly more efficient than carbon tetrachloride but the coextraction of DDC (see below) was also enhanced. The comparatively large volume of the tetrachloride used resulted in a high coextraction of DDC. Comparison of the extractions of lead and DDC, with large volumes of carbon tetrachloride or small volumes of chloroform showed the former method to be superior**.

96% of the lead was extracted (st. dev. 3%). With the exception of bismuth and thallium other metals were not coextracted in appreciable amounts.

Traces of metals which might be coextracted are back-extracted by cyanide together with the DDC. Large amounts of iron and copper prevent the extraction of the lead; other ions including mercury(II) and silver(I) are not active in this way. No explanation for this behaviour of iron and copper could be found.

For small amounts of bismuth and thallium a "blank" can be determined by carrying out the extraction with DDC (with part of the sample) in the presence of cyanide and EDTA: lead is not extracted in contrast to bismuth and thallium (KINNUNEN AND WENNERSTRAND¹¹).

The extraction of lead is slightly influenced by phosphate and pyrophosphate: up to 100 μg of the latter and 10 μg of the former anion do not interfere in the determination of 0.1 μg of lead; when larger amounts are present citrate has to be added to the acid sample solution as described by SANDELL¹⁰ for the extraction of lead with dithizone.

* Not separated from its decay-products. Measurement (2) applied and checked after 5 days ($\tau_{1/2}$ of ^{210}Bi).

** A mixture of 6 ml of tetrachloride and 2 ml of chloroform can be used alternatively when the efficiency of the shaker might go down.

Part of the DDC was coextracted. In the literature only very approximate values are found for this extraction. BODE¹² (using the colour reaction with excess aqueous copper for detection) stated that the extraction of DDC is negligible above pH 8.5, provided that the carbon tetrachloride is dried by filtration.

In our experiments DDC-³⁵S was used to determine the extracted %. As this DDC-³⁵S contained small amounts of decomposition products (some of which were more soluble in carbon tetrachloride than the DDC-³⁵S itself) the solution was back-extracted three or four times. The organic layer was then pipetted on an aluminium dish, dried and measured. The form of the dish promoted a homogeneous distribution and thus minimized the error due to a variable selfadsorption (Fig. 1*).

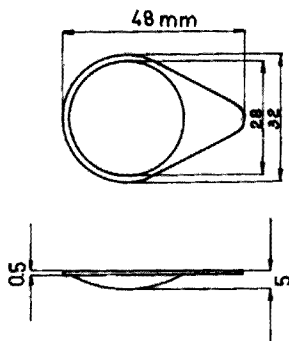


Fig. 1. Aluminium tray.

From 0.2 to 0.4% of the ³⁵S was found in the organic layer. Centrifugation up to 2000 rev/min. (Ø 25 cm) was unsuccessful in lowering this blank**. Filtration decreased the "extracted" percentage to about 0.02 but also removed appreciable amounts of lead when applied to a Pb(DDC)₂ solution***. Thus the tetrachloride layer contains a DDC surplus of 0.2 to 0.4% (corresponding to a blank of 0.3 to 0.6 µg of lead).

A second DDC surplus results from the incomplete removal of the aqueous layer. Provided that this DDC (1 to 2%) is totally extracted with ²⁰⁴Tl⁺³ during the exchange-procedure, it is equivalent to a blank of 1.5 to 3.0 µg of lead.

Back-extraction of DDC

As was to be expected from the figures of BODE¹², strongly alkaline solutions were the most effective, but appreciable amounts of lead were also back-extracted. A solution of pH 10.5 (containing 1% potassium cyanide to prevent the interference of foreign metals) was found to be optimal: 90 to 95% of the DDC and only 1 to 6% of the lead were back-extracted. Again 1 to 2% of the aqueous layer could not be removed. The remaining DDC blank can be calculated to be (theoretically) equivalent to 0.082 µg of lead.

Thus a second back-extraction is required for amounts of lead below 0.5 µg. A

* With the ordinary dishes - which have a rectangular profile - the last drops of the solvent and thus the precipitate are collected in the outer regions.

** Higher velocities are dangerous with regard to the construction of the pill-case.

*** Filtration through hydrophobized paper, as recommended by KOVÁCS¹³ and WEGMANN¹⁴, was found to be equally unsatisfactory.

cyanide-DDC solution (resulting from the purification of cyanide with DDC) was used for both strippings instead of cyanide alone. It can be calculated that theoretically the DDC blanks for 1 and 2 back-extractions are enlarged to 115 (st. dev. 60) and 36 (st. dev. 14) μg of lead respectively by this additional DDC.

It can also be calculated that the whole process is efficient for 87–98 and 81–97% of the lead with 1 and 2 back-extractions respectively. In practice the figures 94 (st. dev. 3) and 89 (st. dev. 7) were found.

Exchange with $^{204}\text{Tl}^{+3}$

To prevent all interferences from traces of mercury, silver, copper, etc. (present in the reagents and in the pill-case), 0.1% potassium cyanide was added to the alkaline $^{204}\text{Tl}^{+3}$ -solution used for the exchange with $\text{Pb}(\text{DDC})_2$.

A pH of 13 proved to be optimal for a high rate of exchange. With a 3.5-fold excess of $^{204}\text{Tl}^{+3}$, the process was effective to 96% (st. dev. 2) within 5 min. Thus the whole procedure was effective to 90% (st. dev. 5) and 85% (st. dev. 9) respectively for the two ranges of lead. For amounts of lead below 0.1 μg the efficiency was only 75% (st. dev. 15).

After the separation of the excess $^{204}\text{Tl}^{+3}$ from the organic layer, the latter had to be washed in order to remove the usual small traces of the aqueous layer (1 to 2%), as well as part of the ^{204}Tl "dissolved" in the carbon tetrachloride.

With regard to the aqueous layer traces: after the washing, this factor still resulted in a blank equivalent to 2.2 (st. dev. 1.4) and 0.5 (st. dev. 0.2) μg of lead for the two amounts of ^{204}Tl applied in our procedure. With regard to "dissolved" ^{204}Tl : experiments with ionic ^{204}Tl and pure carbon tetrachloride indicated a blank of 0.1 to 0.3% (again after the washing)*. This blank was decreased by filtration but again part of the metal-DDC-complex ($\text{Tl}(\text{DDC})_3$ here) was adsorbed by the filter paper. This second factor contributes a Tl-blank of 18 (st. dev. 9) and 3.6 (st. dev. 1.8) μg of lead for the two amounts of ^{204}Tl used above. This is still small compared with the DDC blank.

Measurement of the radioactivity of ^{204}Tl

^{204}Tl can be measured in two ways. The sensitivity of both detectors is about equal, but the GM-tube has a lower (and more stable) zero value and is therefore used to measure the small activities. The crystal has the advantage that separate tubes can be used for the samples and thus the detector need not be cleaned between measurements. With both methods 10^4 counts are registered resulting in a 1% statistical error.

Direct measurement of the carbon tetrachloride (8 ml) is to be preferred when the GM-tube is used (10 ml capacity). Thallium-DDC carrier is added and the pill-case is thoroughly rinsed to prevent adsorption.

Back-extraction of the ^{204}Tl from the tetrachloride with a small volume of an acid thallium carrier is to be preferred when the crystal is used (1 ml capacity). (Since a few percent of the excess $^{204}\text{Tl}^{+3}$ are adsorbed on the walls of the plastic pill-case during the exchange of thallium with lead, this back-extraction has to be carried out in a second container).

* For chloroform a figure of 0.5 to 0.6% was found.

PROCEDURE FOR METHOD A

The procedure is given for a sample containing from 0.1 to 0.5 μg of lead and (per $\mu\text{equiv.}$ of this metal) less than the following amounts of foreign ions (also in $\mu\text{equiv.}$): Bi^{+3} 0.1, Tl^{+3} 0.1, Fe^{+3} 2500, Cu^{+2} 1500, Hg^{+2} 10,000, Zn^{+2} 30,000, Ag^{+} 10,000, PO_4^{-3} 300 and $\text{P}_2\text{O}_7^{-2}$ 1000.

Dissolve in nitric and/or hydrochloric acid, evaporate (when necessary) to about 0.5 ml, place in the pill-case, add 0.3 ml of tartrate and neutralize with ammonia to phenolphthalein. The volume should now be about 1.5 ml.

Add 1.5 ml of the cyanide-DDC solution (a) and extract with 8 ml of carbon tetrachloride by shaking for 5 min (800 to 1000 periods per min). Centrifuge for 1 min at 1000 rev./min (\emptyset 25 cm), remove the aqueous layer with a pipet and shake for 2 min with 2 ml of cyanide-DDC solution (b). Repeat this stripping once, centrifuge and remove the upper layer.

Exchange with $^{204}\text{Tl}^{+3}$ by shaking for 5 min with 0.2 ml of alkaline $^{204}\text{Tl}^{+3}$ and 0.8 ml of cyanide-bicarbonate solution (b). Centrifuge, remove the aqueous layer, shake for 1 min with 2 ml of cyanide-bicarbonate solution (a), centrifuge and separate.

Add 0.5 ml of the thallium-DDC-carrier, transfer to a calibrated glass tube and rinse the pill-case by shaking twice for 10 min with 0.5 ml of the carrier. Adjust with tetrachloride to 10 ml, pipet into the GM-tube and measure*.

RESULTS WITH METHOD A

In Table II the results for the two ranges of lead are shown. To facilitate comparison,

TABLE II
DETERMINATION OF 0.1 TO 3.0 μg OF LEAD WITH DDC AND $^{204}\text{Tl}^{+3}$
(Mean values and standard deviation of 4 experiments each)

1	2	3	4	5	6	7
Lead added ($\mu\text{g} \cdot 10^{-3}$)	C/m ^{204}Tl in CCl_4 (minus blank) ^a	Standard deviation	Lead exchanged ^b ($\mu\text{g} \cdot 10^{-3}$)	Lead corrected ^c ($\mu\text{g} \cdot 10^{-3}$)	Error (%)	Standard deviation (%)
100	770	85	89	104	+4	11
200	1540	160	177	208	+4	10
300	2240	250	258	303	+1	11
400	2980	80	343	402	+0.5	3
500	3900	500	450	500	0	13
1000	7950	550	915	1010	+1	7
2000	14800	800	1700	1890	-5.5	5
3000	23000	1700	2650	2930	-2	7

* 260 and 1000 C/m for 0.1 to 0.4 and 0.5 to 3.0 μg of lead respectively.

^b Calculated from column 2; 0.001 μg of ^{204}Tl in CCl_4 produces 8.7 C/m in the GM-tube.

^c As 85 and 90% of the lead are exchanged in the two ranges respectively.

* With 0.5 to 3.0 μg of lead only one back-extraction is carried out, 1 ml of $^{204}\text{Tl}(\text{III})$ is used (no cyanide-bicarbonate) and the final organic layer is pipetted into a second pill-case. The first one is rinsed twice for 10 min with 2 ml of the thallium-DDC-carrier and the collected solutions are shaken for 4 min with 0.8 ml of the acid Tl-carrier. After centrifugation the aqueous layer is pipetted into a measuring-tube, the pill-case is rinsed with 0.3 ml of the acid carrier and the collected aqueous solutions are measured with the well-type crystal.

all values are corrected for measurement (of the carbon tetrachloride) with the GM-tube*.

For the two ranges (0.1 to 0.5 and 0.5 to 3.0 μg of lead) the blanks were found to be equivalent to 30 and 115 μg of lead respectively (st. dev. 6 and 45). Amounts of iron, copper and zinc up to 1000 μg had no influence on these blanks.

EXPERIMENTAL METHOD B

See also Method A

Materials and methods

²⁰⁴Tl. Dilute 3.4 mg (1 mC) of ²⁰⁴Tl(I) with 0.2 N hydrochloric acid to 10 ml and add 22 mg of thallium as Tl₂SO₄.

²¹⁰Pb. Dilute 12 μg (0.11 mC) of ²¹⁰Pb (Ra - D in equilibrium with its decay products) with 9 N hydrochloric acid to 10 ml.

Bromine water (Merck p.a.); *Diethylamine* (May and Baker).

Cyanide-tartrate solution (a): 1% potassium cyanide (AnalaR), 0.02 M ammonium tartrate (AnalaR) and (2x + 0.1) N sodium hydroxide (Merck p.a.) in water. For the value of x see below.

Cyanide-tartrate solution (b): 0.5% potassium cyanide and 0.01 M ammonium-tartrate in water, adjusted (with x gequiv. of sodium hydroxide/l) to pH 11.5.

Acid Bi-Pb-Tl-carrier: 1 mg of each metal (nitrates) per ml of 2 N nitric acid.

Bi-Pb-Tl-DDC-carrier: 0.5 mg of each metal as the DDC-complex per ml of chloroform.

DDC-solution: A fresh solution of 10 mg of DDC in 10 ml of water.

Preparation of ²⁰⁴Tl-DDC

The stock solution of ²⁰⁴Tl-DDC was prepared in chloroform as this solvent showed the smallest back-extraction of ²⁰⁴Tl during the exchange (see below). The drawback of the co-extraction of DDC was forestalled by using excess ²⁰⁴Tl for the preparation of the complex.

Again cyanide was used to obtain selectivity. Diethylamine was used as a stabilizer (see below). A 3 weeks-old solution, prepared as indicated below, showed a 2% increase of its radio-activity when shaken with ionic-²⁰⁴Tl⁺ of the same specific activity, which indicated that after 3 weeks about 2% of the ²⁰⁴Tl-DDC was decomposed to DDC (or to other molecules able to extract thallium).

Procedure: Pipet 1 ml of ²⁰⁴Tl into a glass tube and neutralize with 2 N ammonia to phenolphthalein. Add 1.1 ml of cyanide-tartrate solution (a) and 2.4 ml of DDC and shake for 3 min at 900 periods per min with 5 ml of chloroform. Centrifuge lightly (1000 r.p.m.; 25 cm Ø) and pipet the aqueous layer into a second tube to repeat the extraction. Strip the collected organic layers 3 times with 2 ml of cyanide-tartrate solution (b), add 1 mmole of diethylamine and adjust the volume to 20 ml. Store in a refrigerator; the solution is stable (enough) for 3 weeks; it contains about 4.0 μC and 100 μg of thallium as ²⁰⁴Tl-DDC per ml.

Factors influencing the stability of the ²⁰⁴Tl-DDC

The instability of the ²⁰⁴Tl-DDC is a drawback: it brings part of the ²⁰⁴Tl back into

* Part of this correction is due to the different detector, and part to the different solvent which is measured.

the aqueous layer during the exchange with lead and thus produces a (variable) blank. The same effect is of course obtained with interfering cations. The influence of several factors on this blank was investigated:

(1) *Organic solvent.* Back-extractions from carbon tetrachloride and *n*-pentanol were higher than from chloroform.

(2) *pH of the sample-solution.* A pH value of 11.5 proved to be optimal for a small blank.

(3) *Concentration of the cyanide.* In order to prevent the interference of foreign cations, 0.5% potassium cyanide had to be added to the sample solution. For amounts of foreign cations below 2 μ equiv., 0.1% potassium cyanide was sufficient. As the stronger solution did not effect the blank, however, it was chosen for all experiments.

(4) *Temperature.* When the room temperature increased to 25° or above, higher blanks were observed. An alcohol envelope was used to keep the temperature below 20° (Figs. 2 and 3).

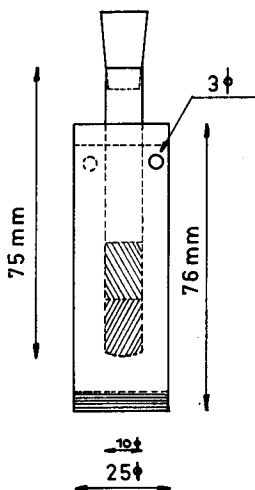


Fig. 2. Polypropylene tube with alcohol envelope.

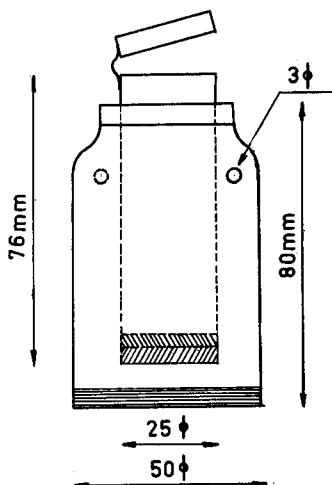


Fig. 3. Polyethylene pill-case with alcohol envelope.

(5) *The influences of (a) the concentration of the ^{204}Tl -DDC, (b) the volume of both layers, (c) the time and (d) the velocity of the shaker, are all shown in Table III. The cyanide-tartrate solution (b) was used as the aqueous layer. The blank after the second back-extraction is given; the further procedure is described below.*

A shorter shaking-time, a lower velocity, smaller volumes, and a higher concentration of the Tl-DDC are all favourable. Neither a constant amount nor a constant percentage is back-extracted (with any of the treatments).

The variation found in all these blanks might be due to a variation in the polypropylene tubes which are manufactured on metal moulds containing small amounts of lead. Although they are purified thoroughly, small differences in their lead content

might exist. However, the smaller standard deviations (in μg of ^{204}Tl) of the blanks obtained with smaller amounts of ^{204}Tl -DDC are an indication that this factor is not of much importance.

TABLE III
BACK-EXTRACTION OF ^{204}Tl FROM ^{204}Tl -DDC IN CHLOROFORM
(Mean values and standard deviations of 8 experiments each)

Treatment ^a	A			B			C			D ^b		
	3-900-1+1			6-900-1+1			6-1400-1+1			6-1400-2+2		
μg of ^{204}Tl as ^{204}Tl -DDC	6	1.5	0.5	6	1.5	0.5	6	1.5	0.5	6	1.5	0.5
$\mu\text{g} \cdot 10^{-3}$ of ^{204}Tl back-extracted	292 ^d	120	55	332	160 ^d	73 ^d	611	352	149	1100	—	—
Standard deviation	20	6	2	21	6	2	176	66	52	360	—	—
% of ^{204}Tl back-extracted ^c	5.3	9.3	13.7	6.3	13.3	19.2	12.2	37.1	49.8	24	>50	<60
Standard deviation	0.36	0.46	0.50	0.39	0.50	0.53	3.5	6.8	17.3	8	—	—

^a Shaking-time in min (*e.g.* 3), shaking velocity in periods per minute (*e.g.* 900) and volumes of both layers in ml (*e.g.* 1+1).

^b Carried out in the pill-case of Fig. 3 (the other treatments in the tubes of Fig. 2).

^c % of the thallium still present as Tl-DDC *after* the first blank.

^d Applied in practice.

(6) *Ageing effect of the ^{204}Tl -DDC.* Older preparations required a preliminary purification: the amounts of thallium back-extracted in the second and third procedures were about equal and were appreciably lower than in the first one. For preparations not older than 2 or 3 weeks, this second or third blank was comparable with the first one of the freshly prepared solution. Evidently decomposition had taken place.

When the addition of diethylamine was omitted, the decomposition increased appreciably. It was not influenced by reducing agents or by a nitrogen atmosphere.

The effect of inactive Tl-DDC or Ag-DDC was only small. As these substances may both be supposed to behave in the same way as ^{204}Tl -DDC, with respect to the (secondary) effects of the β -radiation, this result shows that radiochemical self decomposition was small. However, with an eight times larger specific activity a distinct radio-decomposition was observed. This solution was only stable for 5 days. The addition of a substance, soluble in chloroform, containing a sulfhydryl group and not extracting lead ions, would probably be favourable for the radiochemical stability but such a substance could not be found. A favourable effect was observed when the complex was stored at -5° in a benzol-silicagel substrate. Research on this kind of stabilization is in progress.

(7) *Adsorption of ^{204}Tl ions to the walls.* Apart from the ionic thallium found in the upper layer, 0.45% of the thallium ions were found to be adsorbed to the walls*. These ions are part of the blank or part of the thallium to be evaluated as being ex-

* Apart from the adsorption of the ^{204}Tl ions, adsorption of ^{204}Tl -DDC itself was observed. This ^{204}Tl -DDC had to be removed—before the determination of the adsorbed $^{204}\text{Tl}^+$ —with the help of the Tl-DDC carrier.

changed with lead ions. No influence of the presence of lead ions on the adsorbed amount of ^{204}Tl was observed and thus this adsorption could be neglected.

Exchange with lead ions

The influence of the organic solvent, the pH^* , the concentration of the cyanide, and the age of the ^{204}Tl -DDC, on the rate of exchange, proved to be small. On the other hand, higher temperatures, shaking velocities and concentrations of both components, were favourable for a high rate of exchange. No use of the first two factors could be made, however, because of the higher blank.

With the procedure given below the exchange between $0.5\ \mu\text{g}$ of lead in water and $6\ \mu\text{g}$ of thallium as ^{204}Tl -DDC in chloroform proved to be efficient only to 60–70%. A 25-fold excess of thallium was required for 90% exchange. It is evident (Table III) that the error caused by the variation of the blank then becomes too high. Isotope dilution with ^{210}Pb was introduced and the amount of ^{204}Tl in the aqueous layer was taken as a measure of the exchanged amount of lead.

Isotope dilution with radio-active lead

When a radio-isotope of lead is introduced, it has to be measured in presence of ^{204}Tl (which is the only suitable radio-isotope of thallium). ^{212}Pb (Th-B) can be separated from a thorium source, but not from its decay products (owing to their short half-life). Measurement of ^{204}Tl in the presence of these decay-products is impossible. ^{210}Pb (Ra-D) can be separated from a radium source and also from its decay products. Measurement of ^{210}Pb and ^{204}Tl in the presence of each other is feasible.

^{210}Pb was separated from its decay products (^{210}Bi and ^{210}Po) by anion exchange. The technique consisted in the sorption of the latter two elements from 9 *N* hydrochloric acid in a column (5 cm high, $0.27\ \text{cm}^2$ in diameter) of Dowex 1X10 – 100 to 200 mesh. About 98, 1 and 10% of the three isotopes respectively were found in the eluate; the influence of Pb and Bi carriers was negligible. ^{210}Po does not influence the measurements of ^{210}Pb and ^{204}Tl to a large extent. The ^{210}Bi influences both measurements, but corrections can be made.

^{210}Bi , when carrier-free, exchanged with ^{204}Tl at a lower rate than the lead. This is not in accordance with the sequence of affinities to DDC, and is obviously due to the extremely low concentration of the bismuth. As a consequence, the ratio $^{210}\text{Bi}/^{210}\text{Pb}$ changed during the exchange with ^{204}Tl . A small correction is made for this phenomenon.

Measurement of ^{204}Tl and ^{210}Pb

The GM-tube was preferred for the measurement of ^{204}Tl , as its correction factor for ^{210}Pb (^{210}Bi) was more favourable than with our crystal.

Measurement of the exchanged percentage of lead in the organic layer had to be avoided as this layer generally contained a large excess of ^{204}Tl . Thus the aqueous ^{210}Pb was measured (with the crystal, at the 47 keV-maximum). As about 2% of the lead is adsorbed to the wall during the exchange procedure, the percentage of aqueous ^{210}Pb was subtracted from 98 to find the exchanged percentage.

As indicated above, the measurement of ^{204}Tl had to be corrected with the help

* Between pH 8.5 and 13.5. This is in contrast to the exchange of $^{204}\text{Tl}^{+3}$ with $\text{Pb}-(\text{DDC})_2$ (see method A).

of the "GM%" of ^{210}Pb - ^{210}Bi (10 to 15). On the other hand the measurement of ^{210}Pb had to be corrected for ^{204}Tl ("channel%" about 5 to 7).

With all measurements at least 1000 counts were registered. Including the errors in the correction factors, the total error was about 5%.

PROCEDURE FOR METHOD B

The procedure is given for a sample containing from 0.1 to 0.6 μg of lead and (per $\mu\text{equiv.}$) not more than the following amounts of foreign ions (also in $\mu\text{equiv.}$): Bi^{+3} and Tl^{+3} 0.1; Fe^{+3} 6,000; Cu^{+2} , Hg^{+2} and Ag^{+} 8,000; other heavy metal ions 28,000; $\text{P}_2\text{O}_7^{-2}$ 15,000 and PO_4^{-3} 15,000.

Daily standardizations

Standardize ^{204}Tl and determine the "channel%". Purify ^{210}Pb , standardize and neutralize with ammonia to bromocresol purple (pH 1.0). Correct the volume to a 2-fold of the original ^{210}Pb -solution. Determine the "GM%" at the time of the measurement of the samples (see below) and, when the exchanged percentage of lead is larger than 20, add 1.8 to this "GM%" (because of exchange of Bi).

Weekly determination of the blank

Check the ^{204}Tl -DDC for losses by adsorption to the wall: transfer an aliquot containing about 1.5 μg of ^{204}Tl to a tube (Fig. 2) and adjust the volume with chloroform to 1 ml. Add 1 ml of cyanide-tartrate solution (b), shake for 6 min at 900 p.p.m. and centrifuge for 1 min (1000 r.p.m.; \varnothing 25 cm). Remove the aqueous layer and rinse the chloroform with a second 1-ml portion of cyanide-tartrate solution (b). Repeat the blank; this second time dilute the collected aqueous layers with the acid Bi-Tl-Pb-carrier to 10 ml and measure in the M6-GM-tube.

Determination of 0.1 to 0.6 μg of lead

Dissolve the sample in nitric and/or hydrochloric acid and evaporate to about 0.2 ml; then add 0.02 ml of the neutralized ^{210}Pb -solution, neutralize with concentrated ammonia to bromocresol purple and adjust the volume to 0.5 ml. Now carry out the procedure for the blank, but instead of the third 1-ml portion of cyanide-tartrate solution (b), add 0.5 ml of cyanide-tartrate solution (a). Then add the neutralized sample and carry out the further procedure for the blank as given above. To the collected aqueous layers add only 1 ml of the acid carrier, however, and measure the ^{210}Pb in 1 ml of the mixture. Determine the remaining volume by suction in a pipet, dilute with the acid Bi-Tl-Pb-carrier to 10 ml and measure the radio-activity of ^{204}Tl in the GM-tube. Carry out the calculation as indicated above. Correct the amount of lead found in this way for the lead in the ^{210}Pb (0.010 μg).

For the determination of 0.6 to 3.0 μg of lead use the same amount of ^{210}Pb as above, but 6 μg of ^{204}Tl as ^{204}Tl -DDC. A shaking time of 3 min is sufficient. For 0.05 to 0.15 μg of lead use only 0.005 ml of the neutralized ^{210}Pb -solution and only 0.5 μg of ^{204}Tl as ^{204}Tl -DDC.

RESULTS WITH METHOD B

The values of the blanks are given in Table III, footnote ^a. Some results with standard

TABLE IV
DETERMINATION OF 0.05 TO 0.6 μg OF LEAD WITH ^{204}Tl -DDC

I	2	3	4	5	6	7	8	9	10	II
Experiment No.	Lead added ^a ($\mu\text{g} \cdot 10^{-3}$)	^{204}Tl used as ^{204}Tl -DDC ($\mu\text{g} \cdot 10^{-3}$)	Lead exchanged (%)	^{204}Tl exchanged ^b ($\mu\text{g} \cdot 10^{-3}$)	Lead exchanged (from column 5) ($\mu\text{g} \cdot 10^{-3}$)	Lead found (from columns 4 and 6) ($\mu\text{g} \cdot 10^{-3}$)	Mean value of column 7	Standard deviation ($\mu\text{g} \cdot 10^{-3}$)	Error of mean (%)	Standard deviation (%)
1	600	1500	43	476	245	570	593	46	-1	8
2	600	1500	42	496	255	608				
3	600	1500	40	506	260	650				
4	600	1500	48 ^s	514	264	545				
5	300	1500	26	176	90	346	322	24	+7	7 ^s
6	300	1500	27	153	78	289				
7	300	1500	30	190	97	323				
8	300	1500	38	245	125	328				
9	100	1500	26	56	28 ^s	110	96 ^s	9 ^s	-3 ^s	9 ^s
10	100	1500	45	85	43	95 ^s				
11	100	1500	45	80	40 ^s	90				
12	100	1500	29	51	26	90				
13	150	500	18	50	25 ^s	142				
14	150	500	20	58	29 ^s	148	142	10	-5 ^s	7 ^s
15	150	500	21	62	31 ^s	150				
16	150	500	24	60	30 ^s	127				
17	100	500	20	44	22 ^s	112	112	9 ^s	+6	9
18	100	500	24	53	27	112				
19	100	500	28	53	27	96 ^s				
20	100	500	30	55	28	93 ^s				
21	50	500	18	19	9 ^s	53	51	6	+2	12
22	50	500	22	24	12	54 ^s				
23	50	500	26	27	14	54				
24	50	500	24	20	10	41 ^s				

^a Including the lead in the ^{210}Pb

^b After subtraction of the blank

amounts of lead are given in Table IV. The amounts of lead added are compared with the values calculated from the exchanged amount of thallium and the exchanged percentage of lead.

DISCUSSION OF METHODS A AND B

(A) The blank value is mainly determined by the "DDC-blank" and the "Tl-blank". The former evidently does not reach its theoretical value, owing to an incomplete reaction between DDC and $^{204}\text{Tl}^{+3}$. To obtain a higher sensitivity however, the cyanide should be purified without the use of DDC (MAYNES AND MCBRYDE¹⁵) or the "AnalaR" product should be used (see B).

The standard deviation is due to variations in the blank, the efficiency of the process and the measurement of ^{204}Tl . Better results could perhaps be attained by (1) using AnalaR potassium cyanide; (2) evaporation of the carbon tetrachloride before the exchange (both (1) and (2) resulting in a smaller "DDC-blank"); (3) a higher excess of ^{204}Tl ; (4) prolonged shaking times (both (3) and (4) resulting in a higher efficiency of the process) and finally (5) introduction of isotope dilution with ^{210}Pb to evaluate the efficiency.

(B) The blank value has already been discussed. Only the radiochemical self-decomposition could not be controlled. The blank cannot be lowered by decreasing the excess of Tl-DDC as the actual blank in the experiment would become smaller than the blank determined with the omission of lead.

The standard deviation is due to variations in (1) the blank and (2) the measurement of both isotopes. The influence of both factors increases with smaller amounts of lead: (1) a higher excess of Tl-DDC is required for a reasonable exchange, (2) either the counting error or the self-decomposition increases.

Method B is twice as sensitive as method A and 4, 10 and 20 times more sensitive than the spectrographic, polarographic and spectrophotometric techniques respectively. In addition, it requires only 40 min (30 working min) for a duplicate, which is about twice as quick as method A. Finally larger amounts of (most) foreign ions are permitted. Method A is to be preferred, however, when the sample contains small amounts of bismuth and/or thallium. Larger amounts of these metals should be removed in advance for both methods A and B. Anion exchange in 9 N hydrochloric acid is attractive for this purpose; thallium(I) should be oxidized to thallium(III) (see KRAUS AND NELSON¹⁶).

Both procedures A and B seem to be adaptable for the determination of other cations.

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SUMMARY

Two methods for the determination of submicrogram amounts of lead are described. (A) Lead is selectively extracted with carbon tetrachloride from an alkaline solution containing excess diethyldithiocarbamate (DDC) and cyanide. Traces of DDC are back-extracted. The lead in the DDC complex is exchanged with ^{204}Tl and the amount of ^{204}Tl in the organic layer acts as a measure for the lead. The limit of sensitivity is 0.1 μg ; the standard deviation is 11% (for 0.1 μg). Bismuth and thallium interfere; their influence can be accounted for with the help of EDTA, however.

(B) Excess cyanide is added to the alkaline sample solution and lead is exchanged selectively with ^{204}Tl by shaking with a CHCl_3 solution containing $^{204}\text{Tl}(\text{DDC})_1$. As the process is not 100% effective (with a reasonable excess of the thallium complex) isotope dilution with ^{210}Pb is also carried out. The amount of ^{204}Tl in the aqueous layer acts as a measure for the exchanged lead. The limit of sensitivity is $0.05 \mu\text{g}$ and the standard deviation is 12% (for $0.05 \mu\text{g}$). Bismuth and thallium must be removed in advance, e.g. by anion exchange.

RÉSUMÉ

Deux méthodes sont proposées pour le dosage radiochimique de traces de plomb: (A) Le plomb est extrait dans le tétrachlorure de carbone en présence de diéthylthiocarbamate et de cyanure en solution alcaline. On procède ensuite par échange du plomb extrait par le thallium-204. La mesure de ^{204}Tl dans la phase organique permet de déterminer la teneur en plomb. (B) On procède par échange direct du plomb au moyen du thallium-204, par traitement avec une solution de diéthylthiocarbamate de thallium-204 dans le chloroforme.

ZUSAMMENFASSUNG

Spuren von Blei können radiochemisch nach 2 Methoden bestimmt werden: (A) Man extrahiert das Blei in Gegenwart von Diäthylthiocarbamat und KCN mit Tetrachlorkohlenstoff. Durch Schütteln mit einer ^{204}Tl Thalliumlösung wird das Blei durch ^{204}Tl substituiert. Der ^{204}Tl Gehalt in der organischen Phase entspricht dem Bleigehalt. (B) Man schüttelt die mit KCN versetzte Probelösung mit einer Chloroformlösung von ^{204}Tl -Diäthylthiocarbamat und bestimmt in der wässrigen Phase den Gehalt an ^{204}Tl .

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RADIOMETRIC TRACE ANALYSIS OF COBALT* WITH
DIETHYLDITHIOCARBAMATE-³⁵S, OR ²⁰³Hg

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INTRODUCTION AND PRELIMINARY EXPERIMENTS

BODE¹, and BODE AND TUSCHE² found the extraction of cobalt with diethyldithiocarbamate (DDC) to be effective up to pH 14. The further behaviour of cobalt was found to be exceptional: the extraction was prevented by cyanide, EDTA or reducing agents, but the cobalt-(DDC)₃, once formed, was stable to these reagents. It was also stable to Pb⁺², Cu⁺², Hg⁺² and other ions, but on the other hand exchange between cobalt ions and the DDC-complexes of lead, copper, mercury etc. was negligible.

PŘIBIL³ used this phenomenon for a selective colorimetric determination of cobalt with DDC: interfering metals were exchanged with mercury(II) which has the highest affinity for DDC and forms a colorless complex.

In our work the technique of PŘIBIL is refined with the help of radio-isotopes: DDC-³⁵S is used in method (A): the mercury-DDC-³⁵S is removed with cyanide and the ³⁵S in the extract is taken as a measure for the cobalt; ²⁰³Hg is used in method (B); the explanation of this technique is given below.

(A) In preliminary experiments the co-extraction of DDC-³⁵S was studied with a preparation synthesized from C³⁵S₂ following GLEU AND SCHWAB⁴ and purified by recrystallization from ethyl acetate**. About 0.3% was co-extracted when fresh preparations of DDC-³⁵S were used***. This percentage increased on storage of the DDC-³⁵S; after 1 month 5% and after 2 months 10% of the ³⁵S-activity was co-extracted. Evidently radio-decomposition occurred; for example, free sulphur was formed which was especially evident when the sample was recrystallized. No improvement was observed when the DDC-³⁵S was kept in a high vacuum over phosphorous pentoxide. The admixture of foreign SH-groups was more successful: a 10-fold excess of cysteinamine (in gequivs.) stabilized the DDC-³⁵S. However, this excess of foreign SH-groups decreased the extraction of cobalt appreciably. Extraction of cobalt with a metal-DDC-³⁵S complex (prepared from a stabilized DDC-³⁵S solution with a large excess of the metal) was therefore applied as an alternative.

The larger amounts of mercury(II) ions and cyanide then required for the back-extractions were a disadvantage. Therefore the excess of the metal-DDC complex over the cobalt had to be kept small. To diminish the consumption of this complex by foreign metals, zinc was chosen for the metal-DDC complex as it is nearest to

* Publication 124^a of the Research Institute for Animal Husbandry "Schoonoord".

** Other batches were obtained from the Radiochemical Centre-Amersham, UK.

*** These experiments were all carried out with 500 μg of DDC-³⁵S in order to prevent interference of traces of metal.

cobalt in the sequence of affinities for DDC*. Under these circumstances (a small excess of reagent and a small difference between the affinities of cobalt and zinc for DDC) the process was not 100% effective and isotope dilution with ^{60}Co had to be introduced.

(B) Method B is founded on the same chemical system, but inactive DDC and labelled mercury(II) are used. Cobalt is extracted with a fixed amount of zinc-DDC in chloroform and the excess of the zinc complex is exchanged with $^{203}\text{Hg}^{+2}$ ions. The amount of ^{203}Hg in the organic layer (the difference from the blank) is then taken as a measure of the amount of cobalt extracted. Isotope dilution with ^{60}Co gives the extracted percentage of the cobalt.

EXPERIMENTAL [METHOD A]

Materials and methods

DDC- ^{35}S . (a) Dissolve 100 mg of DDC- ^{35}S dihydrate (3 mC) in 10 ml of 0.01 *N* ammonium tartrate (AnalaR); add 300 mg of cysteinamine hydrochloride (Light & Co.) and adjust the pH to 11 with sodium hydroxide (Merck p.a.). After saturation with pure nitrogen, keep in polyethylene at 4°. (b) As above but with 6 g of cysteinamine hydrochloride.

Zinc-DDC- ^{35}S . See below.

^{60}Co . Dilute (daily) 1 μg of ^{60}Co (10 μC) with 0.1 *N* nitric acid to 30 ml and use 0.3 ml per experiment (0.01 μg ; 0.1 μC).

Ion exchange water; resistivity 3 to 4 Megohms.

The chloroform, carbon tetrachloride, ammonium tartrate, ammonia (s.g. 0.88) and hydrochloric (s.g. 1.18) and nitric (s.g. 1.42) acids used were "AnalaR".

Ammonia-ammonium tartrate solutions. (a) 6 *N* and 0.02 *M* respectively, (b) 1 *N* and 0.02 *M* respectively.

Mercury(II) solutions, (X) and (Y). Each week make fresh dilutions from a stock solution containing 1 mg of mercury(II) per ml of 1 *N* nitric acid: neutralize with sodium hydroxide and adjust with 1% sodium bicarbonate to contain 300 (X) and 60 (Y) μg of mercury(II) per ml respectively.

Cobalt-DDC carrier. 50 μg of cobalt as $\text{Co}-(\text{DDC})_3$ per ml of chloroform.

Zinc-DDC solution. Dissolve 1 mole of zinc sulphate heptahydrate (AnalaR) and 0.14 moles of DDC (Merck p.a.) in 20 ml of 0.01 *M* ammonium tartrate, adjust with sodium hydroxide to pH 11 and extract with 4 successive 20-ml portions of chloroform. After stripping twice with 20 ml, of 0.01 *M* tartrate of pH 8.5, adjust the volume to 100 ml. Keep the chloroform at 4°. It contains about 44 μg of zinc as $\text{Zn}-(\text{DDC})_2$ per ml.

Potassium cyanide-DDC. To 100 ml of 1% potassium cyanide (Merck p.a.) in water add 250 mg of DDC dihydrate and purify from traces of lead, thallium and bismuth by extraction with five 10-ml portions of carbon tetrachloride. Store the aqueous layer over tetrachloride in polyethylene and occasionally clean it — from airborne traces of the above metals — by shaking.

The extractions were carried out in polypropylene tubes. When the room temperature increased above 24°, alcohol envelopes were applied (see Fig. 2 of ref. 5). Shaking was performed with a "Microid Flask Shaker" (Griffin and Tatlock) (see⁵).

The ^{35}S -activity was measured with an end-window GM-tube (Philips Lamp Works

* Thallium is unsuitable since a trace of its DDC complex, if not exchanged with Hg^{+2} , would resist the cyanide treatment.

No. 18506, diameter 3 cm, window 2.5 mg/cm²), combined with a sample changer (Physical Laboratory, University of Utrecht), a scaler (Philips GM 4810-PW 4020) and a printer. The scaler was adjusted to a dead-time of 300 μ sec which resulted in a correction for coincidence loss of 1% per 2000 C/m. The activity of ⁶⁰Co (and of ²⁰³Hg, ⁶⁵Zn etc.) was measured with a well-type NaI-crystal (Philips PW 4111/w, volume 1 ml) and a scaler (Philips PW 4022-4032-4052).

Preparation of zinc-DDC-³⁵S

With three successive extractions of a 2-months old preparation of DDC-³⁵S, 0.6, 0.3 and 0.3% of the ³⁵S remained in the final organic layer (after the treatments with mercury(II) and cyanide). Thus about 0.3% of the DDC-³⁵S was decomposed into chloroform-extractable products (notwithstanding the cysteinamine). These had to be removed before the preparation of zinc-DDC-³⁵S.

For this preparation carbon tetrachloride was preferred to chloroform, as it extracted less DDC-³⁵S. It will be shown that chloroform is to be preferred for the reaction with cobalt ions, thus the tetrachloride extract was diluted with chloroform.

DDC-³⁵S, (b) was used when the preparations were older than three months as it was somewhat better stabilized. The same specific activity was obtained for two samples of zinc-DDC-³⁵S made from the two months old DDC-³⁵S solutions (a) and (b) respectively. This indicated that no exchange of ³⁵SH- and SH-groups had taken place.

Procedure. Dilute 0.1 ml of the DDC-³⁵S solution with 0.01 *M* ammonium tartrate to 10 ml, adjust with sodium hydroxide to pH 11* and extract with 5 ml of chloroform; add 13 mg of zinc sulphate heptahydrate and extract with 4 successive 3-ml portions of carbon tetrachloride. Shake the combined extracts with 2 ml of 0.01 *M* tartrate of pH 8.5, dilute with chloroform to 28 (X) or 140 (Y) ml and store in calibrated glass tubes at 4°. The solutions are stable for only three weeks (owing to some radio-decomposition). They contain about 5 (X) and 1 (Y) μ g of zinc per ml.

Extraction of cobalt with zinc-DDC-³⁵S

Preliminary experiments were carried out with inactive zinc-DDC and ⁶⁰Co. The results for two different concentrations of both reactants, four different compositions of the aqueous layer and two different organic solvents are shown in Table I.

These results show that the extraction from sodium hydroxide solutions is low, especially at small concentrations of cobalt and zinc. Ammonia and chloroform solutions are to be preferred; higher pH values are favourable here. As the zinc complex is not quite stable at pH 10.5, the treatment shown in italics, including a temporary rise of the pH, was chosen.

The foreign ions thallium(I), nickel(II), cadmium(II), zinc(II) and iron(III) reacted only very slowly with zinc-DDC but the ions mercury(I), mercury(II), silver(I), copper(II), thallium(III), bismuth(III) and lead(II) were found to react rapidly. As a large excess of the zinc complex results in a large blank (see below), the amount of the last group of ions in the sample is restricted. In practice a 10-fold excess over the cobalt can be allowed.

A larger excess has to be separated in advance, for instance by: (1) Anion-exchange from concentrated hydrochloric acid. With biological samples precipitates may occur.

* At pH 10 to 10.5 precipitation may occur, which slightly hampers the procedure.

(2) Cation-exchange with selective elution. No precipitation is to be feared with biological samples. (3) Extraction with inactive zinc-DDC in chloroform from a sodium hydroxide solution. μ Equiv. amounts of interfering cations are extracted within 1 min with a 3-fold excess of the zinc complex. Only a few percent of the cobalt is lost (Table I); afterwards the aqueous layer has to be acidified to dissolve colloidal cobalt hydroxide and to decompose traces of inactive zinc-DDC, which would decrease the specific activity of the zinc-DDC- ^{35}S .

TABLE I
PERCENTAGE OF ^{60}Co EXTRACTED WITH ZINC-DDC IN 2 min^a

Amounts of ^{60}Co and Zn (as Zn-DDC)	2		0.1	
	30		1.5	
Aqueous layer (2 ml ^b)	Organic layer (2 ml)			
	CCl_4	CHCl_3	CCl_4	CHCl_3
NaOH pH 8.5	40-60	20-22	1-15	0-5
NH_4OH pH 8.5	60-80	65-85	30-50	30-50
NH_4OH (pH 10.5 \rightarrow) 8.5	70-80	70-85	45-55	65-80
NH_4OH pH 10.5	—	75-85	—	65-80

^a For the further procedure see below.

^b Containing 0.01 M ammonium tartrate

Removal of excess zinc-DDC- ^{35}S and other complexes. Blank value

With regard to the stripping with ionic mercury(II), in the range of 1 to 5 p.p.m. of zinc as zinc-DDC- ^{35}S , a 20-fold excess of mercury(II) was sufficient to complete the process to more than 95% in a few minutes. Other metal-DDC complexes behaved similarly. With the exception of bismuth, lead and thallium, traces of the DDC complexes which might escape the mercury treatment will be decomposed by cyanide.

The decomposition of mercury-DDC by potassium cyanide was studied with a ^{203}Hg -labelled complex. Decomposition by 1% potassium cyanide was complete within a few minutes, but 0.32% (st.dev. 0.06) of the aqueous ^{203}Hg remained suspended in the chloroform*, even with two successive portions of cyanide and intermediate and final centrifugation of the container.

Of course, the same percentage of the aqueous DDC- ^{35}S (resulting from the decomposition of the mercury-DDC- ^{35}S by cyanide) also remained suspended in the chloroform. This factor adds x times 0.32% to the blank when x is the excess of the (remaining) zinc-DDC- ^{35}S over the (extracted) cobalt.

However, in experiments with the ^{35}S -labelled mercury complex the blank value proved to be larger than 0.32% of the complex. Thus other factors must contribute to this result, e.g.: traces of cobalt; traces of decomposition-products of the DDC- ^{35}S ; decomposition of the mercury complex as found below for cobalt-DDC.

"Lead-free" potassium cyanide proved to be favourable for two reasons: traces of

* The greater part of this aqueous layer was removed by filtration, but part of the cobalt-DDC- ^{35}S was also lost.

lead, bismuth and thallium were removed; the residual inactive DDC in this cyanide exchanged with the DDC-³⁵S from the mercury complex.

Two successive treatments with 1% potassium cyanide were more effective than one treatment with 5% potassium cyanide; shaking for 4 min proved to be sufficient.

The mean values of 10 blank experiments with 15 and 3 μg of mercury as mercury-DDC-³⁵S were 1.45% and 3.6% respectively, corresponding to 0.048 (st.dev. 0.005) and 0.024 (st.dev. 0.002) μg of cobalt.

The stability of cobalt-DDC against the mercury and cyanide treatments was tested in experiments with 0.7 to 0.1 μg of ⁶⁰Co as ⁶⁰Co-(DDC-³⁵S)₃; 2% of both ⁶⁰Co and ³⁵S were lost in the mercury treatment; the results of the cyanide treatment are shown in Table II.

As isotope dilution with ⁶⁰Co must in any case be applied in the proposed method, the loss of cobalt as cobalt-DDC in both the mercury and cyanide treatments is not important. However, the loss of cobalt in the ionic form during the cyanide treatment requires a correction. Probably part of the cobalt complex is oxidized to the thiouram compound which in turn forms the monosulfur compound under the influence of the cyanide*.

Evidently no exchange of the DDC-³⁵S from the cobalt complex with aqueous DDC takes place, in contrast to the behaviour of the mercury complex.

TABLE II
BACK-EXTRACTION OF ⁶⁰Co-(DDC-³⁵S)₃ WITH CYANIDE^a
(Experiments in triplicate)

Cobalt as ⁶⁰ Co-(DDC- ³⁵ S) ₃ (μg)	Cobalt back-extracted (%)	
	As ⁶⁰ Co-(DDC- ³⁵ S) ₃	As ⁶⁰ Co ions
0.7	2-3 -2 ^b	3-2 -2 ^b
0.5	6-5 -6 ^b	7-8 -8 ^b
0.3	5-7 ^b -8	9-6 ^b -8
0.1	9-10-8 ^b	6-7 -8 ^b

^a 1 ml of ⁶⁰Co-(DDC-³⁵S)₃ in chloroform was shaken during 4 min with two successive 1-ml portions of 1% potassium cyanide in water.

^b Cyanide-DDC "lead-free" (5 mg DDC), instead of cyanide alone.

Measurement of ⁶⁰Co and ³⁵S

⁶⁰Co was measured with the scintillation detector and the scaler at the discrimination level 200. The background was 60 ± 5 C/m; no correction for ³⁵S was required. At least 1000 counts were registered so as to give a statistical error of 3%.

³⁵S was measured after evaporation on special aluminium dishes (see Fig. 1 of ref. 5) with the end-window GM-tube. The background was 30 ± 3 C/m; corrections for coincidence loss and ⁶⁰Co (C/m Co/2.85 ± 0.02) had to be made. No correction for autoadsorption was required. The error caused by variations in the distribution of the residue was only 6% as compared with 20% for the ordinary flat dishes in which the last traces of chloroform tend to creep to the edges.

* To prevent this decomposition, cobalt-DDC carrier was added; but exchange with the DDC-³⁵S of the mercury complex occurred.

PROCEDURE FOR METHOD A

The procedure is given for a sample containing from 0.1 to 0.5 μg of cobalt and less than a 10-fold excess of the ions Hg^+ , Hg^{+2} , Ag^+ , Cu^{+2} , Tl^{+3} , Bi^{+3} or Pb^{+2} .

Dissolve in nitric and/or hydrochloric acid and evaporate to about 0.5 ml under an infrared heater. Then place in a polypropylene tube (see Fig. 2 of ref.⁵) and add 0.3 ml of ^{60}Co . Neutralize to phenolphthalein with ammonia-ammonium tartrate solution (a) and (b), and add 0.1 ml of solution (b) in excess (pH 10.5). Readjust the pH to the indicator with 1 N hydrochloric acid. Add 1 ml of zinc-DDC- ^{35}S solution (Y), shake for 4 min at 900 rev./min, centrifuge for 1 min at 1000 rev./min (\varnothing 25 cm), and remove the aqueous layer. Add 1 ml of mercury(II) solution (Y), shake for 2 min, centrifuge as above and again remove the upper layer. Add 1 ml of cyanide-DDC, shake for 4 min, centrifuge as above and remove the upper layer. Repeat this cyanide treatment once. Add 1.5 ml of cobalt-DDC carrier and measure the total volume by suction into a pipet. Measure 1 ml for ^{60}Co and two portions of 0.5 ml for ^{35}S .

Corrections. (a) When less than 0.5 μg of cobalt is found in the final organic layer 8% (see Table II) is subtracted from the ^{35}S -value; (b) 0.01 μg is subtracted from the resulting cobalt value to account for the cobalt added as ^{60}Co . For amounts of cobalt from 0.5 to 3.0 μg solutions (X) are used instead of solutions (Y).

RESULTS WITH METHOD A

The results are shown in Tables III and IV. Procedure 1 was given above. In procedure 2 treatment (3) (see above), was applied in advance to remove excess foreign ions.

EXPERIMENTAL [METHOD B]

Materials and methods (see also method A)

Acidic ^{203}Hg solution. 1 mg of ^{203}Hg (7 μC) per ml of 0.5 N nitric acid.

Alkaline ^{203}Hg solution (a) and (b). Neutralize each week 4 ml of the acidic ^{203}Hg solution to phenolphthalein using ammonia, add ammonium tartrate to give a concentration of 0.02 M and adjust the volume to 40 ml (a) or 80 ml (b). These solutions contain 100 (a) and 50 (b) μg and 1.54 (a) and 0.74 (b) μC of ^{203}Hg per ml.

^{60}Co solution. 0.4 μg of ^{60}Co (4 μC) per ml of 1 N hydrochloric acid.

Zinc-DDC solution. See below.

Mercury-DDC-cobalt-DDC carrier. 1000 μg of both metals as the DDC complexes per ml of chloroform.

Tartrate. 0.1 M ammonium tartrate, adjusted to pH 8.5 with ammonia.

Measurement of ^{203}Hg and ^{60}Co in one solution was facilitated by an E.K.A.F. single-channel analyser.

Preparation of zinc-DDC

The amount of inactive complex used here has to be accurately known as it determines the amount of ^{203}Hg in the organic layer (of the blank). This implies that the volume of the zinc-DDC solution must be corrected for evaporation before use and that decomposition of the complex, either before use or during the extraction of cobalt, must be prevented, or accounted for.

Radio-decomposition is of course not to be feared here, thus the addition of cysteine-amine can be omitted. The addition of diethylamine was found to stabilize the complex (compare⁵), but mercury-amine complexes were formed (and extracted into the

TABLE III
DETERMINATION OF 0.1 TO 0.4 μg OF COBALT

Procedure	Co added ($\mu\text{g} \cdot 10^{-3}$)	Cu added (μg)	Co exchanged (%)	⁵⁸ Co in the final organic layer (equiv. of 1 μg Co $\cdot 10^{-3}$)	Idem corrected	Co found (corrected) ($\mu\text{g} \cdot 10^{-3}$)	Co found (mean value) ($\mu\text{g} \cdot 10^{-3}$)	Standard deviation (%)	Error of mean (%)
2	100	6	28	38	35	115	103	15	+3
2	100	6	41	43	39 ^s	86 ^s			
1	100	0	45	62	57	117			
1	100	0	62	68	62 ^s	91			
2	200	6	34	75	68 ^s	192			
2	200	6	36	87	80	212			
2	200	6	56	127	117	198	207	7 ^s	+3 ^s
1	200	0	54	120	110 ^s	195			
1	200	0	55	135	124	215			
1	200	0	64	167	154	231			
2	300	6	18	65	60	323			
2	300	6	26	82	75 ^s	281			
1	300	0	28	96	88 ^s	306	301	6	+0 ^s
1	300	0	49	162	149	294			
2	400	6	22	112	103	457			
2	400	6	31	122	112	353	407	14	+2
1	400	0	35	144	132 ^s	368			
1	400	0	37	185	170	448			

TABLE IV
DETERMINATION OF 0.5 TO 3.0 μg OF COBALT

Procedure	Co added (μg)	Cu added (μg)	Co exchanged (%)	^{55}S in the final organic layer (equiv. of 1 μg Co)	Co found (μg)	Co found (mean value) (μg)	Standard deviation (%)	Error of mean (%)
2	0.5	50	47	0.24	0.50	0.50		
2	0.5	50	54	0.30	0.55	0.55	7	0
1	0.5	0	38	0.19	0.49	0.49		
1	0.5	0	45	0.21	0.46	0.46		
2	1.0	50	38	0.40	1.04	1.01	8	+1
2	1.0	50	46	0.42	0.91	0.91		
1	1.0	0	50	0.55	1.10	1.10		
1	1.0	0	45	0.44	0.97	0.97		
2	2.0	50	36	0.80	2.22	2.01	7 ^s	+0 ^s
2	2.0	50	36	0.73	2.03	2.03		
1	2.0	0	40	0.77	1.93	1.93		
1	2.0	0	38	0.71	1.87	1.87		
2	3.0	50	39	1.16	2.98	3.06	7	+2
2	3.0	50	36	1.10	3.05	3.05		
1	3.0	0	38	1.27	3.35	3.35		
1	3.0	0	47	1.34	2.85	2.85		

chloroform) on shaking with a $^{203}\text{Hg}^{+2}$ solution, thus the amine had to be omitted.

Traces of co-extracted DDC are not detrimental here, as they also react with $^{203}\text{Hg}^{+2}$; thus an excess of DDC is permissible.

Procedure. Dissolve 300 μg of zinc as zinc sulphate heptahydrate and 24 mg of DDC dihydrate (a 10-fold excess) in 1 ml of tartrate solution and adjust the pH to 11 with sodium hydroxide. Extract with four successive 5-ml portions of chloroform, strip the collected organic layers with two successive 10-ml portions of tartrate and dilute to 20 ml. Store in a well-stoppered calibrated glass tube at 4° . The solution contains about 15 μg of zinc as zinc-DDC per ml and is stable for two or three weeks.

Extraction of cobalt with zinc-DDC

Cobalt is determined here as the difference between two measurements of ^{203}Hg . To make this difference as large as possible, the excess of zinc-DDC must be restricted and as much as possible of the zinc must be exchanged with cobalt. In our procedure a 0.5- to 2.0-fold excess is applied (as compared with a 1.3- to 6.5-fold excess with method A). In order to promote the exchange between cobalt and zinc, the procedure is again carried out with an ammonia solution of pH 8.5 which has temporarily been adjusted to pH 10.5 (see Table I); shaking was continued for 10 min.

When the exchange between cobalt and zinc was carried out at pH 10.5 this resulted in a marked fall of the ^{203}Hg value, indicating decomposition of the zinc complex at pH 10.5. The same phenomenon was observed when the temperature rose above 22° . An alcohol envelope was again applied to circumvent the latter difficulty.

With the omission of any cobalt, from 2 to 6 % of the zinc was found in the aqueous layer (experiments with ^{65}Zn -DDC). However, no influence of this effect on the blank (the amount of ^{203}Hg in the final organic layer with the omission of cobalt) was observed. Probably traces of copper and other cations from the reagents and the containers were exchanged with the zinc.

Removal of excess zinc-DDC and foreign DDC complexes with $^{203}\text{Hg}^{+2}$ ions

In contrast to method A, the amount of mercury found in the chloroform after shaking it with an aqueous mercury(II) solution directly contributes to the blank, as here the mercury is labelled. For this reason the excess of ^{203}Hg should be minimized. On the other hand one must be sure that the exchange between zinc and mercury is complete: with method A a small residue of zinc-DDC could be supposed to be removed by cyanide but here the amount of ^{203}Hg exchanged with the zinc is taken as a measure of the cobalt.

Complete exchange of 2.25 μg of ^{65}Zn (as ^{65}Zn -DDC in 1 ml of chloroform) with even 50 μg of ^{203}Hg in 1 ml of tartrate (a 7-fold excess) could not be accomplished in the tubes used in method A, within a reasonable time. A small polyethylene pill-case with a somewhat larger diameter (16 mm) and 29 mm high was found to be more favourable. Now the exchange of the ^{65}Zn was complete to 96.5% (st.dev. 2.3) within 20 min. A smaller excess of ^{203}Hg was not permissible.

The amount of ^{203}Hg in the chloroform — the blank — had a standard deviation of 4% or 0.02 μg . With 7.5 μg of zinc as Zn-DDC and 100 μg of ^{203}Hg the standard deviation of the blank was again 0.02 μg of ^{203}Hg . Experiments with pure chloroform indicated that the greater part of this standard deviation was due to the admixture of a variable amount of ionic ^{203}Hg with the chloroform.

Again this blank was lowered by filtration but again losses of the ^{203}Hg - and ^{60}Co -DDC complexes occurred (notwithstanding the addition of carrier), when filtration was applied in the determination of cobalt. Desiccated filter papers (KOVÁCS⁶; WEGMANN⁷) were also investigated but proved to be unsuccessful. Thus the values found above had to be accepted.

From 10 to 20% of 0.4 to 0.2 μg of cobalt as ^{60}Co -DDC were exchanged with ^{203}Hg within the 20 min required for the exchange of mercury with zinc (2% within 2 min, see method A). This percentage increased with decreasing amounts of cobalt. Especially with the smaller amounts of cobalt this exchange was found to be not quite stoichiometric but extra amounts of ^{203}Hg were found in the chloroform. No explanation of this phenomenon could be found.

Measurement of ^{203}Hg and ^{60}Co

^{203}Hg and ^{60}Co can be measured in the final organic layer with the scintillation detector and the scaler. Discrimination levels of 8 and 200 are then applied respectively. The correction factor ^{60}Co at D8/ ^{60}Co at D200 is about 200%.

With the single-channel analyser better results are obtained. ^{203}Hg is measured at the 0.28-MeV maximum with a channel-width of 20 V. ^{60}Co is measured above 1 MeV. The correction factor of ^{60}Co for the ^{203}Hg measurement is 20% (with a more stable detector the channel-width for ^{203}Hg , and hence the correction factor of ^{60}Co , can be decreased appreciably). No correction for ^{203}Hg need be made in the ^{60}Co measurement.

PROCEDURE FOR METHOD B

The procedure is given for a sample containing from 0.8 to 3.0 μg of cobalt and less than a 4-fold excess of foreign cations able to exchange with zinc-DDC (see method A).

Dissolve in nitric and/or hydrochloric acid and evaporate to less than 0.5 ml; add 0.1 ml of ^{60}Co and 0.1 ml of tartrate. Neutralize to phenolphthalein with concentrated and/or 1 N ammonia. Now add 0.1 ml of 1 N ammonia in excess (pH 10.5), readjust the pH with 1 N hydrochloric acid to phenolphthalein and transfer the mixture to the pill-case.

Add 1 ml of chloroform and 0.15 ml of the zinc-DDC solution, shake the tube for 10 min (900 rev./min) and centrifuge lightly for 1 min (1000 rev./min; \varnothing 25 cm). Remove the aqueous layer and rinse by shaking for 1 min with 1 ml of the tartrate. Centrifuge and remove the rinsing liquid. Add 1 ml of the alkaline ^{203}Hg solution (b). Shake for 20 min, centrifuge and remove the aqueous layer. Finally add 0.2 ml of the mercury-DDC-cobalt-DDC carrier, measure the volume with a pipet and measure the counts of 1 ml in the well-type crystal.

Carry out blank determinations to control the zinc-DDC solution. Measure the ^{203}Hg - and ^{60}Co -standards to control the detector. Subtract the ^{203}Hg -value of the sample (in $\mu\text{equiv.}$) from the ^{203}Hg -value of the blank* to give the amount of cobalt (in $\mu\text{equiv.}$) present in the final organic layer. The ^{60}Co -value for the sample gives the percentage of cobalt in this layer. From the amount of cobalt found, subtract 0.04 μg for the cobalt in the ^{60}Co -solution.

* This value is determined in quadruplicate once a week.

For the determination of 3 to 10 μg of cobalt use 0.5 ml of chloroform and 0.5 ml of the zinc-DDC solution. Furthermore use ^{203}Hg solution (a) instead of (b).

RESULTS WITH METHOD B

The results with 0.4 to 10 μg of cobalt are shown in Table V. For the determination of 0.4 μg of cobalt only 0.075 ml of the zinc-DDC solution and 0.5 ml of ^{203}Hg solution (b) were used. The amount of cobalt from the ^{60}Co is already included in the values given in the second column.

TABLE V
DETERMINATION OF COBALT WITH ZINC-DDC AND $^{203}\text{Hg}^{+2}$

Number of experiments	Cobalt added (μg)	Cobalt found (μg)	Standard deviation (μg of cobalt)	Idem (%)	Error of mean (%)
4	10	10.3	0.80	8	+ 3
4	5	5.0	0.35	7	0
4	2	1.95	0.15	7.5	- 2.5
10	1.4	1.41	0.14	10	+ 1
12	0.8	0.82	0.14	17.5	+ 2.5
7	0.6	0.61	0.17	28	+ 2
6	0.4	0.29	0.07	24	-27

DISCUSSION OF METHODS (A) AND (B)

(A) The factors influencing the blank were discussed above. In the presence of cobalt a (variable) part of the mercury-DDC- ^{35}S complex is replaced by the cobalt complex which does not behave in exactly the same way. Thus the actual blank will probably be (variable and) smaller than the one given above.

The experimental mean of the standard deviation (st.dev.) is 9%. The standard deviation of the measurements of ^{60}Co and ^{35}S is in total about 7% and a standard deviation of 0.4 to 5% is the result of the variable blank (with 40% exchange of cobalt).

The sensitivity limit can be calculated from the amount of cobalt equivalent to a ^{35}S -activity of, say, 3 times the background of the GM-tube (0.0045 μg) and from the percentage of the cobalt which reaches the final ^{35}S -measurement (7 to 10). This limit (about 0.04 μg) could be lowered appreciably with a gas-flow or liquid-scintillation counter.

(B) Neglecting the experiments with 0.4 μg of cobalt, the mean deviation from stoichiometry is 1%. The large deviation from stoichiometry observed with 0.4 μg of cobalt is probably due to the extra ^{203}Hg in the organic layer observed especially with these smaller amounts. The standard deviation of the blank is evidently one of the factors influencing the accuracy of the method. As cobalt is determined as the difference between two ^{203}Hg -measurements the (square values of the) standard deviations must be added. Thus the total effect is 3 to 5.5%.

Another error probably occurs in the determination of the efficiency of the process for the cobalt. When the ^{60}Co in all fractions is measured, not more than 90% (st.dev. 5) of the original amount can be found. Probably adsorption effects occur. The error caused in the measurement of the organic ^{60}Co thus may be a few percent of

the total ^{60}Co or about 6% of the measurement, which accounts for the remaining part of the standard deviation found in Table V.

The main advantages of method *B* over method *A* are (1) the omission of a labelled organic reagent, which is liable to radio-decomposition and (2) the omission of the cyanide treatment. The main drawbacks are (1) the determination of cobalt as a difference of two measurements of ^{203}Hg and (2) the "exchange" of non-stoichiometric amounts of mercury and cobalt in the smaller concentration ranges, which limits the sensitivity.

Both methods show that determinations of cobalt in the submicrogram range are possible using radiometric techniques. The advantage over activation analysis is that no reactor or other source of nuclear particles is required. Comparison with classical techniques shows our methods to be of equal sensitivity. Undoubtedly further refinement of the procedures presented will be possible with continued research.

ACKNOWLEDGEMENT

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SUMMARY

Two radiometric methods for the determination of submicrogram amounts of cobalt are described. (A) Cobalt is extracted from an ammoniacal solution with a zinc-diethylthiocarbamate- ^{35}S solution in chloroform. Excess reagent and interfering metals are removed with mercury(II) and cyanide. The ^{35}S in the final organic layer is a measure of the cobalt in this layer. (B) Cobalt is extracted from an ammoniacal solution with a fixed amount of zinc-DDC in chloroform. Excess reagent and complexes of foreign metals are removed by exchange with $^{203}\text{Hg}^{+2}$ and the ^{203}Hg in the chloroform (compared with a blank) acts as a measure of the cobalt. Method *A* is applicable to 0.1 μg of cobalt and method *B* to 0.8 μg . As the efficiency of both processes is variable, isotope dilution with ^{60}Co is carried out. A 10-fold excess of foreign metals is permitted in method *A* and a 4-fold excess in method *B*; larger amounts are previously removed, e.g. by extraction with inactive zinc-DDC from sodium hydroxide media.

RÉSUMÉ

Deux méthodes sont proposées pour le dosage radiométrique de traces de cobalt: (A) le cobalt est extrait au moyen de zinc-diéthylthiocarbamate- ^{35}S dans le chloroforme. On mesure ^{35}S dans le solvant organique. (B) le cobalt est extrait au moyen de zinc-diéthylthiocarbamate dans le chloroforme. L'excès de réactif est traité par le mercure-203. La mesure de ce dernier permet de déterminer la teneur en cobalt.

ZUSAMMENFASSUNG

Beschreibung von zwei radiochemischen Methoden zur Bestimmung von Spuren von Kobalt: (A) Extraktion mit Chloroform in Gegenwart von Zink-Diäthylthiocarbamat- ^{35}S . Der Überschuss an Reagenz und störende Metalle werden mit Quecksilber(II) und Cyanid entfernt. Die Messung des ^{35}S Gehaltes in der organischen Phase ergibt den Gehalt an Kobalt. Isotopenverdünnung mit ^{60}Co ist notwendig. (B) Extraktion mit Chloroform in Gegenwart einer gemessenen Menge von Zink-Diäthylthiocarbamat. Der Überschuss an Reagenz und andere Metalle werden durch Umsetzung mit $^{203}\text{Hg}^{+2}$ entfernt. Der Gehalt der Chloroformschicht an ^{203}Hg entspricht der Menge an Kobalt.

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POLAROGRAPHIC CHARACTERISTICS AND CONTROLLED-POTENTIAL ELECTRO-REDUCTION OF DIMETHYLGLYOXIME

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INTRODUCTION

Although the polarographic characteristics of several ketoximes have been studied by GARDNER AND GEORGANS¹, and although the amperometric titration of nickel(II) with dimethylglyoxime has been described by KOLTHOFF AND LANGER², there has been no systematic investigation of the polarographic behavior of this substance. The present paper describes the results of a study undertaken partly because of the importance of dimethylglyoxime and other similar compounds in inorganic analysis, partly because of a desire to compare the behavior of a *vic*-dioxime with that characteristic of simple oximes, and partly in connection with a general program of research on the induced currents³ encountered in controlled-potential electrolyses.

EXPERIMENTAL

Polarograms were obtained with a conventional pen-and-ink recording polarograph, dropping mercury electrode assembly, and modified H-cell⁴. Controlled-potential electrolyses were carried out with an Analytical Instruments, Inc. (Wolcott, Conn.) potentiostat and current integrator, using a double-diaphragm cell⁵ in the manner previously described.

All polarographic and kinetic measurements were made at $25.00 \pm 0.01^\circ$. All solutions were deaerated with prepurified nitrogen from which oxygen was removed by passage through either chromous chloride solutions or hot metallic copper. Mercury was purified as described by MEITES AND MOROS³. Dimethylglyoxime, ethanol, and all other chemicals used were ordinary reagent grade and were not further purified. Measurements of pH were made with a Beckman Model G glass electrode pH meter. Except as otherwise noted below, all data were obtained with solutions containing 15% (v/v) ethanol.

DATA AND DISCUSSION

Typical polarograms of freshly prepared 0.1 mM solutions of dimethylglyoxime in

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citrate buffers of various pH values are shown in Fig. 1. A single well-defined wave is observed at pH values below about 3.5. At pH values between about 3.5 and 5.5 the wave appears to divide into two parts, but these coalesce again at about pH 6.

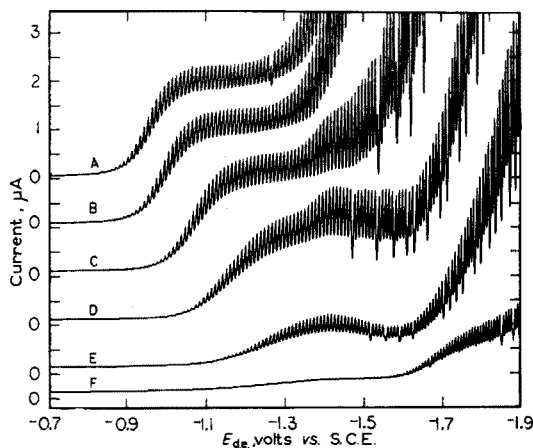


Fig. 1. Polarograms of 0.1 mM dimethylglyoxime in 0.01 *F* citrate-0.09 *F* sodium chloride at pH (a) 2.44, (b) 2.96, (c) 3.90, (d) 4.99, (e) 5.98, (f) 7.03.

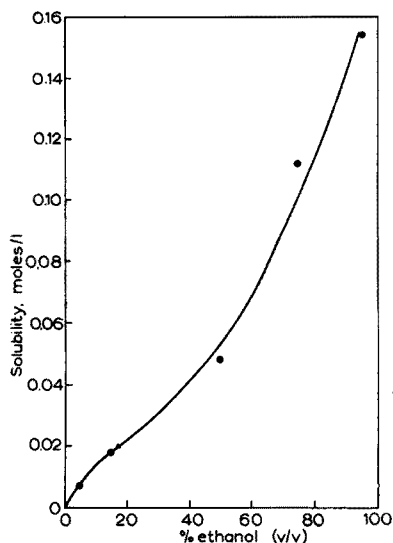


Fig. 2. Solubility of dimethylglyoxime in ethanol-water mixtures at 25°.

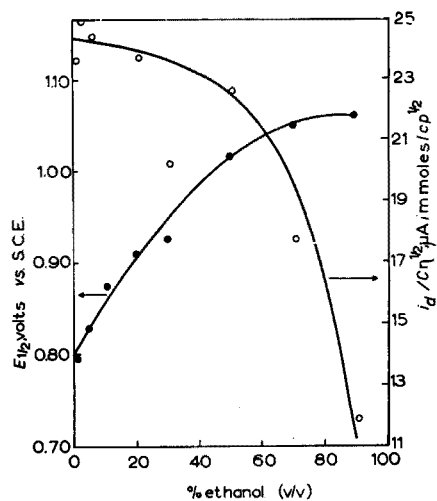


Fig. 3. Effects of ethanol concentration on (a) $-E_{1/2}$ and (b) $i_d/C\eta^{1/2}$ for 0.1 mM dimethylglyoxime in 0.1 *F* hydrochloric acid solutions.

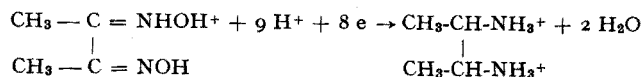
At pH 7 the diffusion current of the wave is only about a tenth of its value in strongly acid solutions; there is also an ill-defined wave at a very negative potential, which is believed to be due to the catalytic reduction of hydrogen ion. Dimethylglyoxime is

polarographically inert in phosphate or borate buffers having pH values above 8, and in sodium hydroxide solutions.

In 0.10 *F* hydrochloric acid the diffusion current of dimethylglyoxime is accurately proportional to its concentration over the range from 0.02 to 2 mM. KOLTHOFF AND LANGER² reported that "at concentrations larger than 0.002 *M*, the diffusion current of dimethylglyoxime soon reaches a value above which it does not increase upon further increase in the concentration". The data shown in Fig. 2 serve to explain this observation. They were obtained by equilibrating excess dimethylglyoxime at 25° with water-alcohol mixtures of known compositions, and determining the concentrations of the saturated solutions gravimetrically⁶. Under the conditions employed by KOLTHOFF AND LANGER, the ethanol content of a titration mixture containing 2 mM dimethylglyoxime would have been approximately 2%; from Fig. 2 the solubility of dimethylglyoxime may be estimated to be about 2.5 mM at this ethanol concentration.

At pH values between 1 and 3 the diffusion current constant of dimethylglyoxime is independent of pH: a capillary which gave $i_a/C = 19.5 \mu A/\text{mmole/l}$ in 0.10 *F* hydrochloric acid gave $i_a/C = 19.3$ in 0.01 *F* citrate-0.09 *F* sodium chloride at pH 3.0. The former value corresponds to $i_a/Cm^{2/3}t^{1/6} = 11.3 \pm 0.3$. This is approximately the expected value for an 8-electron reduction. Controlled-potential electrolysis of a fresh solution of dimethylglyoxime in 0.10 *F* hydrochloric acid at any potential between -0.7 and -1.2 V, followed by evaporation of the ethanol, water, and excess acid and recrystallization of the product, gave a white crystalline material whose physical properties and infrared spectrum agreed with those of 2,3-diaminobutane dihydrochloride.

In this region of pH values, the basic dissociation constants of dimethylglyoxime⁷ lead to the conclusion that it must be present largely or entirely in the form of the mono-protonated species. Hence the overall equation for the reduction under these conditions may be written



Plots of $E_{a.e.}$ vs. $\log i/(i_a - i)$ were found to be strictly linear over the range $0.1 \leq i/i_a \leq 0.95$ at all pH values between 1 and 3. This indicates that the electrode reaction under these conditions involves a single rate-determining electron-transfer step^{8,9}. The mean slope of such a plot was $-0.103 \pm 0.008 \text{ V}$; since this slope is given by the equation

$$\Delta E_{a.e.}/\Delta \log [i/(i_a - i)] = -0.0542/\alpha n_a$$

it follows that $\alpha n_a = 0.53$. Assuming that α is approximately equal to 0.5 gives $n_a = 1$.

The half-wave potential of the dimethylglyoxime wave at pH values between 1 and 3 obeys the equation

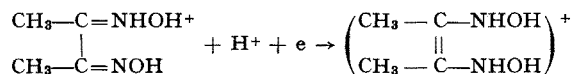
$$E_{1/2} = -0.718 - 0.096 \text{ pH}$$

with a mean deviation of $\pm 4 \text{ mV}$. The theoretical rate of variation of half-wave potential with pH for a totally irreversible wave in which p hydrogen ions are consumed in the rate-determining step and in any fast chemical steps that may precede

it, is given by

$$\Delta E_{1/2}/\Delta pH = -(0.0591/\alpha n_a)p$$

which, together with the above value of αn_a , yields $p = 0.86$. This is equal to 1 within the experimental error of the half-wave potential measurements, and it therefore appears that the rate-determining step may be represented by



GARDNER AND GEORGANS¹ concluded that the reduction of a mono-oxime from acidic solutions also proceeds through its conjugate acid.

Fig. 3 shows data on the effects of ethanol concentration on the wave height and half-wave potential of dimethylglyoxime in solutions containing 0.10 *F* hydrochloric acid. The wave height obtained with a given concentration of dimethylglyoxime decreases slowly with increasing ethanol concentration up to about 30% (v/v), then more rapidly until, with 90% ethanol, it is slightly less than half (after correction for the changing viscosity of the solution) of its value in the presence of 0–10% ethanol. At the same time the half-wave potential shifts to more negative values. It is suggested that these effects, as well as those of increasing the pH above 3 in the presence of 10% ethanol, are due to changes in the position and rate of the equilibrium between dimethylglyoxime and its protonated form, and that the situation is probably very similar to that observed with other substances—*e.g.*, pyruvic acid—for which a proton-transfer step must precede reduction¹⁰. The effect of ethanol concentration on the half-wave potential doubtless also involves changes in the liquid-junction potential and in the electrochemical kinetic parameters that characterize the reduction of the protonated species.

Polarograms of dimethylglyoxime in 0.10 *F* hydrochloric acid exhibit a long flat plateau beginning at about -0.9 V. From the fact that controlled-potential electrolyses under these conditions yielded 2,3-diaminobutane as the sole identifiable product it might be presumed that controlled-potential coulometry would show that 8 electrons were consumed in the reduction of one molecule of dimethylglyoxime at any potential on the rising part of the wave or on its plateau, but actually this is not the case. The experimental *n*-values obtained at potentials between -0.7 and -1.1 V are shown in Fig. 4. The first of these values corresponds to $i/i_a = ca. 0.1$; electrolyses at still more positive potentials, which would be expected to give *n*-values more nearly equal to the expected value of 8, would be too slow to be practical.

To explain these data it appears to be necessary to assume that the stirring employed in the coulometric experiments carried some intermediate away from the surface of the mercury pool before it could undergo further reduction. The identity of this intermediate cannot be inferred from these experiments, although the evidence to be presented strongly suggests that only one intermediate is involved. In other words, it appears that there is only one intermediate for which mass transfer by convection proceeds under these conditions at a rate comparable to that of the electron-transfer process in which it would be consumed in the absence of stirring. Representing this intermediate, for the sake of generality, as R-N·, it is further necessary to assume that on leaving the electrode surface it becomes involved in a

protonation equilibrium, $R-N: + H^+ \rightleftharpoons R-NH^+$, and that the species $R-NH^+$ on again reaching the electrode surface can undergo reduction in either of two ways:

- (1) $R-NH^+ + e \rightarrow H^+ + \text{reduction product of } R-N:$
 (2) $R-NH^+ + e \rightarrow 1/2 H_2 + R-N:$

From these assumptions it follows that the rate of the extraneous process (1) at any instant must be proportional to the concentration of dimethylglyoxime remaining unreduced at that instant. Thus this "induced" reduction of hydrogen ion (in the terminology of MEITES AND MOROS⁹) should give rise to a current which is a constant fraction of the total electrolysis current at any instant. A plot of $\log i$ vs. time should

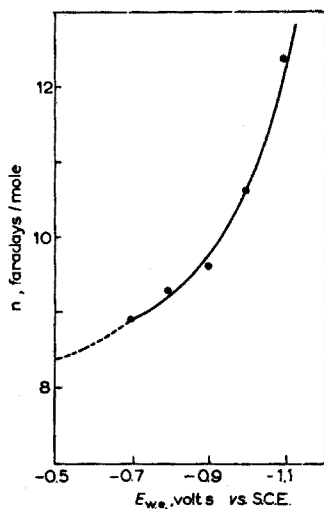


Fig. 4. Variation of apparent n -value with working-electrode potential for the reduction of dimethylglyoxime from 0.1 F hydrochloric acid solutions.

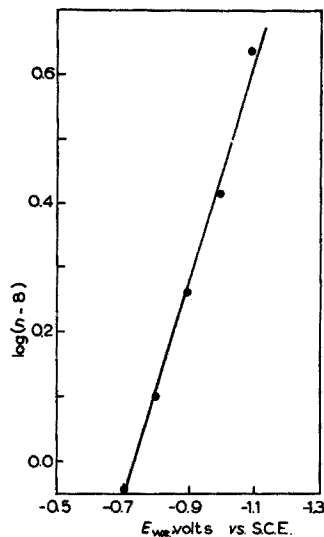


Fig. 5. Plot showing effect of working-electrode potential on the rate of the proton-reduction step accompanying the reduction of dimethylglyoxime from 0.1 F hydrochloric acid solutions.

therefore be linear, as is the case in simple controlled-potential electrolyses that do not involve an induced current. In fact, after excluding the initial regions of constant current that were often obtained because of the high cell resistance¹¹, experimental plots of $\log i$ vs. t were always satisfactorily linear up to at least 95% reduction after appropriate corrections had been applied for the background current (direct reduction of hydrogen ion) observed in the absence of dimethylglyoxime. Small deviations appeared thereafter which could be ascribed to the decomposition of dimethylglyoxime during the first part of the electrolysis (see below).

Integrating the rate equation for the induced process (1) consequently leads to the conclusion that the logarithm of the excess or "induced" quantity of electricity should be a linear function of the working-electrode potential. Since

$$i_i = k^{\circ} j_n n F y A C_i e^{-\alpha n_a F y^2 / RT}$$

where i_i is the induced current at any instant, C_i is the concentration of the assumed

intermediate $R-NH^+$, and the other symbols have their customary significance; since

$$C_t = kC^{\circ} e^{-k_2 t}$$

where C° is the initial concentration of dimethylglyoxime and k_1 and k_2 are constants; and since

$$\int_0^{\infty} i_t dt = (Q - 8 N^{\circ}) F_{\nu} = \left(\frac{Q}{N^{\circ}} - 8 \right) F_{\nu} N^{\circ}$$

where Q is the total number of mF consumed, N° is the number of mmoles of dimethylglyoxime originally present, and Q/N° is the apparent n -value obtained, it follows that

$$-\frac{\alpha n_a}{0.0591} E = \log(n - 8) + k$$

where k is a combination of experimental parameters. A plot of the data in accordance with this equation is shown in Fig. 5. It is the linearity of this plot that leads to the conclusion that the induced quantity of electricity arises from the reduction of a single protonated intermediate: if two such species were involved, the plot would be curved unless the two αn_a values were, by coincidence, nearly equal.

From the slope of the line in Fig. 5 it is possible to deduce the value of αn_a for the induced process; this is found to be 0.11. As this can scarcely correspond to any value for n_a but 1, it may be taken to constitute some slight further support for the above mechanism. The value of α is unexpectedly low, but is not inconsistent with values found by others¹² for processes occurring in the presence of organic materials adsorbed

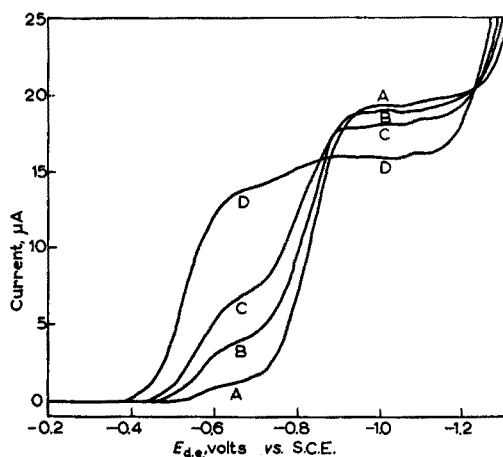


Fig. 6. Polarograms of 1 mM dimethylglyoxime in 0.05 F hydrochloric acid-0.05 F potassium chloride after (a) 0.56, (b) 2.2, (c) 4.7, and (d) 25 h.

on the surfaces of mercury electrodes, and it is not unreasonable to assume that one or more of the substances involved in this complex overall reaction may undergo such adsorption.

Acidic solutions of dimethylglyoxime have been found to be unstable; the polarographic manifestations of this instability are shown in Fig. 6. The height of the original wave, for which $E_{1/2} = -0.84$ V at this pH, decreases, and a new wave, for

which $E_{1/2} = -0.54$ V, grows at its expense. Plots of the logarithm of the diffusion current of the original dimethylglyoxime wave against time were linear, as expected for a process whose rate is proportional to the concentration of unreacted dimethylglyoxime. From the slopes of such plots at several different pH values, all in 15% ethanol at an ionic strength of 0.1, and from data on the relationship between apparent pH and hydrogen-ion concentration under these conditions, the following rate law was deduced:

$$\frac{d[(\text{CH}_3\overset{\text{I}}{\text{C}} = \text{NOH})_2]}{dt} = -(1.13 \pm 0.1) \cdot 10^{-3} [(\text{CH}_3\overset{\text{I}}{\text{C}} = \text{NOH})_2] [\text{H}^+]$$

where the rate constant is in 1/mole/sec. The polarographic rate data were confirmed by the results of an experiment in which aliquots of a dimethylglyoxime solution in a sodium chloride-hydrochloric acid medium in 15% ethanol (ionic strength 0.10, apparent pH 1.21) were added to excess ammoniacal nickel(II) solution. The weight of precipitate thus obtained decreased with increasing age of the dimethylglyoxime solution; though the data obtained were of limited precision because of the small amounts of dimethylglyoxime involved, the rate constant, $(1.04 \pm 0.1) \cdot 10^{-3}$, was in good agreement with that found polarographically.

The half-wave potential of the product of this decomposition is considerably more negative than that of diacetyl. For example, in 0.10 *F* hydrochloric acid $E_{1/2}$ for the decomposition product was found to be -0.54 V *vs.* SCE whereas the corresponding value for diacetyl was found to be -0.42 V, in good agreement with the data of HARRISON¹³. Moreover, the infrared spectrum of the decomposition product, obtained by evaporating an aged solution of dimethylglyoxime to dryness and recrystallizing the residue, showed no carbonyl absorption band, so that the product cannot be either diacetyl or its monoxime. This spectrum is shown in Fig. 7. The bands at 1040, 1090,

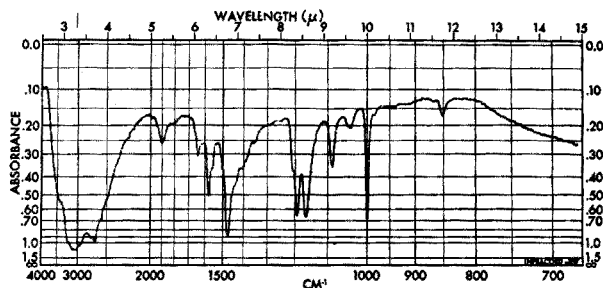


Fig. 7. Infrared spectrum (KBr pellet) of the crystalline product isolated from aged acidic solutions of dimethylglyoxime.

and 3000 cm^{-1} are doubtless due to traces of ethanol occluded in the crystals. Those at 855 , 1170 , 1195 , and 1475 cm^{-1} are consistent with the data of LÜTTKE¹⁴ and TARTE¹⁵ on the spectra of mononitroso compounds. No precedent could be found in the literature for the extraordinarily sharp band at 1000 cm^{-1} , but it does not appear inconsistent with an identification of the decomposition product as 2,3-dinitrosobutane. No compound sufficiently analogous to this to warrant comparison has been studied polarographically.

Although, as was mentioned above, dimethylglyoxime produces no wave in phosphate or borate buffers at pH values above 8, or in dilute sodium hydroxide solutions, a fairly well-defined wave was obtained in 0.1 *F* ammonia–0.1 *F* ammonium chloride (apparent pH 8.9). The half-wave potential of this wave, -1.56 V vs. SCE, is far too negative to correspond to either diacetyl or its imine¹⁶, and its diffusion current constant, 6.2 ± 0.3 , is about 20 times as great as that reported¹⁶ for the latter.

SUMMARY

Acidic solutions of dimethylglyoxime produce a well-defined polarographic wave corresponding to an 8-electron reduction to 2,3-diaminobutane. The effects of various experimental variables on the characteristics of the wave are described, and an equation is advanced for its rate-determining step. The reduction of dimethylglyoxime at a large mercury electrode at controlled potential induces the reduction of hydrogen ion, and the mechanism of this process is discussed on the basis of coulometric evidence. Acidic solutions of dimethylglyoxime slowly decompose, by a reaction whose rate law is given, yielding what is believed to be 2,3-dinitrosobutane as the principal product.

RÉSUMÉ

La diméthylglyoxime en solution acide donne une vague polarographique bien définie correspondant à une réduction en diamino-2,3-butane, où interviennent 8 électrons. L'influence de divers facteurs a été examinée.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das polarographische Verhalten von Dimethylglyoxim in saurer Lösung. Die gut definierte polarographische Welle entspricht einer 8-Elektronen Reduktion des Dimethylglyoxims zu 2,3-Diaminobutan. Der Einfluss verschiedener Faktoren wurde untersucht. Diskussion des Reaktionsmechanismus.

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HIGH PRECISION COMPARATIVE POLAROGRAPHY

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INTRODUCTION

Differential polarography^{1,2} is a general technique in which the current flowing in one polarographic cell is subtracted from that flowing in another. When one cell contains an accurately known solution and the other a similar but unknown solution, the small current difference can be amplified and precisely measured; this technique, which has been called "comparative polarography"³, allows the precision of polarographic determinations to be greatly improved⁴.

The new Differential Cathode Ray Polarograph (DCRP) described by DAVIS AND SEABORN³ can be connected to two polarographic cells, either or both of which can be switched into circuit. A current fed into one of the input channels, cell 1, gives rise to a positive or upward deflection of the cathode ray tube trace; the other channel, cell 2, gives a negative deflection. Hence if equal currents are fed into both channels there is no resultant vertical movement of the trace.

In order that the same solution in two polarographic cells will give rise to equal current inputs to the polarograph, the two dropping mercury electrodes must have identical capillary characteristics². This is achieved by mechanically synchronising the fall of the mercury drops and arranging that the diameters of the capillary orifices, and the rate of flow of mercury through them, are equal.

Performance trials of the new polarograph were carried out⁴ using a conventional electrode stand and thermostated bath (manufactured by the Cambridge Instrument Co. Ltd.), modified to carry the two dropping mercury electrodes and the drop synchronising mechanism. With this apparatus it was shown that for comparative polarography the two cells should have similar internal diameters and that the coefficient of variation of a determination could be reduced to as little as 0.14%.

The practical difficulties which occurred during this work were principally due to the method of excluding atmospheric oxygen from the solutions. Glass sleeves, mounted on a rubber bung on each capillary, dipped into the thermostat bath water, and owing to variations in the dimensions of the cells, the position of these sleeves had frequently to be adjusted to allow the drop synchronising mechanism to function satisfactorily. Furthermore, it was difficult to be certain that no contamination of the solutions occurred during deoxygenation (when a rapid stream of nitrogen was passed through the solution) or when the dropping mercury electrodes were being manipulated.

Therefore, a new stand was designed in which two matched cells are permanently mounted in a box which contains an oxygen-free atmosphere. No further manipula-

tion of the cells or electrodes was required after the initial setting up operation and the coefficient of variation of comparative polarographic determinations was then found to be considerably reduced. A detailed description of the design and construction of the stand is given below.

CONSTRUCTIONAL DETAILS

Polarographic cell

The cells were made of pyrex glass and one is shown in Fig. 1. The tube A contains the mercury pool anode B and the solution to be analysed, C; electrical contact to the anode is made by a platinum seal D and mercury contact tube E. Nitrogen is

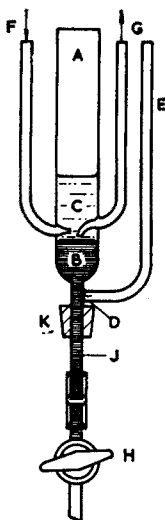


Fig. 1. The polarographic cell.

passed through tube F to remove dissolved oxygen from the solution and to remove used solutions from the cell suction is applied to tube G. The cell may be drained completely for cleaning and mercury replacement by means of the stopcock H, connected to tube J by neoprene tubing. Tube A has the same internal diameter (13 mm) as a conventional polarographic cell but is 13.5 cm long, which permits about 5 ml of a solution to be deoxygenated by a rapid stream of nitrogen without any danger of the solution frothing or splashing at the top of the cell.

The rubber bung K on the tube J serves to mount the cell in a hole in the base of the box. Connections to the cell are made through glass tubes in rubber bungs fitted into suitable holes in the top of the box.

Cell container

$\frac{3}{8}$ in. perspex sheets were butt jointed, glued and screwed together to form a rectangular box $11 \times 9\frac{1}{2} \times 5\frac{3}{4}$ in., and holes were bored at suitable points to carry the various inlet and outlet tubes as shown in Fig. 2. Two sides were extended

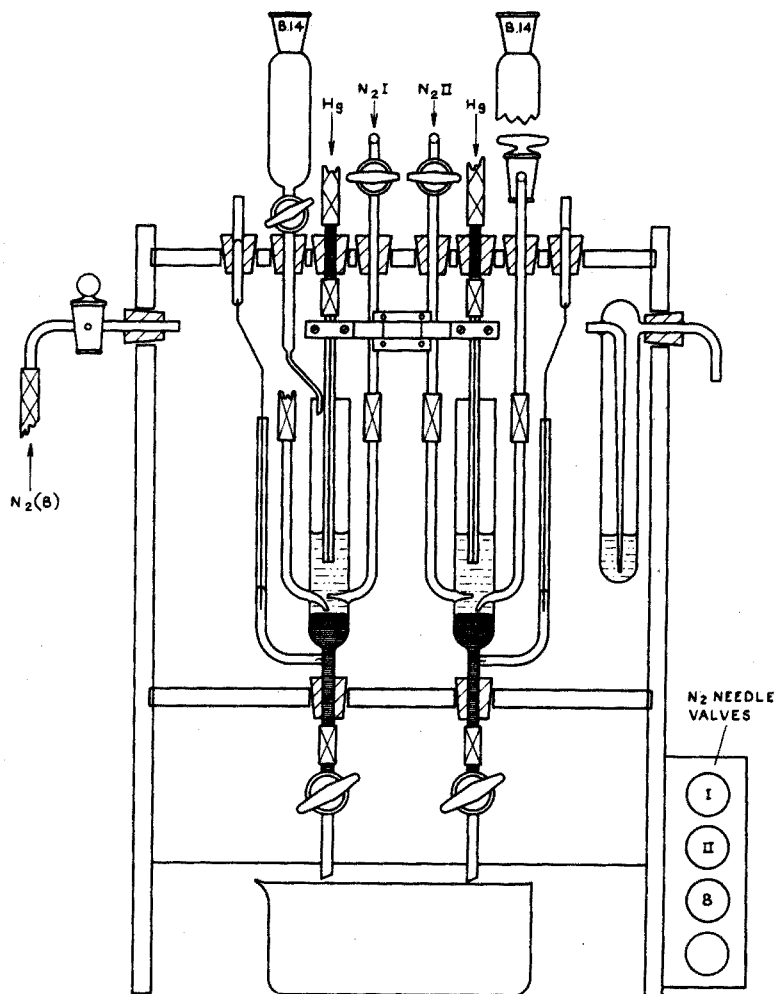


Fig. 2. The cell container.

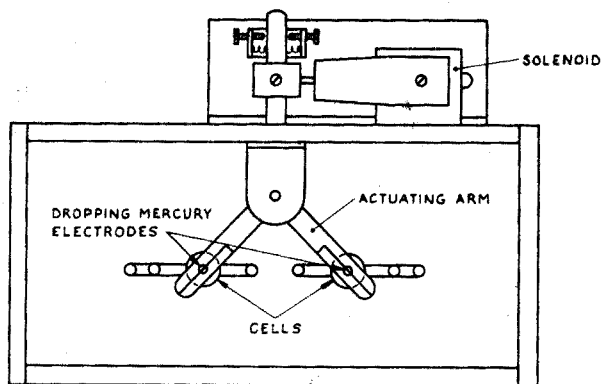


Fig. 3. Simplified plan view of the drop synchronising mechanism.

downwards by 6 in. to act as a stand thus permitting access to the drainage taps; removable panels were provided at the front and rear of the box.

Electrodes and synchronising mechanism

The method of clamping each dropping mercury electrode in the actuating arm and connecting it to the mercury reservoir through the top of the box can be seen in Fig. 2.

A simplified plan view of the drop synchronising mechanism is shown in Fig. 3 and full details have been reported elsewhere⁵. The slot through which the pivoting arm passes out of the box is sealed from the atmosphere by a flexible gasket made from one finger of a surgical rubber glove.

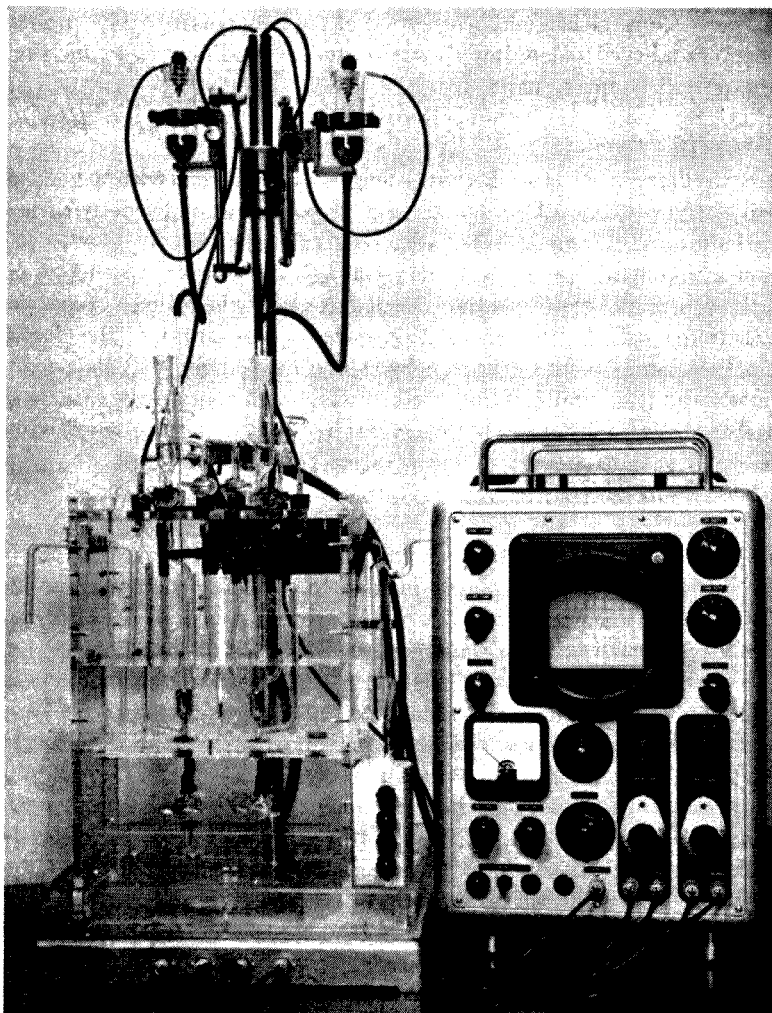


Fig. 4. The complete cell stand.

Reservoir stand

A hollow stainless steel graduated column 1 in. diameter \times 36 in. long was bolted

to a base made from $\frac{1}{4}$ in. steel plate. Two holders for the mercury reservoirs are mounted on a carriage which can be clamped at any desired height on the column. Each reservoir holder can be independently moved over a distance of 7 in., one of them being provided with a rack and pinion drive to permit fine adjustment. The electrical leads to the cells are carried down the centre of the column to sockets on the front of the base, on which is mounted a shallow perspex mercury tray.

A distribution box with needle valves allows the rate of flow of nitrogen to the cells and the cell box to be smoothly controlled. A photograph of the complete assembly is shown in Fig. 4.

METHOD OF OPERATION

Some differences from the original description of the new polarograph³ and its method of use⁴ may be observed below but these are due to modifications which have been made to the prototype instrument.

Dropping mercury electrodes

The glass capillary used is such that a length of 10–12 cm with a head of 70 cm mercury gives a drop time of 10–15 sec in 1 *M* potassium chloride with no applied potential; the internal diameter is between 0.01 and 0.05 mm.

To obtain a matched pair of electrodes a length of between 20 and 25 cm is cut exactly in the centre and the two adjacent cut faces form the orifices of the electrodes. After the clean dry cells have been positioned in the cell container the electrodes are mounted in the clamps of the drop synchronising mechanism. All electrical connections are made and it is arranged that the cell which will contain the sample solutions is connected to the cell 1 input of the polarograph so that a positive result will indicate that the sample contains a greater concentration than the standard.

Balancing procedure

The dropping electrodes must be tested and balanced under polarographic working conditions. Sufficient mercury is placed in each cell to bring the levels just up to the lower end of tube G (Fig. 1). 5–6 ml of a solution of 10^{-4} *M* lead in 0.1 *M* potassium chloride is added to each cell and deoxygenated.

(1) With the start potential set to -0.2 V the height and position of the peak due to the reduction of lead in each cell is measured separately, in its appropriate channel. The heights of the mercury reservoirs are adjusted so as to make the observed peak heights as similar as is possible under these conditions.

(2) Both cells are then switched into circuit so that the differential peak height may be observed and the potential balance and sensitivity control are set to give a trace having both a negative and a positive peak as shown in Fig. 5. The potential balance control is then adjusted until the negative peak has just disappeared and the trace has the conventional form given by a cathode ray polarograph shown in Fig. 6.

(3) One reservoir is then adjusted to reduce the peak height until as near a straight line as possible is obtained. It may now be necessary to readjust the potential balance control, and, following this, make further fine changes in the height of the reservoir. The sensitivity of the instrument may now be increased and if any imbalance is then revealed further fine adjustments must be made to the reservoir height and potential balance controls. The traces shown in Figs. 5 and 6 indicate that the reservoir

of cell 1 is too high and must be lowered to secure balance. However, the traces will appear inverted if this reservoir is initially too low.

Finally, the trace should appear as a horizontal straight line, but it invariably possesses slight deviations, the maximum extent of which is noted. No further changes in the heights of the mercury reservoirs should be made unless the whole of this balancing procedure is repeated.

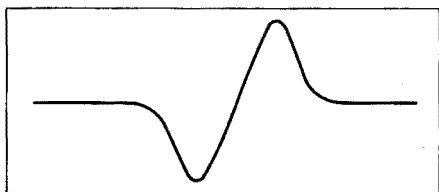


Fig. 5. Shape of wave before adjustment of the potential balance control.

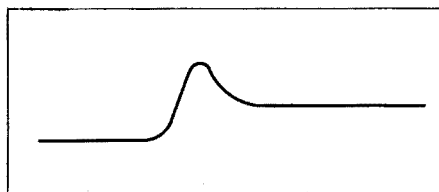


Fig. 6. The correct shape of the wave.

Reproducibility of the balance

In order to determine the reproducibility of the balance, the solution used above is replaced by fresh aliquots in each cell. After deoxygenation the differential trace is examined and, if necessary, the potential balance control adjusted to give the best straight line in the region of the peak potentials. The maximum deviation from linearity is noted and the experiment repeated to obtain a sufficient number of observations to allow the coefficient of variation of the deviations to be calculated (normally not less than 10 determinations).

The mercury pool anodes are not changed unless significantly different peak potentials are observed with the same solution in each cell; the mercury which falls into the anode from the dropping electrodes is removed through the tube G when the solution in the cell is being replaced.

Comparative polarographic determinations

Before attempting a new determination by comparative polarography, the balancing procedure should be carried out using a solution as similar as possible to those which will subsequently be analysed. It is also desirable that the coefficient of variation of the balance be determined so that the best possible precision of the method is known under the particular conditions of the new determination. The accuracy of the balance should be checked before and after each series of determinations or at the beginning and end of each day.

Each determination is carried out as follows. The sample solution is placed in cell 1, deoxygenated and the start potential and sensitivity set to suitable values to observe and note the height and potential of the peak, as with the original Cathode Ray Polarograph^{6,7}. A suitable standard solution is selected and placed in cell 2; the factors which govern the choice of the standard will be discussed later. The height and potential of the peak obtained with the standard solution are noted. The procedure is then that described in section (2) of the *Balancing procedure* above; it should be remembered that if the sample has a smaller concentration of the ion being determined than the standard, then the traces observed will be the inverse of those shown in Figs. 5 and 6.

To relate the measured differential peak height to concentration, a calibration graph is prepared using a series of standard solutions having accurately known small differences in concentration of the ion being determined. Care must be taken that these solutions are similar in all other respects.

RESULTS

The reproducibility of the balance has been determined using the new cell stand and several different solutions, and the results are given in Table I. For comparison two

TABLE I

Solution	Number of determinations	New stand coefficient of variation (%)	Original stand coefficient of variation (%)
10^{-3} M Cd in 0.1 M KCl	10	0.04	—
	10	0.02	—
10^{-3} M Pb in 1 M KCl	10	0.12	—
10^{-4} M Pb in 1 M KCl	10	0.07	0.28
10^{-3} M U in H_3PO_4/H_2SO_4	10	0.10	—
10^{-4} M U in H_3PO_4/H_2SO_4	27	0.10	0.76

results obtained with the original cell stand are also given. The standard deviation, obtained as described above, is expressed in these tables as a percentage of the peak height measured with a single cell (all measured values being corrected to the same sensitivity setting).

10 measurements of the differential peak height were made using two solutions containing 23 and 25 $\mu\text{g/ml}$ uranium in the phosphoric/sulfuric acid base electrolyte. The average differential peak height was 82.6 mm (using $\frac{1}{4}$ maximum sensitivity), the coefficient of variation being 2.2%. The mean calibration factor was therefore 0.0061 $\mu\text{g/ml/mm}$ on maximum sensitivity.

DISCUSSION

Precision of comparative polarography

It is hoped that the simple treatment given below will serve to show how to carry out a comparative polarographic determination with a given coefficient of variation using the minimum number of standard solutions. It is not an exhaustive or rigorous study of the factors affecting the precision of the technique; these will be discussed in another paper.

If the concentration of the ion of interest in the sample solution is C' , the concentration in the standard solution, C , and the measured difference in concentration, ΔC , then:

$$C' = C + \Delta C$$

The coefficient of variation, V , of the measured differential concentration is given by:

$$V = \frac{s}{\Delta C} \cdot 100$$

where s is the standard deviation of ΔC .

For the present it may be assumed that errors in the value of C are negligible and,

therefore, any uncertainty in the value of C' is due solely to uncertainty in the value of ΔC . The coefficient of variation, V' , of C' will then be given by:

$$V' = \frac{s}{C + \Delta C} \cdot 100$$

and

$$\frac{V'}{V} = \frac{\Delta C}{C + \Delta C} = \frac{1}{C/\Delta C + 1} \quad (1)$$

Now provided that the differential peak height (which is assumed to be directly proportional to ΔC) can be amplified to at least one half of full-scale deflection on maximum sensitivity, errors in the physical measurement of the height will be relatively small and the coefficient of variation, V , will be a constant of the same order as the coefficient of variation found in measuring diffusion currents at a single dropping mercury electrode; in practice V was found to be between 1% and 2%.

Concentration of the standard solutions

Table II shows the variation of V'/V with $C/\Delta C$.

TABLE II

$C/\Delta C$	100	10	5	1	0.3	0.1	0.01
V'/V	0.01	0.09	0.17	0.5	0.75	0.95	0.99

If V is 2% then in order that V' shall be less than 0.2%, $C/\Delta C$ must be greater than 10. If $C/\Delta C$ is made much smaller than this it is doubtful whether the additional effort of a comparative polarographic determination would be worthwhile. On the other hand there is nothing to be gained by making $C/\Delta C$ very large since, in the limit, when the two cells contain identical solutions, the coefficient of variation is not zero but has a small finite value.

For example, in the determination of uranium in a phosphoric/sulfuric acid medium, the minimum value of V' was found to be 0.1% and from eqn. (1), the corresponding value of $C/\Delta C$ is 20. Even if $C/\Delta C$ is made larger than this, the coefficient of variation will not be reduced beyond the limiting value imposed by the reproducibility of the balance *i.e.* 0.1%. Thus if it were necessary to carry out many such determinations with this precision it would be most economical to prepare a series of standard solutions having concentrations differing by 10%. A sample having a concentration midway between those of two adjacent standard solutions would differ from them by 5%, *i.e.* $C/\Delta C$ would be 20.

The minimum number of standard solutions which should be prepared for any given determination cannot be predicted but must be calculated from the precision of the differential peak height measurement, V , determined with the actual solutions and from a knowledge of the precision required, V' . It must of course be confirmed, by a determination of the reproducibility of the balance, that the desired precision can be achieved.

Preparation of solutions

JONES⁸ has given an excellent account of the factors which must be considered when carrying out precise analytical determinations by means of differential spectro-

photometry. Much of his discussion is relevant to comparative polarography *e.g.* the purity of starting materials, the accuracy of weight and volume measurement and the efficiency of sampling procedures should be examined to ensure that they do not impair the precision and accuracy of the result.

Unlike differential spectrophotometry where there is usually a wide choice of suitable absorbing species, polarographic determinations can be carried out in relatively few base electrolytes. For comparative determinations a solution which gives a reversible electrode reaction is to be preferred and the ionic species of the element being determined must be stable.

It was assumed above that the differential peak height could be amplified to at least one-half of full scale deflection on maximum sensitivity and in order that this shall be so, the concentration of the solutions being examined must generally be at least about 10^{-4} M. The single cell peak heights can then be amplified about 50-fold for a differential measurement. More concentrated solutions may be used but do not improve the precision since greater amplification reveals variations in the current due, presumably, to fluctuations in the sizes of the mercury drops.

It appears as though the limit has been reached with a conventional dropping mercury electrode but some modified form of capillary and perhaps further development of the drop synchronising mechanism might allow the precision of polarographic determinations to be improved yet further.

ACKNOWLEDGEMENTS

The authors are indebted to H. M. DAVIS and JOYCE E. SEABORN for their advice and encouragement in carrying out this work.

SUMMARY

A new cell assembly for use with the differential cathode ray polarograph is described together with full practical details of its use in comparative polarography. The difficulties of manipulating the cells and dropping mercury electrodes have been greatly reduced. Results obtained show that the coefficient of variation of a polarographic determination can be as low as 0.04%. Some general aspects of the technique are discussed.

RÉSUMÉ

Un nouveau dispositif est proposé pour la polarographie différentielle à rayon cathodique. Les difficultés de manipulation de la cellule et de l'électrode à gouttes de mercure sont ainsi considérablement réduites.

ZUSAMMENFASSUNG

Beschreibung einer neuen Zellenkombination für die differentielle Kathodenstrahlen-Polarographie, wobei die Schwierigkeiten bei der Handhabung der Zellen und der Quecksilber-Tropfelektrode stark vermindert werden.

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NEW METHOD FOR DETERMINING SMALL CONCENTRATIONS OF CHLORIDE ION

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During the course of an investigation of chloride-containing films on platinum electrodes, the need arose for a precise method for determining chloride ion in aqueous media in the concentration range from 10^{-6} to 10^{-5} *M*. For this purpose the new method described herein was devised.

The method rests on the familiar solubility product principle that in a solution saturated with silver chloride the silver ion concentration is governed by the chloride ion concentration. Thus, the chloride ion concentration can be evaluated if the silver ion concentration is determined. The test solution is equilibrated with excess silver chloride, and the silver ion concentration is then determined by potentiometric titration with iodide ion.

EXPERIMENTAL

Reagents

Pure silver chloride was prepared by dissolving stoichiometric weights of silver nitrate and sodium chloride in water and mixing them in a paraffin-lined brown glass bottle. The silver chloride was washed repeatedly with water by decantation, and stored as an aqueous suspension in the same container. The paraffin lining precluded the possibility of exchange adsorption of silver ion with ions from the glass.

Distilled water with a specific conductance not greater than $0.9 \cdot 10^{-6}$ $\text{ohm}^{-1}\text{cm}^{-1}$ was used. Nitric acid for the supporting electrolyte was purified by distilling concentrated reagent acid from a quartz still. Chloride test solutions were prepared from sodium chloride, and nitric acid was added to adjust the ionic strength to 0.0250 *M*. Standard iodide solutions were prepared from potassium iodide.

Procedure

The experiments were carried out in a dark room. A 0.5–1.0-g sample of the silver chloride was transferred onto a filter paper in a glass funnel and washed first with 100 ml of 0.0250 *N* nitric acid and then with 50 ml of the test solution. The silver chloride was transferred directly to the equilibrating bottle by puncturing the filter and washing the silver chloride into the bottle with 150–200 ml of the test solution.

The equilibrating vessels were brown glass bottles coated with paraffin. Equilibration was facilitated by mechanically stirring the test solution with a Pyrex pro-

pellor which had been coated with paraffin. All equilibrations were done in a water bath maintained at $25.00^\circ \pm 0.03^\circ$. No difference in the experimental results was noted for equilibration periods of from 5 to 24 h; the effect of a shorter equilibration time was not investigated. The attainment of solubility equilibrium was not affected by approaching 25° from either higher or lower temperatures.

A sample of the solution was taken (while the equilibrating bottle remained in the water bath) by applying suction to a pipet to whose tip was attached a fine porosity immersion filter. The silver ion concentration in the sample was determined by potentiometric titration with iodide ion by the technique described in detail by KOLTHOFF AND LINGANE¹.

THEORY

At solubility equilibrium, and provided that silver ion is the only ionic species of dissolved silver in the solution, the total concentration of chloride ion will be that originally present, which we represent by C , plus that contributed by the dissolution of the silver chloride, which is equal to the silver ion concentration $[Ag^+]$. Under these conditions

$$(C + [Ag^+]) [Ag^+] \gamma_{\pm}^2 = K_{AgCl} \quad (1)$$

or

$$C = \frac{K_{AgCl}}{\gamma_{\pm}^2 [Ag^+]} - [Ag^+] \quad (2)$$

where K_{AgCl} is the thermodynamic activity product of silver chloride and γ_{\pm} is the mean activity coefficient of silver and chloride ions in the particular solution.

In general, to evaluate C from measured values of $[Ag^+]$, it is necessary to know γ_{\pm} as well as K_{AgCl} . However, when, as in the experiments with which we were concerned, the ionic composition of the test solutions is constant, except for slight variations in the very small concentrations of silver and chloride ions, γ_{\pm} becomes a constant. Therefore a "concentration solubility product" $S_{AgCl} = K_{AgCl} / \gamma_{\pm}^2$ can be determined by measuring the solubility of silver chloride in the supporting electrolyte alone without added chloride, and we then have the relation

$$C = \frac{S_{AgCl}}{[Ag^+]} - [Ag^+] \quad (3)$$

From eqn. (3) the relative error dC/C in the determination of C is related to the relative error in the evaluation of the silver ion concentration $d[Ag^+]/[Ag^+]$ by

$$\frac{dC}{C} = - \frac{d[Ag^+] (S_{AgCl} + [Ag^+]^2)}{[Ag^+] (S_{AgCl} - [Ag^+]^2)} \quad (4)$$

Thus the error in C caused by a given relative error in evaluating the silver ion concentration increases rapidly when $[Ag^+]$ approaches $S_{AgCl}^{1/2}$; *i.e.*, when C becomes small compared to $S_{AgCl}^{1/2}$. Conversely, as C becomes large compared to $S_{AgCl}^{1/2}$, $[Ag^+]$ becomes small compared to $S_{AgCl}^{1/2}$, and dC/C approaches $-d[Ag^+]/[Ag^+]$. It follows, however, that the relative error in C will always be larger than the relative error in determining the silver ion concentration, so that a relatively highly precise method of determining $[Ag^+]$ is necessary to achieve even modest precision in the evaluation of C .

In round numbers S_{AgCl} is $2 \cdot 10^{-10}$, so that the silver ion concentration will be approximately $1.4 \cdot 10^{-5} M$ or smaller. A precise method for determining such small concentrations of silver ion is potentiometric titration with iodide ion which has been studied thoroughly by KOLTHOFF AND LINGANE¹. These authors demonstrated that $10^{-5} M$ silver ion can be titrated with a relative error within $\pm 0.3\%$; with $10^{-6} M$ silver ion the error is $\pm 1-2\%$ and with only $10^{-7} M$ silver ion the error is within $\pm 10\%$. From these data and eqn. (4), one can expect for $C = 1 \cdot 10^{-5} M$, corresponding to $[\text{Ag}^+] = 0.50 S_{\text{AgCl}}^0$, that $dC/C = -2 d[\text{Ag}^+]/[\text{Ag}^+]$, and that C should be determinable with a relative error of about $\pm 0.6\%$. If C is $1 \cdot 10^{-6} M$, corresponding to $[\text{Ag}^+] = 0.97 S_{\text{AgCl}}^0$, $dC/C = -28 d[\text{Ag}^+]/[\text{Ag}^+]$ and C should be determinable to about $\pm 9\%$. For smaller values of C the error increases very rapidly; hence, it is not feasible to attempt to determine C at values much lower than $10^{-6} M$. For values of C larger than $10^{-5} M$, dC/C approaches $-d[\text{Ag}^+]/[\text{Ag}^+]$.

The potentiometric iodide titration actually determines the total concentration of all forms of dissolved silver. In the solutions studied in this investigation, most of the dissolved silver is present as silver ion, Ag^+ . However, as FORBES AND COLE² demonstrated, there is a small and constant amount of dissolved, undissociated silver chloride, $\text{AgCl} (aq.)$, in equilibrium with solid silver chloride. In the present study we have found that the concentration of $\text{AgCl} (aq.)$ in equilibrium with solid silver chloride is $(1.8 \pm 0.3) \cdot 10^{-7} M$ at 25° and an ionic strength of $0.0250 M$. Literature values³ for this quantity at zero ionic strength range from $1.4 \cdot 10^{-7} M$ obtained by PINKUS AND HAUGEN⁴ to $6.2 \cdot 10^{-7} M$ reported by FORBES AND COLE². The variations in the value reported doubtless stem from the fact that the $\text{AgCl} (aq.)$ concentration is relatively quite small, and that it cannot be determined directly but must be calculated indirectly from solubility measurements. Since this small concentration of $\text{AgCl} (aq.)$ is independent of the concentration of added chloride C , it will always be titrated by the iodide method and, therefore, must be subtracted from the total determined concentration of dissolved silver to obtain the silver ion concentration $[\text{Ag}^+]$.

As the chloride concentration C increases above $10^{-4} M$, the formation of anion complexes such as AgCl_2^- becomes an important enhancing factor in the solubility of silver chloride. The equilibrium constant K for the reaction $\text{AgCl} (s) + \text{Cl}^- = \text{AgCl}_2^-$ has been determined by numerous workers⁵; K is about $3.6 \cdot 10^{-5}$ at 25° .

At $C = 2.3 \cdot 10^{-4} M$ the concentration of AgCl_2^- will be very nearly 1% of the silver ion concentration, $[\text{Ag}^+]$. Under conditions where the concentration of AgCl_2^- does become significant, *i.e.*, C greater than $10^{-4} M$, eqn. (3) is no longer valid because the total chloride concentration, given by $(C + [\text{Ag}^+])$ in eqn. (1), is decreased by the chloride ion consumed in the formation of AgCl_2^- . Instead the chloride concentration is given by $(C + [\text{Ag}^+] - [\text{AgCl}_2^-])$ and the expression for the calculation of C (analogous to eqn. (3)) becomes

$$C = \frac{S_{\text{AgCl}}}{[\text{Ag}^+]} - [\text{Ag}^+] + [\text{AgCl}_2^-] \quad (5)$$

Both $[\text{Ag}^+]$ and $[\text{AgCl}_2^-]$ must be known in order for C to be calculated. The sum of these concentrations ($[\text{Ag}^+] + [\text{AgCl}_2^-]$) can be obtained by subtracting the known concentration of $\text{AgCl} (aq.)$ from the total determined concentration of dissolved silver. Then the concentration of AgCl_2^- can be expressed in terms of $[\text{Ag}^+]$ by com-

binning the relation for the "concentration solubility product" of silver chloride, *i.e.*, $[Ag^+][Cl^-] = S_{AgCl} = K_{AgCl}/\gamma_{\pm}^2$, with the equilibrium constant K for the reaction $AgCl(s) + Cl^- = AgCl_2^-$ (*vide supra*). The result is

$$[AgCl_2^-] = \frac{S_{AgCl} \cdot K}{[Ag^+]} \quad (6)$$

From the sum of the concentrations of Ag^+ and $AgCl_2^-$ and from eqn. (6), the individual values for $[Ag^+]$ and $[AgCl_2^-]$ may be computed and C may be calculated from eqn. (5). In practice the use of eqn. (5) would necessitate a precise evaluation of K as well as of S_{AgCl} under the exact experimental conditions. For values of C less than $10^{-4} M$, the simpler eqn. (3) is applicable because the concentration of $AgCl_2^-$ is extremely small. However, for C greater than $10^{-4} M$ the more rigorous eqn. (5) must be used.

PERFORMANCE DATA

By potentiometric titration with iodide ion of the total dissolved silver, the solubility of silver chloride in $0.0250 M$ nitric acid at 25° was found to be $(1.527 \pm 0.003) \cdot 10^{-5} F$. This value includes a small concentration due to dissolved, undissociated silver chloride. This concentration of $AgCl(aq.)$ was determined by measuring the solubility of silver chloride in a $1.110 \cdot 10^{-4} M$ chloride solution containing nitric acid to provide an ionic strength of $0.0250 M$. The solubility of silver chloride was $0.2217 \cdot 10^{-5} F$. This value corresponds to the sum of the concentrations of Ag^+ , $AgCl(aq.)$ and $AgCl_2^-$. The concentration of $AgCl_2^-$ was evaluated from the equilibrium $AgCl(s) + Cl^- = AgCl_2^-$ ($K = 3.6 \cdot 10^{-5}$) on the assumption that $[Cl^-]$ was $1.1 \cdot 10^{-4} M$. The concentration of $AgCl_2^-$ thus obtained was $4.0 \cdot 10^{-9} M$. This value was subtracted from the total solubility of silver chloride in $1.110 \cdot 10^{-4} M$ chloride ($0.2217 \cdot 10^{-5} F$) to give $0.2213 \cdot 10^{-5} F$ as the sum of the concentrations of Ag^+ and $AgCl(aq.)$. Therefore $[Ag^+] = 0.2213 \cdot 10^{-5} - [AgCl(aq.)]$. In the absence of added chloride ion there is virtually no $AgCl_2^-$ present, so that $[Ag^+] = 1.527 \cdot 10^{-5} - [AgCl(aq.)]$ and $S_{AgCl} = [Ag^+]^2 = (1.527 \cdot 10^{-5} - [AgCl(aq.)])^2$. From eqn. (3), for $1.110 \cdot 10^{-4} M$ added chloride, we have

$$1.110 \cdot 10^{-4} = \frac{(1.527 \cdot 10^{-5} - [AgCl(aq.)])^2}{(0.2213 \cdot 10^{-5} - [AgCl(aq.)])} - (0.2213 \cdot 10^{-5} - [AgCl(aq.)]) \quad (7)$$

Solution of eqn. (7) gives $(2.0 \pm 0.2) \cdot 10^{-7} M$ for $[AgCl(aq.)]$. The limits of error are those which are in harmony with the known accuracy of the potentiometric iodide titration of silver ion as studied by KOLTHOFF AND LINGANE¹. Similarly, the solubility of silver chloride was found to be $0.1180 \cdot 10^{-5} F$ for $C = 2.220 \cdot 10^{-4} M$ and $\mu = 0.0250 M$. The concentration of $AgCl_2^-$ was estimated to be $7.9 \cdot 10^{-9} M$. The value calculated for $[AgCl(aq.)]$ was $(1.5 \pm 0.2) \cdot 10^{-7} M$.

Taking $1.8 \cdot 10^{-7} M$ as the average value of $[AgCl(aq.)]$ in $0.0250 M$ nitric acid and subtracting it from the formal solubility of silver chloride ($1.527 \cdot 10^{-5} F$) in $0.0250 M$ nitric acid at 25° , we obtain a value for the "concentration solubility product" S_{AgCl} of silver chloride of $2.277 \cdot 10^{-10}$. Since the mean ion activity coefficient for $\mu = 0.0250 M$ is 0.852 , we calculate $1.654 \cdot 10^{-10}$ for the thermodynamic activity product K_{AgCl} of silver chloride at 25° .

Typical values for K_{AgCl} reported in the literature are $1.615 \cdot 10^{-10}$ by NEUMAN⁵, $1.618 \cdot 10^{-10}$ by POPOFF AND NEUMAN⁶, $1.621 \cdot 10^{-10}$ by PINKUS AND SCHEPMANS⁷, $1.695 \cdot 10^{-10}$ by KOHLRAUSCH⁸, and $1.721 \cdot 10^{-10}$ by BROWN AND MACINNES⁹.

The proposed method has been tested with known concentrations of chloride ion and the results are presented in Table I. In all cases the temperature was 25° and the ionic strength was 0.0250 *M* (nitric acid). The chloride concentration *C* was calculated from eqn. (3) with the value for S_{AgCl} of $2.277 \cdot 10^{-10}$ obtained in this study. To obtain the silver ion concentration $[\text{Ag}^+]$, we subtracted $1.8 \cdot 10^{-7}$ *M* (the concentration of AgCl (*aq.*)) from the total concentration of dissolved silver found by the potentiometric iodide titration. In none of the experiments was the contribution due to AgCl_2^- significant.

TABLE I
PERFORMANCE DATA

$[\text{Cl}^-] \cdot 10^5$ <i>M</i> Taken	$[\text{Ag}^+] \cdot 10^5$ <i>M</i> Found	$[\text{Ag}^+] \cdot 10^5$ <i>M</i> Corr.	$[\text{Cl}^-] \cdot 10^5$ <i>M</i> Found	Error %
0.111	1.474	1.456	0.108	-2.7
0.111	1.475	1.457	0.106	-4.5
0.696	1.219	1.201	0.695	-0.1
0.974	1.116	1.098	0.976	+0.2
1.662	0.909	0.891	1.665	+0.2
5.552	0.404	0.386	5.513	-0.7

The results demonstrate that chloride concentrations as small as 10^{-6} *M*, or slightly lower, can be determined with an error of approximately $\pm 5\%$. For $C = 1 \cdot 10^{-5}$ *M* the error is *ca.* $\pm 0.5\%$. At higher chloride concentrations the silver ion concentration decreases and, correspondingly, the precision of its determination decreases. At the same time, as can be seen from eqn. (4), the error in the silver ion concentration does not magnify the error in the chloride concentration *C* so much as it does at the lower chloride concentrations. The applicability of the present method is limited principally by the fact that as *C* increases above 10^{-4} *M* the silver ion concentration $[\text{Ag}^+]$ becomes smaller and smaller and increasingly difficult to evaluate precisely. We conclude, therefore, that the range of chloride concentrations most suitable for determination by this method is from 10^{-6} to 10^{-4} *M*.

Besides the usefulness of this method for determining small concentrations of chloride, the technique should be particularly valuable as a tool in the study of the solubility of silver chloride in solutions up to several molar in chloride ion. The equilibria involved in the formation of the various chloro-complexes of silver ion, *i.e.*, AgCl_2^- , AgCl_3^{2-} , can be studied and the equilibrium constants evaluated. The method may also be adaptable to studies of other slightly soluble silver compounds.

The method will, of course, have as possible interferences any of the many ions and molecules which form either slightly soluble compounds or complex ions with silver ion.

ACKNOWLEDGEMENT

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SUMMARY

A new method has been devised for the determination of concentrations of chloride ion from approximately 10^{-6} to $2 \cdot 10^{-4}$ *M*. The test solution is equilibrated with solid silver chloride, the silver ion concentration is determined by potentiometric titration with iodide ion, and the chloride concentration is calculated by the solubility product principle. Chloride concentrations near 10^{-6} *M* can be determined with an accuracy of about $\pm 5\%$, and at 10^{-5} *M* the error is within $\pm 0.5\%$. Chloride concentrations above $2 \cdot 3 \cdot 10^{-4}$ *M* cannot be accurately determined because of the formation of AgCl_2^- .

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage des chlorures en concentrations de 10^{-6} à $2 \cdot 10^{-4}$ *M*. La solution à analyser est additionnée de chlorure d'argent solide; la teneur en ion argent est déterminée par titrage potentiométrique au moyen d'iode.

ZUSAMMENFASSUNG

Beschreibung einer neuen Methode zur Bestimmung von Chlorid-Ion im Konzentrationsbereich von 10^{-6} bis 10^{-5} *M*. Die Probelösung wird mit festem Silberchlorid versetzt; man wartet zur Einstellung des Gleichgewichts einige Stunden und titriert dann das Silber-Ion potentiometrisch mit Jodidlösung.

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TÜPFELREAKTIONEN VON RHODANID DURCH REDUKTIVE AUFSPALTUNG

EIN BEITRAG ZUR CHEMIE DER SPEZIFISCHEN, SELEKTIVEN UND EMPFINDLICHEN REAKTIONEN

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In der qualitativen organischen Analyse ist häufig darauf zu achten, dass Eintritt und Ausmass von charakteristischen Fällungs- und Farbreaktionen durch Lösungsgenossen verhindert oder eingeschränkt wird, die durch Umsetzung mit an der Nachweisreaktion beteiligten Ionen deren Konzentration weitgehend herabsetzen. Ein hierhergehöriges Beispiel ist die zu rotem Eisen(III)Rhodanid führende Umsetzung von SCN^- - und Fe^{+3} -Ionen. Diese empfindliche Farbreaktion ist an sich weitgehend selektiv, da lediglich N_3^- -Ionen rotes wasserlösliches Eisen(III)azid bilden. Enthält die Probelösung ausser SCN^- -Ionen nur N_3^- -Ionen, so können letztere durch Erwärmung der sauren Lösung unter Bildung von flüchtiger Stickstoffwasserstoffsäure leicht entfernt werden. Erheblich grössere und zumeist nicht leicht zu behebende Störungen verursacht die Anwesenheit von Anionen, die stabile Eisen(III)Komplexsalze bilden oder eine Reduktion von Ferri- zu Ferrosalzen herbeiführen. Hierher gehören Fluoride, Phosphate, Oxalate, Citrate, sowie Sulfide, Sulfite, Thiosulfate und Jodide. Desgleichen stören oxidierende Anionen, die in saurer Lösung Rhodanid in Sulfat und Cyanat überführen. In Betracht kommen Chlorate, Bromate, Jodate und Chromate. Zu beachten ist auch, dass die Bildung kleiner Mengen von Eisen(III)-Rhodanid in farbigen Lösungen (Farbstoffe) nicht unmittelbar zu erkennen ist.

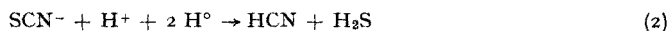
Von den angeführten Beeinträchtigungen ist bisher lediglich die durch Jod-ionen bewirkte in einfacher Weise behoben worden. WEISZ¹ hat gezeigt, dass in einer Eisen(III)Salzlösung, die viel Eisen(II)Salz enthält, die reversible Redoxreaktion $2 \text{Fe}^{+3} + 2\text{J}' \rightleftharpoons \text{Fe}^{+2} + \text{J}_2$ nicht eintritt, während die zu $\text{Fe}(\text{SCN})_3$ führende Umsetzung, die vom Redoxpotential des Eisens unabhängig ist, nicht behindert wird.

Wegen der vielen Beeinträchtigungen, denen die Eisen(III)Rhodanidreaktion ausgesetzt ist, erschien es wünschenswert, nach weniger beirraren analytisch auswertbaren Reaktionen von Alkalirhodaniden zu suchen. Einen diesbezüglichen Hinweis boten die Angaben², dass Rhodanide bei Behandlung mit Zink und Salzsäure Schwefelwasserstoff abspalten, und dass bei Destillation von Kaliumrhodanid mit Aluminium und Salzsäure die Umsetzung



erfolgen soll. Für eine analytische Verwertung scheidet die Destillation aus und ist

lediglich die Entbindung von Schwefelwasserstoff bei Erwärmung von Rhodaniden mit Zink und Säure von Interesse, wofür die Umsetzung

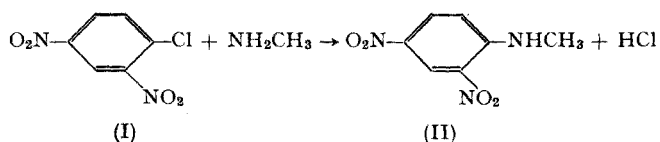


in Betracht zu ziehen ist. Zur Prüfung dieses Reaktionsverlaufes war die gleichzeitige Bildung von Schwefelwasserstoff und Blausäure nachzuweisen, wofür folgendes Verfahren sich als brauchbar erwiesen hat: In einer Mikroeprouvette wurde ein Tropfen einer 5%-igen Kaliumrhodanidlösung mit etwas Devarda-Legierung und Salzsäure vereinigt. In die Epruvette wurde ein mit Bleiacetat getränkter und hierauf getrockneter Wattebausch eingeführt und auf das offene Ende der Epruvette ein Scheibchen Filterpapier gelegt, das mit einer frisch bereiteten Lösung von Kupferacetat und Benzidinacetat befeuchtet wurde. Im Falle der Entbindung von H_2S und HCN war bei Erwärmung die Abscheidung von schwarzem Bleisulfid auf der Watte und die Bildung eines blauen Fleckes auf dem Reagenspapier zu erwarten³. Da beides zutrifft, kann der Eintritt von (2) als erwiesen gelten.

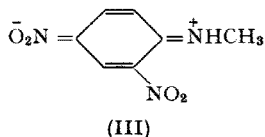
Zufolge der grossen Empfindlichkeit der oben angeführten Nachweise sollte durch diese der Ablauf von (2) und damit Rhodanide empfindlich nachweisbar sein. Diesbezügliche Versuche in der Arbeitsweise der Tüpfelanalyse haben ergeben, dass durch die Bildung von H_2S und HCN 0.2 μg bzw. 15 μg Kaliumrhodanid nachweisbar ist. Die Ursache dieses grossen Empfindlichkeitsunterschiedes dürfte darin zu suchen sein, dass Blausäure durch nascenten Wasserstoff teilweise zu Methylamin reduziert wird, was zuerst von MENDIUS⁴ festgestellt worden ist.

Durch Verwendung der zu Schwefelwasserstoff führenden Reduktion von Rhodaniden lassen sich diese neben vielen Anionen nachweisen, welche die Eisenrhodanidreaktion beeinträchtigen. Nicht anwendbar ist dieses Verfahren bei Anwesenheit von Sulfiden, Sulfiten und Thiosulfaten, da diese mit Säure und Devarda-Legierung reagieren. Beachtenswert dürfte sein, dass durch die saure Reduktion von Rhodaniden auch deren Nachweis neben Cyaniden möglich ist.

Die leichte Reduzierbarkeit von Rhodaniden in saurer Lösung, wobei eine zusätzliche Reduktion von Blausäure zu Methylamin erfolgt, verwies auf die Möglichkeit einer reduktiven Aufspaltung in alkalischer Lösung und deren allfällige Verwendung. Die unmittelbare Anregung für diesbezügliche Versuche war die von FEIGLUND HAGUENAUER-CASTRO⁵ gemachte Beobachtung, dass organische Rhodanide bei Erwärmung mit Lauge und Devarda-Legierung Methylamin abspalten, was zum Nachweis von organischen Rhodaniden in der Tüpfelanalyse verwendet werden kann. Bei Übertragung dieses Verfahrens auf Alkalirhodanide wurde festgestellt, dass basische Dämpfe entstehen, die sowohl Ammoniak als auch Methylamin enthalten. Ersteres wurde durch die Nessler'sche Reaktion, letzteres durch die Farbreaktion (Gelbfärbung) mit 2,4-Dinitrochlorbenzol⁶ nachgewiesen. Die Farbreaktion des Methylamins beruht auf der Umsetzung von 2,4-Dinitrochlorbenzol(I) unter Bildung von 2,4-Dinitro-N-Methylanilin(II)

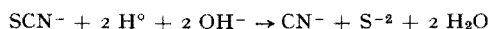


Nach FEIGL⁷ beruht die intensive Farbigekeit des Dinitromethylanilins darauf, dass dieses in der chinoiden Zwitterform(III) vorliegt



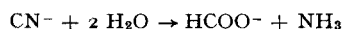
Die Kondensation von (I) mit Aminen zu N-substituierten Dinitroanilinen verläuft sehr schnell bei Vereinigung und Abdampfen von ätherischen Lösungen der Komponenten⁷. Beim Nachweis von aus Rhodaniden abgespaltenem Methylamin kommt dieses zugleich mit Wasserdämpfen zur Einwirkung auf ein mit dem Reagens imprägniertes Filterpapier. Dabei wurde festgestellt, dass die Farbreaktion nicht sofort, sondern erst nach einigen Minuten Erwärmung eintritt.

Es erhebt sich die Frage, auf welche Weise es bei der alkalischen Reduktion von Rhodanid zur Abspaltung von Ammoniak und Methylamin kommt. Naheliegend war die Annahme, dass der aus Devarda-Legierung und Lauge gebildete nascente Wasserstoff zunächst eine Entschwefelung gemäss

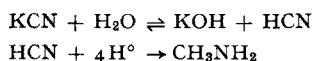


herbeiführt und im Anschluss daran Cyanid zu Ammoniak und Methylamin reduziert wird. Dass ersteres der Fall ist, konnte durch folgenden Versuch bewiesen werden: Zu einer alkalischen 2%-igen Kaliumrhodanidlösung wurden einige cg Devarda-Legierung zugesetzt, einige Minuten erwärmt und das Gemisch zentrifugiert. Nach Abgiessen der Lösung und einmaligem Waschen des Rückstandes mit Wasser wurde neuerlich zentrifugiert, der Rückstand mit verdünnter Salzsäure versetzt, auf das offene Ende der Epruvette ein Scheibchen Bleiacetatpapier gelegt und schwach erwärmt. Hierbei erfolgte sofortige Schwärzung des Reagenspapiers. Zum Beweis dafür, dass das bei alkalischer Reduktion von Kaliumrhodanid entstehende Ammoniak und Methylamin aus dem primär gebildeten Cyanid stammt wurden Versuche über das Verhalten von Cyanid bei alkalischer Reduktion mit Devarda-Legierung angestellt. Es zeigte sich hierbei, dass basische Dämpfe entstehen, die nach dem Ausfall der Nessler-Reaktion und der Farbreaktion mit 2,4-Dinitrochlorbenzol unzweifelhaft Ammoniak und Methylamin enthalten.

Die Bildung von Ammoniak aus Cyanid kann auf die bekannte Hydrolyse



zurückgeführt werden. Die Bildung von Methylamin kann wohl nur auf der Reduktion von Blausäure beruhen, die infolge Hydrolyse in wässrigen Lösungen von Alkalicyanid in merklichen Mengen vorliegt. Es kommen demnach hierfür nachstehende Teilreaktionen in Betracht:



Die Tatsache, dass bei der Reduktion von Rhodanid in alkalischer Lösung mit Devarda-Legierung Indikatorpapier umfärbende Dämpfe von Ammoniak und Methylamin entstehen, ermöglicht einen neuen empfindlichen und bemerkenswert selektiven Nachweis von Rhodaniden. Der Nachweis kann auch in Gegenwart von Ammon-

salzen angewendet werden, da diese durch Abdampfen mit Lauge leicht entfernt werden können, wobei Rhodanid unverändert bleibt. Nicht anwendbar ist der Nachweis in Gegenwart von Nitraten, Nitriten, Hydrazin- und Hydroxylaminsalzen, da diese Verbindungen in alkalischer Lösung durch Devarda-Legierung zu Ammoniak reduziert werden. Desgleichen ist der Nachweis in Gegenwart von Cyaniden nicht anwendbar; in diesem Falle ist die oben beschriebene zu Schwefelwasserstoff führende Reduktion in saurer Lösung empfehlenswert, sofern Sulfide, Sulfite und Thiosulfate abwesend sind.

ARBEITSWEISE

In eine Mikroeprouvette werden 1 Tropfen der Probelösung, 1 Tropfen 5%-ige Natronlauge und einige mg Devarda-Legierung gebracht, auf das offene Ende der Eprouvette ein Scheibchen Indikatorpapier gelegt und im Wasserbad erwärmt. Die Bildung von basischen Dämpfen beweist das Vorliegen von Rhodanid. (Erfassungsgrenze: 0.2 μg SCN).

In der angeführten Arbeitsweise war es möglich, 3 μg Rhodanid neben

5.000 μg Natriumphosphat	10.000 μg Natriumoxalat
5.000 μg Natriumfluorid	5.000 μg Kaliumchromat
5.000 μg Natriumsulfit	5.000 μg Natriumthiosulfat

nachzuweisen.

Zum Nachweis von Rhodanid in Gegenwart von Ammonsalzen müssen letztere vor der Reduktion entfernt werden. Dies ist durch Abdampfen eines Tropfens der Probelösung mit einem Tropfen 20%-iger Natronlauge im Trockenschrank bei 140–150° leicht zu erreichen. Es ist zweckmässig, die Abdampfung in einer Mikroeprouvette durchzuführen und die oben beschriebene Reduktion anzuschliessen. Es waren 1.5 μg Rhodanid neben 2.000 μg Ammoniumchlorid nachweisbar.

DANK

An dieser Stelle sei Herrn Prof. Dr. F. FEIGL für seine wertvollen Anregungen und Ratschläge, sowie dem Conselho Nacional de Pesquisas für seine Unterstützung bei Durchführung dieser Arbeit gedankt.

ZUSAMMENFASSUNG

Bei der Reduktion von Rhodaniden in saurer oder alkalischer Lösung durch Devarda-Legierung entsteht als Folge von experimentell ermittelten Teilreaktionen Schwefelwasserstoff, bzw. ein Gemisch von Methylamin und Ammoniak. Durch den Nachweis dieses Reaktionsproduktes in der Gasphase wird, in der Arbeitsweise der Tüpfelanalyse, zu weitgehend selektiven Nachweisen von Rhodanid gelangt.

Hierbei wurden Erfassungsgrenzen von 0.12 μg bzw. 0.2 μg Rhodanid erreicht.

SUMMARY

In the reduction of thiocyanates in acidic or alkaline solution by Devarda alloy, respectively hydrogen sulfide or a mixture of methylamine and ammonia is formed. The identification of these reaction products in the vapor phase allows a fairly selective test for thiocyanates by means of spot test methods.

Limits of identification of 0.12 μg resp. 0.2 μg thiocyanate were obtained.

RÉSUMÉ

Une nouvelle réaction à la touche, sélective, est proposée pour l'identification des thiocyanates, par réduction au moyen de l'alliage Devarda, en milieu acide (formation d'hydrogène sulfuré) ou

en milieu alcalin (formation d'un mélange de méthylamine et d'ammoniac) et identification de ces produits de réaction. Limite d'identification: 0.12 μg et 0.2 μg de thiocyanate, respectivement.

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Anal. Chim. Acta, 26 (1962) 81-85

SOLVENT EXTRACTION STUDIES OF PHOSPHONIUM SALTS AND THEIR ANALYTICAL APPLICATIONS

II. DIFFERENTIATION OF *n*- AND ISOPROPYL HALIDES

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A systematic study of the extractability of phosphonium salts of metal halide and pseudo halide complexes is in course in this laboratory. This study has shown that in some cases salts of triphenyl *n*-propyl phosphonium may differ markedly from the analogous triphenylisopropyl phosphonium salts with respect to their extractability into organic solvents¹.

Among others, the copper and cobalt thiocyanate complexes were found to form insoluble colored salts with triphenyl *n*-propyl phosphonium which could be extracted by different solvents giving rise to intensely colored solutions, whereas the corresponding triphenylisopropyl phosphonium compounds remained precipitated and unextracted.

This peculiar behavior, resulting merely from the isomerism of the alkyl ligand of the phosphonium cation, can be used as the basis of a test to differentiate *n*-propyl from isopropyl halides. This is possible also because the synthesis of propyl and isopropyl phosphonium halides can be performed by very simple techniques on the micro scale.

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EXPERIMENTAL

The extractability of triphenyl n-propyl and triphenylisopropyl phosphonium salts of copper(II) and cobalt(II) thiocyanato complexes

Experiments with both copper(II) and cobalt(II) ions were carried out by adding to the acidic aqueous solutions of the metal ion excess sodium thiocyanate and the chloride of either triphenyl *n*-propyl or triphenylisopropyl phosphonium. A number of solvents were tested to study the extractability of the precipitate formed.

The results obtained, which are partially reported in Table I, show that several solvents could be selected for the proposed test. In the procedure given below, however, *n*-butyl acetate was chosen as a matter of convenience.

The organic solutions obtained by extracting the copper compounds were always wine-red and those of the cobalt salts blue. The cobalt precipitate was also blue but the product obtained by precipitating copper in the presence of excess thiocyanate and triphenylisopropyl phosphonium changed rapidly from wine-red to brown yellow, this color being persistent.

TABLE I

EXTRACTABILITY INTO ORGANIC SOLVENTS OF TRIPHENYL *n*-PROPYL AND TRIPHENYLISOPROPYL PHOSPHONIUM SALTS OF COPPER(II) AND COBALT(II) THIOCYANATO COMPLEXES

Experiments were carried out with 10 μ g of metal ion in 0.5 ml of aqueous solution and 0.5 ml of solvent

Solvent	Copper(II)		Cobalt(II)	
	<i>n</i> -propyl	isopropyl	<i>n</i> -propyl	isopropyl
<i>n</i> -Butyl alcohol	+++ ^a	o	+++	o
Isobutyl alcohol	+++ ^a	o	+++	o
Amyl alcohol	+++ ^a	o	++	o
Isoamyl alcohol	+++ ^a	o	++	o
Ethyl acetate	+++	o	+++	++
<i>n</i> -Butyl acetate	+++	o	+++	o
<i>n</i> -Amyl acetate	+	o	+	o
Isoamyl acetate	++	o	++	o
Tri- <i>n</i> -butyl phosphate	+++	o	+++	+++
Methylisobutyl ketone	+++	+++	+++	+++
Diisobutyl ketone	+++	o	+++	o
Anisole	+++	o	+++	+++
Phenetole	+++	o	+++	+++

+ Extracted; ++ well extracted; +++ very well extracted; o not extracted

^a Extract is rapidly decolorized.

*Synthesis and identification of the phosphonium halides**Pure alkyl halides*

Experiments were carried out in a small glass sealed tube containing a micro drop of the halide and a slight excess of triphenylphosphine. The temperature necessary to bring the reaction to completion was found to depend on the reactivity of the halide and on the time of heating. Thus with iodides, which are more reactive than bromides

and chlorides, the synthesis could be performed in 3 min at 150° while with the other halides heating at 230° was necessary to keep the time within 3 min. Tests showed that if the temperature is maintained at 150° with bromides and chlorides, the time of heating must be considerably increased. As it seemed desirable to elaborate a rapid test, it was felt that the time of heating should be kept always at 3 min and the temperature raised when necessary.

The test was always performed in the same tube care being taken to remove the excess triphenylphosphine by rinsing with ether previously. The reaction with copper ions was preferred when chlorides and bromides were employed on account of the more pronounced distinction between extract and precipitate than in the case of cobalt. Copper ions, however, could not be employed when iodides were used because of the interaction of these ions leading to the formation of iodine.

Solutions of halides

The same technique was applied to solutions of either *n*- or isopropyl halides in ether and acetone as well as in the corresponding alcohol, *i.e.*, *n*- and isopropyl alcohol respectively. Completely satisfactory results were obtained up to a dilution of 2% by volume of *n*-propyl halide in ethereal, acetone or alcoholic solution and of 10% of isopropyl halide in the same solvents.

Mixtures of n-propyl and isopropyl halides

Experiments were carried out with the technique described above. The identification of both halides through the formation of a precipitate which was partially extractable in a suitable solvent was unambiguous in cases of mixtures containing about the same amount of each halide or an excess of isopropyl halide. The test was not plainly satisfactory for the detection of isopropyl halide in mixtures containing an excess of *n*-propyl halide since the small amounts of precipitate obtained could not be clearly identified.

Identification of both halides in mixtures containing from 50 to 5% of *n*-propyl halide was found to be possible.

Reagents and solutions

Ethyl ether and *n*-butyl acetate were distilled before use.

RECOMMENDED PROCEDURE

(1) Detection of n-propyl or isopropyl chloride and bromide

Place in a micro tube a few grains of pure triphenylphosphine (about 10 mg) and a micro drop of the halide or of its solutions in ether, acetone or in the corresponding alcohol. Seal the tube and heat it for 3 min in an oil bath at 230°. Open the sealed tube and twice rinse the product of the reaction with 2–3 drops of ether. Add to the residue two drops of 1:8 sulfuric acid. If a turbidity appears, add 3–4 drops of ether, shake gently and remove the ethereal layer with a medicine dropper. After complete evaporation of the ether add a drop of copper chloride dihydrate solution (0.05%), a drop of sodium thiocyanate solution (5%) and finally 5 drops of *n*-butyl acetate. Shake and swirl gently. If *n*-propyl halide was present in the original sample a wine-

red color appears in the organic layer, while a yellowish brown precipitate not extractable by the solvent indicates isopropyl halide in the sample.

(2) *Detection of n-propyl or isopropyl iodide*

Proceed exactly as outlined above with the following modifications: (a) heat the sealed tube for 3 min at 150°; (b) perform the identification test using cobalt chloride hexahydrate (0.1%) instead of copper chloride solution. A blue colored extract indicates *n*-propyl iodide whereas a light blue unextracted precipitate shows the presence of isopropyl iodide in the original sample.

(3) *Detection of n-propyl and isopropyl halides in mixtures*

Follow procedure (1) for mixtures of chlorides or bromides and procedure (2) for mixtures of iodides, taking care to employ 30% sodium thiocyanate solution and, respectively, 0.25% copper chloride dihydrate or 0.5% cobalt chloride hexahydrate solution.

ACKNOWLEDGEMENT

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SUMMARY

A test is described for identification and differentiation of *n*-propyl and isopropyl halides. The halide is reacted with triphenylphosphine to form the phosphonium salt, and thiocyanate and copper or cobalt solutions are added. Extraction of the colored precipitate into a suitable solvent indicates *n*-propyl halide whereas isopropyl halides yield unextractable products. The test is applicable to solutions of each halide in the corresponding alcohol as well as to mixtures of both halides.

RÉSUMÉ

Une réaction est proposée pour l'identification et la différenciation des halogénures de *n*-propyle et d'isopropyle, au moyen de triphénylphosphine. Le sel de phosphonium formé est traité par un thiocyanate et une solution de cuivre ou de cobalt; le précipité coloré obtenu, extrait dans un solvant approprié, indique l'halogénure de *n*-propyle, tandis que l'halogénure d'isopropyle n'est pas extrait.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Identifizierung und Unterscheidung von *n*-Propyl- und Isopropylhalogenid mit Hilfe von Triphenylphosphin. Zu dem gebildeten Triphenylphosphoniumsalz gibt man Thiocyanat und eine Kupfer- oder Kobaltlösung, wobei gefärbte Niederschläge entstehen; die *n*-Propylverbindung kann mit einem organischen Lösungsmittel extrahiert werden, während die Isopropylverbindung nicht extrahierbar ist.

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SOLVENT EXTRACTION STUDIES OF PHOSPHONIUM SALTS AND THEIR ANALYTICAL APPLICATIONS

III. DETECTION OF GOLD. IDENTIFICATION OF GOLD AND MINOR CONSTITUENTS IN GOLD ALLOYS

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In previous papers^{1,2} marked differences of solubility in organic solvents of triphenyl-*n*-propyl and triphenylisopropyl phosphonium salts with metal thiocyanato complexes have been described.

A thorough study¹ has shown that the extractability of these compounds depends on the solvent employed as well as on the nature of the metal ion complexed with thiocyanate. It has also been observed that these differences of solubility are more likely to appear among the triphenylisopropyl phosphonium salts since many such compounds tend to remain precipitated, whereas in the series of the triphenyl-*n*-propyl phosphonium salts, extraction into organic media is more frequent.

Most of the products obtained by adding excess thiocyanate and a triphenylisopropyl phosphonium halide to the aqueous solution of a number of metal ions were found not to be extracted by benzene or toluene. Both solvents, however, extract very efficiently the corresponding compound obtained from gold solutions. This property allows the detection of gold and provides a suitable means of separating this element, especially in large amounts, from other metals.

Furthermore, the behavior of the corresponding phosphonium compounds with other metal ions is so highly selective with regard to the solubility in organic solvents, that in many cases separation and detection of minor constituents of gold alloys is possible merely by a proper selection of solvents.

EXPERIMENTAL

Extraction study

Experiments were run with aqueous hydrochloric acid solutions with pH adjusted between 0 and 1. The efficiency of the extraction was determined both with 0.5 and 1.0 ml of aqueous solution with equal volumes of benzene and toluene. The gold extracted was determined in the aqueous residue by the method of ONISHI³ after destruction of excess thiocyanate and phosphonium. The gold content was varied from 5 to 100 $\mu\text{g/ml}$ and it was found that extraction was 80 to 90% complete in a single operation with both solvents. These experiments were performed in ground

glass stoppered test tubes and the organic phase was removed with a medicine dropper or an extraction pipet of the type described by CARLTON⁴.

Detection of gold and interference study

The detection was carried out according to the recommended procedure given below and was based on the color of the organic extract. This color is not sufficiently intense to allow a low limit of identification but since extraction is very efficient, 0.5 μg of gold can be detected by identification in the extract by the benzidine test⁵.

With respect to the behavior of foreign ions, the extractability of a number of metal ions with benzene and toluene was first investigated. The results (Table I) show that

TABLE I

EXTRACTABILITY INTO TOLUENE OF METAL IONS FROM AQUEOUS SOLUTIONS (PH 0-1) CONTAINING THIOCYANATE AND TRIPHENYLISOPROPYL PHOSPHONIUM IONS

Experiments carried out with 500 μg of metal ion in 0.5 ml of aqueous solution and 0.5 ml of solvent

Au(III)	+++ (orange)	Fe(III)	o	Cu(II)	o	Sn(II)	o
Zn(II)	+ (colorless)	Fe(II)	o	Ag(I)	o	Sn(IV)	o
		Co(II)	o	Hg(II)	o	Ti(IV)	o
		Ni(II)	o	Be(II)	o	Zr(IV)	o
		Ru(III)	o	Al(III)	o	Bi(III)	o
Cd(II)	+ (colorless)	Rh(III)	o	Ga(III)	o	V(V)	o
		Pd(II)	o	In(III)	o	Cr(III)	o
		Os(III)	o	Tl(I)	o	Mo(VI)	o
Sb(III)	+ (colorless)	Ir(III)	o	Ge(IV)	o	W(VI)	o
		Pt(IV)	o	Pb(II)	o	Th(IV)	o
Sb(V)	+ (colorless)					U(VI)	o

+++ very well extracted; + extracted; o not extracted

only four of the ions tested were partially extracted with toluene giving colorless extracts. Mercury(II) and titanium(IV) were found to be also partially extracted with benzene, the latter giving rise to a yellow-orange extract whereas with the former no color was observed.

For identification purposes the extraction with toluene should thus provide a practically specific test for gold.

The influence of the above-mentioned ions on the test was studied by taking in every case one drop of solution containing 5 μg of gold and 100 μg of the foreign ion except in the case of platinum(IV) and palladium(II), the amounts of which were increased to 200 μg . No interference was observed with any of the ions tested. Experiments were also run with gold and groups of ions, by taking: 5 μg Au + 50 μg Cu + 50 μg Fe(III); 5 μg Au + 50 μg Cu + 50 μg Ag; 5 μg Au + 100 μg Pt + 100 μg Pd; 5 μg Au + 50 μg Fe(III) + 100 μg Pd. In all these cases it was always possible to detect gold and no color was observed in corresponding blanks run with the same elements but in the absence of gold.

With regard to anions it was observed that cyanide, iodide, thiosulfate, sulfite and phosphate inhibit the test and should be eliminated previously. Nitrate and perchlor-

ate which form precipitates with the phosphonium ion should preferably be absent. Substances which reduce gold ions to the metal in acidic solution, *e.g.* oxalate or hypophosphite, as well as strong oxidants which may destroy thiocyanate or phosphonium ions, should obviously be absent.

Gold alloys

On the basis of results obtained in a survey study¹ a scheme of separation was worked out by careful choice of solvents with the purpose of identifying the compounds of gold alloys which might contain as minor constituents any of the following metals: iron, copper, silver, platinum and palladium.

The scheme given in Table II was first applied to solutions which were specially prepared and which contained, besides large amounts of gold(III), variable amounts of one or more of the ions, Fe(III), Ag, Cu(II), Pt(IV) and Pd(II). The procedure recommended below was followed.

TABLE II

IDENTIFICATION OF GOLD AND OTHER METAL COMPONENTS OF GOLD ALLOYS BY THE SELECTIVE EXTRACTION FROM ACIDIC AQUEOUS SOLUTION, OF THE TRIPHENYLISOPROPYL PHOSPHONIUM SALTS OF THE CORRESPONDING THIOCYANATO COMPLEXES

<i>Metal components</i>	<i>Solvent</i>	<i>Extract</i>
Au	toluene (benzene)	orange
Fe	tri- <i>n</i> -butylphosphate	red
Ag	2-methylcyclohexanol	colorless
Pt	tri- <i>n</i> -butylphosphate (after previous heating at 65–70°)	yellow
Cu	methylisobutyl ketone	wine-red
Pd	cyclohexanone	yellow

The solvents should be used in the sequence given in order to attain the desired selectivity.

As shown in the above scheme, the detection of metal ions is based on the color of the extract, with the exception of silver which may be identified in the organic phase with a suitable reagent. It should be noted that the separation of platinum is based on the fact that no complex is formed with thiocyanate at room temperature; complexing occurs quantitatively at higher temperatures. The corresponding phosphonium salt of this thiocyanato complex, however, is extracted by all the solvents employed except benzene and toluene. It is thus important not to heat the mixture before completing the extraction of silver in order to obtain the desired separation.

Experiments were also performed with three different gold alloys which were dissolved as recommended below. The percentage composition of the metal components in the solutions obtained, to which a small amount of ferric chloride was intentionally added, was:

Sample I: 79.4% Au; 0.8% Fe; 11.9% Ag; 7.9% Cu
 Sample II: 90.1% Au; 0.9% Fe; 9.0% Pd
 Sample III: 70.9% Au; 0.7% Fe; 7.1% Pt; 21.3% Ag

In order to prove the versatility of the extraction procedure and the possibility of developing further methods of quantitative determination, the separations of the metal components were carried out not only according to the scheme outlined above but also with other solvents. Thus in the case of sample I, since platinum and palladium were known to be absent, copper was extracted with cyclohexanone. Iron in sample II was alternately extracted with methylisobutyl ketone and 2-methylcyclohexanol. A different sequence of separation was also studied for the analysis of sample III, *i.e.*, after completing the separation of gold and iron through extraction with toluene and tri-*n*-butyl phosphate respectively, platinum was separated by extracting with methylisobutyl ketone (after previous heating at 70°) and silver, left in the aqueous phase, was finally extracted with cyclohexanone.

For every metal present in the alloys analysed, extraction with the corresponding solvent in the conditions of the test was carefully checked and it was always found to provide quantitative separation. Furthermore, for each step parallel blanks were run which confirmed complete separation.

Solvents, reagents and solutions

The solvents used were all distilled. Freshly prepared alkaline stannite solution consisted of equal volumes of 25% sodium hydroxide and of a solution of 5 g of stannous chloride in 5 ml of concentrated hydrochloric acid, diluted to 100 ml with water⁶.

RECOMMENDED PROCEDURES

(1) Detection of gold

Place in a microtube a drop of the nitrate free solution (pH 0–1), add a drop of 2% triphenylisopropyl phosphonium chloride solution, a drop of 10% sodium thiocyanate solution and 3 drops of benzene or toluene. Shake and allow the phases to separate. A yellow-orange color appears in the organic layer if gold is present. Limit of identification: 2 μg .

If very large amounts of iron(III) are suspected to be present, it is advisable to use more concentrated thiocyanate (20–30%) and phosphonium (5%) solutions.

To detect lower amounts of gold proceed as described and transfer the organic extract, with the help of a medicine dropper, to a small porcelain dish. Let the solvent evaporate, add 3 drops of concentrated hydrochloric acid and one drop of concentrated nitric acid. Evaporate to dryness in a water bath taking care to eliminate all the nitric acid. To the residue add a drop of 1% benzidine solution in 10% acetic acid. A blue color indicates gold. Limit of identification: 0.5 μg . Run a blank with all the reagents.

(2) Identification of gold and other metal components in gold alloys

Dissolve about 10 mg of the alloy in aqua regia. Evaporate to dryness to remove nitric acid completely. Add 1 ml of concentrated hydrochloric acid and dilute to about 5 ml in order to adjust the pH to between 0 and 1. If silver is present use sufficient hydrochloric acid to keep the solution clear. Place a drop of this solution in a small glass test tube (about 0.8 cm diameter) and add 2 drops of 2% triphenylisopropyl chloride, a drop of 10% sodium thiocyanate solution and 6 drops of benzene or toluene and shake. An orange color in the organic layer indicates gold.

Centrifuge and remove the extract with a medicine dropper or an extraction pipet⁴ and discard it. Repeat the extraction twice with 4 drops of solvent each time. Employ the same technique in subsequent steps taking care to add a drop of hydrochloric acid (1:1) as well as an additional drop of phosphonium chloride and of thiocyanate solution before each extraction. These steps should conform to the scheme given above.

In order to detect and separate platinum, as shown in Table II, after completing the separation of silver, rinse the aqueous residue with 3-4 drops of toluene (or benzene), discard the solvent, heat for 10 min in a water-bath at 65-70° and allow to cool before extracting with tri-*n*-butylphosphate.

Silver may be identified by the black color obtained by treating a drop of the organic extract with a drop of saturated lead chloride solution, a drop of 25% sodium hydroxide solution and a drop of alkaline stannite solution in a spot plate⁶.

According to the foregoing procedures the limits of identification of the metals studied are: 0.1 μg Fe; 1.0 μg Ag; 2.5 μg Pt; 0.5 μg Cu; 2.5 μg Pd. These limits were found to be practically independent of the dilution of the aqueous phase.

ACKNOWLEDGEMENTS

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SUMMARY

Gold is very efficiently extracted with benzene or toluene after precipitation in acidic solution by excess thiocyanate and triphenylisopropyl phosphonium ions. An almost specific test for gold is thus possible and large amounts of gold can be separated from other elements. A scheme of separation is described for the identification of gold and other metal components in gold alloys, based on selective extraction of the triphenylisopropyl phosphonium salts of the corresponding thiocyanato complexes.

RÉSUMÉ

Une réaction est proposée pour l'identification de l'or par précipitation au moyen de thiocyanate et d'ions triphényl-isopropyl-phosphonium et extraction dans le benzène ou dans le toluène.

ZUSAMMENFASSUNG

Beschreibung eines Extraktionsverfahrens zum Nachweis und zur Abtrennung von Gold durch Fällung mit Thiocyanat- und Triphenyl-isopropyl-phosphonium Ionen.

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ADSORPTION OF SOME METALS ON ANION-EXCHANGE RESINS FROM POTASSIUM THIOCYANATE SOLUTIONS

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In recent years a large amount of information has been reported on the anion-exchange behavior of metals in a number of media. Chloride media, especially hydrochloric acid solutions, have received most attention, and KRAUS AND NELSON¹ have reported the behavior of most metals in the periodic table over a broad range of hydrochloric acid concentrations. Numerous separations are feasible by proper control of hydrochloric acid concentrations and many have been reported in the literature.

A number of elements are not adsorbed by an anion-exchange resin at any hydrochloric acid concentration and hence cannot be separated in this manner. Other complexing agents are available, of course, and many have been studied². This paper reports the results we obtained with a number of metals using thiocyanate ion as the ligand. Since many metals form thiocyanate complexes it was thought worthwhile to investigate the adsorption of metals from potassium thiocyanate media and to see if any useful separations could be achieved. The metals studied were scandium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silver, thorium and uranium. For those metals which showed appreciable adsorption, distribution coefficients were determined at various thiocyanate concentrations and some separations were found to be feasible.

EXPERIMENTAL

Resin

The resin used in all experiments was Dowex-I, 80-100 mesh, with 8% divinyl benzene. The chloride form of the resin was converted to the thiocyanate form by shaking with 6 M KSCN for several days. This procedure does not completely remove chloride from the resin, but the resin was assumed to be principally in the thiocyanate form in view of the higher selectivity for thiocyanate ions than for chloride ions³. The resin was then washed and air-dried at room temperature. The percentage moisture was found to be 5.6% by drying a sample over "Anhydrone" at 65° overnight in a vacuum desiccator. The bed density of the resin in the thiocyanate form was found to be 0.62 g/ml.

Adsorbabilities

The adsorbabilities of elements showing appreciable adsorption were determined by

column and equilibration methods at room temperature (usually 25–30°). In the "column" method⁴ (not the more common "band elution" method) a known amount of the element of interest was first adsorbed on a weighed portion of the resin and the resulting uniformly loaded resin was placed in a column. Eluting solutions of different thiocyanate concentrations were then passed through the column and the effluent was analyzed by the radiometric technique.

Batch equilibrations were employed in cases where the distribution coefficients were not extremely large. Measured amounts of solution and resin were shaken overnight to establish equilibrium. In several instances, even with very large distribution coefficients, batch equilibrations were tried using quantities of resin as small as 1 mg, weighed on a Cahn Electrobalance. Care was taken to ensure that the loading of the resin did not exceed 1%. Results obtained by this technique compared favorably with those by the column method, but since there were occasional indications that equilibrium was being reached rather slowly, only values obtained by the column method are reported here.

Tracers and solutions

Standard solutions of potassium thiocyanate were prepared by direct weighing of the salt and dilution in a volumetric flask. The tracers employed for radiometric analysis were as follows: ⁵¹Cr ($T_{\frac{1}{2}} = 27$ day), ⁴⁶Sc ($T_{\frac{1}{2}} = 85$ day), ⁶⁰Co ($T_{\frac{1}{2}} = 5.2$ year), ¹¹⁵Cd ($T_{\frac{1}{2}} = 53$ h), ⁶⁵Zn ($T_{\frac{1}{2}} = 245$ day), and ¹¹⁰Ag ($T_{\frac{1}{2}} = 270$ day). These were obtained from the Radioisotope Division of the Oak Ridge National Laboratory in a high state of purity. A well-type scintillation counter was employed in assaying the solutions.

Vanadium, uranium, and thorium were detected by spot-tests⁵, vanadium with hydrogen peroxide, uranium with 8-hydroxyquinoline, and thorium with quinalizarin.

RESULTS AND DISCUSSION

Of the various metals studied, chromium, manganese, and nickel were found to be non-adsorbable from solutions up to 8 M in thiocyanate. This behavior is similar, of course, to that in hydrochloric acid media. Neither copper nor mercury could be

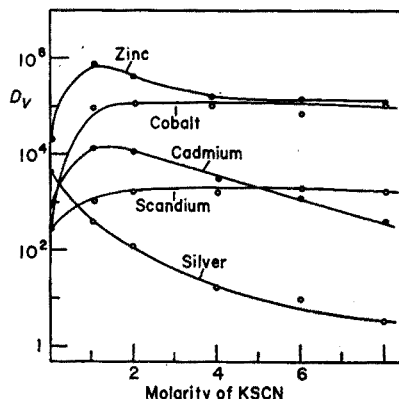


Fig. 1. Distribution coefficients at various concentrations of cyanate.

conveniently studied in thiocyanate media, both forming precipitates with this anion. It was observed, however, that at the tracer level mercury was held strongly by the resin, probably as the well-known $\text{Hg}(\text{SCN})_4^{-2}$ complex. Vanadium(IV) was retained by the resin from 8 *M* thiocyanate, but a black precipitate formed on the resin when 1 *M* thiocyanate was employed in an attempt to elute the metal. Neither thorium nor uranium (uranyl) showed appreciable adsorption from thiocyanate solutions up to 8 *M*.

In Fig. 1 the distribution coefficient, D_v , is plotted against the molarity of potassium thiocyanate for the elements zinc, cobalt, cadmium, scandium, and silver, all of which show appreciable adsorption from this medium. Iron is also strongly adsorbed on the resin, but no attempt was made to measure the adsorbability quantitatively since the distribution coefficient is so large. It was found difficult to remove iron from the resin by elution. One method that was successful was to remove the thiocyanate by washing with concentrated hydrochloric acid, followed by a very dilute hydrochloric acid or water wash (see below).

Scandium is only slightly adsorbed from hydrochloric acid solutions by Dowex-1 but is rather strongly adsorbed as the thiocyanate¹. The fact that the element can be extracted by ether from a thiocyanate-hydrochloric acid solution suggests that the metal may form complexes with thiocyanate⁶. The behavior here offers a convenient method of separating scandium from other elements in the first long row of the periodic table which are non-adsorbable from hydrochloric acid or thiocyanate media. Fig. 2 shows such a separation of chromium and scandium. Scandium is held strongly in 1 *M* thiocyanate while chromium passes through the column. The scandium can be eluted with 0.025 *M* thiocyanate.

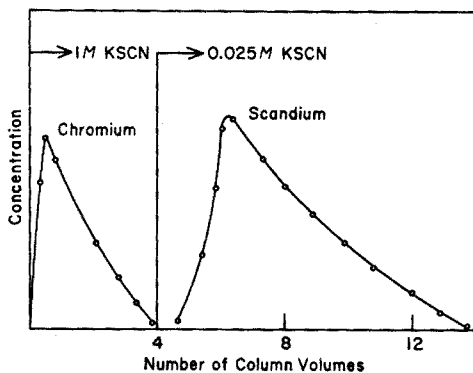


Fig. 2. Separation of chromium and scandium.

Cobalt is known to form stable complexes with thiocyanate and the blue color which results is used as the basis of a colorimetric determination of the metal⁷. It was not surprising to find that cobalt is strongly adsorbed from thiocyanate solutions and the distribution coefficient is even larger than that in hydrochloric acid media. The coefficient is as large as 10^5 above 1 *M* thiocyanate, but drops rapidly at low concentrations, and cobalt can be eluted with 0.02 *M* thiocyanate. Since the adsorption of cobalt from thiocyanate occurs at much lower concentrations of the complexing

agent than from hydrochloric acid media, the familiar separation of nickel and cobalt on Dowex-1 can be carried out in solutions of quite low ionic strength by using thiocyanate rather than hydrochloric acid.

The adsorption curves for both zinc and cadmium are similar in shape to those obtained for these metals from hydrochloric acid media. However, both are more strongly adsorbed from the thiocyanate medium, and in both cases the adsorption remains large even to quite low concentrations of the complexing agent. Hence, it is difficult to elute either metal with thiocyanate solutions.

Although silver forms a precipitate with thiocyanate ion, apparently this is converted into a negatively charged ion, such as $\text{Ag}(\text{SCN})_2^-$, with excess thiocyanate. The variation of the distribution coefficient with thiocyanate concentration is very similar to that found in hydrochloric acid solutions¹, the value of D_0 steadily decreasing with increasing concentration of thiocyanate.

Separations

As previously mentioned, Fig. 2 shows a separation of scandium and chromium that cannot be carried out conveniently in hydrochloric acid media. It should be noted that a third element, such as zinc or cadmium, which is strongly held even at low thiocyanate concentrations would still be retained by the resin and could also be separated. It is apparent from the non-symmetrical appearance of the elution bands that the rate of equilibration was slow (note also Fig. 3). Sharper elution bands would

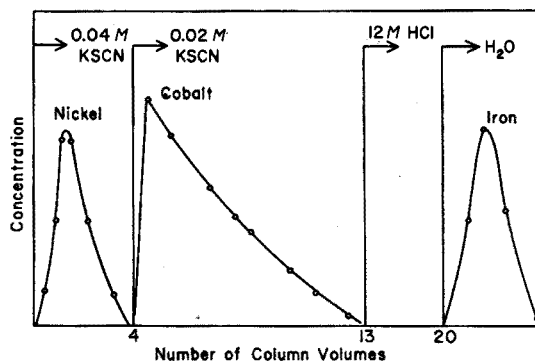


Fig. 3. Separation of iron, cobalt and nickel.

be expected, of course, with a finer resin and with slower flow rates. The flow rate employed was of the order of 1 ml/cm²/min.

Fig. 3 shows a separation of iron, cobalt, and nickel using thiocyanate solutions. Nickel is not adsorbed from 0.04 M thiocyanate whereas cobalt and ferric iron are strongly adsorbed. Cobalt can be removed by eluting with 0.02 M thiocyanate. The iron was removed by washing the column with 12 M hydrochloric acid, followed by a very dilute hydrochloric acid solution.

A number of other separations are possible, of course, using thiocyanate as the complexing agent. Any non-adsorbable element can be separated from one which is strongly held by the resin. However, this complexing agent does not seem to be as versatile as is hydrochloric acid for such purposes, but it does offer some additional methods for the separation of metals.

ACKNOWLEDGEMENT

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SUMMARY

The adsorption of a number of metals on Dowex-1 from potassium thiocyanate solutions has been studied. Distribution coefficients were measured as a function of thiocyanate concentration for zinc, cobalt, cadmium, scandium, and silver. Some separations of metals employing thiocyanate as the complexing agent are reported.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'adsorption d'une série de métaux sur dowex-1, à partir de solutions de thiocyanate de potassium. Les coefficients de distribution ont été mesurés, en fonction de la concentration en thiocyanate, pour le zinc, le cobalt, le cadmium, le scandium et l'argent.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Adsorption einer Anzahl Metalle an Dowex-1 aus Kaliumthiocyanatlösung. Die Verteilungskoeffizienten für Zink, Kobalt, Cadmium, Scandium und Silber wurden als Funktion der Thiocyanat-Konzentration bestimmt.

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Short Communication

The ageing of ammonium molybdate reagent

It is well known that acidified solutions of ammonium molybdate, used as a reagent for orthophosphate, deposit yellow crystals on ageing. During the past 20 years a number of workers have commented on this effect^{1-3,6}. The general conclusion has been that the yellow crystals formed are molybdic acid $\text{MoO}_3 \cdot 2 \text{H}_2\text{O}$, contaminated with small amounts of ammonium polymolybdates. AUGER¹ investigated the formation of this acid and LINDQVIST² determined the structure by X-ray methods. AUGER stated that the yellow colour was due to traces of silicomolybdate, the silica originating from the glass vessel. Storage of the reagent in dark bottles has been recommended in order to minimise the formation of this deposit. BIRNBAUM AND WALDEN³ reported a variation in the phosphorus content of ammonium 12-molybdophosphate which has been formed from an ammonium molybdate reagent contaminated with silica from the container.

The present author, in using large quantities of ammonium molybdate reagent, has stored the solution in a variety of containers under various conditions and his observations differ from those previously reported.

Experimental

Ammonium molybdate reagent was prepared by THISTLETHWAITE's method⁴. 35 g of A.R. ammonium molybdate was dissolved in 50 ml of 0.880 s.g. ammonia solution and 50 ml of water. This solution was poured slowly into cold nitric acid (168 ml of concentrated A.R. nitric acid diluted to 360 ml) with constant stirring. The solution was allowed to stand for 24 h in a polythene bottle, after which it was filtered through a No. 3 porosity sintered glass funnel and diluted to 900 ml. This reagent was divided into 4 equal parts, which were used to fill 2 identical polythene bottles and 2 identical glass bottles. One polythene and one glass bottle were kept in direct daylight whilst the remaining bottles were stored in complete darkness; all were tightly stoppered. The mean temperature was around 15°. The contents of the bottles were examined at monthly intervals. The experiment was later repeated with varying molybdate concentrations.

Observations and discussion

After 4 months, isolated yellow crystals started to develop in all 4 bottles. After another 2 months these crystals reached their maximum size (up to 2 mm long) but a white crystalline deposit had also started to form. In all the bottles, the net result after 8 months was that the bottoms were covered with a number of yellow crystals embedded in a matrix of fine needle shaped white crystals. The mother liquor in each case was colourless with the exception of that in the glass bottle which had been kept in direct light; the latter solution had a faint yellow colour. After 18 months there were no further developments except that the mother liquor in the last mentioned bottle had become progressively more yellow, reaching a pale straw colour.

The deposits were filtered off, washed with a little ice-cold water, followed by ethanol and ether. In each case about 3–3.5 g of mixed crystals were obtained. The yellow and white crystals were separated from each other manually, analysed for ammonia and molybdenum and X-ray powder photographs were taken.

The X-ray powder photographs showed the two types of crystals to be completely different in nature. The pattern given by the yellow crystals corresponded in many ways to that reported for molybdic acid $\text{MoO}_3 \cdot 2 \text{H}_2\text{O}$; there were a number of extra lines which can probably be accounted for by the presence of a small amount of ammonia. The pattern given by the white crystals could not be identified with that of any known molybdate.

The percentages of ammonium ion and molybdenum in the yellow crystals were respectively 1.1 and 53.9% (theoretical values for $\text{MoO}_3 \cdot 2 \text{H}_2\text{O}$ are 0 and 54.5%). For the white crystals, the respective percentages were 5.5 and 61.7% (theoretical values for $(\text{NH}_4)_2 \text{Mo}_4\text{O}_{26}$ are 5.8 and 61.1%). No nitrate was found in either of the compounds.

Thus it seems likely that the yellow crystals are a slightly impure form of the well known yellow molybdic acid whilst the white crystals are ammonium tetramolybdate. The tetramolybdates have been described by LINDQVIST² and the existence of the tetramolybdate ion in acid solutions is more or less certain⁵.

Variation of the concentration of the molybdate in the reagent caused a variation in the time taken for the deposit to appear. Keeping the nitric acid and ammonia concentrations constant, it was found that if only 20 g of ammonium molybdate are used (per 900 ml of reagent) no deposit is formed even after 6 months. If 67 g of ammonium molybdate are used deposition of the yellow crystals starts in less than a month.

In the original experiment it was found that the aged reagent still remained effective for the quantitative precipitation of phosphate.

Conclusion

It has been shown that the ageing of the given ammonium molybdate reagent, with the deposition of two types of crystals, takes place irrespective of the nature of the containing vessel and is unaffected by the presence or absence of light. However, the presence of light appears to aid the dissolution of silica from the glass vessel giving rise to a pale yellow colour in the solution (after some months): this effect is dependent on the nature of the glass. To prepare a reagent which will remain clear and colourless for many months, an ammonium molybdate concentration of less than 20 g/l and storage in a polythene bottle are recommended.

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Slough (Great Britain)*

H. BUCHWALD

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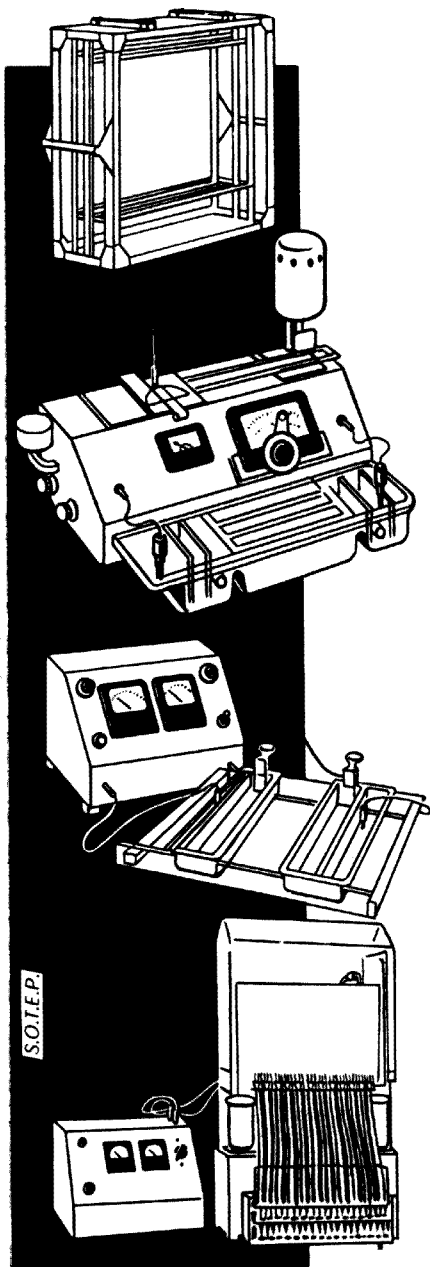
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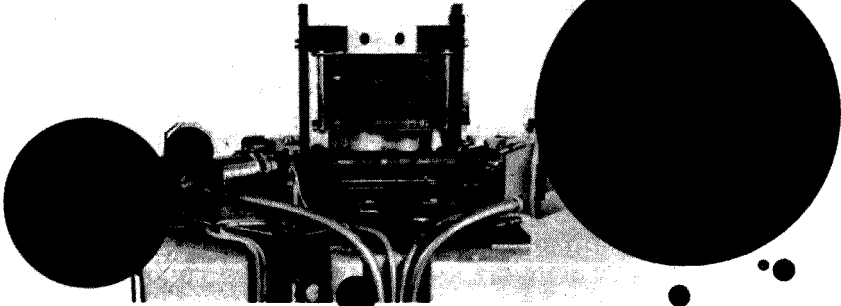
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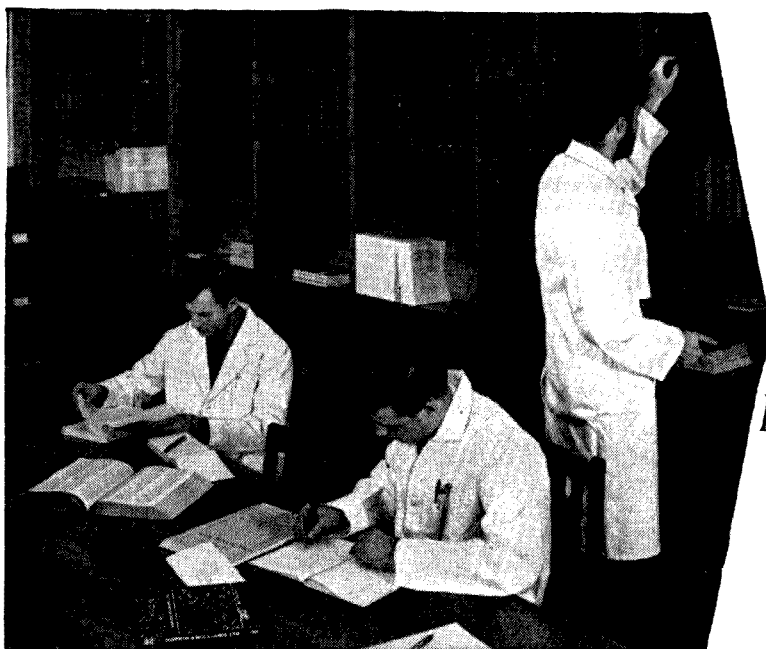
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