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ANALYTICAL CHEMISTRY OF THE SULPHUR ACIDS

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Summary—A comprehensive review is made of the analytical methods available for the inorganic acids derived from sulphur.

Sulphur is one of nature's very reactive elements, and it combines with most of the elements to form chemical compounds. Most of these sulphur compounds are either acids or their salts, because the oxygen and halogen derivatives of sulphur react with water to yield sulphur acids.

Most of the sulphur acids are very reactive and thus unstable; they can react with each other, and many can undergo decomposition or air oxidation. As a consequence the analytical determination of the sulphur acids usually presents a difficult problem, namely that of the analysis of a complex mixture of sulphur compounds.

It is often necessary or desirable to analyse for several or even all of the individual components of such a complex mixture, since the measurement of total sulphur content does not usually provide sufficient information.

A collective series of articles describing in great detail the then available methods of sulphur analysis was published by Kurtenacker in 1938 under the title "Analytische Chemie der Sauerstoffsäuren des Schwefels".[1] Several monographs published later have reviewed this very complex problem in lesser detail.

A review and evaluation of the analytical methods for the determination of H_2S, H_2S_x, H_2SO_3, $H_2S_2O_4$, H_2SO_4, $H_2S_2O_3$, $H_2S_xO_6$, H_2SO_5, $H_2S_2O_8$, and the corresponding salts, comprises the subject of this article.

In addition to the above-mentioned sulphur-containing acids, some authors[2] have suggested the existence of H_2SO, H_2SO_2 and $H_2S_2O_2$ in the form of intermediates or organic derivatives. However the analytical methods—if any—for the determination of these highly unstable compounds are not reviewed here.

DETERMINATION OF SULPHIDES

Titrimetric determinations

Analysis with iodine. Several methods are based on the reaction of H_2S with iodine to give elemental sulphur and iodide ions.

$$H_2S + I_2 \longrightarrow S + 2H^+ + 2I^- \qquad \text{I}$$

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* For reprints of this review, see Publisher's announcement near the end of this issue.

Since direct titration of sulphides with iodine does not give accurate results,[3] an excess of iodine is added to the H_2S solution and the excess of iodine is titrated with thiosulphate. Another method is based on the reaction of sulphide ions with iodine in alkaline medium to yield sulphate.[4]

$$S^{2-} + 4I_2 + 8OH^- \longrightarrow SO_4^{2-} + 8I^- + 4H_2O \qquad \text{II}$$

After acidification of the reaction medium the excess of iodine is back-titrated with thiosulphate.

Because aqueous H_2S solutions lose H_2S gas very readily, some authors recommend the precipitation of the sulphide with cadmium or zinc acetate solution. Excess of acidic iodine solution is then added to the precipitate, followed by back-titration of the excess of iodine with thiosulphate.[5,6] Concentrations as low as 0·2 ppm of sulphide can be accurately measured according to this principle.[7]

An aqueous solution of alkali and alkaline earth metal sulphides is of strongly alkaline pH, and usually contains sulphites, thiosulphates and in certain cases even polysulphides as contaminants.[8,9] In order to avoid the reaction of sulphides with iodine in alkaline medium (equation II) it is necessary to use an iodine solution containing enough mineral acid when the iodometric sulphide determination is carried out according to equation I.[10,11]

The determination of sulphides and hydrogen sulphides in the presence of each other can be done on the basis of reactions III and IV

$$S^{2-} + I_2 \longrightarrow 2I^- + S \qquad \text{III}$$

$$SH^- + I_2 \longrightarrow 2I^- + H^+ + S \qquad \text{IV}$$

The amount of acid formed according to equation IV can be measured alkalimetrically.[12]

Iodometric determination of sulphide in the presence of sulphite and thiosulphate. Sulphide ions can be selectively precipitated as zinc or cadmium sulphide even in the presence of sulphites and thiosulphates.[13–17] After filtration the precipitate is reacted with acidic iodine solution and the excess of iodine is back-titrated.[35]

Sulphide is practically always contaminated with its oxidation products, which also react with iodine. After precipitation and filtration of zinc or cadmium sulphide, the amounts of sulphite and thiosulphate can be determined in aliquots of the filtrate.[18] The total amount of sulphite and thiosulphate is measured with iodine according to equations V and VI, and the thiosulphate is selectively titrated with iodine in a separate aliquot in the presence of formaldehyde which masks sulphite according to equation VII.[29–34]

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \qquad \text{V}$$

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+ \qquad \text{VI}$$

$$HCHO + SO_3^{2-} + H^+ \longrightarrow CH_2OH.SO_3^- \qquad \text{VII}$$

The method of Wollak can also be utilized for the determination of sulphide, sulphite and thiosulphate in the presence of each other.[19] According to this method the total amount of the three ions is determined iodometrically, in one aliquot. To another aliquot zinc acetate is added, the sulphite is masked with formaldehyde, and iodine is added to the solution, which still contains the zinc sulphide precipitate. Back-titration of the excess of iodine gives the total amount of sulphide and thiosulphate. In order to determine the amount of thiosulphate, a third aliquot is carefully oxidized with iodine, and the excess of I_2 is removed by addition of Na_2SO_3 to a colourless end-point. The tetrathionate formed from the original thiosulphate is reacted with potassium cyanide (equation VIII), to produce half the amount of thiosulphate originally present, and this is titrated with iodine.

$$3CN^- + S_4O_6^{2-} + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 2HCN + SCN^- \qquad \text{VIII}$$

Sulphite can be selectively precipitated as $SrSO_3$ in the presence of sulphide and thiosulphate.[20]

The accuracy of the methods involving filtration of a precipitate is often unsatisfactory owing to adsorption of various ions on the precipitate. Wollak's method in particular does not give accurate results for thiosulphate when only a small amount of that ion is present.

An altogether different principle for the determination of sulphides, sulphites and thiosulphates in the presence of each other is utilized when the volatile H_2S is removed from the solution by treatment with a weak acid such as carbonic or boric acid. The H_2S is absorbed in iodine, bromine or alkaline peroxide solution.[21-23] The amount of sulphite and thiosulphate can then be measured iodometrically in the sulphide-free solution. The accuracy of this method can be greatly reduced by the concentration-dependent side-reaction of SO_3^{2-} ions with HS^- ions (equation IX).

$$4H^+ + 2HS^- + 4SO_3^{2-} \longrightarrow 3S_2O_3^{2-} + 3H_2O \qquad \text{IX}$$

In order to circumvent this difficulty Szekeres recommended the determination of the sulphide, sulphite and thiosulphate content of alkali metal sulphides by four titrations.[24,25] According to this method one aliquot is titrated with iodine, and another with bromine (bromide/bromate mixture) which reacts with three species according to equations X, XI and XII.

$$S^{2-} + 4H_2O + 4Br_2 \longrightarrow SO_4^{2-} + 8H^+ + 8Br^- \qquad \text{X}$$

$$S_2O_3^{2-} + 5H_2O + 4Br_2 \longrightarrow 2SO_4^{2-} + 10H^+ + 8Br^- \qquad \text{XI}$$

$$SO_3^{2-} + H_2O + Br_2 \longrightarrow SO_4^{2-} + 2H^+ + 2Br^- \qquad \text{XII}$$

These two determinations give the total amount of sulphide, sulphite and thiosulphate ions. From the other two aliquots the sulphide is removed by boiling with boric acid, and the total amount of sulphite and thiosulphate is determined by titration of one aliquot with iodine and the other with bromine. From these four measurements the amount of S^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ can be calculated and the amount of sulphide converted into thiosulphate according to equation IX can also be calculated.[25]

Mixtures containing elemental sulphur in addition to sulphide, sulphite and thiosulphate can be analysed by the above-described iodometric methods, and by measuring the total sulphur content.[26]

Erdey recommended the use of ascorbic acid (with Variamine Blue or dichlorophenol–indophenol as indicator) for the back-titration of iodine in the iodometric determination of sulphide.[27,28] Since the titre of ascorbic acid solutions changes much more rapidly than that of thiosulphate solutions this method offers no advantage, and is of limited practical utility. Furthermore, as already pointed out, sulphides cannot be determined accurately by a simple iodometric titration since with the exception of H_2S they are always contaminated with sulphite, thiosulphate and/or polysulphides.[8,9]

Determination of sulphides by other redox titrations. Sulphide is oxidized to sulphate by potassium iodate in boiling strongly alkaline aqueous solutions, but iodate also reacts with the other sulphur compounds which usually contaminate sulphides, and its utility for the determination of sulphide is rather restricted.[5,36] In these methods excess of iodate is added, and the surplus back-titrated iodometrically.

Bromide/bromine solution has been recommended for the determination of sulphides, with irreversible organic-dye indicators.[37,38] Some authors have used bromate or bromide/bromate with iodometric back-titration of the excess of reagent.[39–41]

Sulphide can also be oxidized to sulphate with hypochlorite (equation XIII), again with iodometric determination of the excess of reagent.[42]

$$S^{2-} + 4OCl^- \longrightarrow SO_4^{2-} + 4Cl^- \qquad \text{XIII}$$

Hypoiodite has also been used.[43]

Erdey used hypobromite or hypochlorite solution for the direct titration of sulphide.[44–46] Since these reagents are comparatively unstable and are non-selective as reagents for sulphide, these hypohalite methods are of limited practical utility.

Kolthoff oxidized sulphide with permanganate in alkaline medium and used iodometric back-titration of the excess.[47] However, the reaction of permanganate with the usual sulphur-containing contaminants of sulphides diminishes the accuracy of this method too.

Murthy used chloramine-T solution for the determination of sulphide, sulphite and thiosulphate ions.[48] The total amount of the three ions was obtained by iodometric back-titration of excess of chloramine-T; the sulphide content was measured *via* CdS, and the sulphite/thiosulphate content was obtained by the usual iodometric methods.

Periodate has also been used for the oxidation of sulphides.[49] It also oxidizes sulphite, thiosulphate and dithionite. The simplest way to measure the excess of periodate is by iodometric titration.

Mixtures of sulphide, sulphite and thiosulphate can also be titrated with sodium nitrite solution in mildly acidic medium,[50] with chloroform and a trace of potassium iodide as indicator. When periodate or nitrite is used the amounts of sulphite and thiosulphate present in the mixture must be determined by separate measurement.

A theoretically interesting though less practical method for the determination of sulphide is oxidation by the Ag(III) tellurate complex. The excess of the oxidizing agent is reduced with arsenite solution, and the excess of arsenite is back-titrated with iodine.[51]

Potassium ferricyanide solution has been used for the oxidation of sulphide (equation XIV).[51–57]

$$S^{2-} + 2[Fe(CN)_6]^{3-} \longrightarrow S + 2[Fe(CN)_6]^{4-} \qquad \text{XIV}$$

Above pH 9·4 sulphide is oxidized to sulphate by potassium ferricyanide.[52] Sodium nitroprusside or ferrous dimethylglyoximate is used for end-point indication. Potentiometric indication has been recommended by several authors.[52,53,56] At pH 9·4 ferricyanide does not react with sulphite and thiosulphate. The sulphite content of the mixture can be removed from solution by precipitation as barium sulphite.[52,53] Sulphide, sulphite, tetrathionate and dithionite can be titrated with potassium ferricyanide solution in strongly alkaline medium in the presence of osmium tetroxide as catalyst.[58–60] Either dead-stop or potentiometric end-point detection can be used.

Determination of sulphides by precipitation titration. Sulphide can be titrated with zinc sulphate in the presence of ammonia. The end-point is indicated potentiometrically[76,102] or by metallochromic indicators.[61–63]

The sulphide content of polysulphides can also be determined by a modification of this method. The polysulphide is reacted with sulphite (equation XV), to give thiosulphate and sulphide, and the sulphite and thiosulphate do not interfere with the precipitation titration of sulphide.[63,64]

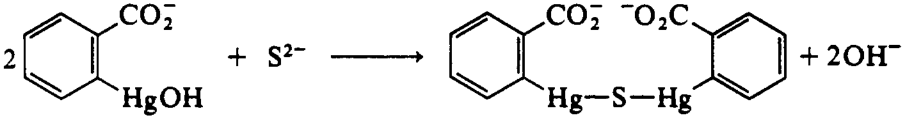
$$S_x^{2-} + (x-1)SO_3^{2-} \longrightarrow S^{2-} + (x-1)S_2O_3^{2-} \qquad \text{XV}$$

Complexometric determination of sulphide. The indirect chelatometric determination of sulphide is based on the insolubility of copper, cadmium and zinc sulphides. In Kivalo's procedure excess of copper perchlorate is added to the solution of sulphide, the precipitate is filtered off, and the excess of copper ion is titrated complexometrically.[65] Variations based on the same principle have been recommended.[66–71] Buděšínský precipitated cadmium sulphide by addition of Cd–EDTA complex to sulphide solutions and titrated the liberated EDTA with calcium chloride solution.[72]

Sulphide and thiosulphide can be determined in the presence of each other according to the method of de Sousa.[73] The sulphide is precipitated as cadmium sulphide and the excess of cadmium is measured in the filtrate by complexometric titration. In another aliquot all the sulphur species are oxidized to sulphate with bromine, the sulphate is precipitated with excess of barium chloride and after filtration the excess of barium is titrated with EDTA. Similar methods for the determination of sulphide and sulphite have also been worked out by de Sousa.[74,108]

Szekeres oxidized sulphide to sulphate and determined the latter by precipitation titration with barium chloride, using a metallochromic indicator.[75] Phosphate and arsenate did not interfere.

Mercurimetric determination of sulphide. The reaction of sulphide with *o*-hydroxymercurybenzoic acid (HMB) in alkaline medium can often be utilized (equation XVI). Since HMB does not react with sulphite and thiosulphate, sulphide can be titrated directly with HMB in the presence of these ions.[77–86] Thiofluorescein,[81–83] dithizone[78,84,86] and sodium nitroprusside[79] were recommended as indicators in these titrations.



XVI

Acrylonitrile reacts relatively rapidly with compounds of the general structure R–SH, including sulphides and polysulphides.[85] Since the products of these reactions are inert to HMB, various sulphur compounds can be determined in the presence of each other by appropriate combination of masking with acrylonitrile and various iodometric procedures.[83,85]

Another mercurimetric method is based on the colour reaction of mercury(II) and diphenylcarbazone.[87] Combinations of methods based on this principle with various iodometric procedures have been used for the determination of sulphide, sulphite and thiosulphate in the presence of each other.[88]

Determination of sulphides by argentometry and other methods requiring instrumental end-point indication. The reaction of sulphide ions with silver nitrate (equation XVII) has been the basis of various analytical methods, which differ mainly in the mode of end-point indication.

$$2Ag^+ + S^{2-} \longrightarrow Ag_2S \qquad \text{XVII}$$

When silver nitrate solution is added in excess, it can be back-titrated with thiocyanate.[89,90]

A similar procedure utilizes mercuric nitrate solution as the precipitating titrant.[90] Various other argentometric methods coupled with instrumental end-point indication have been recommended for the determination of sulphides.[91–101]

Kramer *et al.*, used lead nitrate solution in alkaline medium, with potentiometric end-point indication. Under these conditions sulphate, carbonate, thiocyanate, chloride, ferrocyanide and thiosulphate do not interfere.[103] Kiss recommended cadmium acetate solution as titrant, with a dead-stop end-point.[104,105]

Determination of sulphide by metathesis. Use of the methathetic reaction between sulphide and silver chromate or lead oxalate has been suggested by Erdey and Bányai,[106,107] equations XVIII and XIX.

$$Ag_2CrO_4 + S^{2-} \longrightarrow Ag_2S + CrO_4{}^{2-} \qquad \text{XVIII}$$

$$PbC_2O_4 + S^{2-} \longrightarrow PbS + C_2O_4{}^{2-} \qquad \text{XIX}$$

The amount of chromate or oxalate ions liberated was measured by iodometric or permanganometric methods. Since both iodine and permanganate react with the usual contaminants of alkali sulphides, these methods, too, are of limited accuracy.

Determination of sulphide by the iodine–azide reaction

The reaction of H_2S with iodine is instantaneous; in contrast the reaction of azide ions with iodine (equation XX) to give nitrogen is slow.

$$2N_3{}^- + I_2 \longrightarrow 2I^- + 3N_2 \qquad \text{XX}$$

However, elemental sulphur (obtained from sulphide by oxidation with iodine) in the presence of iodide ions reacts rapidly with azide ions to give nitrogen (equation XXI). Thiocyanate and thiosulphate give similar reactions.

$$S + 2N_3{}^- \longrightarrow S^{2-} + 3N_2 \qquad \text{XXI}$$

Thus sulphide can be determined by measuring the volume of nitrogen liberated.[109–120] This method is also suitable for microscale determinations.[111,113,119] Thiosulphate and thiocyanate interfere.

Determination of sulphide by physical methods

Polarography. The polarographic method is often used advantageously for the determination of small amounts of H_2S, or for the determination of traces of H_2S in other gases.[121–128] Roubal *et al.*, have described an indirect method:[129] the gas mixture containing H_2S was passed through cadmium acetate–acetic acid solution and after removal of cadmium sulphide by filtration, the residual cadmium content was measured by polarography.

Photometric and colorimetric methods. Amino-*N*,*N*-dimethylaniline reacts with dilute ferric chloride solution in the presence of H_2S to form Methylene Blue, which can be measured spectrophotometrically. This method is suitable for the determination of as little as 1 μg of H_2S.[130–137] The conditions are rather critical and have been examined by several workers.[137a–c] Kato *et al.*, described the use of *p*-phenylenediamine, which forms Lauth Purple with sulphide ions.[138] Several other colour reactions of sulphide ions suitable for quantitative determination have been described.[139–144] Sodium nitroprusside reacts with sulphide in alkaline medium to give an intensely violet complex, which can be measured photometrically.[145–148]

The blue colour of alkaline thiofluorescein solution is quenched by mercury(II) or silver ions, and reappears on treatment with sulphide.[149] The red reaction product of Hg–diphenylcarbazone and sulphide ions can be measured colorimetrically.[150,151] Sulphide ions displace diphenylthiocarbazone from its complex with silver ions, and the liberated organic base can be measured spectrophotometrically.[152] Sulphide quenches the fluorescence of the fluorescein–mercury–acetate complex and this reaction can be used for the microdetermination of sulphide.[153]

Ammonium molybdate is reduced by H_2S in the presence of hydrochloric acid and the resulting molybdenum(III) can be treated with thiocyanate to yield a red complex. This reaction is applicable to the determination of sulphide.[154]

Of the many colloidal metal sulphides suitable for the photometric determination of sulphide, PbS and Bi_2S_3 gave the best results[155–157] but the sulphides of Ag, Pd, As, Hg, Sb Sn, Ni, Cd and Cu have also been used.[158,159]

The reduction of silver bromide to metallic silver is accelerated by catalytic amounts of sulphide. This reaction has been used for the measurement of traces of sulphide, *e.g.*, the darkening of photographic film exposed to traces of sulphide was measured after development of the film.[160–162]

Rapid semi-quantatitive methods for the determination of sulphide have been based on the use of filter paper impregnated with silver chromate or lead acetate.[163–166] A similar rapid method utilizes lead acetate finely dispersed in a gelatine film, and photometric measurement.[167]

Sulphide quenches the chemiluminiescence of hypoiodite with luminol, and this phenomenon is the basis of a photometric method for the determination of sulphides.[168]

A colour reaction for the semi-quantatitive microdetermination of ZnS, CdS, MnS, Bi_2S_3, SnS, SnS_2, UO_2S and As_2S_3 has been described by Feigl *et al.*[169] The sulphide is heated with mercuric cyanide in a test-tube, the top of which is covered with filter paper impregnated with a chloroform solution of copper ethylacetoacetate and "tetrabase" (4,4′-tetramethyldiaminodiphenylmethane). Metathesis gives mercuric sulphide which then reacts according to

$$2HgS + Hg(CN)_2 \longrightarrow 3Hg + (CNS)_2 \qquad \text{XXII}$$

followed by

$$(CNS)_2 + Hg(CN)_2 \longrightarrow Hg(CNS)CN + (CN)_2S \qquad \text{XXIII}$$

and the $(CN)_2S$ gives the blue colour with the copper–tetrabase mixture. The reaction is not specific, however, and is given by elemental sulphur and by any species which will release HCN from the mercuric cyanide.

Chromatography. Birk *et al.* described the GLC determination of sulphide and sulphite by measurement of the H_2S liberated from sulphides by treatment with sulphuric acid or obtained by reduction of sulphite.[170] The main advantage is speed. Sulphide, sulphite, sulphate and thiosulphate have been determined by thin-layer chromatography and ring-colorimetry.[170a]

Elbein *et al.*, described a paper chromatographic system for the separation of sulphide and arsenate;[171] however, the liability of sulphide to undergo air oxidation renders these paper chromatographic methods of limited practical utility.

Gravimetric determination of sulphide

Sulphide can be oxidized to sulphate which is then determined gravimetrically as barium sulphate. However, because the usual sulphur-containing contaminants[8,9] of alkali metal sulphides are also converted into sulphates by oxidation, the results are not accurate.[75] The oxidation can be done with alkaline hydrogen peroxide or sodium peroxide, hypobromite, bromine in hydrochloric acid, *aqua regia*,, or by heating with a mixture of sodium carbonate and nitrate.[13,180–195]

Sulphide can be precipitated with lead nitrate and the lead sulphide can be dried and weighed.[172,173] The thio-salt contamination of lead sulphide can be removed by treatment with ammonium acetate or 2% sodium hydroxide solution.[175]

Sulphides can also be precipitated as cadmium sulphide.[176] From certain insoluble sulphides (FeS, ZnS, CdS, PbS, Sb_2S_3, CuS, HgS) H_2S is said to be released by treatment with concentrated hydrochloric acid and trapped in cadmium acetate solution.[177,178] Since the CdS precipitate is not stoichiometric it is converted into CuS by treatment with acidic cupric sulphate solution (equation XXIV).

$$CdS + CuSO_4 \longrightarrow CdSO_4 + CuS \qquad \text{XXIV}$$

The Cus is then converted into CuO by heating, and weighed.

Water-soluble sulphides can be analysed directly by precipitation of CuS.[3,179] In this case too it is desirable to weigh as CuO.

POLYSULPHIDES

Titrimetric analysis

Most alkali and alkaline earth metal polysulphides will contain thiosulphate as contaminant,[196–198] mainly because their manufacture usually involves heating the metal hydroxide with elemental sulphur (equation XXV),

$$Ca(OH)_2 + 12S \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O \qquad \text{XXV}$$

Thus it is usually desirable to determine the monosulphide moiety, the polysulphide and the thiosulphide content of these mixtures.

Iodometric determination. Only the monosulphide moiety of polysulphides can be measured by simple iodometric titration in acidic medium (equation XXVI),

$$H_2SS_x + I_2 \longrightarrow 2H^+ + 2I^- + (x+1)S \qquad \text{XXVI}$$

Since carbon disulphide dissolves the elemental sulphur formed in the course of this titration Feher *et al.*, recommended its use as a co-solvent.[199]

Szekeres has described several methods for the determination of sulphide, polysulphide and thiosulphate and in the presence of each other.[200–202] These methods are based on the following reactions. Though iodine oxidizes only monosuphide (equation XXVI) and thiosulphate (equation V) in acidic medium, bromine (bromate/bromide) or hypobromite oxidizes both these and the polysulphide sulphur to sulphate (equations X, XI). Each polysulphide sulphur atom requires 3 molecules of bromine for this oxidation (equation XXVII).

$$S + 4H_2O + 3Br_2 \longrightarrow SO_4{}^{2-} + 8H^+ + 6Br^- \qquad \text{XXVII}$$

Both elemental and polysulphide sulphur are hydrolysed by hot water to give H_2S and thiosulphate (equation XXVIII); this reaction takes place rapidly in boiling alkaline solutions.[2,203–206]

$$4S + 3H_2O \longrightarrow S_2O_3{}^{2-} + 2H_2S + 2H^+ \qquad \text{XXVIII}$$

Polysulphides react with cyanide to give thiocyanates (equation XXIX), and the thiocyanates are oxidized by bromine but not by iodine in acidic solution (equation XXX).

$$H_2SS_x + xCN^- \longrightarrow H_2S + xSCN^- \qquad \text{XXIX}$$

$$SCN^- + 4H_2O + 3Br_2 \longrightarrow SO_4{}^{2-} + 7H^+ + 6Br^- + HCN \qquad \text{XXX}$$

In utilization of these reactions, one aliquot of the sulphide–polysulphide–thiosulphate solution is treated with iodine and another with bromine. A third aliquot is treated with potassium cyanide in order to mask polysulphide–sulphur as thiocyanate and prevent its hydrolysis on heating the solution with boric acid. This latter treatment removes the monosulphide moiety as H_2S. Finally the thiocyanate and thiosulphate content of this aliquot is determined by oxidation with bromine. The quantities of monosulphide, polysulphide and thiosulphate originally present in the solution are calculated from these three titrations.[200] A side-reaction that occurs to a small extent on boiling the third aliquot with boric acid (equation XXXI) somewhat diminishes the accuracy of this method.

$$2SH^- + S_2O_3{}^{2-} + 4HCN \longrightarrow 3H_2O + 4SCN^- \qquad \text{XXXI}$$

The monosulphide moiety of polysulphides can be measured accurately if the polysulphide sulphur is masked as thiocyanate and the monosulphide precipitated as cadmium sulphide, which is filtered off and determined iodometrically.

In an alternative method the polysulphide–sulphur is converted into cadmium sulphide and thiosulphate by heating with cadmium carbonate (equation XXXII), and these can be determined by the procedures above.[202]

$$4S + 2CdCO_3 + H_2O \longrightarrow 2CdS + S_2O_3{}^{2-} + 2H^+ + 2CO_2 \qquad \text{XXXII}$$

The main advantage of the latter two methods is that heating with boric acid and the resulting undesirable side-reaction (XXXI) is avoided.

Schulek's widely used method for the determination of polysulphide sulphur consists of the following steps.[23,197,207,208] Potassium cyanide and the sample containing polysulphide are added to boiling boric acid solution, and boiling continued for a few minutes. During this step the polysulphide–sulphur is converted into thiocyanate (equation XXIX), and H_2S and excess of cyanide are removed from the solution. In the next step thiosulphate is oxidized into sulphate, and thiocyanate is either determined photometrically[213] or converted into sulphate and cyanogen bromide by addition of excess of bromide (equation XXXIII). After the excess of bromine has been masked with phenol the cyanogen bromide is titrated iodometrically (equation XXXIV),

$$SCN^- + 4H_2O + 4Br_2 \longrightarrow SO_4{}^{2-} + 7Br^- + 8H^+ + BrCN \qquad \text{XXXIII}$$

$$BrCN + 2I^- + H^+ \longrightarrow HCN + Br^- + I_2 \qquad \text{XXXIV}$$

Iodine monochloride has also been used instead of bromine for the oxidation of thiocyanate.[209]

The reaction of polysulphide–sulphur with sodium sulphite to give thiosulphate renders the polysulphide–sulphur measurable by iodometric titration (equation XXXV).

$$SS_x{}^{2-} + xSO_3{}^{2-} \longrightarrow S^{2-} + xS_2O_3{}^{2-} \qquad \text{XXXV}$$

The excess of sulphite is either masked with formaldehyde (equation VII) or precipitated as strontium sulphite, before the iodometric titration. In combination with this method the monosulphide moiety can be determined by precipitation as zinc sulphide.[31,210–214,218]

Schmidt and Waegerle used arsenite to convert polysulphides into a thioarsenate which could be titrated iodometrically (equation XXXVI).[215]

$$SSx^{2-} + xAsO_3{}^{3-} \longrightarrow S^{2-} + xAsO_3S^{3-} \qquad \text{XXXVI}$$

Polysulphide–sulphur is converted into monosulphide by reaction with sodium metal or sodium amalgam (equation XXXVII).[216]

$$Na_2SS_x + 2Na \longrightarrow (x+1)Na_2S \qquad \text{XXXVII}$$

The resulting sulphide is titrated iodometrically. The amount of polysulphide–sulphur is calculated as the difference between the monosulphide moiety and the total sulphur content, provided the amount of thiosulphate in the sample is negligible or is disregarded. Copper metal has also been used for the reduction of polysulphides to sulphides.[217]

Other titrimetric methods. Heating a solution of polysulphides with magnesium chloride—preferably in a nitrogen atmosphere—removes the monosulphide content as H_2S, which is absorbed in hydrogen peroxide solution and oxidized to sulphate which is determined as barium sulphate.[219] Owing to the slow hydrolysis of polysulphide–sulphur[2,203–206] the determination often yields values that are too high.

The total sulphur content of polysulphides can be measured by oxidation with alkaline peroxide solution (equation XXXVIII), the excess of alkali being simply back-titrated with sulphuric acid.[220,221]

$$Na_2S_x + (2x-2)NaOH + (3x+1)H_2O_2 \longrightarrow xNa_2SO_4 + 4xH_2O \qquad \text{XXXVIII}$$

Légrádi used a combination of iodometric, complexometric and acidimetric methods.[222] According to this procedure the polysulphide is precipitated as ZnS_x with an ammoniacal zinc solution and removed by filtration. The thiosulphate content of the sample is titrated iodometrically in the filtrate. The ZnS_x is decomposed by boiling with hydrochloric acid, the resulting elemental sulphur is oxidized with alkaline peroxide, and the excess of alkali is back-titrated with acid. The total sulphur content is determined in another aliquot by conversion into sulphate with bromine, and complexometric determination of barium sulphate. Since the polysulphide–sulphur is converted in a small extent into sulphide on boiling with hydrochloric acid, this method often gives low values for polysulphide–sulphur.

Wronski described several methods for the titration of the monosulphide moiety in polysulphides, with *o*-hydroxymercurybenzoic acid solution.[84,85,223] According to one of these procedures the polysulphide is first treated with sodium sulphite and the resulting monosulphate titrated with *o*-hydroxymercurybenzoic acid.

The monosulphide moiety of polysulphides can be measured indirectly by argentometric methods (equation XXXIX).[199]

$$H_2SS_x + 2Ag^+ \longrightarrow Ag_2S + xS + 2H^+ \qquad \text{XXXIX}$$

The elemental sulphur formed is removed with carbon disulphide, and the excess of silver back-titrated with thiocyanate.

Kiss used diamminoargentate(I) and dead-stop end-point indication to measure the monosulphide content of polysulphides. H_2S was removed from a second aliquot by heating with boric acid, and the thiosulphate content was titrated with mercuric chloride. The polysulphide–sulphur content of the sample was measured in a third aliquot by treatment with sulphite, followed by iodometric titration.[224] Owing to the hydrolysis of polysulphide-sulphur on heating with boric acid this procedure often yields high values for thiosulphate.

Gravimetric methods

Since polysulphanes and polysulphides are readily converted into elemental sulphur and H_2S by heating in benzene or carbon disulphide, the polysulphide–sulphur content can be measured by weighing the residual sulphur obtained after evaporation of the organic solvent.[225,226,230,231] Other authors prefer to measure the H_2S formed in the thermal decomposition of polysulphanes.[227–229]

The polysulphide–sulphur content of technical grade calcium polysulphide has been measured by weighing the amount of elemental sulphur obtained on treatment of the samples with acid.[232,233]

Some authors recommend the determination of total sulphur content of polysulphides *via* oxidation with alkaline peroxide or bromine, and gravimetric determination as barium sulphate.[234–242] The monosulphide moiety is measured separately by iodometric methods[233] or isolated and determined gravimetrically as cadmium sulphide.[242]

These gravimetric methods disregard the thiosulphate content of polysulphides, even though thiosulphate is practically always present. Even an Na_2S_x solution freshly prepared by dissolving sulphur in sodium sulphide solution contains thiosulphate as a contaminant.[8,9]

SULPHITE

Titrimetric determination

Sulphites are technologically important reducing agents. Most of the quantitative analytical methods designed for the determination of sulphites utilize their reducing properties, but the aqueous solution of sulphur dioxide or the acid salts of sulphurous acid (*e.g.*, $NaHSO_3$) can also be titrated alkalimetrically.

Alkali metal sulphites usually contain sulphates as contaminants, and alkali metal sulphides and dithionites always contain sulphite contaminants.

Iodometric determination. This is based on equation VI. Since sulphites undergo air-oxidation to sulphates quite readily it is advantageous to add the sample to standard iodine solution, and back-titrate the excess of iodine with thiosulphate,[243–248] ascorbic acid or hydrazine.[249,250] The last two reagents seem to have no advantage over thiosulphate.

The direct titration of sulphite with iodine (thyodine as indicator)[251] or in alkaline medium (luminol as indicator) has been recommended.[252]

Numerous iodometric methods have been described for the determination of sulphite and thiosulphate in the presence of each other.[19,29,253–264] They take advantage of the reaction of thiosulphate with iodine to give tetrathionate (equation V), with bromine to give sulphate (equation XI)[265,266] and of the fact that sulphite ions can be masked from oxidation with iodine by reaction with formaldehyde (equation VII).[18,267,268]

Even sulphite, thiosulphate and tetrathionate can be determined in the presence of each other *via* oxidation with iodine, and bromine, and masking the sulphite with formaldehyde.[269] This method utilizes the fact that tetrathionate does not react with iodine, but is oxidized to sulphate with bromine (equation XL).

$$S_4O_6^{2-} + 7Br_2 + 10H_2O \longrightarrow 4SO_4^{2-} + 20H^+ + 14Br^- \qquad \text{XL}$$

Sulphite, thiosulphate and sulphate can be determined in the presence of each other by utilizing the above-described reactions, and by measuring the total sulphur content—after oxidation—as barium sulphate.[270]

Other oxidative titrations. Sulphite (and thiosulphate) reacts with iodine monochloride to give sulphate and iodine (equation XLI); the excess of ICI can be back-titrated with arsenite, or the iodine formed in the reaction can be titrated with periodate in the presence of hydrochloric acid and potassium bromide (equation XLII)[271,272] with an Andrews' titration end-point.[273]

$$SO_3^{2-} + 2I^+ + H_2O \longrightarrow SO_4^{2-} + I_2 + 2H^+ \qquad XLI$$

$$3I_2 + IO_4^- + 7Br^- + 8H^+ \longrightarrow 7IBr + 4H_2O \qquad XLII$$

Van Eck described the determination of sulphite *via* oxidation with chloramine-T solution and iodometric back-titration of excess of reagent.[274] Others also recommend methods based on the same principle.[275–277] Murthy combined the use of chloramine-T with various iodometric methods to determine sulphite, thiosulphate and sulphide in the presence of each other.[48]

The reaction of sulphite with iodate to give sulphate (equation XLIII) also serves as the basis of a volumetric method.[278–280]

$$2IO_3^- + 6SO_3^{2-} \longrightarrow 6SO_4^{2-} + 2I^- \qquad XLIII$$

In strongly acidic (hydrochloric acid) solution sulphite can be directly titrated with iodate, iodine monochloride being formed (Andrews' titration, equation XLIV).[281,282]

$$IO_3^- + 2SO_3^{2-} + Cl^- + 2H^+ \longrightarrow ICl + H_2O + 2SO_4^{2-} \qquad XLIV$$

Manchot and Oberhauser used excess of bromate/bromide mixture to convert sulphite into sulphate, and back-titrated with arsenite in the presence of indigo carmine as indicator.[283–285] Hypobromite was also used for this oxidation[283,286] and the excess of oxidizing agent can also be back-titrated iodometrically.[287] Sulphite can be titrated directly with hypobromite in alkaline medium, and nickel hydroxide,[288] luminol or lucigenin[280,290] can serve as indicator.

Several authors recommend hypochlorite as titrant, either in direct titration or *via* back-titration.[286,291–294]

Potassium bromate solution was used by Mayr and Peyfuss for the determination of sulphite, with iodometric back-titration.[259] The oxidation of sulphite with bromate, dichromate, permanganate or hypochlorite does not always yield sulphate exclusively, since dithionate is also formed to some extent,[278,295] the amount depending on the exact conditions of the reaction. Hypobromite undergoes disproportionation on standing, and its use is often not recommended.

Hydrogen peroxide[290,296] and peroxybenzoic acid[297] have also been used for the titration of sulphite. Some authors recommend titration of the peroxide solution with the sulphite sample to be determined.[298] Because of the instability of the peroxide and peroxybenzoic acid solutions these methods have little practical utility.

On the other hand the determination of sulphite by treatment with excess of permanganate followed by back-titration with ferrous sulphate is recommended.[299] Iodine monochloride in dilute sulphuric acid or cupric sulphate in acetic acid is used as catalyst for the oxidation.

The oxidation of sulphite to sulphate with dichromate should be conducted in strongly acidic medium in the presence of iodine monochloride catalyst, otherwise dithionate is also formed as a side-product. The excess of dichromate can be back-titrated with a ferrous solution.[278,295,299,300]

Ceric sulphate has also been used in the presence of iodine monochloride as catalyst for oxidation of sulphite to sulphate, with back-titration with ferrous solution (ferroin as indicator).[299]

Lang and Kurtenacker used hot ammonium vanadate solution to oxidize sulphite to sulphate, and titrated the resulting vanadium(IV) with permanganate.[301] In a variation of this procedure Rao and Rao back-titrated the excess of vanadate with ferrous solution.[302] Thiosulphate and polythionates interfere.

Sulphite (and other reducing sulphur compounds) can be titrated with ferricyanide in strongly alkaline medium in the presence of osmium tetroxide as catalyst.[58–60] It can also be directly titrated with chlorite solution in the presence of potassium iodide and acetic acid, either potentiometrically or with starch, as indicator.[303–305]

Erler[306] recommended oxidation of sulphite with a cupric solution (equation XLV), followed by iodometric back-titration of excess of copper(II).

$$2(CuBr_4)^{2-} + SO_3^{2-} + H_2O \longrightarrow 2(CuBr4)^{3-} + SO_4^{2-} + 2H^+ \qquad XLV$$

An indirect ascorbimetric method has also been described for the determination of sulphite.[307] Sulphite is oxidized with an excess of mercurous nitrate, giving rise to sulphate and metallic mercury. The excess of mercury(I) is back-titrated with ascorbic acid in the presence of Variamine Blue as indicator. Because of the instability of the ascorbic acid solution this method offers little practical utility.

Acid–base titration. The alkalimetric titration of sulphurous acid requires two equivalents of base if phenolphthalein is used as indicator, and one with Methyl–Orange (equations XLVI and XLVII).

$$H_2SO_3 + 2NaOH \longrightarrow 2H_2O + Na_2SO_3 \qquad XLVI$$

$$H_2SO_3 + NaOH \longrightarrow H_2O + NaHSO_3 \qquad XLVII$$

Consequently $NaHSO_3$ can be titrated with base in the presence of phenolphthalein, and Na_2SO_3 can be titrated with acid in the presence of Methyl–Orange as indicator.[308]

The reaction of neutral sulphite salts with formaldehyde results in the formation of one equivalent of base (equation XLVIII) which can be titrated with acid.[309–311]

$$Na_2SO_3 + HCHO + H_2O \longrightarrow CH_2(OH)SO_3Na + NaOH \qquad XLVIII$$

Another method for the determination of sulphurous acid (the aqueous solution of sulphur dioxide) involves oxidation with neutral hydrogen peroxide and alkalimetric titration of the resulting sulphuric acid.[312]

Since the reaction of sulphurous acid with mercuric chloride (equation XLIX) renders the second proton of sulphurous acid strongly acidic, sulphurous acid can be titrated as a dibasic acid with alkali in the presence of mercuric chloride even with Methyl–Orange as indicator.[313,314]

$$HgCl_2 + H_2SO_3 \longrightarrow HgClSO_3^- + Cl^- + 2H^+ \qquad XLIX$$

Indirect complexometric titrations. Since sulphites are practically always contaminated with sulphate the determination of these two species in the presence of each other is of great practical significance. De Sousa's method involves heating an aliquot of the sample with hydrochloric acid to remove sulphur dioxide, followed by precipitation of sulphate with barium chloride and back-titration of the excess of barium with EDTA.[315] The total amount of sulphite and sulphate is determined complexometrically *via* barium sulphate in another aliquot after oxidation with bromine. Szekeres used thallium(III) for the oxidation of sulphite and back-titrated the excess of thallium with EDTA.[316]

Other complexometric methods[317] as well as total sulphur determination[318] have been recommended for the analysis of mineral waters. These methods can be used even in the presence of phosphate and arsenate.

Physical methods

Sulphite can be determined simply by adding iodine to the sample and measuring the excess of iodine photometrically.[319] A similar method employs dichromate.[320]

In another photometric method sulphite ions (and other sulphur compounds) are reduced to H_2S with aluminium metal and acid. The H_2S is absorbed in lead citrate solution, and the resulting colloidal lead sulphide is measured photometrically.[158]

The complex of Methylene Blue with iodine reacts with sulphite and the Methylene Blue liberated can be measured photometrically.[321] Fuchsin and *p*-rosaniline form a coloured complex with sulphite in the presence of formaldehyde and this can be measured colorimetrically.[322–324] Sulphite also forms a coloured compound with sodium tetrachloromercurate(II) in the presence of Methyl–Violet and hydrochloric acid. This complex too is suitable for colorimetric determination.[325] The fading of Methyl–Green or Malachite–Green as a result of their reaction with sulphite has also been utilized for the colorimetric determination of sulphites. [326,327] The red complex of sodium nitroprusside with sulphite in the presence of zinc has also been utilized in colorimetric determinations.[328,329]

Some authors recommend atomic-absorption spectroscopy for the determination of sulphite.[330]

Methods for the polarographic determination of sulphites have been described by several authors,[331–334] the main advantage being the sensitivity. However, thiosulphate and other sulphur compounds interfere.

Birk *et al.*, described a gas chromatographic method for the determination of sulphite, sulphide and carbonate in the presence of each other.[335]

Sulphite has been separated from sulphide, sulphate and thiosulphate by thin-layer chromatography.[170a]

Gravimetric methods

Sulphite can be determined gravimetrically as barium sulphate[189–195,240,336,337] after oxidation, but since sulphites are usually contaminated with sulphate the oxidative titration methods generally yield better results. Suitable oxidants include chlorine or bromine water, sodium or hydrogen peroxide, hypochlorite and hypobromite, or the dry sulphite sample can be fused with a mixture of sodium carbonate and potassium nitrate or with potassium chlorate.

DITHIONITE

Dithionites are very strong reducing agents. They are also labile compounds which undergo rapid disproportionation in aqueous solution. In the crystalline state the disproportionation is much slower (equations L, LI),[263,338–340]

$$2S_2O_4{}^{2-} + H_2O \longrightarrow 2HSO_3{}^- + S_2O_3{}^{2-} \qquad \text{L}$$

$$2Na_2S_2O_4 \longrightarrow Na_2S_2O_3 + Na_2S_2O_5 \qquad \text{LI}$$

Because of these disproportionation reactions dithionite samples always contain sulphite and thiosulphate. For this reason dithionite samples can be analysed acccurately only by determination of all three species.

Iodometric methods

Dithionite is oxidized to sulphate by iodine[341,342] (equation LII). The reaction of dithionite and formaldehyde yields formaldehyde bisulphite and formaldehyde sulphoxylate[343,344] (equation LIII). Formaldehyde bisulphite does not react with iodine but formaldehyde sulphoxylate is oxidized by iodine to sulphate (equation LIV).

$$S_2O_4^{2-} + 3I_2 + 4H_2O \longrightarrow 2SO_4^{2-} + 6I^- + 8H^+ \qquad \text{LII}$$

$$S_2O_4^{2-} + 2HCHO + H_2O \longrightarrow HCHO.HSO_3^- + HCHO.HSO_2^- \qquad \text{LIII}$$

$$HCHO.HSO_2^- + 2I_2 + 2H_2O \longrightarrow SO_4^{2-} + 4I^- + 5H^+ + HCHO \qquad \text{LIV}$$

Utilizing these reactions, Wollak[344] recommended the following method. Excess of iodine is added to the sample in the presence of formaldehyde, and the excess of iodine is back-titrated with thiosulphate. In this manner the amount of iodine necessary for the oxidation of dithionite and thiosulphate is measured. A second aliquot is first treated with the calculated equivalent amount of iodine, then excess of sulphite is added, which reacts with the tetrathionate ions present in the mixture (equation LV)

$$S_4O_6^{2-} + SO_3^{2-} \longrightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad \text{LV}$$

The excess of sulphite is then masked with formaldehyde and the thiosulphate content is titrated with iodine. The accuracy of this method is slightly limited by the fact that it measures only the equivalent of 50 % of the original thiosulphate content of the sample.

Schulek and co-workers utilized the disproportionation reaction for the determination of dithionites.[263,340] They took advantage of the fact that 1 mole of dithionite reacts with 6 equivalents of iodine, whereas the disproportionation products react with only 5 equivalents.

Szekeres[345] noted the quantatitive conversion of dithionite into sulphite, pyrosulphite and elemental sulphur which takes place in the presence of hydrochloric acid (equation LVI).

$$2S_2O_4^{2-} \longrightarrow SO_3^{2-} + S_2O_5^{2-} + S \qquad \text{LVI}$$

Dithionite can be determined on the basis of this reaction as follows. One aliquot is titrated with iodine, and another aliquot is treated with hydrochloric acid and then titrated with iodine. The thiosulphate content of the sample can be measured by separate iodometric and bromometric titrations (equations V and XI).

Binz and Sontag[346] assumed that only the dithionite content of a "typical dithionite sample" is oxidized to sulphate by aerial oxygen, and so subjected the alkaline solution of a dithionite sample to oxidation with air and then performed an iodometric titration. Since the disproportionation of dithionite is rather rapid in alkaline solution this method gives quite inaccurate results. This is one of the reasons why the analytical chemistry of dithionite has been considered vague and unreliable.[347]

Other titrimetric methods

Dithionite reduces diamminoargentate(I) to metallic silver,[347-350] which can be determined gravimetrically[348] or by Volhard's method [349] after dissolution in nitric acid, or by potentiometric methods.[350] Dithionite also reduces potassium iodomercurate(II), mercuric chloride, or mercuric cyanide, giving rise to metallic mercury[351–353] which is measured iodometrically or by Volhard's method after dissolution in nitric acid.[353]

Helvig[354] recommended tetra-amminocuprate(II) solution for the analysis of dithionites of technical purity. The cupric reagent was titrated to a colourless end-point with the unknown dithionite solution.

Ekker[355] was the first to utilize potassium ferricyanide solution for the determination of dithionite, by forming sulphite from the dithionite in mildly acidic or mildly alkaline medium,[59,60,356–360] and oxidizing the sulphite to sulphate with ferricyanide in strongly alkaline medium in the presence of osmium tetroxide as catalyst.[59,60] The end-point can be indicated with ferrous solution[355–358] or potentiometrically.[59,60,359]

Dithionite has been titrated with ferricyanide under an argon atmosphere in the presence of ferrous dimethylglyoximate as indicator.[360]

The use of a ferric solution for the determination of dithionite was first described by Mohr.[361] Feibelmann and Meves[362] use ferric thiocyanate solution for this purpose; others used ferric sulphate solution with potassium thiocyanate[363,364] or ferrocyanide[365] as indicator, or a potentiometric end-point.[366] Errors arise in these methods, however, from slow aerial oxidation of dithionite, though this can be avoided to some extent by use of an inert gas atmosphere.

Thallic chloride solution has been used for the potentiometric titration of dithionite and sulphite.[367] The method of Kauhik *et al.*,[368] by selective titration with periodate is based on the fact that in the presence of formaldehyde and acetic acid only the formaldehyde sulphoxylate formed from dithionite reacts with periodate, to give sulphate and iodate. Formaldehyde bisulphite does not react under these conditions.

Fülöp and Blazsek[369] oxidized dithionites with an excess of potassium tetraiodomercurate(II) solution and measured the excess of oxidizing agent complexometrically. Rostovsev and Gromova[370] oxidized dithionite with oxygen in a closed system (equation LVII), measuring volumetrically the amount of oxygen used.

$$S_2O_4^{2-} + H_2O + O_2 \longrightarrow HSO_4^- + HSO_3^- \qquad \text{LVII}$$

As an alternative to this method the bisulphate can be measured alkalimetrically, with Methyl–Orange as indicator.

Colorimetric determinations

The ability of dithionites to reduce certain dyes to colourless leuco-dyes has been utilized in colorimetric determinations. The excess of the dye can be measured colorimetrically. Methylene–Blue and indigo,[371–374] safranine,[375] Napthol Yellow S[376] and other dyes[377–380] have been used.

Small amounts of dithionite can be measured by indirect colorimetric methods. For example the dithionite is oxidized with chromate, the excess of which is determined colorimetrically by means of its complex with bis-*o*-anisidine.[381] Artigas[382] used ferricyanide in a similar way. Because sulphite reacts with ferricyanide only in strongly alkaline medium it does not interfere.

SULPHATE

Because of the wide and extensive use of sulphuric acid in chemical industry, the determination of sulphate plays a very important role in analytical chemistry. Sulphur in many compounds is determined in the form of sulphate. Because of the insolubility of barium, lead and benzidine sulphates, most of the determinations are based on the use of these compounds, as discussed below.

Titrimetric determinations

Direct titration with barium solution. The oldest volumetric method for the determination of sulphate involves a titration with barium chloride, (or some other water-soluble barium salt) in the presence of sodium rhodizonate as indicator.[383–387] Rhodizonate has also been used extensively as an external indicator.[388–397] Several other indicators can be used, which have certain specific advantages over rhodizonate. For instance, Schroeder[398] recommended tetrahydroxyquinone because it gives a sharper end-point, and its use was later studied by many other investigators.[399–405]

Small amounts of sulphate can be determined by titration with barium perchlorate solution in the presence of Thorin as indicator. The interfering ions can be eliminated by using ion-exchange resins.[387,406–415] A photometric titration can be used.[409,412,413]

In weakly acidic aqueous alcohol solutions, sulphate can be determined by titration with barium chloride solution with Alizarin Red S as adsorption indicator.[406] The interfering tervalent cations can be removed by ion-exchange resins.[407] Further applications of Alizarin Red S as indicator were studied by many authors.[387,408,416–424]

Kuznetsov and Basargin[425] and others[426–430] recommended nitrochromazo as indicator for the barium chloride titration of alcoholic solutions of sulphate at pH 2. This indicator is especially useful in the presence of phosphate and arsenate ions. Other indicators suggested include stilbnaphthazo,[431] chlorphosphonazo III,[432,433] carboxyarsenazo,[434] Bromopyrogallol Red, Methylthymol Blue, Eriochrome Black T–magnesium–EDTA[435–438] *etc.*[439–448]

Conductometric[449–456] and potentiometric methods are also used.[457–459]

Direct titration with lead solution. Lead acetate or nitrate solution is used[460] and the first indicator was dithizone.[382,461–469] In recent years the following indicators have been found to work better: PAR [pyridyl-(2-azo-4)-resorcinol],[465] diphenylcarbazol[470] and diphenylcarbazone.[471–474]

Several instrumental techniques such as photometric titration with dithizone as indicator,[475] potentiometric,[476–478], high-frequency,[450,479], and amperometric titration[480–483] have been developed.

Complexometric titration. Munger *et al.*,[484] were the first investigators to use complexometric determination of sulphate. In recent years many authors have studied this important method. The basic principle is addition of excess of barium solution and back-titration with EDTA.[484–513] The first indicator used was Eriochrome Black T.[485–495] Subsequently, other indicators such as phthaleincomplexone[495–500,502–504] and Eriochrome Black T–rhodizonic acid[501,506–508] have been used. In principle, any metallochromic indicator for barium is suitable.[509–515] Certain bivalent and tervalent cations interfere, but can be removed by ion-exchange.[486,495,516–520]

Several modifications of the method have been developed. In one, the barium sulphate is filtered off and dissolved in excess of EDTA solution, which is then back-titrated with a magnesium or zinc solution.[521–527]

Similar back-titration procedures are based on lead sulphate, the solubility being decreased by the addition of alcohol or some other suitable water-miscible solvent.[528,529] Again, some prefer to dissolve the precipitate with ammonium tartrate, sodium acetate or other complex-forming agents and determine the lead in it complexometrically.[530–533] The precipitate can also be dissolved in ammoniacal EDTA solution and the excess of EDTA back-titrated with zinc or magnesium solution.[534–542]

Indirect titrations. A known quantity of a barium solution is added and the excess back-titrated with sulphate in the presence of rhodizonate as indicator[543–546] or amperometrically with chromate.[547]

In another method the sulphate is precipitated with barium acetate in aqueous acetic acid medium. The water is removed by addition of acetic anhydride and the excess of barium acetate titrated with perchloric acid, potentiometrically or conductometrically.[548,549] A few other methods, of largely theoretical interest, are also known.[550–552]

An excess of lead can be added and back-titrated with ferrocyanide potentiometrically or in the presence of Variamine Blue as indicator,[553–556] or with chromate either in the presence of siloxan as luminescence indicator[557] or by end-point detection with a glass electrode.[558]

Andrews,[559] Köszegi,[560] Houser[561] and Bányai and Erdey[107,562] recommended the metathesis of barium chromate with sulphate followed by iodometric determination of the chromate liberated. A similar reaction with barium iodate can be used,[562,563] but it is best to use an acetone–water medium, because barium iodate is not completely insoluble in water. Barium oxalate was used similarly, first by Nechamkin[564] and later by Bányai and Erdey,[562] the liberated oxalate being titrated with permanganate.

The barium chromate reaction has other variants. The chromate can be reduced with arsenite, the excess of which is titrated with bromate.[565] The chromate can be titrated more conveniently by reductometric methods,[566–571] *e.g.*, with ferrous sulphate,[566] hydroquinone,[567] or stannous chloride,[568]

In other indirect methods, the sulphate is reduced to H_2S with Ti and H_3PO_4, or with HI and H_3PO_2 or with other reducing agents. H_2S can then be determined by precipitation with zinc or cadmium, followed by iodometric determination,[572,573] or by absorption in a suitable solution and titration with cadmium in the presence of dithizone as incidator, or with mercuric acetate with diphenylthiocarbazone as indicator.[387,575]

The sulphide can also be titrated with lead in the presence of the hexacyanoferrate(II/III) electrode which is very sensitive to any changes in the concentration of lead ions, and small amounts of sulphate can be determined indirectly in this way.[577,580]

The sulphate can also be reduced to sulphur dioxide with metallic copper and the SO_2 determined iodometrically.[576]

Shinkai[581] and later others[582] recommended an indirect acidimetric prodecure for sulphate determination. The neutral sulphate solution is treated with a known quantity of barium chloride solution followed by a known quantity of sodium carbonate solution. The barium carbonate and sulphate are removed by centrifugation and the excess of sodium carbonate determined acidimetrically. Alkalimetric methods are also known for the determination of bisulphate and pyrosulphate.[583]

Physical methods

Physical methods are used mostly but not exclusively for the determination of micro amounts of sulphate.

Photometric and colorimetric methods. Sulphate can be determined indirectly with barium. The excess of barium is precipitated with chromate and the excess of chromate determined colorimetrically[584,588] or photometrically after treatment with diphenylcarbazide.[589,590]

Some complexes of thorium, zirconium and cerium can be decomposed with sulphate and the liberated coloured compound determined colorimetrically.[591–599] Barium chloranilate is decomposed with sulphate and the liberated chloranilic acid measured at 530 nm.[600–608] Barium nitrochromazo complex[609] and barium rhodizonate[610] are utilized similarly. Thoron has been used in an automatic spectrophotometric titration.[611]

The amount of lead in a lead sulphate precipitate can be determined spectrophotometrically with a chloroform solution of dithizone,[612] and hence the amount of sulphate.

A solution of benzidine sulphate in hydrochloric acid can be measured spectrophotometrically at 248 nm.[613,614] The sulphate can also be reduced to H_2S which may be transformed into Methylene Blue[615,616] or used to form molybdenum blue.[617] The complexes of ferric sulphate can be directly measured photometrically at 325–360 nm.[618] In recent years certain infrared spectrophotometric methods have been used for the determination of sulphate.[619,620]

Polarography. Sulphate can be determined directly by oscillographic polarography[621] and indirectly *via* lead by simple polarography.[622–624] Polarography can also be used to measure the chromate liberated from barium chromate by sulphate.[625,626]

It should be mentioned here that Pungor *et al.*,[627] recommended the application of a silicone–rubber membrane electrode for the automatic determination of sulphate ions.

Nephelometry and turbidimetry. Small amounts of sulphate can be determined as barium sulphate suspension by nephelometric[628–636] and turbidimetric[637–645] methods. The accuracy of these determinations depends upon the experimental conditions used. Photochronometric methods utilizing the rate of precipitation are known.[646,647]

Flame photometry. Determination of sulphate by flame photometry is based on the determination of either the excess of barium used,[649–652] or the amount of barium in the precipitate.[653–655]

Radiometry. This determination can be carried out with barium chloride containing ^{135}Ba, the radioactivity of the barium sulphate precipitate being measured. Alternatively an inactive precipitate is treated with chromate containing ^{50}Cr and the radioactivity of the resulting barium chromate is determined.[656–660]

Thermometric methods. The formation of barium sulphate is an exothermic reaction. The end-point can easily be determined from the temperature curve obtained during the titration.[661] Sajó recommended an automatic equipment for thermometric methods.[662]

Determination of sulphate by benzidine

Benzidine (4,4′-diaminobiphenyl) is a very weak base. Its hydrochloride is soluble in water but its sulphate is practically insoluble, and sulphate can be determined as benzidine sulphate.[663–673] Benzidine hydrochloride is also used in the conductometric titration of sulphate ions.[674] Belcher *et al.*,[675] recommended 4-amino-4′-chlorodiphenyl hydrochloride for the titrimetric determination of sulphate. This compound is similar to benzidine in structure. The precipitate of benzidine sulphate can be determined gravimetrically,[665–673] or (after washing with water) by titrating it with sodium hydroxide solution in the presence of phenolphthalein as indicator.[663,664,676] The latter procedure is known as the Raschig method.[676]

According to Keller and Munch[677] benzidine sulphate can be determined by diazotitration. In this case the precipitated benzidine sulphate is filtered off, dissolved in hydrochloric acid and titrated potentiometrically with potassium nitrite solution in the presence of potassium bromide.

Gravimetric determination

Usually the sulphate is precipitated as barium sulphate, which is filtered off, washed, dried and finally ignited.[678,679] Although barium sulphate is practically insoluble in water, filtration is sometimes difficult.[680] The precipitate is invariably impure, owing to adsorption, occlusion or mixed crystal formation.[681–686] Interfering cations commonly present can be eliminated by ion-exchange.[687–688] Any iron(III) can be masked with EDTA.[689–691]

The precipitate retains water even up to a temperature of about 600°, and if ignited in the presence of filter paper is apt to be partially reducted to sulphide. Treatment with sulphuric acid eliminates the error from this source.

Several other factors can also cause problems.[692–693] Winkler *et al.*,[240,694–697] studied the optimal conditions for precipitation and several authors have investigated applications of this procedure for the determination of sulphate in the presence of chromate, phosphate, *etc.*[698–702] Measurement of the volume of the precipitate has been suggested.[648]

THIOSULPHATE

The most important titrimetric methods for the determination of thiosulphate are based on its oxidation. For gravimetric determination, the thiosulphate can either be oxidized to sulphate or reduced to H_2S. The alkali metal sulphides, polysulphides and dithionites are always contaminated with thiosulphate. Therefore the determination of thiosulphate in the presence of these compounds was mentioned earlier in the sections dealing with these species.

Titrimetric determinations

Oxidative titrations. Iodine oxidizes thiosulphate to tetrathionate (equation V). The iodometric method based on this reaction is the simplest and the best method for the determination of thiosulphate, because between pH 4·5 and 9·5 the formation of tetrathionate is quantitative.[703] The end-point of the reaction can be detected visually (with starch solution) or potentiometrically.[704]

Several methods for the determination of thiosulphate in the presence of other ions have been suggested.[705,706] Procedures based on the indirect iodometric determination of thiosulphate are of theoretical interest only[215,707] For example iodine oxidizes thiosulphate to sulphate in strongly alkaline medium, and after acidification the excess of iodine can be determined by back-titration.[708,709] Similarly potassium metaperiodate oxidizes thiosulphate to sulphate in acidic medium in the presence of bromide[273,368] (equation LVIII).

$$3S_2O_3^{2-} + 4IO_4^- + 8Br^- + 2H^+ \longrightarrow H_2O + 4IBr_2^- + 6SO_4^{2-} \qquad \text{LVIII}$$

Bromine also oxidizes thiosulphate (equation XI). According to this reaction thiosulphate can be titrated directly with either hydrochloric acid/bromine or glacial acetic acid/bromine. The end-point can be detected with irreversible dye indicators.[283]

Perhaps a better way of oxidizing is by using bromate/bromide or periodate/bromide in acidic medium. The excess of bromine can then be determined iodometrically by back-titration.[39–41,259,273,278,710,711] A direct method of determining thiosulphate utilizes ceric sulphate solution[712,713] in the presence of potassium iodide and starch as indicator.

In another method, thiosulphate is heated with perchloric acid and excess of ceric sulphate. The excess of Ce(IV) can be back-titrated with ferrous sulphate or sodium oxalate.[714]

Ferric chloride oxidizes thiosulphate to tetrathionate.[715] Methylene Blue can be used as indicator, being reduced by the excess of thiosulphate to a colourless base. The ferrous chloride generated can also be measured cerimetrically.[301] Thiosulphate can also be oxidized to tetrathionate with an acetic acid solution of vanadate in the presence of copper(II) as catalyst. In the presence of hydrochloric acid and iodine monochloride as catalyst vanadate oxidizes thiosulphate to sulphate. The resulting vanadium(IV) can be determined with permanganate, or the excess of vanadate can be titrated with ferrous sulphate solution.[301,716] Thiosulphate can also be oxidized to sulphate with ferricyanide in strongly alkaline medium in the presence of osmium tetroxide as catalyst.[58,59,717] The end-point may be detected amperometrically or potentiometrically.

Several other oxidizing agents have been recommended for the oxidation of thiosulphate: hypochlorite, hypobromite, chloramine-T, iodine monochloride, iodate, permanganate, potassium periodate–cuprate, perbenzoate *etc.*[45,48,272,275,289,291,297,718–727] Recently lead tetra-acetate[728] and lead tetraformamide $[Pb(HCOHN_2)_4]$[729] have been recommended for the titration of thiosulphate. The end-point can be determined potentiometrically. For all practical purposes only iodine and bromate are important for the determination of thiosulphate.

Other titrimetric methods. Thiosulphate reacts with mercuric chloride to form the unstable $[Hg(S_2O_3)_2]^{2-}$. The end-point can be indicated either potentiometrically,[730] or by the dead-stop method.[731]

Thiosulphate also reacts with excess of cyanide to form thiocyanate. The excess of cyanide ions and the sulphite generated can be masked with formaldehyde so that they do not interfere with the determination of the thiocyanate. Alternatively the excess of cyanide can be determined.[732]

During the oxidation of thiosulphate with bromine, sulphate and bromide and hydrogen ions are produced. The excess of bromine can be boiled out and the acids estimated alkalimetrically.[733] The following reactions (equations LIX and LX) can also be utilized to determine thiosulphate alkalimetrically.[734,735]

$$2S_2O_3^{2-} + 2H_2O + 3HgCl_2 \longrightarrow HgCl_2.2HgS + 2SO_4^{2-} + 4Cl^- + 4H^+ \qquad \text{LIX}$$

$$S_2O_3^{2-} + H_2O + 2AgNO_3 \longrightarrow Ag_2S + SO_4^{2-} + 2NO_3^- + 2H^+ \qquad \text{LX}$$

Thiosulphate can be oxidized with hydrogen peroxide in the presence of alkali according to the equation

$$S_2O_3^{2-} + 2OH^- + 4H_2O_2 \longrightarrow 5H_2O + 2SO_4^{2-} \qquad \text{LXI}$$

and the consumption of alkali can be determined acidimetrically.[736,737]

Thiosulphate can be titrated with *o*-hydroxymercurybenzoic acid (HMB) solution in the presence of diphenylcarbazone as indicator.[78,84] Thiosulphate can be oxidized to sulphate, which is then titrated with barium,[445,754] or can be reduced with sodium carbonate and magnesium to sulphide, which is determined as lead or cadmium sulphide.[755] Ganchev and Koev[738] suggested that micro amounts of thiosulphate ions can be determined by measuring the extent of their migration on a filter paper impregnated with AgCl.

Kinetic method

The slow reaction between iodine and azide can be catalysed by sulphide, thiosulphate and thiocyanate. This reaction has been used for the determination of thiosulphate.[115,117,739,740]

Photometric and colorimetric determination

Thiosulphate reacts with cyanide in the presence of copper(II) to form thiocyanate, which can be determined photometrically as the ferric complex at 496 nm.[741,742] Thiosulphate can also be oxidized by ferric ions to tetrathionate and the excess of ferric salt determined photometrically as the thiocyanate complex.[743] A precipitate of CuSCN may be dissolved in thiosulphate solution and the thiocyanate liberated can be determined as the ferric complex photometrically.[144] Thiosulphate can also be determined by oxidation with iodine and estimation of excess of iodine photometrically at 365 nm.[744]

In the presence of thiosulphate copper salts oxidize *o*-toluidine to a blue compound which may be determined photometrically.[745] Schöön[746] utilized the reaction between *p*-benzoquinone and thiosulphate. Several other colour reactions have been suggested.[140,747–749]

Physical methods

For the radiometric determination of thiosulphate, Schöön[750] recommended use of silver thiocyanate labelled with ^{110}Ag. The silver thiocyanate is soluble in thiosulphate and the radioactivity of the solution can be measured. Tölgyessy and Sarsunova[751] recommended another radiometric method for the determination of thiosulphate.

The reaction with mercuric chloride can be used for a polarographic determination of thiosulphate.[752]

Gravimetric determination

Thiosulphate can be determined gravimetrically by oxidation to sulphate and determination as barium sulphate.[189–195,237,240,336,337,736,753] In hot solution silver thiosulphate forms a precipitate of silver sulphide which can be determined gravimetrically.[243]

DITHIONATE AND POLYTHIONATES

The polythionic acids ($H_2S_xO_6$ where $x = 2$–6) are known only in aqueous solution, but their salts are sufficiently stable to be isolated. Dithionic acid ($H_2S_2O_6$) has more resistance to oxidizing agents than have the other members of this series. The polythionates are usually produced as mixtures (Wackenroder liquid), except the dithionate, which can be obtained in relatively pure form. Methods of producing tri, tetra, penta and hexathionates are known, but they have largely theoretical interest. It is desirable to discuss the determination of dithionate and the polythionates separately.

Determination of dithionate

Several authors tried to determine dithionate with oxidizing agents such as bromate, chlorate, vanadate, ceric sulphate and permanganate.[259,756–759] However, it can be correctly determined only by oxidation with dichromate in sulphuric acid medium.[760–762]

Murthy[763] determined dithionate in the presence of sulphide, sulphite and thiosulphate. The mixture was boiled with alkaline permanganate solution in order to oxidize all sulphur compounds, except the dithionate, to sulphate. The excess of permanganate was reduced to manganese dioxide with manganous sulphate. The manganese dioxide precipitate was filtered off and the dithionate in the filtrate determined by oxidation with dichromate.

Soffer[764] used the decomposition of dithionic acid in the presence of hydrochloric acid ($H_2S_2O_6 \longrightarrow H_2SO_4 + SO_2$) for the estimation of dithionic acid by determining the liberated sulphur dioxide iodometrically.

Determination of pure individual polythionates

The simplest method for the determination of individual polythionates is based on the determination of the total sulphur content. The oxidation of polythionates gives sulphate which can be determined gravimetrically.[765–767] In another method, the total sulphur content can be determined by reducing the polythionate with metallic aluminium in the presence of hydrochloric acid. The resulting sulphides can be measured iodometrically.[768]

The tri, tetra and pentathionates yield thiosulphate and sulphite on boiling with alkali (equation LXII).

$$2S_xO_6{}^{2-} + 6OH^- \longrightarrow (2x-5)\,S_2O_3{}^{2-} + (10-2x)SO_3{}^{2-} + 3H_2O \qquad \text{LXII}$$

The thiosulphate and sulphite can be simultaneously determined iodometrically.[769]

Polythionates can be determined cerimetrically,[770] or by oxidation with vanadium(V),[301] hypoiodite[708,771] or iodate in the presence of mineral acids.[772]

The tetra and pentathionates react with sodium sulphide (the trithionate practically does not react at room temperature) according to equation LXIII.

$$S_xO_6{}^{2-} + S^{2-} \longrightarrow 2S_2O_3{}^{2-} + (x+3)S \qquad \text{LXIII}$$

The resulting thiosulphate is determined iodometrically. The excess of sulphide in the mixture can be eliminated by treatment with zinc carbonate suspension.[769,773] Hansen[774] recommended the determination of polythionates by direct titration with sodium sulphide, with lead acetate paper as external indicator. The disadvantage is that sodium sulphide is always contaminated with its oxidation products[8,9] and this diminishes the accuracy of the determination. Therefore the quality of the sulphide used is important.

Jay[775] suggested an alkalimetric method for the determination of polythionates. All the polythionates react with mercuric chloride, and the resulting acid can be titrated alkalimetrically. Thiosulphate and sulphide present as contaminants in the sample affect the accuracy. Some authors recommend mercuric cyanide or silver nitrate for the determination of polythionate (equations LXIV and LXV).

$$S_xO_6{}^{2-} + Hg(CN)_2 + 2H_2O \longrightarrow 2SO_4{}^{2-} + (x-3)S + HgS + 2\,HCN + 2H^+ \qquad \text{LXIV}$$

$$S_xO_6{}^{2-} + 2Ag^+ + 2H_2O \longrightarrow Ag_2S + 2\,SO_4{}^{2-} + (x-3)S + 4\,H^+ \qquad \text{LXV}$$

The sulphur content of the precipitate of sulphur silver or mercuric sulphide can be determined according to well-known principles.[776–778] These do not offer any significant advantage over the simple methods of determining the total sulphur content.[765–767]

Trithionate can be determined by its reaction with cupric sulphate to form sulphuric acid and copper sulphide. The latter can be estimated gravimetrically[779,780]or the sulphuric acid can be determined alkalimetrically or as barium sulphate.[781]

Tetrathionate can be determined by oxidation with peroxide in the presence of alkali. The excess of alkali can be determined acidimetrically[782] According to a method recommended by Iwasaki.[783] tetrathionate is treated with sulphite and the resulting thiosulphate determined iodometrically. The excess of sulphite can be masked with formaldehyde.

The tetra, penta and hexathionates undergo a fast reaction with cyanide,[784–785] whereas cyanolysis of trithionate is slow[786] (equation LXVI).

$$S_xO_6{}^{2-} + (x-1)CN^- + H_2O \longrightarrow S_2O_3{}^{2-} + 2HCN + SO_4{}^{2-} + (x-3)SCN^- \qquad \text{LXVI}$$

The resulting thiosulphate can be titrated iodometrically. Sharada and Murthy oxidized polythionates with chloramine-T and determined the excess of the oxidizing agent iodometrically.[787]

Analysis of polythionates in mixtures

Kurtenacker and Goldbach[769] analysed mixtures of polythionate, thiosulphate, sulphite and sulphide (in the presence of one other) by the examination of five aliquots. If there is only a small amount of sulphide in the solution it can be removed with zinc carbonate suspension. A large amount of sulphide in the mixture cannot be tolerated, because according to equation LXIII it reacts with tetra and pentathionates. Since polythionates do not react with iodine, the sulphite and thiosulphate can be determined in the first aliquot iodometrically. In the second aliquot the sulphite is masked with formaldehyde and the thiosulphate determined iodometrically. Sodium sulphite solution is added to the third aliquot, which is then neutralized. The tetra, penta and hexathionates react[788] according to equation LXVII.

$$S_xO_6^{2-} + (x-3)SO_3^{2-} \longrightarrow S_3O_6^{2-} + (x-3)S_2O_3^{2-} \qquad \text{LXVII}$$

The excess of sulphite is masked with formaldehyde and the thiosulphate titrated with standard iodine solution. This reaction was also utilized for the determination of the individual polythionates.[789–791] In the fourth aliquot the sulphite and thiosulphate are oxidized with iodine and then a solution of potassium cyanide is added. In this case (equation LXVI), from each mole of tetra, penta and hexathionate, 1 mole of thiosulphate is formed.[258] The excess of cyanide is masked with formaldehyde and the thiosulphate determined by iodometric titration.

From the results for the titrations of the third and fourth aliquots the quantity of the tetra and pentathionate can be calculated. The fifth aliquot is needed on account of the trithionate. This aliquot is boiled with sodium sulphide solution and the excess of sulphide removed with zinc carbonate suspension. The precipitate is filtered off and the thiosulphate content of the filtrate determined by iodometric titration. Polythionates are known to react with sulphide to form elemental sulphur and thiosulphate[791] (equation LXIII). Trithionates react with sodium sulphide only slowly at room temperature whereas the other polythionates react completely.

From the results of the five titrations the amounts of all the components can be calculated, but the results are usually high. According to Kolthoff[792] the trithionate–sulphide reaction is not exactly stoichiometric, because some sulphite is also liberated. Also, the alkali sulphides always contain thiosulphate and sometimes other sulphur compounds,[8,9] so the quantity of iodine consumed in the titration of the fifth aliquot is more than the amount required for the polythionate present in the original mixture.

For the determination of hexathionate Goehring *et al.*,[793] treated a sixth aliquot with alkali. The hexa, penta and tetrathionate react with dilute alkali at room temperature to give thiosulphate (equations LXVIII, LXIX, LXX).

$$S_6O_6^{2-} \longrightarrow S_5O_6^{2-} + S \qquad \text{LXVIII}$$

$$2S_5O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 3H_2O \qquad \text{LXIX}$$

$$4S_4O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3\,H_2O \qquad \text{LXX}$$

With more concentrated base the trithionate also reacts (equation LXXI).

$$2S_3O_6^{2-} + 6OH^- \longrightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \qquad \text{LXXI}$$

The liberated thiosulphate can be titrated iodometrically. In this method it is impossible to avoid the hydrolysis of the elemental sulphur which is formed from the hexathionate. This process takes place rapidly in alkaline solution.[2,203–206]

As can be seen from the discussion above, there are many difficulties in the analysis of polythionate mixtures (Wackenroder liquid). But the problem of analysing individual polythionates can be regarded as completely solved.

Determination of polythionates by physical methods

The tetra, penta and hexathionates react rapidly with alkali metal cyanides to form thiocyanate. Trithionate gives the reaction only slowly, and thiosulphate does so only in the presence of copper(II) as catalyst. The thiocyanate can be determined as the ferric complex colorimetrically.[784,786,794–796]

The polarographic analyses of mixtures containing polythionates are difficult and further investigations are needed.[797–800] Schmidt and Sand[801–802] examined the ultraviolet and infrared absorption spectra of polythionates. The ultraviolet absorption is not specific, but the infrared is suitable for the differentiation of pure polythionates.

Weitz *et al.*,[803,804] separated polythionates by fractional crystallization of their benzidine salts. Later the use of the pyridinocuprate complexes of the polythionates was recommended for this purpose.[805,806] Several authors[807–809] have used anion-exchange columns for the separation of polythionates, but the results were not accurate. The separation of polythionates by paper chromatography is also difficult since the components of the mixture may undergo changes on the surface of the paper.[810–817] Much better results can be obtained by high-tension paper ionophoresis. This method was utilized by many authors,[813,818–824] who combined it with classical microanalytical methods.

Analysis of mixtures of dithionate and polythionate and other sulphur compounds.

The simplest way to determine dithionate in the presence of other sulphur compounds is by Murthy's method[763] (see section on dithionate). Sulphate can be separated from dithionate by precipitation with barium. The dithionate in the filtrate can be oxidized and determined. Sulphite ions can be removed from dithionate as sulphur dioxide.[760,825,826]

Polythionate, dithionate, sulphite, sulphide and thiosulphate cannot form stable mixtures, because the sulphide and sulphite react with the polythionates. In acidic medium H_2S and sulphurous acid react with each other and in alkaline solutions the polythionates decompose, forming thiosulphate and sulphite.[793] The dithionates in such artificially produced equilibrium-mixtures can be determined by known methods after oxidation of the other ions.[762,827]

Dithionate and polythionates can be separated from sulphate, thiosulphate and sulphide, owing to the solubility of their lead salts.[828] For the simultaneous determination of polythionates, sulphide, sulphite and thiosulphate a titration procedure using Methylene-Blue has been recommended. The iodometric and cyanide–sulphite determinations can also be used.[829]

PEROXO COMPOUNDS

Peroxodisulphate

The peroxodisulphates are often utilized as strong oxidizing agents. During the hydrolysis of peroxodisulphates hydrogen peroxide is evolved. The determination of peroxodisulphates is primarily based on their oxidizing properties. For example, the $S_2O_8{}^{2-}$ can be reduced with iodide in alkaline or neutral medium, and the liberated iodine titrated with thiosulphate.[830–834] The hydrolysis of peroxodisulphate in concentrated sulphuric acid yields hydrogen peroxide, which can be determined iodometrically[835] or with permanganate.[836] Dyufur *et al.*,[837] and later Sierra-Monzon[838] titrated peroxodisulphate with ferrous sulphate potentiometrically. Other authors add excess of ferrous sulphate to the solution of $S_2O_8{}^{2-}$, and back-titrate with permanganate.[839,840] The ferric iron formed during the reaction can be titrated with ascorbic acid.[841]

Vulterin[842] used vanadium(II) sulphate for the reduction of $S_2O_8{}^{2-}$, and back-titrated the excess with permanganate; vanadium(II) sulphate can be prepared by reducing ammonium vanadate with metallic zinc in sulphuric acid medium. The peroxodisulphates can also be reduced with hydroquinone and the excess of hydroquinone determined cerimetrically,[842] or can be reduced with thiosulphate in the presence of small amounts of copper(II) and excess of thiosulphate determined iodometrically.[843] A solution of arsenic(III) is also suitable for the reduction of peroxodisulphate.[844,845]

Sierra and Sanchez[846] titrated peroxodisulphate with $HgNO_3$ solution potentiometrically. Schwicker[847] titrated peroxodisulphate with potassium ferrocyanide at 60°. Erdey *et al.*,[848,849] added excess of ferrocyanide and titrated the resulting ferricyanide with ascorbic acid.

The iodometric and permanganometric methods are the only redox methods of any practical use. Methods based on vanadium(II), hydroquinone, or other reducing agents have no significant advantage over them.

Hydrolysis of $S_2O_8{}^{2-}$, producing sulphate and hydrogen ions, can be used for an alkalimetric determination.[839] Peroxodisulphate can be reduced to sulphate with ethanol, and de Sousa[74] used this reaction and determined the sulphate complexometrically as barium sulphate. Doležal and Zýka[850] reduced $S_2O_8{}^{2-}$ with zinc or cadmium amalgam and titrated the resulting zinc or cadmium ions complexometrically. Kellner and Szekeres[851] reduced $S_2O_8{}^{2-}$ with thallium(I) nitrate and titrated the resultant thallium(III) with EDTA.

The peroxodisulphates can also be determined gravimetrically *via* their water-insoluble salts, *e.g.*, with strychnine.[852,853] Several other suitable precipitates[854,855] are known. After the hydrolysis of peroxodisulphate, the resulting sulphate can be determined gravimetrically.[839,856]

Photometric methods are the best-known physical methods for the determination of peroxodisulphate.[857–861] Some authors have also recommended the use of infrared spectroscopy[862] and polarography.[863–865]

Determination of peroxomonosulphuric acid (Caro's acid).

Two important methods of producing Caro's acid involve the hydrolysis of peroxodisulphate or the reaction of hydrogen peroxide with sulphur trioxide. The analysis of this acid is important, mainly in its mixtures with hydrogenperoxide and peroxodisulphate.

Peroxomonosulphate reacts with arsenic(III) very slowly in acidic medium, but the reaction is very rapid in the presence of iodide, and can be used in a direct potentiometric titration.[866] Peroxomonosulphate can be reduced by vanadyl sulphate solution, the excess of reductant being titrated with permanganate.[867] Peroxomonosulphate can also be reduced to sulphate with sulphite in the presence of iodide. The end-point can be detected visually or potentiometrically.[868,869]

Analysis of mixtures of peroxodisulphate and hydrogen peroxide

Peroxodisulphates usually contain hydrogen peroxide as impurity. Van der Meulen[870] reduced this mixture with ferrous sulphate and back-titrated the excess of ferrous sulphate with permanganate. He determined the peroxodisulphate in another alqiquot. The solution was made weakly alkaline and the hydrogen peroxide in it decomposed with a trace of osmium tetroxide as catalyst. Then sulphuric acid was added to the solution and the peroxodisulphate again reduced with ferrous sulphate and the excess back-titrated with permanganate.

Schulek *et al.*,[871] reduced the peroxide in peroxodisulphate peroxide mixtures selectively with hypochlorite. They eliminated the excess of hypochlorite with cyanide. The resulting cyanogen chloride forms an inactive polymer. The excess of cyanide can be eliminated by passing a stream of carbon dioxide through the solution. The peroxodisulphate can then be determined iodometrically. Hydrogen peroxide can also be reduced with hypobromite or with thiocyanate in the presence of ammonium molybdate as catalyst.[872,873] Chromous sulphate solution has been suggested for the simultaneous reduction of peroxodisulphate and hydrogen peroxide.[874]

Analysis of mixtures of peroxomonosulphuric acid and hydrogen peroxide

Thiocyanate reacts slowly with peroxide but rapidly with SO_5^{2-}. In the presence of ammonium molybdate thiocyanate reacts rapidly with peroxide but not with peroxodisulphate. Therefore it is possible to reduce peroxomonosulphuric acid selectively and determine hydrogen peroxide iodometrically. The total peroxo compounds can be determined iodometrically in a separate aliquot.[873]

Determination of peroxodisulphate, peroxomonosulphate and hydrogen peroxide in the presence of each other

Berry[867] titrated a mixture of peroxo compounds with ceric sulphate, which reacted with the peroxide present. Then vanadyl sulphate solution was added to the mixture. This reduced the Caro's acid; the excess of vanadyl sulphate was back-titrated with permanganate. In another aliquot the total content of H_2SO_5, $H_2S_2O_6$ and H_2O_2 was determined by reducing them with ferrous sulphate and back-titrating the excess with permanganate.

According to Gleu[863] Caro's acid can be reduced with hydrobromic acid in the presence of arsenious oxide, which speeds up the reaction. The bromine liberated during this reaction oxidizes the arsenious oxide immediately. The unchanged As_2O_3 is titrated with bromate and the peroxide in the titrated solution is determined with permanganate. Then excess of arsenious oxide is added to the solution still containing peroxodisulphate. Boiling the solution reduces the peroxodisulphate, and the excess of As_2O_3 is again titrated with bromate. The end-points of these titrations can be determined visually or potentiometrically. [875]

Schulek *et al.*,[873,876] utilized the reductive effect of thiocyanate ions for the analysis of peroxo compounds (see previous section). In one aliquot of sample the total amount of the three peroxo compounds was determined iodometrically. Addition of thiocyanate to a second aliquot selectively reduced H_2SO_5, so the amounts of H_2O_2 and $H_2S_2O_8$ in it could be determined iodometrically. Ammonium molybdate and thiocyanate were added to a third aliquot to reduce H_2SO_5 and H_2O_2, then $H_2S_2O_8$ was determined iodometrically. Since this method is based on time reactions and can be applied only to very dilute solutions, it has limited application.

Csányi and Solymosi[877,878] added arsenious oxide to a mixture of the peroxo compounds, in dilute sulphuric acid, and titrated the peroxide with ceric sulphate, with ferroin as indicator. Caro's acid can also be reduced selectively with arsenious oxide in the presence of a trace of osmium tetroxide as catalyst. The H_2SO_5 content of the solution can be calculated from the excess of arsenious oxide, determined by cerimetric titration. After the second titration the sulphuric acid content of the mixture is increased to approximately 10–12%. Addition of arsenious oxide and boiling reduces the $H_2S_2O_8$. The excess of As_2O_3 is again determined cerimetrically and the amount of $H_2S_2O_8$ calculated as before.

Csányi and Solymosi[879] reported another method based on the observation made by Gleu[863] that H_2SO_5 can be reduced by hydrobromic acid. They first titrated the liberated bromine with arsenite solution, and then determined the H_2O_2 content of that solution by titration with arsenic acid in the presence of osmium tetroxide and ammonium molybdate as catalysts. Finally the concentration of sulphuric acid in the solution was increased to about $5N$ and the $H_2S_2O_8$ content determined by titration with arsenite solution at 60–70°. In this titration the end-point was determined by using polarized platinum electrodes.

Famina *et al.*,[880] used a potentiometric method for the analysis of peroxo compounds. The H_2O_2 content of the solution was determined by titration with permanganate at pH 1·8, after which the pH of the solution was adjusted to 4 with sodium acetate and the H_2SO_5 content determined by titration with thiosulphate. Finally, the catalysts potassium iodide and cupric sulphate were added to the mixture in order to reduce $H_2S_2O_8$. The liberated elemental iodine was determined by titration with thiosulphate.

Potentiometric methods have been recommended for the titration of peroxo compounds.[881]

Kyrki[882] suggested an infrared spectrometric method for the determination of peroxodisulphate and peroxomonosulphate. Raspi and Venturini[883] solved this problem polarographically.

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APPLICATION OF THE DAVIDON–FLETCHER–POWELL METHOD TO THE CALCULATION OF STABILITY CONSTANTS

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Summary—The Davidon–Fletcher–Powell method of function minimization has been modified and successfully applied to the calculation of stability constants of species of the type $H_pM_qL_r$ in solution. It is shown that the refinement with respect to the logarithms of the stability constants is intrinsically ill-conditioned, leading to convergence difficulties when poor initial parameter estimates are used, and to failures when one or more parameters are experimentally indeterminate.

The computation of the equilibrium constants for the formation of complex species in solution (stability constants) is a complicated one, and has recently been reviewed.[1,2] None of the published programmes is completely satisfactory. Sillén's method of pit-mapping[3] (LETAGROP) was the first to find wide application. This method effectively uses the Newton–Raphson (NR) approach,[4] adopting a numerical calculation of the requisite derivatives. Despite continuous development[5] LETAGROP suffers from the defect inherent in the NR method that it does not distinguish between maxima, saddle points and minima. Thus, a poor initial estimate of the parameters, *i.e.*, the stability constants, may lead to the sum of squares tending to be maximized instead of minimized. This is commonly avoided by performing (sometimes extensive) pre-calculations using, for example, an axial iteration method.[4]

The programme SCOGS[6] is also generally applicable to pH titration data. It is based on the Gauss–Newton (GN) method[4] and also uses numerical differentiation. It has proved difficult to implement in various laboratories because of deficiencies[6] in the subroutine COGSNR. However, after these deficiencies were remedied[7] the programme still appears to require good initial parameter estimates, otherwise it is liable to produce "extreme overshifts" to the calculated parameters, a condition that requires arbitrary and unpredictable intervention in the programme. The performance of SCOGS is also critically dependent upon the values of the increments given for the numerical differentiation, and does not work well if bad values are chosen.

The recently published[7] programme LEAST, which may use either the GN or the NR method, employs analytical expressions for the derivatives, and has been shown to have markedly better convergence properties than either LETAGROP or SCOGS. As presently constituted, however, it is capable of treating only systems containing one metal and one ligand, with pH titration data.

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As the Davidon–Fletcher–Powell (DFP) method[8,9] has recently been applied with encouraging success in a limited calculation[10] we have developed a programme "STEW"* based on this method and having the same scope as the published version of LEAST. Davidon's method has previously been used in connection with the stability constants of fluoro-complexes, but no details of the implementation were given.[11]

THEORY

The equilibrium concentrations of the species in solutions containing one metal and one ligand, including polynuclear and hydrolysed species, are defined by the three mass-balance equations (1) applicable to each experimental data point, k.

$$T_H = [H] + \Sigma p\beta_{pqr}[H]^p[M]^q[L]^r. \tag{1a}$$

$$T_M = [M] + \Sigma q\beta_{pqr}[H]^p[M]^q[L]^r. \tag{1b}$$

$$T_L = [L] + \Sigma r\beta_{pqr}[H]^p[M]^q[L]^r. \tag{1c}$$

T_H, T_M and T_L are the total concentrations of hydrogen ion, metal ion and ligand respectively, and [H], [M] and [L] are the corresponding values of the concentration of the uncomplexed form. The n stability constants β_{pqr} (denoted collectively by the vector $\boldsymbol{\beta}$) are the parameters to be refined and each term $\beta_{pqr}[H]^p[M]^q[L]^r$ is the concentration of the chemical compound $H_pM_qL_r$. The summation is extended over all the species $H_pM_qL_r$ assumed to be present in the solution.

The parameters are varied so as to minimize U, defined by equation (2),

$$U = \sum^{k} (T_H{}^{\text{obs}} - T_H{}^{\text{calc}})^2, \tag{2}$$

where $T_H{}^{\text{calc}}$ is the value of T_H calculated from the current estimates of [M], [L] and $\boldsymbol{\beta}$ *via* equation (1a). [L] and [M] are determined at each point k by solving equations (1b) and (1c) simultaneously by using the NR technique. This process is also used in LETAGROP and SCOGS (COGSNR).

The function U was minimized by the DFP method. The theory of this method is as described in detail for the calculation of vibrational force constants,[12] and will not be repeated. The basis of this iterative method is that a proportion λs of the correction vector s calculated from equation (3) is added to the vector $\boldsymbol{\beta}$ as in equation (4).

$$s = -Hg \tag{3}$$

$$\boldsymbol{\beta}^{i+1} = \boldsymbol{\beta}^i + \lambda s, \tag{4}$$

λ is determined as the value which optimizes the reduction in U for the iteration cycle. The vector g, the gradient of the function U with respect to $\boldsymbol{\beta}$ is given by equation (5)

$$g_j = \frac{\partial U}{\partial \beta_j}, \tag{5}$$

and H is a positive definite approximation to the inverse of the Hessian G defined in equation (6).

$$G_{ij} = \partial^2 U/\partial\beta_i\,\partial\beta_j. \tag{6}$$

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* Copies of this programme are available on request.

H is updated from the information obtained in previous iteration cycles so that after at least n cycles the DFP method becomes equivalent to the NR method. The elements of g must be obtained by numerical differentiation, so that the original DFP method,[9] which requires analytical expressions for g, is not applicable, but Stewart's modification[13] must be used. We initially used a FORTRAN subroutine very similar to the ALGOL procedure Dapodmin[14] used earlier.[10]

In working up the programme we made one modification to "Dapodmin" which may be of general interest. An initial diagonal approximation to H was obtained as follows. The increment δ_i used to calculate g_i according to equation (7), was also used to provide a third function value, as shown by equations (8).

$$g_i = (U^+ - U)/\delta_i \tag{7}$$

$$U = U(\beta_1 \cdots \beta_i \cdots \beta_n) \tag{8a}$$

$$U^+ = U(\beta_1 \cdots (\beta_i + \delta_i) \cdots \beta_n) \tag{8b}$$

$$U^- = U(\beta_1 \cdots (\beta_i - \delta_i) \cdots \beta_n) \tag{8c}$$

If it is assumed that U is a quadratic function of β_i (the other parameters $\beta_j, j \neq i$, remaining constant) the equations (8) may be rewritten in the form (9)

$$U = U^0 + g_i\beta_i + \tfrac{1}{2}G_{ii}\beta_i^2 \tag{9a}$$

$$U^+ = U^0 + g_i(\beta_i + \delta_i) + \tfrac{1}{2}G_{ii}(\beta_i + \delta_i)^2 \tag{9b}$$

$$U^- = U^0 + g_i(\beta_i - \delta_i) + \tfrac{1}{2}G_{ii}(\beta_i - \delta_i)^2 \tag{9c}$$

whence equation (10) results:

$$U^+ + U^- = 2U^0 + 2g_i\beta_i + G_{ii}(\beta_i^2 + \delta_i^2) = 2U + G_{ii}\delta_i^2 \tag{10}$$

Therefore an approximate value of H_{ii} is given by equation (11).

$$H_{ii} = 1/G_{ii} = \left|\frac{\delta_i^2}{U^+ + U^- - 2U}\right| \tag{11}$$

The absolute value in equation (11) is necessary so that H_{ii} is positive, since it may happen that $U^+ + U^- - 2U$ is negative. This method of calculating the diagonal elements of H is derived from a similar calculation in LETAGROP.[3] As a further safeguard we check that the quantities $(U^+ - U)$ and $(U^- - U)$ are significant with respect to an estimate of the precision to which U may be calculated; if they are not, δ_i is arbitrarily multiplied by 10 until the check is satisfied.

RESULTS AND DISCUSSION

Trials using $H_{ii} = 1$ $(i = 1 \cdots n)$, $H_{ij} = 0$ $(i \neq j,\ i, j = 1 \cdots n)$ as the initial estimate of H were unsatisfactory. According to equation (3) the first cycle is then one of steepest descent, $s = -g$. If the gradient vector contains elements of widely differing magnitude the linear minimization effectively reduces some elements of λs virtually to zero and so some parameters are not refined. The use of equation (11) overcomes this problem by effectively scaling the gradient so that all elements of λs are of comparable magnitude, at least for the first cycle. The parameters chosen to be minimized were the logarithms of the formation constants, log β, as in SCOGS and for the same reason—to bring all parameters on to a scale of comparable magnitude. The programme STEW worked well on three test problems, involving two, four and six parameters, as shown in Table 1. All data points were given equal weight.

Tests starting from very poor initial estimates of the log β values revealed a most interesting property of stability-constant calculations in general—the refinement of log β is intrinsically ill-conditioned, whereas the refinement of β values as parameters is not. This is illustrated in the figures. Figure 1 shows the contours of U for the 2-dimensional problem

Table 1. Logarithms of formation constants obtained by using different methods of refinement[a]

Problem	Complex	Parameter	SCOGS 1	LG/3	LEAST-GN	STEW
A	$NiHL^{3+}$	β_1	15·78(3)	15·78(3)	15·76(4)	15·78(2)[e]
L = tpt[b]	NiL^{2+}	β_2	8·702(2)	8·702(2)	8·702(2)	8·702(1)
	CuH_2L^{4+}	β_1	24·618(6)	24·619(4)	24·613(4)	24·619(3)[f]
B	$CuHL^{3+}$	β_2	20·05(2)	20·05(2)	20·07(1)	20·04(1)
L = Me_7tetren[c]	CuL^{2+}	β_3	12·34(3)	12·32(4)	12·32(3)	12·32(2)
	$Cu(OH)L^+$	β_4	3·06(3)	3·02(2)	3·04(3)	3·01(2)
	CuL^{2+}	β_1	7·376(1)	7·377(2)	7·376(1)	7·376(1)[g]
	$Cu(OH)L^+$	β_2	−0·65(7)	−0·66(7)	−0·64(4)	−0·64(4)
L = Me_4en[d]	$Cu_2(OH)_2L^{2+}$	β_3	−3·66(5)	−3·65(5)	−3·65(5)	−3·65(3)
C	$Cu_2(OH)_2L_2{}^{2+}$	β_4	2·59(2)	2·59(2)	2·59(2)	2·58(1)
	$Cu_3(OH)_4L_2{}^{2+}$	β_5	−8·18(3)	−8·14(6)	−8·15(6)	−8·14(4)
	$Cu(OH)_2L$	β_6	−10·91(2)	−10·91(2)	−10·91(2)	−10·91(1)

[a] Values for SCOGS 1, LG/3 and LEAST-GN are taken from reference 7. The figures in parentheses are the standard deviations of the last decimal figure and reflect only the random errors in the titration data.
[b] tpt = $N(CH_2CH_2CH_2NH_2)_3$.
[c] Me_7tetren = $Me_2N(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2NMe_2$
[d] Me_4en = $Me_2N(CH_2)_2NMe_2$.
[e] Initial values: log β_1 8·7, log β_2 12·0. An automatic restart occurred at log $\beta_1 = 8{\cdot}71$, log $\beta_2 = 15{\cdot}00$.
[f] Initial values: log β_1 26·6, log β_2 19·0, log β_3 13·2, log β_4 1·1.
[g] Initial values: log β_1 7·4, log β_2 −0·4, log β_3 −3·8, log β_4 2·5, log β_5 −7·9, log β_6 10·9.

(*A*), plotted in (*a*) as a function of log β_1 and log β_2, and in (*b*) as a function of β_1 and β_2. A section in relief through the plane at log $\beta_2 = 8{\cdot}70$ is shown in Fig. 2 as a function of log β_1 and of β_1. It will be seen that the U *vs.* log β contours form a convex–concave shell-shaped cavity, whereas the U *vs.* β contours form an (apparently parabolic) concave cavity. The fact that the U *vs.* log β surface is partly convex means that at those points in which it becomes concave the Hessian and its inverse become singular. Hence the DFP method, which depends on the assumption that H is a positive definite matrix, must fail if it has not reached the concave region after n cycles. Such failures were observed in problem (*A*) when starting from log $\beta_1 < 14$. The failures could be overcome by restarting with H calculated from equation (11) since this guarantees a positive definite matrix.

The significant point, however, is that the convexity in the U contours is artificially introduced by the change of variable from β to log β.

Consider y, a parabolic function of x, $y = ax^2 + bx + c$, and change the variable to z, where $z = \log x$, *i.e.*, $x = \exp(z)$. The function in terms of z is $y = a \exp(2z) + b \exp(z) + c$ and its first derivative $dy/dz = 2a \exp(2z) + b \exp(z)$. The function has a minimum at $dy/dz = 0$, *i.e.*, $z = \log(-b/2a)$, so that $b/2a$ must be negative. The second derivative,

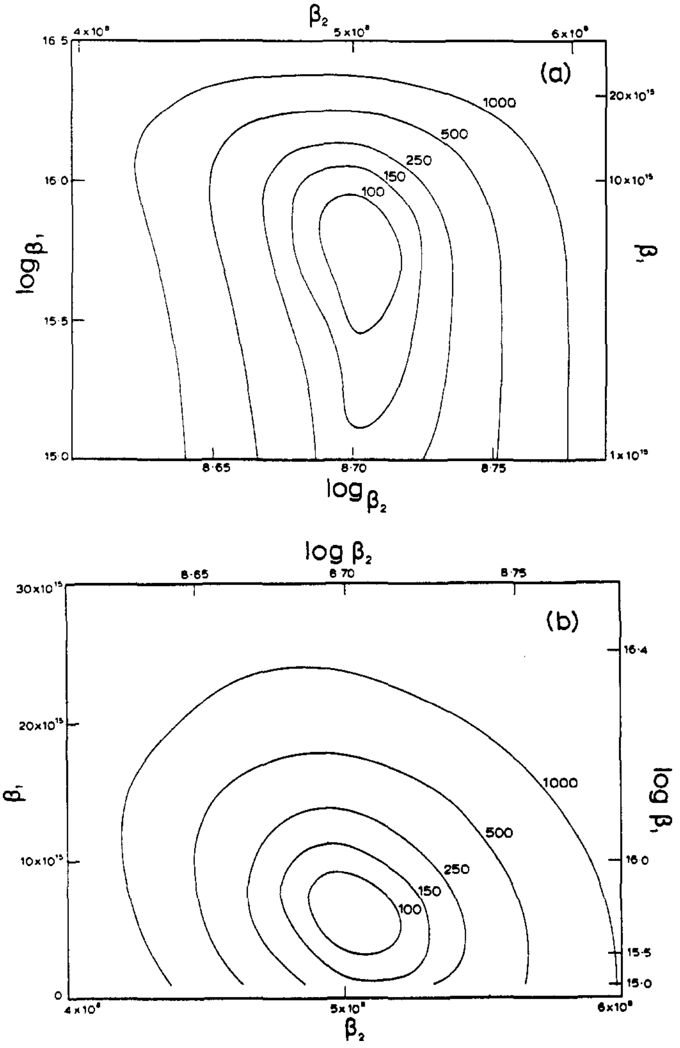

Fig. 1. Contours of U [equation (2)] for the system Ni–tpt, plotted (*a*) linearly with respect to $\log \beta_1$ and $\log \beta_2$, and (*b*) linearly with respect to β_1 and β_2. U has been multiplied by 10^8 for clarity.

$d^2y/dz^2 = 4a \exp(2z) + b \exp(z)$, is positive only when $z > \log(-b/4a)$. In other words, the function is concave only when x is not less than half its optimal value. It will be clear that any function which is paraboloid with respect to some parameter vector x will become convex–concave with respect to $\log x$, and there will be a region in which the matrix of second derivatives is not positive definite.

Since U is an almost parabolic function of $\boldsymbol{\beta}$ the change of scale from $\boldsymbol{\beta}$ to $\log \boldsymbol{\beta}$, instead of just scaling the parameters, transforms U into a highly non-linear, non-concave function which must be difficult to minimize by any method.[4] SCOGS uses such a change of variable, but LETAGROP and LEAST do not. It is possible that many of the difficulties experienced in stability-constant calculations[1] could be due to an unlucky choice of an ill-conditioned

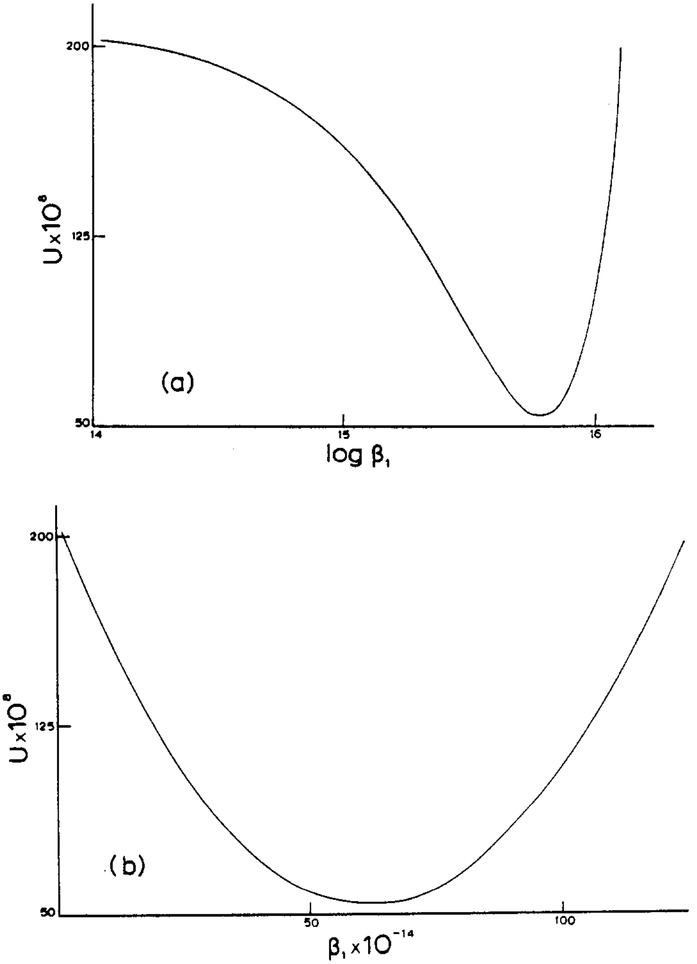

Fig. 2. A relief section through the contour maps of Fig. 1 at log $\beta_2 = 8{\cdot}70$, plotted (*a*) as a function of log β_1 and (*b*) as a function of β_1. The curve (*a*) is convex for log $\beta_1 <$ *ca.* 15·4.

function, the evils of which can sometimes be mitigated be introducing a scheme for weighting the experimental observations.[1]

A further difficulty arises when it is assumed that a species is present which has an actual concentration so low as to have little or no influence on the observed pH. The corresponding stability constant β_j is indeterminate. In an ideal calculation the value of β_j would tend to zero, its standard deviation would tend to infinity and H would tend to become singular. In practice it is usually found that β_j soon assumes a negative value, and in LETAGROP such constants are removed from the calculation.[3] Log β_j in such a situation would tend rather rapidly to minus infinity, this giving the refinement a tendency to move away from the minimum, as will be seen by considering Figs. 1(*a*) and 2(*a*). This property will also apply in the GN refinement, so that refinements which include an indeterminate log β_j must always fail to converge. Refinements that include an indeterminate β_j can converge if the offending parameter is removed when it becomes negative.

After changing to refinement of **β**, "STEWβ" successfully minimized functions from very poor initial parameter estimates, *e.g.*, $\beta_1 = 1 \times 10^{12}$ for problem (A).

The results agreed well with those obtained previously on the test data. STEWβ is much faster and more stable than LETAGROP and SCOGS, and is not very sensitive to the values of δ_i initially used in equation (7), as the increment for differentiation is automatically recalculated on each cycle after the first.[13] In the optimization of shifts, equation (4) confers a notable stability on the refinement and is one reason why STEWβ works with very poor parameter estimates.

The performance of STEWβ seems to be comparable to that of LEAST-GN, being better in terms of storage requirements and poorer in terms of speed. As our next step in the development of programmes for the computation of stability constants we have chosen to develop a generalized version of LEAST-GN, known as MINIQUAD.[15] Experience with this programme will give us an indication as to the desirability of implementing a generalized programme using the Davidon–Fletcher–Powell approach.

Acknowledgement—We thank Professor L. Sacconi for his interest and encouragement and the C.N.R. for a Fellowship and other financial support.

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Résumé—La méthode de Davidon–Fletcher–Powell de minimisation de fonction a été modifiée et appliquée avec succès au calcul des constantes de stabilité d'espèces du type $H_pM_qL_r$ en solution. On a montré que le perfectionnement en ce qui concerne les logarithmes des constantes de stabilité est intrinsèquement mal établi, menant à des difficultés de convergence quand on utilise des estimations initiales de paramètres médiocres, et à des échecs quand un ou davantage de paramètres sont expérimentalement indéterminés.

Zusammenfassung—Die Methode der Funktionsminimierung nach Davidon, Fletcher und Powell wurde modifiziert und mit Erfolg auf die Berechnung der Stabilitätskonstanten von Spezies vom Typ $H_pM_qL_r$ in Lösung angewandt. Es wird gezeigt, daß die iterative Verbesserung der' Logarithmen def Stabilitätskonstanten unter schlechten Bedingungen abläuft; daher kommt es zu Konvergenzschwierigkeiten, wenn schlechte Anfangs-Schätzwerte der Parameter verwendet werden, und zu Fehlschlägen, wenn ein oder mehrere Parameter experimentell unbestimmt sind.

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MINIQUAD—A GENERAL COMPUTER PROGRAMME FOR THE COMPUTATION OF FORMATION CONSTANTS FROM POTENTIOMETRIC DATA

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Summary—A new computer programme for the computation of formation constants of complex species in solution is presented. The programme can be applied to all kinds of potentiometric titration data, including multi-reactant and multi-electrode systems. A statistical analysis is made of the results in order to assess their validity, and to assist in hypothesis testing.

Many computer programmes for the computation of formation constants of complex compounds in solution equilibria have been described,[1] but only two of these have wide applications, LETAGROP[2] and SCOGS.[3] SCOGS can deal with multi-reactant systems but is limited to pH titration data. LETAGROP can additionally deal with many types of data, but each type requires the use of one or more purpose-written sub-programmes. Both programmes have certain mathematical defects which may cause them to fail to converge to satisfactory solutions.[4] A need was therefore felt for a programme with guaranteed convergence properties that could be applied to a wide variety of problems with the minimum of modification.

We have developed such a programme to deal with potentiometric titration data. Named MINIQUAD from the Italian for least squares, *minimi quadrati*, this programme can in principle treat data from systems containing any number of reactant species and potentiometric electrodes, and all commonly found types of complex, *e.g.*, mononuclear, polynuclear, hydrolysed complexes.

After a brief résumé of the theory we shall discuss the advantages of the new programme, its organization, and pertinent programming details. There follows the text of the programme, which is amply annotated to facilitate comprehension.

THEORY

Let there be n_k formation constants β_j of which n are to be determined. For each of $n_{\rm mbe}$ reactants there is a mass-balance equation (1)

$$T_i = C_i + \sum_j q_{ij} C'_j \tag{1}$$

where T_i is the total (analytical) concentration of reactant i, C_i is the concentration of free (uncomplexed) reactant and C'_j is the concentration of the complex j as shown by equation (2).

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$$C'_j = \beta_j \prod_k C_k^{q_{jk}} \tag{2}$$

The indices q_{jk} are the stoichiometric coefficients of reaction (see Appendix for an explanation).

There are n_{mbe} mass-balance equations at each point. If there are n_{p} titration points there will be a total of $n_{\mathrm{p}} \times n_{\mathrm{mbe}} = m$ mass-balance equations. The free concentrations C_i may be determined potentiometrically, by using appropriate electrodes sensitive to reactant concentrations. Let there be n_{emf} such electrodes. This leaves $n_{\mathrm{c}} = n_{\mathrm{mbe}} - n_{\mathrm{emf}}$ free concentrations unknown at each titration point. These will be called the unknown free concentrations, denoted for each data point by C''_k. There are $n_{\mathrm{p}} \times n_{\mathrm{c}}$ unknown free concentrations and a total of $n_{\mathrm{p}} \times n_{\mathrm{c}} + n$ parameters to be determined.

The method used is the Gauss–Newton least-squares method, similar to the method used in LEAST-GN,[5] but made general. The sum of squares, U, to be minimized is given in equation (3).

$$U = \sum_{i=1}^{i=m} (T_i^{\mathrm{calc}} - T_i^{\mathrm{obs}})^2 = \sum_{i=1}^{i=m} (\Delta T_i)^2 \tag{3}$$

Thus U is the sum of squared residuals for all the mass-balance equations. Equal weights are used, for the reasons discussed previously.[5] The parameters, now to be denoted for mathematical purposes by the vector x, are refined iteratively by calculating a shift s to be applied according to the standard least-squares expression (4)

$$J^{\mathrm{T}}Js = J^{\mathrm{T}}\,\Delta T \tag{4}$$

where J is the Jacobian, or design, matrix given by $J_{ij} = \partial T_i/\partial x_j$. The shifts s are linearly optimized with respect to the scalar t, the fraction of s required for the minimum value of U^{i+1}, equation (5).

$$x^{i+1} = x^i + ts^i \tag{5}$$

The normal equations (4) are first scaled by multiplying each column of J by the appropriate parameter x_j to form a scaled design matrix A where $A_{ij} = x_j J_{ij} = x_j\,\partial T_i/\partial x_j$. In matrix notation this is given by equation (6)

$$A^{\mathrm{T}}As' = A^{\mathrm{T}}\,\Delta T \tag{6}$$

which is equivalent to equation (7)

$$X^{\mathrm{T}}J^{\mathrm{T}}JXs' = X^{\mathrm{T}}J^{\mathrm{T}}\,\Delta T \tag{7}$$

where $X = diag(x_1 \ldots)$. Clearly the shifts are related by equation (8).

$$s = Xs' \tag{8}$$

In other words, s' is a vector of "relative shifts" with elements given by $s'_k = s_k/x_k$.

In order to render the problem tractable, the scaled normal equations (6) are factorized to block diagonal form so that n_{p} systems of equations of order n_{c} and one of order n are solved. The factorization is a generalized version of the one used[5] in LEAST, in which the blocks may have the variable dimension n_{c} instead of the fixed dimension 2. The transformed equations are given in (9)

$$D^{\mathrm{T}}(A^{\mathrm{T}}A)D(D^{-1}s') = D^{\mathrm{T}}A^{\mathrm{T}}\,\Delta T \tag{9}$$

where D is the triangular factorization matrix. Thus, $D^{-1}s'$ is first calculated and is next converted into s' and then into s. Further details concerning the calculation of D will be found elsewhere.[5]

The refinement may be terminated when the elements of the relative shift vector s' are less than a predetermined quantity, *e.g.*, each element of x changes by less than 0·1%. Alternatively the refinement may be terminated when the decrease in U is smaller than some predetermined tolerance. MINIQUAD terminates only when both convergence criteria are satisfied, or when a predetermined number of iteration cycles has been performed.

DISCUSSION

MINIQUAD possesses the following advantages over other programmes for formation-constant calculation.

(*i*) It uses the Gauss–Newton method of refinement. Previous work[5] showed that this method is to be preferred to the Newton–Raphson method in spite of the better ultimate theoretical convergence properties of the latter. LETAGROP effectively uses the Newton–Raphson method.

(*ii*) The refinement is protected against divergence by the linear optimization of shifts. Indeed, it has been proved[6] that optimization of shifts confers a guaranteed convergence property on the refinement. Consequently the initial estimates for the parameters need not be very accurate, and guessed values are usually satisfactory.

(*iii*) All differential coefficients are calculated from analytical expressions. This eliminates the errors inevitably introduced during numerical differentiation (such as occurs in both LETAGROP and SCOGS) and avoids the problem of choosing suitable increments for the differencing formulae.

The elements of the scaled design matrix are particularly easy to calculate. Differentiation of equations (1) and (2) gives, at the kth titration point,

$$A_{ij} = \beta_j \frac{\partial T_i}{\partial \beta_j} = q_{ij} C'_j \tag{10a}$$

$$A_{ij} = C''_j \frac{\partial T_i}{\partial C''_j} = \delta_{ij} C''_j + \sum_l q_{jl} q_{il} C'_l \tag{10b}$$

where $\delta_{ij} = 0$ for $j \neq i$ and $\delta_{ij} = 1$ for $j = i$. Thus the derivatives are calculated simply by assembling the already calculated concentrations of the complexes with appropriate coefficients. Moreover, the "relative derivatives" A_{ij} in equations (10a) and (10b) are bounded in magnitude by the values of the concentrations of the complexes, thus ensuring that the elements of the normal equations matrix are not greatly dissimilar. The unscaled derivatives J_{ij} vary over a much larger range of scale since, for example, the expressions in equation (10a) must then be divided by the formation constants.

(*iv*) The parameters refined are all the unknown quantities, *i.e.*, they include the unknown free concentrations. U involves all the mass-balance equations equally, so there is no bias in favour of any individual reactant and all total reactant concentrations are assumed to be subject to experimental error.

(*v*) The formation constants β_j are refined, as in LETAGROP. This form of scaling the parameters is satisfactory, in contrast to the use of log β_j which can cause serious difficulties.[4] The programme allows the parameters to assume negative values during the linear minimization but rejects negative β_j values at the end of an iteration cycle. Formation constants are stored in mantissa and exponent form (a, b), *i.e.* $\beta = a \times 10^b$, but the concentrations in equation (2) are calculated first in logarithmic form so that the partial products in that equation are not fortuitously larger or smaller than can be held in the computer's store. In addition, the "absolute shifts" s of equation (8) are made to refer to the mantissa of the formation constants only, the exponent remaining unchanged during the refinement. This allows formation constants of any magnitude to be determined, regardless of the numerical capacity of the computer. A similar device is used in LETAGROP.[2]

(*vi*) The factorized normal equations matrix $D^T(A^TA)D$ consists of n_p blocks of order n_c and one block of order n. The unknown free concentrations are thus refined simultaneously with the formation constants, each iteration involving the solution of linear equations only. Because of this, MINIQUAD (like LEAST[5]) is a fast programme. In both LETAGROP and SCOGS the unknown free concentrations are usually found once each iteration from a set of non-linear equations.

(*vii*) A proper convergence criterion has been introduced for the termination of the refinement.

(*viii*) Because the mass-balance equations are not tied to any chemical system the programme is extremely flexible. It has been tested on a variety of pH-titrations of polyfunctional bases and their metal complexes, with up to 300 titration points and 20 complex species in equilibrium, and with use of both a glass electrode and a metal electrode. Other calculations that could be performed include: hydrolysis of metal ions; mixed metal and/or mixed ligand complexes; competitive equilibria.

(*ix*) The residuals on the mass-balance equations are analysed upon convergence to see how nearly they follow a Gaussian (normal) distribution. The final output also includes a complete species-distribution analysis.

PROGRAMMING DETAILS

The programme is written in a simple subset of FORTRAN IV, and has been run on IBM 360, CDC 6600 and ICL 1906A computers. The following comments are mainly directed at potential users of the programme who might wish to consider making their own modifications.

MINIQUAD consists of a main programme which reads only a title and those numbers needed for run-time array dimensions. It then calls subroutines as follows.

DINP—data input. The formation constants and their coefficients are read in. β's may be held constant (KEY = 0) or varied (KEY = 1) at will. The titration data are then read in. The free concentrations are obtained from the potentiometric data, *via* the Nernst equation if e.m.f. values are read in, or directly from the decimal cologarithm (*e.g.*, pH). Other forms of potentiometric data (*e.g.*, a concentration cell with transference) would require very small modifications to the programme. The unknown free concentrations are calculated for each point in ML, by Newton–Raphson iteration on the relevant mass-balance equations, as in COGSNR.[3] These values are stored in CONC for use as initial estimates in the subsequent refinement. The potentiometrically determined free concentrations are also stored in CONC, and the total reactant concentrations are stored in T. The titration points are counted and checked to see that the maximum numbers permitted are not exceeded.

MINIM—this routine performs the main minimization. The first part goes through each data point, calling CALC to calculate all species concentrations C'_j, the elements of the scaled design matrix, and the partial value of U. The elements of the factorization matrix D

are also computed point by point. Since they are subsequently recalled (for the calculation of the shifts in the unknown free concentrations) pointwise, D may easily be placed in a backing-store device, rather than in the main store, and recalled point by point. This saves considerably on the main core requirement, at the expense of time lost in backing-store manipulation. A version of MINIQUAD which uses the 16 K IBM 1130 with disc backing-store is available, upon request, from A. Vacca.

Once the normal equations matrix has been set up and factorized the shifts s are linearly optimized in LIMIN. This is a linear minimization routine based on the method of Powell[7] and derived from a well-tried coding of the method. LIMIN in turn calls FUNCT, which is similar to CALC except that its main purpose is to calculate U only.

The linearly optimized shifts are then tested to see if they give rise to any negative formation constants, in NEG. In such an event, the fraction t of equation (5) is reduced so that one formation constant β_j goes to zero and it is then eliminated from the refinement by making its key, KEY(J) equal to -1. However, in order that n can be reduced by one, it is then necessary to exit from MINIM and re-enter with $n' = n - 1$. The progress of the minimization may optionally be monitored *via* MON1.

LINEQ is a general purpose symmetric linear equations solver used at various points in the programme. The method used is based on Choleski factorization, and is believed to be the method that introduces the smallest rounding errors.[8] Such errors could be further reduced by using double-length arithmetic for forming all inner-products, but we have not included this process, since the refinement is protected against an inaccurate shift vector by the shift optimization.

DOUT—when the minimization is terminated this routine causes print-out of all the relevant information on the computed formation constants, *e.g.*, value, standard deviation, correlation coefficients. Also, if the refinement has failed, a concise failure message is printed. The programme is protected throughout against hard failure (*e.g.*, due to overflow) so that usually numerical failure results in a message being printed here. The main exception is with faulty data input.

STATS—after DOUT the residuals on all the mass-balance equations are subjected to a statistical analysis. If there are no systematic errors present in the data or the chemical model, the residuals should have a Gaussian distribution. The actual distribution can then be compared with the Gaussian to see if systematic errors are present.

The concentrations of all species present may then be calculated and printed out as fractions of a given reactant concentration. In an optional output, these fractions are printed out in graphical form, as shown by the example in Fig. 1.

INTERPRETATION OF OUTPUT

The values of standard deviation of log β are only approximate, and can be expected to be seriously in error if the corresponding standard deviation of β is large, since $\mathrm{d}\log\beta = \mathrm{d}\beta/\beta$ and $\sigma(\log\beta) \sim \sigma(\beta)/\beta$.

With regard to the output from STATS, a Gaussian (normal) distribution has the following properties: arithmetic mean zero, standard deviation σ, mean deviation $(\sqrt{2/\pi})\sigma \sim 0{\cdot}8\sigma$, variance σ^2, moment coefficient of skewness zero and moment coefficient of kurtosis 3.[9] The residuals are then divided into eight classes inside which there would be a "normal" probability of 12·5% of all residuals. Thus the classes are defined by the limits $-\infty$, $-1{\cdot}15\sigma$, $-0{\cdot}675\sigma$, $-0{\cdot}319\sigma$, $0{\cdot}0$, $0{\cdot}319\sigma$, $0{\cdot}675\sigma$, $1{\cdot}150\sigma$, ∞. A goodness-of-fit statistic χ^2 is then derived from the difference in observed and calculated probability. Since the standard deviation σ must be computed from the residuals themselves, the total χ^2 has 6 degrees of freedom.

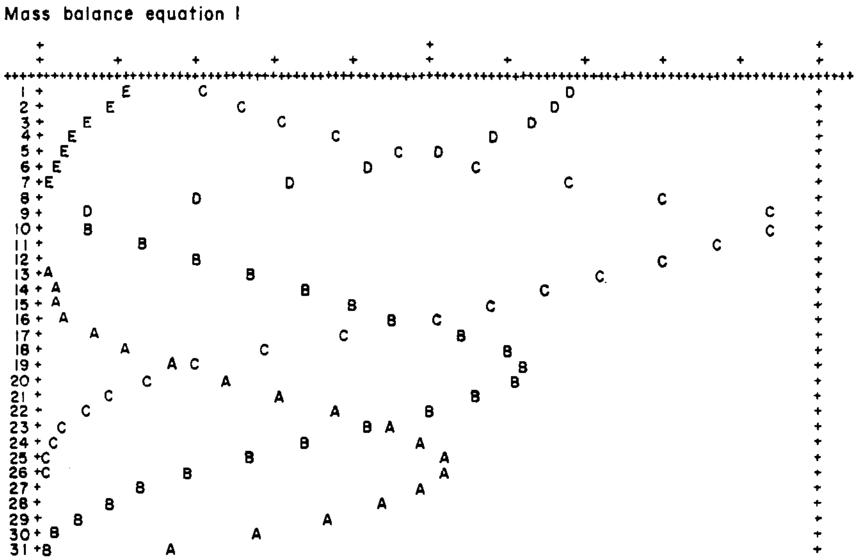

Fig. 1. Per cent formation of the species present for each point of a curve obtained by titrating an acidic solution of a pentabasic ligand L (Me_7tetren) with a solution of potassium hydroxide. During the course of the titration the species LH_5, LH_4, LH_3, LH_2 and LH are formed, denoted by E, D, C, B and A. The percentages are relative to the analytical (total) concentration of the ligand, T_L. The numbers at the left index the titration points.

Values of χ^2 for various confidence levels can be found in reference 9, Appendix IV. A fit can be accepted at the appropriate confidence level if the observed value of χ^2 is less than the value expected. The crystallographic *R* factor is also printed out for possible use in connection with significance tests.[10,11]

We do not expect that real experimental data will give a very good Gaussian distribution of residuals. However, when comparing two chemical models it may perhaps be detected that one model is "wrong," through the systematic errors introduced by postulating the presence of a complex which is actually absent. Therefore, these statistics supply information, additional to the value of the sum of squares and the *R* factor, which may be of assistance in hypothesis testing.

Specimen data input and output listings are available, on request, from P. Gans.

COMPUTER IMPLEMENTATION

The user must supply his own input and output channel numbers for JINP and JOUT and specify the total number of points NP. The convergence tolerances TOL and TOLU may also be altered though we have found the values given satisfactory on computers of different precision (8 or 12 decimal digits). The present implementation can take up to 300 data points (NP), 5 reactants (NMBE), 3 electrodes (NEMF), 20 complexes (NK) and 20 variable β's (N). All arrays have run-time dimensions, so if a change of dimensions is required, only those of the main segment are affected, *i.e.*, HLNB, JPOT, BETA, KEY, CI (NK); JQR (NMBE, NK); T, CONC (NP, NMBE); A, B (NMBE, NK + NC); CX, TT, HX, EPS, TOTC, ADDC, TITRE (NMBE); JEL, EZERO, EMF (NEMF); BETAV, IVAR, DGB, SB, SIGMA, DBR (N); BB (N, N); GC, TOLC, DT (NC); DDT (NC, NC); SC (NP × NC); D (NP × NC, N); D1 (NEMF, NK). NC is the number of unknown free concentrations, NC = NMBE − NEMF.

```
      DIMENSION TITLE(20)
      DIMENSION HLNB(20),JPOT(20),BETA(20),KEY(20),CI(20),JS(20)
      DIMENSION JQR(5,20)
      DIMENSION T(300,5),CONC(300,5)
      DIMENSION A(5,25),B(3,25)
      DIMENSION CX(5),TT(5),HX(5),EPS(5),TOTC(5),ADDC(5),TITRE(5),JP(5)
      DIMENSION JEL(3),EZERO(3),EMF(3)
      DIMENSION BETAV(20),IVAR(20),DGB(20),SB(20),BB(20,20),
     *          SIGMA(20),DBR(20)
      DIMENSION GC(3),TOLC(3),DT(3),DDT(3,3),D1(3,20)
      DIMENSION SC(900),D(900,20)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C          PROGRAM MINIQUAD  -  MAIN SEGMENT
    1 FORMAT (20A4)
    2 FORMAT ('1 MINIQUAD ',20A4/)
    3 FORMAT (10I5)
    4 FORMAT (' NO FREE CONCENTRATIONS TO CALCULATE. RUN ABANDONED BEFOR
     *E REFINEMENT')
C          INPUT AND OUTPUT CHANNELS DEFINED TO SUIT THE USER
      JINP=5
      JOUT=6
C          CONVERGENCE CRITERIA
C          A) RELATIVE SHIFTS OF THE PARAMETERS LESS THAN TOL
C          B) RELATIVE DECREASE OF THE ERROR SQUARE SUM LESS THAN TOLU
      TOL=1.E-03
      TOLU=1.E-04
C          AUTOMATIC CALCULATION OF ACCM (THE ABSOLUTE MACHINE ACCURACY)
      ACCM=1.
   10 X=ACCM/10
      IF (X) 12,12,11
   11 ACCM=X
      GO TO 10
   12 AL10=ALOG(10.)
      NP=300
      NSET=0
      LP=0
  100 READ (JINP,1) TITLE
      WRITE(JOUT,2) TITLE
      IFAIL=0
      READ (JINP,3) LARS,NK,N,MAXIT,IPRIN,NMBE,NC
      IF(NC)130,130,138
  130 WRITE (JOUT,4)
      STOP
  138 NEMF=NMBE-NC
C          CALL THE DATA INPUT ROUTINE
      CALL DINP (NK,N,NMBE,NEMF,NP,NC,BETA,JPOT,JQR,KEY,HLNB,T,CONC,
     *           BETAV,IVAR,JEL,EZERO,EMF,TOTC,ADDC,TITRE,CX,TT,CI,HX,
     *          TOLC,DT,DDT,LP,NSET)
C          CHECK THAT ML HAS OPERATED SUCCESSFULLY
      IF(IFAIL)120,120,150
  120 PERC1=0.
      PERC2=1.
      NRUN=0
      NM=LP*NC
      NF=0
      JF=0
  140 NPNC=N+NC
C          CALL THE MINIMISATION ROUTINE
      CALL MINIM (NK,N,NMBE,NC,NEMF,NP,BETAV,JPOT,JQR,HLNB,T,CONC,IVAR,
     *                  A,GC,DGB,EPS,HX,TT,CI,CX,BB,SB,SC,SIGMA,BETA,LP,
     *          NPNC,NM,U,KEY,B,D,DBR,DDT,PERC1,PERC2,D1,JF)
      IF(IFAIL) 145,150,150
  145 N=N-1
      IFAIL=0
      IF (N) 160,160,140
C          CALL THE DATA OUTPUT ROUTINES
  150 CALL DOUT (NK,N,NMBE,BETAV,JPOT,JQR,IVAR,SIGMA,U,KEY,BB,HLNB)
      NKE=NK+NMBE
      CALL STATS (NK,N,NMBE,NC,BETAV,JPOT,JQR,HLNB,T,CONC,IVAR,DU.A,GC,
     *            DGB,EPS,HX,TT,CI,CX,NPNC,LP,NP,NM,U,D,KEY,JS,JP,NKE)
```

```
  160 READ (JINP,3) NSET
      IF (NSET) 200,100,100
  200 STOP
      END


      SUBROUTINE DINP (NK,N,NMBE,NEMF,NP,NC,BETA,JPOT,JQR,KEY,HLNB,T,
     *           CONC,BETAV,IVAR,JEL,EZERO,EMF,TOTC,ADDC,TITRE,CX,TT,CI,
     *           HX,TOLC,DT,DDT,IP,NSET)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),JPOT(NK),BETA(NK),KEY(NK),CI(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),CONC(NP,NMBE)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE),TOTC(NMBE),ADDC(NMBE),TITRE
     *          (NMBE)
      DIMENSION JEL(NEMF),EZERO(NEMF),EMF(NEMF)
      DIMENSION BETAV(N),IVAR(N)
      DIMENSION TOLC(NC),DT(NC),DDT(NC,NC)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *          ,NRUN,TITLE,IFAIL
C         INPUT ROUTINE APPLICABLE TO DATA FROM POTENTIOMETRIC TITRATIONS.
C         THE TITRATION DATA ARE READ IN AND THE INITIAL VALUES OF THE UNKNOWN
C         FREE CONCENTRATIONS ARE CALCULATED IN ML
    1 FORMAT (' (',I2,')',F11.4,'E',I3,I8,7X,5I4)
    2 FORMAT (//10X,'FORMATION    REFINEMENT    STOICHEIOMETRIC'/
     *         10X,'CONSTANTS        KEYS          COEFFICIENTS'/)
    3 FORMAT (6I5)
    4 FORMAT (F10.6,7I5)
    5 FORMAT (8F10.6)
    6 FORMAT (I5,8F8.3)
    7 FORMAT (6E10.3)
    8 FORMAT ('0    LARS    MAXIT   IPRIN        TOL              TOLU
     *     ACCM' ,/3I8,3E15.3/'0     THERE ARE',I3,' EQUILIBRIUM CONSTA
     *NTS,',I3,' OF WHICH ARE TO BE REFINED'//'      THERE ARE',I3,
     *' MASS-BALANCE EQUATIONS AND',I3,' UNKNOWN FREE CONCENTRATION(S)
     *PER DATA POINT'//6X,'REACTION TEMPERATURE ',F6.2,
     *' DEGREES CENTIGRADE'/)
    9 FORMAT (1H0,' THEREFORE RUN ABANDONED BEFORE REFINEMENT')
   10 FORMAT (1H0,I5,' DATA POINTS HAVE BEEN READ IN AND',I5,
     *' MAXIMUM WERE EXPECTED'/)
   11 FORMAT ('0   THE NUMBER N OF CONSTANTS TO BE REFINED DOES NOT AGREE
     *WITH THE NUMBER OF POSITIVE KEYS')
   12 FORMAT (/8X,'CURVE',I3,8E12.4/18X,6E12.4)
      READ (JINP,5) TEMP
      WRITE (JOUT,8) LARS,MAXIT,IPRIN,TOL,TOLU,ACCM,NK,N,NMBE,NC,TEMP
      J=0
C         READ IN VALUES OF PARAMETERS, THEIR INDICES AND REFINEMENT KEYS.
C         THE STABILITY CONSTANT IS EQUAL TO BETA TIMES 10 TO THE POWER JPOT,
C         BUT THE PARAMETER VARIED IS BETA
      WRITE (JOUT,2)
      DO 105 I=1,NK
      READ (JINP,4) BETA(I),JPOT(I),(JQR(K,I),K=1,NMBE),KEY(I)
      WRITE(JOUT,1) I,BETA(I),JPOT(I),KEY(I),(JQR(K,I),K=1,NMBE)
C         IF KEY=1 THE PARAMETER IS TO BE REFINED AND THE BETA VALUE IS STORED
C         IN BETAV. THE CORRESPONDING INDEX OF BETA IS STORED IN IVAR.
      IF(KEY(I))105,105,103
  103 J=J+1
      BETAV(J)=BETA(I)
      IVAR(J)=I
C         THE LOGARITHM OF THE STABILITY CONSTANT IS CALCULATED IN HLNB
  105 HLNB(I)=ALOG(BETA(I))+AL10*JPOT(I)
C         CHECK THAT THE NUMBER OF REFINABLE CONSTANTS IS CORRECT
      IF (N-J) 106,107,106
  106 WRITE (JOUT,11)
      WRITE (JOUT,9)
      STOP
  107 NP=IP
      IP=0
      NTC=1
      DO 108 I=1,NC
  108 CX(I)=1.E-07
      IF (NSET) 112,110,112
C         JEL (L) IS THE NUMBER OF ELECTRONS TRANSFERRED AT THE ELECTRODE L.
C         IF JEL(L)=0 THE DECIMAL COLOGARITHM OF THE FREE CONCENTRATION OF THE
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C          SPECIES DETERMINED BY THE ELECTRODE L WILL BE READ IN INSTEAD OF THE
C          E.M.F. VALUE (E.G., PH INSTEAD OF E.M.F.).
  110 READ(JINP,3) (JEL(L),L=1,NEMF)
C          INITIAL READ-IN OF CONCENTRATIONS OF SOLUTION, STANDARD POTENTIALS OF
C          ELECTRODES, CONCENTRATIONS OF TITRANTS AND INITIAL VOL OF SOLUTION
  111 READ(JINP,5) (TOTC(K),K=1,NMBE),(EZERO(L),L=1,NEMF),(ADDC(K),K=1,
     *            NMBE),VINIT
      WRITE(JOUT,12)NTC,(TOTC(K),K=1,NMBE),(EZERO(L),L=1,NEMF),
     *                 (ADDC(K),K=1,NMBE),VINIT
      NTC=NTC+1
  112 IP=IP+1
      IS=LARS
      IF(NSET) 1122,113,1122
 1122 IF (IP-MP) 1126,1126,1124
 1124 IP=IP-1
      RETURN
 1126 DO 1128 L=1,NMBE
      TT(L)=T(IP,L)
 1128 CX(L)=CONC(IP,L)
      GO TO 125
C          POINT-WISE READ-IN OF AMOUNTS OF TITRANT ADDED AND THE MEASURED
C          POTENTIALS. LUIGI IS AN END OF TITRATION CURVE INDICATOR.
  113 READ (JINP,6) LUIGI,(TITRE(K),K=1,NMBE),(EMF(L),L=1,NEMF)
      IS=IS-1
      IF(LUIGI)115,114,115
  114 IF(IS)115,115,113
  115 WRITE(JOUT,6) IP,(TITRE(K),K=1,NMBE),(EMF(L),L=1,NEMF)
      IF (IP-NP)1115,1115,140
 1115 DO 118 L=1,NEMF
      NCPL=NC+L
      IF (JEL(L))116,117,116
  116 CX(NCPL)=EXP((EMF(L)-EZERO(L))*JEL(L)*11.6049/(TEMP+273.16))
      GO TO 118
  117 CX(NCPL)=EXP(-EMF(L)*AL10)
  118 CONTINUE
      VOL=VINIT
      DO 119 K=1,NMBE
  119 VOL=VOL+TITRE(K)
      DO 120 K=1,NMBE
      TT(K)=(TOTC(K)+TITRE(K)*ADDC(K))/VOL
  120 T(IP,K)=TT(K)
C          T(IP,K) HOLDS THE TOTAL CONCENTRATION AT POINT IP OF THE REACTANT K
  125 CALL ML (NK,NMBE,NEMF,NC,HLNB,CI,CX,TT,HX,TOLC,DT,DDT,JQR)
      IF (IFAIL) 129,129,300
  129 DO 130 K=1,NMBE
  130 CONC(IP,K)=CX(K)
C          CONC(IP,K) HOLDS THE FREE CONCENTRATION AT POINT IP OF THE REACTANT K
      IF (NSET) 112,140,112
  140 IF(LUIGI) 200,112,111
  200 WRITE (JOUT,10) IP,NP
C          CHECK THAT THE NUMBER OF POINTS DOES NOT EXCEED THE TOTAL STATED
C          INITIALLY
      IF (IP-NP) 300,300,250
  250 WRITE (JOUT,9)
      STOP
  300 RETURN
      END



      SUBROUTINE ML (NK,NMBE,NEMF,NC,HLNB,CI,CX,TT,HX,TOLC,DT,DDT,JQR)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),CI(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE)
      DIMENSION TOLC(NC),DT(NC),DDT(NC,NC)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCN,NF,IPRIN
     *        ,NRUN,TITLE,IFAIL
C          THIS ROUTINE CALCULATES ESTIMATES OF THE FREE CONCENTRATIONS OF METAL,
C          LIGAND ETC.  USING A NUMBER OF MASS-BALANCE EQUATIONS EQUAL TO THE
C          NUMBER OF UNKNOWNS (THOSE FOR WHICH THERE IS NO POTENTIAL). THE
C          'NEWTON-RAPHSON' METHOD IS USED, WITH FIRST DERIVATIVES ONLY. INITIAL
C          ESTIMATES ARE ALSO REQUIRED FOR THIS ROUTINE, BUT 1.E-07, FOR THE
C          FIRST POINT IN THE FIRST TITRATION CURVE IS SATISFACTORY. INITIAL
C          ESTIMATES FOR THE OTHER POINTS ARE TAKEN AS THE VALUE OBTAINED FOR THE
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C         PREVIOUS POINT.
      DO 102 I=1,NEMF
      IPNC=I+NC
  102 HX(IPNC)=ALOG(CX(IPNC))
      NCICL=0
C         A CYCLE COUNTER. 100 CYCLES ARE PERMITTED AS MAXIMUM.
      DO 105 I=1,NC
C         TOLC(I) PROVIDES A RELATIVE TOLERANCE FOR USE WITH THE CONVERGENCE
C         CRITERION
  105 TOLC(I)=TT(I)*TOL
  121 NCICL=NCICL+1
      DO 125 J=1,NC
C         CX(J) IS ONE OF THE UNKNOWN CONCENTRATIONS THAT ARE BEING CALCULATED.
C         AS IT CANNOT TAKE A NEGATIVE VALUE, THE STEP LENGTH OF THE CORRECTION
C         VECTOR HX IS REDUCED SO THAT NONE OF THEM TAKES A NEGATIVE VALUE
  122 IF(CX(J))123,123,125
  123 DO 124 I=1,NC
      HX(I)=0.5*HX(I)
  124 CX(I)=CX(I)-HX(I)
      GO TO 122
  125 CONTINUE
      DO 126 I=1,NC
      HX(I)=ALOG(CX(I))
C         DT(I) IS THE DIFFERENCE BETWEEN T OBSERVED AND T CALCULATED FOR THE
C         MASS-BALANCE EQUATION (I), I.E. IT IS THE RESIDUAL.
  126 DT(I)=CX(I)-TT(I)
      DO 1128 J=1,NK
      W=HLNB(J)
      DO 1127 I=1,NMBE
      IF (JQR(I,J))127,1127,127
  127 W=W+HX(I)*JQR(I,J)
 1127 CONTINUE
C         CI(J) IS THE CONCENTRATION OF THE SPECIES (J) DEFINED BY THE INDICES
C         IN JQR
      CI(J)=EXP(W)
      DO 128 I=1,NC
      IF (JQR(I,J))128,1128,128
  128 DT(I)=DT(I)+JQR(I,J)*CI(J)
 1128 CONTINUE
      DO 129 I=1,NC
C         CONVERGENCE CRITERION. WHEN ALL THE MASS-BALANCE EQUATIONS ARE
C         SATISFIED TO THE REQUIRED RELATIVE TOLERANCE, CONTROL IS PASSED BACK
C         TO DINP
      IF(ABS(DT(I))-TOLC(I))129,129,131
  129 CONTINUE
      GO TO 190
  131 DO 152 I=1,NC
      DO 151 J=1,NC
C         DDT IS THE JACOBIAN FOR THE SYSTEM, AND IT IS SYMMETRICAL AND SQUARE.
C         ITS ELEMENTS ARE THE RELATIVE DERIVATIVES, SO THAT THEY ARE OBTAINED
C         DIRECTLY FROM THE CONCENTRATION TERMS PREVIOUSLY CALCULATED.
      DDT(I,J)=0.
      DO 151 L=1,NK
      IF(JQR(I,L))149,151,149
  149 IF(JQR(J,L))150,151,150
  150 W=JQR(I,L)*JQR(J,L)*CI(L)
      DDT(I,J)=DDT(I,J)+W
  151 CONTINUE
  152 DDT(I,I)=DDT(I,I)+CX(I)
      CALL LINEQ(DDT,NC,DT,1,4)
      IF (IFAIL) 160,160,190
C         DT CONTAINS THE RELATIVE CORRECTIONS TO THE PARAMETERS. HX WILL
C         CONTAIN THE ABSOLUTE CORRECTIONS.
  160 DO 165 I=1,NC
      HX(I)=-DT(I)*CX(I)
  165 CX(I)=CX(I)+HX(I)
C         IF 100 CYCLES HAVE BEEN EXCEEDED, WHICH IS MOST UNLIKELY, CONTROL IS
C         PASSED BACK TO DINP WITHOUT ANY FAILURE INDICATION. THIS IS BECAUSE
C         ML IS ONLY USED TO CALCULATE INITIAL ESTIMATES FOR MINIM, AND THESE
C         NEED NOT BE VERY GOOD.
      IF(NCICL -100) 121,121,190
  190 RETURN
      END
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      SUBROUTINE LINEQ (A,N,B,M,JFAIL)
      DIMENSION TITLE(20),A(N,N),B(N,M)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *        ,NRUN,TITLE,IFAIL
C          SOLVES THE N SIMULTANEOUS LINEAR EQUATIONS A*X=B WITH M RIGHT-HAND
C          SIDES IN B. THE SOLUTION VECTORS ARE LEFT IN B AND THE MATRIX IS
C          REPLACED BY ITS INVERSE. AFTER CHOLESKI FACTORING OF A TO GIVE A=L*LT,
C          THE FORWARD SUBSTITUTIONS L*Y=B AND L*Z=E AND THE BACKWARD SUBSITUTION
C          LT*X=Y AND LT*AINV=Z ARE PERFORMED
      IF (N-1) 45,5,9
    5 T=A(1,1)
      IF (T-ACCM) 45,45,6
    6 A(1,1)=1./T
      DO 7 J=1,M
    7 B(1,J)=B(1,J)/T
      RETURN
    9 DO 80 I=1,N
      I1=I-1
      DO 70 J=I,N
      S=A(I,J)
      IF (I1) 10,30,10
   10 DO 20 K=1,I1
   20 S=S-A(I,K)*A(J,K)
   30 X=S
      IF (J-I) 60,40,60
   40 IF (X) 45,45,50
   45 IFAIL=JFAIL
      GO TO 400
   50 A(I,I)=1./SQRT(X)
      GO TO 70
   60 A(J,I)=X*A(I,I)
   70 CONTINUE
   80 CONTINUE
C          FORWARD SUBSTITUTION ON RIGHT HAND SIDES
      DO 125 J=1,M
      B(1,J)=B(1,J)*A(1,1)
      DO 120 I=2,N
      I1=I-1
      S=B(I,J)
      DO 110 K=1,I1
  110 S=S-A(I,K)*B(K,J)
  120 B(I,J)=S*A(I,I)
  125 CONTINUE
C          FORWARD SUBSTITUTION FOR INVERSION
      DO 170 J=1,N
      J1=J+1
      IF (J1-N) 140,140,170
  140 DO 160 I=J1,N
      I1=I-1
      S=0.
      DO 150 K=J,I1
  150 S=S-A(I,K)*A(J,K)
  160 A(J,I)=S*A(I,I)
  170 CONTINUE
C          BACKWARD SUBSTITUTION
      DO 210 J=1,M
  210 B(N,J)=B(N,J)*A(N,N)
      DO 220 J=1,N
  220 A(J,N)=A(J,N)*A(N,N)
      DO 290 II=2,N
      I=N-II+1
      T=A(I,I)
      I1=I+1
      DO 245 J=1,M
      S=B(I,J)
      DO 240 K=I1,N
  240 S=S-A(K,I)*B(K,J)
  245 B(I,J)=S*T
      DO 280 J=1,I
      S=A(J,I)
      DO 270 K=I1,N
  270 S=S-A(K,I)*A(J,K)
      A(J,I)=S*T
  280 CONTINUE
```

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  290 CONTINUE
      DO 300 I=2,N
      I1=I-1
      DO 300 J=1,I1
  300 A(I,J)=A(J,I)
  400 RETURN
      END



      SUBROUTINE CALC (NK,N,NMBE,NC,IP,BETAV,JPOT,JQR,HLNB,T,CONC,IVAR,
     *                 U,A,GC,DGB,EPS,HX,TT,CI,CX,NPNC,NP,KEY)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),JPOT(NK),CI(NK),KEY(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),CONC(NP,NMBE)
      DIMENSION A(NMBE,NPNC)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE),EPS(NMBE)
      DIMENSION BETAV(N),IVAR(N),DGB(N)
      DIMENSION GC(NC)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         THIS SUBROUTINE CALCULATES, FOR ONE DATA POINT AT A TIME, THE ELEMENTS
C         OF THE DESIGN MATRIX AND GRADIENT VECTOR. IT ALSO CALCULATES THE
C         SQUARED TERM THAT GOES TO MAKE UP THE SUM OF SQUARES.
C
C         IP IS THE INDEX OF THE DATA POINT. THE VALUES OF THE LOGARITHMS OF THE
C         PARAMETERS ARE CALCULATED AT THE FIRST DATA POINT , AND CAN THEN BE
C         USED FOR ALL. IVAR IS AN INDEX VECTOR RELATING THE REFINABLE
C         PARAMETERS, BETAV, TO THE VECTOR BETA.
      IF(IP-1) 100,100,110
  100 DO 102 I=1,N
      IV=IVAR(I)
  102 HLNB(IV)=ALOG(BETAV(I))+AL10*JPOT(IV)
      NF=NF+1
  110 DO 112 K=1,NMBE
      CX(K)=CONC(IP,K)
      HX(K)=ALOG (ABS(CX(K)))
  112 TT(K)=T(IP,K)
      DO 122 I=1,NK
      IF (KEY(I)) 122,116,116
  116 W=HLNB(I)
      DO 120 J=1,NMBE
      IF(JQR(J,I))118,120,118
  118 W=W+JQR(J,I)*HX(J)
  120 CONTINUE
      CI(I)=EXP(W)
  122 CONTINUE
C         CI NOW HOLDS THE CONCENTRATIONS OF ALL THE SPECIES IN SOLUTION. TT(I)
C         IS THE OBSERVED TOTAL CONCENTRATION FOR MASS-BALANCE EQUATION (I),
C         EPS(I) WILL BE THE RESIDUAL, CALCULATED-OBSERVED. THE SUM OF SQUARES I
C         ACCUMULATED IN U.
      DO 136 I=1,NC
      IF(CX(I))132,136,136
  132 DO 135 J=1,NK
      IF (JQR(I,J))133,135,133
  133 CI(J)=CI(J)*((-1.)**JQR(I,J))
  135 CONTINUE
  136 CONTINUE
      DO 205 I=1,NMBE
      EPS(I)=CX(I)-TT(I)
      DO 204 J=1,NK
      IF (JQR(I,J)) 203,204,203
  203 EPS(I)=EPS(I)+JQR(I,J)*CI(J)
  204 CONTINUE
  205 U= U+EPS(I)*EPS(I)
C         THE MATRIX A WILL HOLD THE ELEMENTS OF THE DESIGN MATRIX. THE BLOCK
C         RELATIVE TO THE UNKNOWN FREE CONCENTRATIONS  IS PLACED IN THE FIRST NC
C         COLUMNS, AND THE BLOCK RELATING TO THE PARAMETERS BETAV IN THE LAST N
C         COLUMNS. SINCE THE FACTORISATION CAN PROCEED POINT BY POINT, NOT ALL
C         OF THE DESIGN MATRIX  NEED BE STORED.
      DO 209 I=1,NMBE
      DO 209 J=1,NPNC
  209 A(I,J)=0.
      DO 210 J=1,NC
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  210 A(J,J)=CX(J)
      DO 215 I=1,NMBE
      DO 213 J=1,NC
      DO 213 L=1,NK
      IF(JQR(J,L))211,213,211
  211 IF(JQR(I,L))212,213,212
  212 A(I,J)=A(I,J)+JQR(J,L)*JQR(I,L)*CI(L)
  213 CONTINUE
      DO 215 J=1,N
      IV=IVAR(J)
      IF (JQR(I,IV)) 214,215,214
  214 JPNC=J+NC
      A(I,JPNC)=JQR(I,IV)*CI(IV)
  215 CONTINUE
C         GC WILL HOLD THAT PART OF THE GRADIENT VECTOR RELATING TO POINT IP AND
C         THE UNKNOWN FREE CONCENTRATIONS AT THAT POINT. DGB WILL DO THE SAME
C         FOR THE PARAMETERS BETAV.
      DO 232 I=1,NC
      GC(I)=0.
      DO 232 J=1,NMBE
  232 GC(I)=GC(I)-A(J,I)*EPS(J)
      DO 235 I=1,N
      DGB(I)=0.
      IPNC=I+NC
      DO 235 J=1,NMBE
  235 DGB(I)=DGB(I)-A(J,IPNC)*EPS(J)
      RETURN
      END



      SUBROUTINE LIMIN (X,F,XSTEP,RACC,MAXFN,NK ,N ,NMBE,NC,NEMF,LP,
     * NP,BETAV,BETA,JPOT,JQR,HLNB,T,CONC,IVAR,CX,SB,SC,HX,TT,CI,NM,KEY)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),JPOT(NK),BETA(NK),CI(NK),KEY(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),CONC(NP,NMBE)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE)
      DIMENSION BETAV(N),IVAR(N),SB(N)
      DIMENSION SC(NM)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         LINEAR MINIMISATION. A QUADRATIC FUNCTION IS MINIMISED WITH
C         CALCULATION OF FUNCTION VALUES ONLY.
  100 FORMAT (1H0,'LINEAR MINIMIZATION'//12X,1HX,15X,2HFA,15X,2HFB,
     * 15X,2HFC,/E17.7)
  101 FORMAT (1H+,17X,3E17.7/E17.7)
      IF (IPRIN) 48,49,48
   48 WRITE (JOUT,100) X
   49 IS=4
      IFAIL=-1
      IINC=1
      XINC=XSTEP+XSTEP
      MC=1
      FA=0.
      FB=0.
      GOTO 1
    3 IF (IPRIN) 46,47,46
   46 WRITE (JOUT,101) FA,FB,FC,X
   47 MC=MC+1
      IF (MAXFN-MC) 12,15,15
   12 IFAIL=1
C         ITERATION CYCLES EXHAUSTED BEFORE REACHING MINIMUM WITH REQUIRED
C         TOLERANCE.
   43 X=DB
      F=FB
      IF (FB-FC) 15,15,44
   44 X=DC
      F=FC
   15 IF (IFAIL) 2,50,50
    2 CALL FUNCT (NK ,N,NMBE,NC,NEMF,LP,NP,BETAV,BETA,JPOT,JQR,HLNB,
     *              T,CONC,IVAR,CX,SB,SC,X,HX,TT,CI,F,NM,KEY)
    1 GOTO (5,6,7,8), IS
    8 IS=3
    4 DC=X
```

```
      FC=F
      X=X+XSTEP
      GOTO 3
    7 IF (FC-F) 9,10,11
   10 X=X+XINC
      XINC=XINC+XINC
      GOTO 3
    9 DB=X
      FB=F
      XINC=-XINC
      GOTO 13
   11 DB=DC
      FB=FC
      DC=X
      FC=F
   13 X=DC+DC-DB
      IS=2
      GOTO 3
    6 DA=DB
      DB=DC
      FA=FB
      FB=FC
   32 DC=X
      FC=F
      GOTO 14
    5 IF (FB-FC) 16,17,17
   17 IF (F-FB) 18,32,32
   18 FA=FB
      DA=DB
   19 FB=F
      DB=X
      GOTO 14
   16 IF (FA-FC) 21,21,20
   20 XINC=FA
      FA=FC
      FC=XINC
      XINC=DA
      DA=DC
      DC=XINC
   21 XINC=DC
      IF ((D-DB)*(D-DC)) 32,22,22
   22 IF (F-FA) 23,24,24
   23 FC=FB
      DC=DB
      GOTO 19
   24 FA=F
      DA=X
   14 IF (FB-FC) 25,25,29
   25 IINC=2
      XINC=DC
      IF (FB-FC) 29,45,29
   29 D=(FA-FB)/(DA-DB)-(FA-FC)/(DA-DC)
      IF (D*(DB-DC)) 33,33,37
   37 D=0.5*(DB+DC-(FB-FC)/D)
      IF (ABS(D-X)-ABS(D*RACC)) 34,34,36
   34 IFAIL=0
      GOTO 43
   36 IS=1
      X=D
      IF ((DA-DC)*(DC-D))3,26,38
   38 IS=2
      GOTO (39,40),IINC
   39 IF (ABS(XINC)-ABS(DC-D)) 41,3,3
   33 IS=2
      GOTO (41,42),IINC
   41 X=DC
      GOTO 10
   40 IF (ABS(XINC-X)-ABS(X-DC)) 42,42,3
   42 X=0.5*(XINC+DC)
      IF ((XINC-X)*(X-DC)) 26,26,3
   45 X=0.5*(DB+DC)
      IF ((DB-X)*(X-DC))26,26,3
   26 IFAIL=2
C          THE FUNCTION CANNOT BE MINIMISED.
      GOTO 43
```

```
   50 RETURN
      END



      SUBROUTINE MON1 (N,M,U,T,X,JPOT,S,SD,IVAR,JF)
      DIMENSION X(N),S(N),SD(N),IVAR(N),JPOT(M)
      DIMENSION TITLE(20)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         OPTIONAL MONITOR OF THE PROGRESS OF THE MINIMIZATION
      IF (IPRIN) 1,3,1
    1 WRITE (JOUT,4) NRUN,U,JF,T
      WRITE (JOUT,5)
      DO 2 I=1,N
      K=IVAR(I)
    2 WRITE (JOUT,6) K,X(I),JPOT(K),S(I),SD(I)
    3 RETURN
    4 FORMAT (7H0 CYCLE,I4,5H  U =,E14.7/
     * 10X,I4,' FUNCTIONS CALCULATED'/
     * 10X,' FRACTION OF STEP LENGTH TAKEN',F10.4/)
    5 FORMAT (1H ,21X,'    VALUE     REL. SHIFT  STD.DEVN.(REL.PERCENT
     * )')
    6 FORMAT (17H           BETA (,I2,1H),F10.5,'E',I3,E13.5,F14.2)
      END



      SUBROUTINE DOUT (M,N,NMBE,X,JPOT,JQR,IVAR,SD,U,KEY,COCO,HLNB)
      DIMENSION IVAR(N),SD(N),COCO(N,N),X(N)
      DIMENSION JPOT(M),KEY(M),HLNB(M)
      DIMENSION JQR(NMBE,M)
      DIMENSION TITLE(20)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         GENERAL OUTPUT ROUTINE
      WRITE (JOUT,100) TITLE
      IF (IFAIL) 7,8,7
    7 GOTO (1,2,3,4,5,6),IFAIL
    1 WRITE (JOUT,101)
      GOTO 9
    2 WRITE (JOUT,102)
      GOTO 9
    3 WRITE (JOUT,103)
      GOTO 16
    4 WRITE (JOUT,104)
      GOTO 16
    5 WRITE (JOUT,105)
      GOTO 16
    6 WRITE (JOUT,106)
      GOTO 9
    8 WRITE (JOUT,107)
    9 WRITE (JOUT,108) NRUN,NF,U
      K=1
      DO 13 I=1,M
      WRITE (JOUT,109) I,(JQR(J,I),J=1,NMBE)
      IF (KEY(I)) 10,11,12
   10 WRITE (JOUT,110)
      GOTO 13
   11 WRITE (JOUT,111)
      XC=EXP(HLNB(I)-AL10*JPOT(I))
      WRITE (JOUT,113) XC,JPOT(I)
      GOTO 13
   12 WRITE (JOUT,112)
      IV=IVAR(K)
      SDC=SD(K)*X(K)/100.
      XL=ALOG(X(K))/AL10+JPOT(IV)
      SDL=SD(K)/100./AL10
      WRITE (JOUT,114) X(K),JPOT(IV),SDC,JPOT(IV),XL,SDL
      K=K+1
   13 CONTINUE
      IF (N-1) 16,16,130
  130 WRITE (JOUT,115)
      DO 15 I=2,N
      IM=I-1
```

```
      WRITE (JOUT,116) IVAR(I),(COCO(I,J),J=1,IM)
   15 CONTINUE
      WRITE (JOUT,117) (IVAR(J),J=1,IM)
   16 RETURN
  100 FORMAT (1H1,20A4)
  101 FORMAT (1H ,'LINEAR MINIMIZATION FAILED, BUT REFINEMENT CONTINUED
     * TO EVENTUAL SUCCESS')
  102 FORMAT (1H ,'FAILURE IN LINEAR MINIMIZATION, REFINEMENT TERMINATED
     *')
  103 FORMAT (1H ,'MATRIX OF NORMAL EQUATIONS NOT POSITIVE DEFINITE, REF
     *INEMENT ABANDONED')
  104 FORMAT (1H ,'FAILURE TO CALCULATE INITIAL FREE CONCENTRATIONS,
     *NO REFINEMENT ATTEMPTED')
  105 FORMAT (1H ,'FAILURE IN FACTORIZATION PROCESS, REFINEMENT ABANDONED

  106 FORMAT (1H ,'MAXIMIMUM NO. OF ITERATIONS PERFORMED, REFINEMENT TER
     *MINATED')
  107 FORMAT (1H ,'REFINEMENT CONVERGED SUCCESSFULLY')
  108 FORMAT (I4,' ITERATIONS',I4,' FUNCTION CALLS'/
     *' SUM OF SQUARES =',E17.9//32X,'    VALUE     STD. DEVIATION   LO
     *G BETA   STD. DEVIATION'//)
  109 FORMAT (' BETA (',I2,')  ',5I2)
  110 FORMAT (32H+                              NEGATIVE)
  111 FORMAT (32H+                              CONSTANT)
  112 FORMAT (32H+                              REFINED )
  113 FORMAT (1H+,32X,F10.5,'E',I3)
  114 FORMAT (1H+,32X,2(F10.5,'E',I3),2F12.5)
  115 FORMAT (1H0,'MATRIX OF CORRELATION COEFFICIENTS RHO I,J'//4H   I/)
  116 FORMAT (I4,11F10.3/5X,11F10.3)
  117 FORMAT (6H0  J   ,I5,10I10/11I10)
      END


      SUBROUTINE NEG (N,M,X,T,SHIFT,KEY,IVAR,HLNB,JPOT,CI)
      DIMENSION X(N),SHIFT(N),IVAR(N),HLNB(M),JPOT(M),KEY(M),CI(M)
      DIMENSION TITLE(20)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         CHECK FOR NEGATIVE FORMATION CONSTANTS. IF ANY ARE FOUND, THE FRACTION
C         T OF THE VECTOR SHIFT IS ALTERED SO THAT ONE OF THE PARAMETERS GOES TO
C         ZERO AND THE OTHERS REMAIN POSITIVE. THE CONCENTRATION OF THE SPECIES,
C         THUS ELIMINATED, IS SET EQUAL TO ZERO AND ITS KEY TO -1. THE VECTORS
C         IVAR, X, AND SHIFT ARE COMPACTED, IF NECESSARY.
      J=0
      DO 4 I=1,N
      XT=X(I)+T*SHIFT(I)
      IF (XT) 1,1,4
    1 T=-X(I)/SHIFT(I)
      J=I
    4 CONTINUE
C         IF J .NE. 0 IT HOLDS THE INDEX OF THE PARAMETER TO BE ELIMINATED.
      IF (J) 5,9,5
    5 IV=IVAR(J)
      KEY(IV)=-1
      CI(IV)=0.
      IF (J-N) 6,8,8
    6 NM=N-1
      DO 7 I=J,NM
      IP=I+1
      IVAR(I)=IVAR(IP)
      SHIFT(I)=SHIFT(IP)
    7 X(I)=X(IP)
    8 IFAIL=-1
      WRITE (JOUT,100) IV
  100 FORMAT ('0BETA (',I2,') NEGATIVE')
    9 RETURN
      END


      SUBROUTINE MINIM (NK,N,NMBE,NC,NEMF,NP,BETAV,JPOT,JQR,HLNB,T,C,
     *          IVAR,A,X1,Y1,EPS,HX,TT,CI,CX,BB,SB,SC,SIGMA,BETA,LP,
     *          NPNC,NM,U,KEY,B,D,DY,B1,PERC1,PERC2,D1,JF)
      DIMENSION TITLE(20)
```

```
      DIMENSION HLNB(NK),JPOT(NK),BETA(NK),KEY(NK),CI(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),C(NP,NMBE)
      DIMENSION A(NMBE,NPNC),B(NC,NPNC)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE),EPS(NMBE)
      DIMENSION BETAV(N),IVAR(N),Y1(N),SB(N),BB(N,N),SIGMA(N),DY(N)
      DIMENSION X1(NC),B1(NC,NC),D1(NC,N)
      DIMENSION SC(NM),D(NM,N)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *    ,NRUN,TITLE,IFAIL
C         A GENERAL MINIMISATION ROUTINE USING THE GAUSS-NEWTON METHOD WITH
C         LINEAR OPTIMISATION OF THE SHIFTS. THE ROUTINE ALSO CONTAINS THE
C         FACTORISATION OF THE MATRIX OF THE NORMAL EQUATIONS APPROPRIATE TO
C         EQUILIBRIA IN SOLUTION. THE PARAMETERS ARE DIVIDED IN TWO KINDS, THE
C         UNKNOWNS FREE CONCENTRATIONS AND THE FORMATION CONSTANTS BETAV. THE
C         SUM OF SQUARES IS DENOTED BY U.
      NC1=NC+1
  100 U=0.
      NN=0
C         IEXIT IS USED TO TEST THE CONVERGENCE CRITERIA
      IEXIT=2
      DO 101 I=1,N
      SB(I)=0.
      DO 101 J=1,N
  101 BB(I,J)=0.
C         LOOP FOR EACH EXPERIMENTAL DATA POINT.
      DO 200 IP=1,LP
      CALL CALC (NK,N,NMBE,NC,IP,BETAV,JPOT,JQR,HLNB,T,C,IVAR, U,A,X1,
     *           Y1,EPS,HX,TT,CI,CX,NPNC,NP,KEY)
C         RECOVER THE PARTIAL DESIGN MATRIX FROM CALC AND FORM THE UNFACTORISED
C         NORMAL EQUATION MATRIX WITH RESPECT TO THE UNKNOWN FREE CONCENTRATIONS
C         IN B.
      DO 110 I=1,NC
      DO 110 J=1,NPNC
      B(I,J)=0.
      DO 110 K=1,NMBE
  110 B(I,J)=B(I,J)+A(K,I)*A(K,J)
C         THE FACTORISATION PROCESS BEGINS HERE.
      DO 132 I=1,NC
      DO 131 J=1,N
      K=J+NC
  131 D1(I,J)=-B(I,K)
      DO 132 J=1,NC
  132 B1(I,J)=B(I,J)
      CALL LINEQ (B1,NC,D1,N,5)
      IF (IFAIL-5) 140,400,140
C         CALCULATE THE FACTORISATION MATRIX D.
  140 DO 160 I=1,NC
      L=I+NN
      DO 150 J=1,N
  150 D(L,J)=D1(I,J)
C         SINCE THE FACTORISATION PROCESS DOES NOT ALTER THAT PART OF THE NORMAL
C         EQUATIONS MATRIX PERTAINING TO THE UNKNOWN FREE CONCENTRATIONS, THE
C         SHIFTS IN THESE MAY NOW BE CALCULATED, AND PLACED IN SC.
      SC(L)=0.
      DO 160 K=1,NC
  160 SC(L)=SC(L)+B1(I,K)*X1(K)
C         THE CALCULATION OF THE SHIFTS TO BE APPLIED TO THE PARAMETERS BETAV
C         BEGINS. THE FACTORISED NORMAL EQUATION MATRIX IS TOTALISED IN BB, AND
C         THE GRADIENT OF U WITH RESPECT TO BETAV IS CORRECTED FOR THE
C         FACTORISATION AND TOTALISED IN SB.
      DO 190 I=NC1,NPNC
      L=I-NC
      DO 180 J=1,NPNC
      M=J-NC
      DO 170 K=1,NMBE
  170 BB(L,M)=BB(L,M)+A(K,I)*A(K,J)
      DO 180 K=1,NC
      KN=K+NN
  180 BB(L,M)=BB(L,M)+D(KN,L)*B(K,J)
      SB(L)=SB(L)+Y1(L)
      DO 190 K=1,NC
      KN=K+NN
  190 SB(L)=SB(L)+D(KN,L)*X1(K)
  200 NN=NN+NC
```

```
C         END OF THE POINT BY POINT LOOP. THE SHIFTS AND STANDARD DEVIATIONS IN
C         BETAV CAN NOW BE CALCULATED.
      DO 210 I=1,N
  210 DY(I)=SB(I)
      CALL LINEQ (BB,N,DY,1,3)
      IF (IFAIL-3) 214,400,214
C         THE SHIFTS FOR BETAV WILL BE IN DY. IF THEY ARE ALL LESS THAN THE
C         TOLERANCE SPECIFIED AS A CONVERGENCE CRITERION, THE MINIMISATION IS
C         STOPPED.
  214 DO 223 I=1,N
      IF (ABS(DY(I))-TOL) 223,223,222
  222 IEXIT=1
      GO TO 225
  223 CONTINUE
C         THE SHIFTS IN THE CONCENTRATIONS MUST AGAIN BE CORRECTED FOR THE
C         EFFECTS OF THE FACTORISATION (SHIFT=D*(D INV*SHIFT)), THIS CORRECTION
C         WAS NOT NEEDED FOR THE SHIFTS IN BETAV. THE CORRECTED SHIFTS ARE THEN
C         ALSO SUBJECTED TO A CONVERGENCE TEST.
  225 DO 233 I=1,NM
      DO 230 J=1,N
  230 SC(I)=SC(I)+D(I,J)*DY(J)
      GO TO (233,231),IEXIT
  231 IF (ABS(SC(I))-TOL) 233,233,232
  232 IEXIT=1
  233 CONTINUE
C         CONVERT THE RELATIVE SHIFTS IN SC AND SB TO ABSOLUTE SHIFTS
      K=0
      DO 240 I=1,LP
      DO 240 J=1,NC
      K=K+1
  240 SC(K)=SC(K)*C(I,J)
      DO 250 I=1,N
  250 SB(I)=DY(I)*BETAV(I)
C         CALCULATE THE STANDARD DEVIATIONS IN SIGMA AND THE MATRIX OF
C         CORRELATION COEFFICIENTS IN BB.
      W=FLOAT((NMBE-NC)*LP-N)
      W=SQRT(U/W)*100
      DO 260 I=1,N
      Y1(I)=SQRT(BB(I,I))
  260 SIGMA(I)=Y1(I)*W
      DO 265 I=1,N
      DO 265 J=1,I
  265 BB(I,J)=BB(I,J)/Y1(I)/Y1(J)
C         CHECK ON THE NUMBER OF ITERATION CYCLES PERFORMED
      IF (NRUN-MAXIT) 270,390,390
  270 IF (NRUN) 300,300,280
  280 GO TO (300,290),IEXIT
C         FINAL CONVERGENCE TEST
  290 IF ((U1-U)/U-TOLU) 400,300,300
  300 U1=U
      JF=NF-JF
      CALL MON1 (N,NK,U,PERC1,BETAV,JPOT,DY,SIGMA,IVAR,JF)
      JF=NF
      PERC1=0.
      CALL LIMIN (PERC1,U,PERC2,.2,10,NK,N,NMBE,NC,NENF,LP,NP,BETAV,
     *          BETA,JPOT,JQR,HLNB,T,C,IVAR,CX,SB,SC,HX,TT,CI,NM,KEY)
C         SET THE LINEARLY MINIMISED PARAMETER FOR THE NEXT CYCLE
      PERC2=PERC1
      IF (IFAIL-1) 330,310,400
C         IF THE LINEAR MINIMISATION HAD NOT CONVERGED AFTER TEN CYCLES CONTROL
C         IS PASSED BACK TO THE MAIN PROGRAM IF U HAS NOT BEEN DECREASED AT ALL.
  310 IF (U-U1) 330,320,320
  320 IFAIL=2
      GO TO 400
  330 CALL NEG (N,NK,BETAV,PERC1,SB,KEY,IVAR,HLNB,JPOT,CI)
C         APPLY THE ABSOLUTE SHIFTS TO THE UNKNOWN FREE CONCENTRATIONS AND THE
C         BETAV.
      DO 340 I=1,N
  340 BETAV(I)=BETAV(I)+PERC1*SB(I)
      K=0
      DO 350 IP=1,LP
      DO 350 J=1,NC
      K=K+1
  350 C(IP,J)=C(IP,J)+PERC1*SC(K)
      NRUN=NRUN+1
```

```
      IF(IFAIL)400,100,100
  390 IFAIL=6
  400 RETURN
      END



      SUBROUTINE FUNCT (NK,N,NMBE,NC,NEMF,LP,NP,BETAV,BETA,JPOT,JQR,HLNB
     *                 ,T,CONC,IVAR,CX,SB,SC,PERC,HX,TT,CI,U,NM,KEY)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),JPOT(NK),BETA(NK),CI(NK),KEY(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),CONC(NP,NMBE)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE)
      DIMENSION BETAV(N),IVAR(N),SB(N)
      DIMENSION SC(NM)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
C         THIS SUBROUTINE CALCULATES ONLY THE SUM OF SQUARES FOR ALL THE DATA
C         POINTS, AND IS CALLED BY THE LINEAR MINIMISATION ROUTINE LIMIN. THE
C         LENGTH OF THE SHIFT VECTORS (SC FOR THE UNKNOWN FREE CONCENTRATIONS,
C         SB FOR THE PARAMETERS BETAV) ARE MULTIPLIED BY THE SCALAR PERC WHICH
C         IS THE VARIABLE BEING OPTIMISED IN LIMIN. THE CALCULATION IS SIMILAR TO
C         THE ONE PERFORMED IN CALC, EXCEPT THAT NO DESIGN MATRIX OR GRADIENT IS
C         COMPUTED.
      U=0.
      NF=NF+1
      DO 102 I=1,N
      IV=IVAR(I)
C         THE INITIAL VALUE IN BETA(IV) IS NO LONGER REQUIRED SINCE THE UPDATED
C         VALUE IS IN BETAV. BETA(IV) THEREFORE IS USED TO STORE THE TEMPORARY
C         VALUE NEEDED BY THE LINEAR MINIMISATION. CX WILL HOLD THE TRIAL VALUES
C         OF THE UNKNOWN FREE CONCENTRATIONS.
      BETA(IV)=BETAV(I)+PERC*SB(I)
      W=ABS(BETA(IV))
  102 HLNB(IV)=ALOG(W)+AL10*JPOT(IV)
      KP=0
      DO 300 IP=1,LP
      DO 120 I=1,NEMF
      IPNC=I+NC
  120 CX(IPNC)=CONC(IP,IPNC)
      DO 130 I=1,NC
      KP=KP+1
  130 CX(I)=CONC(IP,I)+PERC*SC(KP)
      DO 140 I=1,NMBE
      HX(I)=ALOG(ABS(CX(I)))
  140 TT(I)=T(IP,I)
      DO 152 I=1,NK
      IF (KEY(I)) 152,146,146
  146 W=HLNB(I)
      DO 149 J=1,NMBE
      IF(JQR(J,I))148,149,148
  148 W=W+JQR(J,I)*HX(J)
  149 CONTINUE
      CI(I)=EXP(W)
  152 CONTINUE
      DO 160 I=1,N
      IV=IVAR(I)
C         THE PARAMETERS BETA ARE PERMITTED NEGATIVE VALUES DURING THE LINEAR
C         MINIMISATION, BUT SINCE THE ABSOLUTE VALUE WAS TAKEN AT STATEMENT 102
C         A CHECK IS NEEDED HERE TO SEE IF BETA(IV) IS REALLY NEGATIVE.
      IF(BETA(IV))158,160,160
  158 CI(IV)=-CI(IV)
  160 CONTINUE
      DO 166 I=1,NC
      IF (CX(I)) 162,166,166
  162 DO 165 J=1,NK
      IF (JQR(I,J))163,165,163
  163 CI(J)=CI(J)*((-1.)**JQR(I,J))
  165 CONTINUE
  166 CONTINUE
      DO 170 I=1,NMBE
      EPS=CX(I)-TT(I)
      DO 168 J=1,NK
  168 EPS=EPS+JQR(I,J)*CI(J)
```

```
  170 U=U+EPS*EPS
  300 CONTINUE
      RETURN
      END



      SUBROUTINE STATS (NK,N,NMBE,NC,BETAV,JPOT,JQR,HLNB,T,CONC,IVAR,DU,
     *                  A,GC,DGB,EPS,HX,TT,CI,CX,NPNC,LP,NP,NM,U,D,KEY,
     *                  JS,JP,NKE)
      INTEGER PLUS,BLANK,STAR,SYM(20),PT(116)
      DIMENSION JPOP(8),CLIM(8),EXFR(8)
      DIMENSION TITLE(20)
      DIMENSION HLNB(NK),JPOT(NK),CI(NK),KEY(NK),JS(NK)
      DIMENSION JQR(NMBE,NK)
      DIMENSION T(NP,NMBE),CONC(NP,NMBE)
      DIMENSION A(NMBE,NPNC)
      DIMENSION CX(NMBE),TT(NMBE),HX(NMBE),EPS(NMBE),JP(NMBE)
      DIMENSION BETAV(N),IVAR(N),DGB(N)
      DIMENSION GC(NC)
      DIMENSION D(LP,NKE)
      COMMON JINP,JOUT,AL10,LARS,MAXIT,TOL,TOLU,ACCM,NF,IPRIN
     *       ,NRUN,TITLE,IFAIL
      DATA PLUS,BLANK,STAR,SYM/'+',' ','*','A','B','C','D','E','F','G',
     *     'H','I','J','K','L','M','N','O','P','Q','R','S','T'/
C          A STATISTICAL ANALYSIS OF THE RESIDUALS OF ALL THE MASS BALANCE
C          EQUATIONS. FOR FURTHER DETAILS SEE M.R. SPIEGEL,
C          THEORY AND PROBLEMS OF STATISTICS, MC GRAW HILL.
    1 FORMAT ('1 STATISTICS ON', 20A4//)
    2 FORMAT(I5,5X,10E11.3)
    3 FORMAT (7I5)
    4 FORMAT (//' R FACTOR =', F12.6)
    6 FORMAT (I5,E13.4,4X,12F8.2/18X,8F8.2)
    7 FORMAT (1H1,' TABLE OF FORMATION PERCENTAGES'/)
   10 FORMAT (//E15.5,'      ARITHMETIC MEAN'/
     *          E15.5,'      MEAN DEVIATION'/
     *          E15.5,'      STANDARD DEVIATION'/
     *          E15.5,'      VARIANCE'/
     *          E15.5,'      MOMENT COEFFICIENT OF SKEWNESS'/
     *          E15.5,'      MOMENT COEFFICIENT OF KURTOSIS'//)
   11 FORMAT (' CONCENTRATIONS AND RESIDUALS TABLE'/
     *' COLS 1 -',I2,' TOTAL REACTANT CONCENTRATIONS'/
     *' COLS',I2,3H - ,I2,' RESIDUALS ON MASS BALANCE EQUATIONS'//)
   12 FORMAT (16X,'CLASS  LIMITS',13X,'PROBABILITY',10X,'FREQUENCY',8X,
     *'PARTIAL'/12X,'LOWER',10X,'HIGHER',7X,'CALC',7X,'OBS',7X,'CALC',
     *5X,'OBS',5X,'CHI-SQUARE'//)
   17 FORMAT (I5,2E15.5,2F10.4,F10.1,I8,F12.3)
   18 FORMAT (//' OBSERVED CHI SQUARE IS', F10.2/
     *          ' CHI SQUARE (6,0.95) SHOULD BE ', F10.2/)
   20 FORMAT (////' MASS-BALANCE EQUATION',I2)
   21 FORMAT (I4,116A1)
   22 FORMAT (//' PLOTS OF FORMATION PERCENTAGES'/)
   23 FORMAT ('0POINT  FREE CONCN. ',12I8/16X,8I8/)
   24 FORMAT (/' RESIDUALS PLOT'/)
   25 FORMAT (/5X,A1,2(49X,A1)/5X,A1,10(9X,A1)/1X,119A1)
      READ (JINP,3) JPRIN,NT,(JP(I),I=1,NT)
      NR=8
      WRITE (JOUT,1) TITLE
      NTOT=LP*NMBE
      W=FLOAT(NTOT)
      SD=SQRT(U/W)
      CLIM(1)=-1.150*SD
      CLIM(2)=-0.675*SD
      CLIM(3)=-0.319*SD
      CLIM(4)= 0.000
      CLIM(5)= 0.319*SD
      CLIM(6)= 0.675*SD
      CLIM(7)= 1.150*SD
      CLIM(8)=SD/ACCM
      DO 108 I=1,NR
  108 JPOP(I)=0
      AM=0.
      DM=0.
      VAR=0.
      COSQ=0.
```

```
      COKU=0.
      RDEN=0.
      GO TO (114,112,114,112),JPRIN
  112 N1=NMBE+1
      N2=NMBE+NMBE
      WRITE (JOUT,11) NMBE,N1,N2
  114 DO 200 IP=1,LP
      CALL CALC (NK,N,NMBE,NC,IP,BETAV,JPOT,JQR,NLNB,T,CONC,IVAR,DU,A,
     *              GC,DGB,EPS,HX,TT,CI,CX,NPNC,NP,KEY)
      DO 130 I=1,NMBE
      DO 119 K=1,NR
      IF (EPS(I)-CLIM(K)) 118,118,119
  118 JPOP(K)=JPOP(K)+1
      GO TO 120
  119 CONTINUE
      JPOP(NR)=JPOP(NR)+1
  120 AM=AM+EPS(I)
      RDEN=RDEN+TT(I)*TT(I)
      DM=DM+ABS(EPS(I))
      VAR=VAR+EPS(I)**2
      COSQ=COSQ+EPS(I)**3
  130 COKU=COKU+EPS(I)**4
      GO TO (200,131,132,131),JPRIN
  131 WRITE (JOUT,2)IP,(TT(I),I=1,NMBE),(EPS(I),I=1,NMBE)
  132 DO 135 J=1,NK
  135 D(IP,J)=CI(J)
      DO 136 J=1,NMBE
      JPNK=J+NK
  136 D(IP,JPNK)=EPS(J)
  200 CONTINUE
      GO TO (270,270,202,202),JPRIN
  202 WRITE (JOUT,24)
      DO 260 IP=1,LP
      DO 207 J=1,NK
  207 CI(J)=D(IP,J)
      DO 208 J=1,NMBE
      JPNK=J+NK
  208 EPS(J)=D(IP,JPNK)
      DO 210 I=1,116
  210 PT(I)=BLANK
      DO 220 I=2,116,19
  220 PT(I)=PLUS
      DO 250 I=1,NMBE
      X=EPS(I)/SD*19.+59.5
      J=IFIX(X)
      IF(J-1) 230,230,235
  230 J=2
      GO TO 250
  235 IF(J-116) 250,250,240
  240 J=116
  250 PT(J)=SYM(I)
  260 WRITE (JOUT,21) IP,PT
  270 AM=AM/NTOT
      DM=DM/NTOT
      VAR=VAR/W
      COSQ=COSQ/(NTOT*VAR*SD)
      COKU=COKU/(NTOT*VAR*VAR)
      WRITE (JOUT,10) AM,DM,SD,VAR,COSQ,COKU
      DO 270 I=1,NR
  270 EXFR(I)= 0.125
      OBSCH=0.
      WRITE (JOUT,12)
      R1=-CLIM(NR)
      DO 350 K=1,NR
      EXPOP=EXFR(K)*W
      OBFR=FLOAT(JPOP(K))/W
      RAPP=((JPOP(K)-EXPOP)**2)/EXPOP
      WRITE (JOUT,17) K,R1,CLIM(K),EXFR(K),OBFR,EXPOP,JPOP(K),RAPP
      R1=CLIM(K)
  350 OBSCH=OBSCH+RAPP
C          OBSCH AND EXPCH ARE THE OBSERVED  AND EXPECTED VALUES OF
C          CHI-SQUARED
      EXPCH=12.6
      WRITE (JOUT,13) OBSCH,EXPCH
      RFACT=SQRT(U/RDEN)
```

```
      WRITE (JOUT,4) RFACT
      GO TO (500,351,366,351),JPRIN
  351 WRITE (JOUT,7)
      DO 365 I=1,NT
      JT=JP(I)
      WRITE (JOUT,20) JT
      NS=0
      DO 353 J=1,NK
      IF(JQR(JT,J)) 352,353,352
  352 NS=NS+1
      JS(NS)=J
  353 CONTINUE
      WRITE (JOUT,23) (JS(J),J=1,NS)
      DO 358 IP=1,LP
      DO 354 J=1,NK
  354 CI(J)=D(IP,J)
      DO 355 J=1,NMBE
      JPNK=J+NK
  355 EPS(J)=D(IP,JPNK)
      TS=T(IP,JT)+EPS(JT)
      DO 357 J=1,NS
      JJ=JS(J)
  357 CI(J)=CI(JJ)*JQR(JT,JJ)*100./TS
  358 WRITE (JOUT,6) IP,CONC(IP,JT),(CI(J),J=1,NS)
  365 CONTINUE
      GO TO (500,500,366,366),JPRIN
  366 WRITE (JOUT,22)
      DO 480 I=1,NT
      JT=JP(I)
      WRITE (JOUT,20) JT
      WRITE (JOUT,25) (PLUS,K=1,133)
      DO 470 IP=1,LP
      DO 435 J=1,NK
  435 CI(J)=D(IP,J)
      DO 436 J=1,NMBE
      JPNK=J+NK
  436 EPS(J)=D(IP,JPNK)
      TS=T(IP,JT)+EPS(JT)
      DO 440 K=1,116
  440 PT(K)=BLANK
      PT(2)=PLUS
      PT(102)=PLUS
      DO 460 J=1,NK
      X=CI(J)*JQR(JT,J)*100./TS+0.5
      K=IFIX(X)
      IF(K-100)450,457,445
  445 K=102
  450 IF(K)460,460,455
  455 K=K+2
      IF(PT(K)-BLANK)456,458,456
  456 PT(K)=STAR
      GO TO 460
  457 K=102
  458 PT(K)=SYM(J)
  460 CONTINUE
  470 WRITE (JOUT,21) IP,PT
  480 CONTINUE
  500 RETURN
      END
```

DATA INPUT INSTRUCTIONS FOR MINIQUAD

Format specifications are in square brackets.

(*i*) 1 card: descriptive title [20A4].

(*ii*) 1 card: LARS [I5], with LARS = 1 all data points are used, with LARS = 2 alternate points, LARS = 3 every third point *etc.* First and last points on all titration curves are always used. NK [I5], total number of formation constants; N [I5], the number of formation constants to be determined; MAXIT [I5], the maximum number of iteration cycles to be performed (Note *a*); IPRIN [I5], IPRIN = 0 is normal, IPRIN = 1 monitors the minimization; NMBE [I5], the number of reactants (mass-balance equations); NC [I5] the number of unknown free concentrations at each titration point, *i.e.*, the number of electrodes NEMF = NMBE − NC.

(*iii*) 1 card: TEMP [F10·6], reaction temperature in °C.

(*iv*) NK cards: each one specifies a formation constant as follows—BETA (I) [F10·6], JPOT (I) [I5], JQR (J, I) [I5] (NMBE values), KEY (I) [I5]; $\beta_i = \text{BETA (I)} \times 10^{\text{JPOT (I)}}$, JQR holds the stoichiometric coefficients (Note *b*) and KEY is a refinement key, 0 for constants, 1 for parameters.

(*v*) 1 card: JEL [I5] (NEMF values), the number of electrons transferred at each electrode (Note *c*).

(*vi*) The following set of cards for each titration curve.

1 card: TOTC [F10·6] (NMBE values), the initial number of millimoles of reactants in solution (Note *d*); E° [F10·6] (NEMF values) the standard potentials of the electrodes (mV) (Note *e*); ADDC [F10·6] (NMBE values) the concentrations (*M*) of titrant solutions (there is one for each mass-balance equation (Notes *d*, *f*)); VINIT [F10·6] the initial solution volume (ml).

1 card for each point on the titration curve with LUIGI [I5], 0 is normal, LUIGI > 0 indicates the end of a titration curve, LUIGI < 0 indicates the end of all titration curves; TITRE [F8·3] (NMBE values), volumes (ml) of titrant solutions added (Note *f*); EMF [F8·3] (NEMF values), potentials (mV) measured on each electrode with non-zero JEL value, otherwise the decimal cologarithm of concentration.

(*vii*) 1 card: this card controls the amount and type of output produced by STATS. JPRIN [I5], NT [I5], JT [I5] (NT values). JT contains the indices of the NT mass-balance equations relative to which the formation fractions are to be calculated. JPRIN controls the print-out of these fractions as follows: 1, no tables or graphs; 2, tables only; 3, graphs only; 4, both tables and graphs.

(*viii*) 1 card: NSET [I5], 1 for another set of formation constants (items *i–iv* above), 0 for another complete set of data, −1 for termination of the run.

Notes

a With MAXIT = 0 a species distribution is evaluated for the given formation constants and conditions.

b The order of coefficients is arbitrary except that those referring to reactants of which the free concentration is determined potentiometrically must come last; however, the order of coefficients given here determines the order of the concentrations given later.

c If the decimal cologarithm of concentration (*e.g.*, pH) is to be read in put JEL (J) = 0.

d The order of reactants is the same as the JQR.

e The value is ignored if JEL (I) = 0.

f If one solution contains more than one reactant, simulate the appropriate number of titrant solutions with adjusted concentration and volume. Example 1: NMBE = 3, one titrant solution containing reactant 3: ADDC (1) = 0·0, ADDC (2) = 0·0, ADDC (3) = C_3. Example 2: NMBE = 3, one titrant solution containing reactants 2 and 3: ADDC (1) = 0, ADDC (2) = $2C_2$, ADDC (3) = $2C_3$. In this case the volumes added of reactants 2 and 3 must be half the amount added from the burette [TITRE (2) and TITRE (3)].

APPENDIX

Equation (2) may be written out as (A1)

$$C'_j = \beta_j C_1^{f\,j1} C_2^{f\,j2} C_3^{f\,j3} \cdots \tag{A1}$$

where C'_j is the concentration of complex *j* and C_1 and C_2 *etc*. are the free concentrations of reactants 1, 2 *etc*. Example 1: a complex ML_2 would be defined by (A2):

$$[ML_2] = \beta_1 [M][L]^2[H]^0 \tag{A2}$$

hence for this complex JQR is (1, 2, 0). Example 2: a complex $M(LH)_2$ would be defined by (A3):

$$[M(LH)_2] = \beta_2 [M][L]^2[H]^2 \tag{A3}$$

i.e., JQR = (1, 2, 2). Example 3: a complex $ML_2(OH_2)$ would be defined by (A4):

$$[ML_2(OH)_2] = \beta_3 [M][L]^2[H]^{-2} \tag{A4}$$

i.e., JQR = (1, 2, −2). β_3 is not in fact the formation constant for the complex $ML_2(OH)_2$ but is related to it through $K_w = [H][OH]$ since $\beta'_3[M][L]^2[OH]^2 = \beta'_3[M][L]^2[H]^{-2}K_w^2$, *i.e.*, $\beta_3 = \beta'_3 \times K_w^2$, where β'_3 is the true formation constant for $ML_2(OH)_2$.

Following this convention, if hydroxide ion is being added as titrant its concentration should be given a negative sign, assuming that the mass-balance equation is expressed in terms of hydrogen-ion concentration.

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Zusammenfassung—Ein neues Computerprogramm zur Berechnung der Bildungskonstanten von Komplexspezies in Lösung wird angegeben. Man kann das Programm bei allen Arten von potentiometrischen Titrationsdaten verwenden, auch bei Systemen mit mehreren Reaktanten und mehreren Elektroden. Die Ergebnisse werden statistisch analysiert, um ihre Richtigkeit zu bewerten und um bei der Prüfung von Hypothesen zu helfen.

Résumé—On présente un nouveau programme de calculatrice pour le calcul de constantes de formation d'espèces complexes en solution. Le programme peut être appliqué à toutes espèces de données de titrages potentiométriques, y compris les systèmes à multi-corps réagissants et multiélectrodes. On fait une analyse statistique des résultats afin d'apprécier leur validité, et d'aider dans l'examen d'hypothèses.

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FORMATION CONSTANTS OF ZINC(II) COMPLEXES WITH SEMI-XYLENOL ORANGE

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Summary—A potentiometric and spectrophotometric investigation on the formation of zinc(II) complexes with Semi-Xylenol Orange (SXO or H_4L) is reported. In an aqueous solution ($\mu = 0{\cdot}1$), three 1 : 1 complex species, MH_2L, MHL^-, ML^{2-}, and a 1 : 2 complex, ML_2^{6-}, seem to exist. In a strongly alkaline medium (above pH 12·5) the complexes may dissociate to give zinc hydroxide and L^{4-}. The formation of a hydroxy complex is not observed. The absorption maxima are at 445 nm (MH_2L), 466 nm (MHL^-) and 561 nm (ML^{2-}), the molar absorptivities being $2{\cdot}34 \times 10^4$, $2{\cdot}42 \times 10^4$ and $3{\cdot}14 \times 10^4$ $l.mole^{-1}.cm^{-1}$ respectively. The formation constants are (at 25 ± 0·1°) $\log K^{M}_{ML} = 11{\cdot}84$, $\log K^{M}_{MHL} = 7{\cdot}13$, $\log K^{M}_{MH_2L} = 2{\cdot}70$, $\log K^{M}_{ML_2} = 16{\cdot}60$.

The mono-substituted product Semi-Xylenol Orange, 3-[*N*,*N*′-di(carboxymethyl)aminomethyl]-*o*-cresolsulphonphthalein, SXO, is synthesized when Xylenol Orange, XO, is prepared.[1–3] In previous work,[4] we separated SXO from XO and investigated the acid formation constants and the molar absorptivities of SXO. Its value as a metallochromic indicator or analytical reagent for the determination of several metals has been investigated.[3–6]

The present work reports on the species in an aqueous solution containing zinc(II) and SXO.

EXPERIMENTAL

Reagents

SXO. Synthesized and purified[4] by means of cellulose column chromatography and ion-exchange (batch method instead of the chromatographic one used previously). The purity was nearly 100%, as measured by potentiometric titration with a standard sodium hydroxide. This SXO was weighed and dissolved in water for each experimental solution.

Standard sodium hydroxide solution, 0·1*M*. Free from carbonate.

Stock solution of zinc nitrate, $1 \times 10^{-2}M$. Standardized with EDTA, and diluted as required.

Buffers. The pH was controlled with 0·1*M* sodium acetate–0·1*M* perchloric acid at pH 1·0–3·5, 0·1*M* acetic acid–0·1*M* sodium acetate at pH 3·5–7·0, 0·05*M* veronal–0·1*M* perchloric acid at pH 6·7–9·0, 0·1*M* and 1*M* sodium hydroxide at pH 9·0–14·0.

All reagents were analytical grade materials.

Apparatus

Titration vessel. A 200-ml glass flask with 4 necks to accommodate a Metrohm Model E-274 piston burette, glass and calomel electrodes, gas inlet and outlet.

Procedures

Potentiometric measurements. The tetrabasic SXO was titrated potentiometrically at 25±0·1° under nitrogen, with sodium hydroxide solution in the absence and presence of zinc(II) at 1 : 2, 1 : 1 and 4:1 molar ratios of metal to ligand. The concentration of ligand was approximately $1 \times 10^{-3}M$ and the volume of the experimental solution was 50 ml. The ionic strength was maintained at 0·1 with potassium nitrate.

Photometric measurements. To a solution containing enough $1 \times 10^{-4}M$ zinc(II) to give the desired molar ratio of metal to ligand, in a 25-ml volumetric flask, were added 2 ml of $5 \times 10^{-4}M$ SXO, buffer solution, the amount of $1M$ potassium nitrate required for an ionic strength of 0·1, and water to the mark. The solution was mixed and the spectrum obtained immediately, against water as reference, in 1-cm quartz cells. All measurements were performed at room temperature.

CALCULATIONS

In the mathematical treatment, the following symbols are used: T_L = total analytical concentration of ligand; T_M = total analytical concentration of metal ion; a = moles of base added per mole of ligand; k_i = acid formation constant of the ligand, $k_i = [H_iL]/[H_{i-1}L][H]$; $K^{M}_{MH_iL}$ = formation constant of complex MH_iL, $K^{M}_{MH_iL} = [MH_iL]/[M][H_iL]$; $K^{H}_{MH_iL}$ = acid formation constant of complex MH_iL, $K^{H}_{MH_iL} = [MH_iL]/[MH_{i-1}L][H]$. The acid formation constants of SXO determined previously[4] are: $\log k_1 = 10{\cdot}90$, $\log k_2 = 7{\cdot}44$, $\log k_3 = 2{\cdot}60$, $\log k_4 = 1{\cdot}5$.

Formation constants of 1 : 1 *complexes MH_nL*

The equations can be derived by modifying Schwarzenbach's[7] and Martell's.[8,9] For the system of the ligand H_4L and the metal ion M, where the complexes MH_iL ($i = 0, 1, \ldots, N$) are formed, equations describing the total analytical concentration of ligand, total metal ion concentration and electroneutrality can be written as follows.

$$T_L = \sum_{i=0}^{4} [H_iL] + \sum_{i=0}^{N} [MH_iL] \tag{1}$$

$$T_M = [M] + \sum_{i=0}^{N} [MH_iL] \tag{2}$$

$$(4 - a)T_L = [H] - [OH] + \sum_{i=1}^{4} i[H_iL] + \sum_{i=1}^{N} i[MH_iL] \tag{3}$$

Equations (1), (2) and (3) are written in terms of $[MH_nL]$, $[H_nL]$ and [M] as follows.

$$T_L = A_n[H_nL] + B_n[MH_nL] \tag{4}$$

$$T_M = [M] + B_n[MH_nL] \tag{5}$$

$$T_H = C_n[H_nL] + D_n[MH_nL] \tag{6}$$

where

$$A_n = \sum_{i=0}^{4} [H]^iK_i/[H]^nK_n,\ B_n = \sum_{i=0}^{N} [H]^iK_i^{1}/[H]^nK_n^{1}$$

$$C_n = \sum_{i=1}^{4} i[H]^iK_i/[H]^nK_n,\ D_n = \sum_{i=1}^{N} i[H]^iK_i^{1}/[H]^nK_n^{1}$$

$$T_H = (4 - a)T_L - [H] + [OH],\ K_i = k_1\,k_2, \ldots, k_i\ \ (K_0 = 1)$$

$$K_i^{1} = K^{H}_{MHL}\,K^{H}_{MH_2L} \cdot \ldots\, K^{H}_{MH_iL}\ \ (K_0^{1} = 1).$$

Equations (4), (5) and (6) can be solved simultaneously for the quantities $[MH_nL]$, $[H_nL]$ and [M], and the formation constant of the complex MH_nL given by the equation

$$K^{M}_{MH_nL} = \frac{[MH_nL]}{[M][H_nL]} = \frac{(B_nC_n - A_nD_n)(C_nT_L - A_nT_H)}{(B_nT_H - D_nT_L)(A_nB_nT_H + B_nC_nT_M - A_nD_nT_M - B_nC_nT_L)} \tag{7}$$

The value for $K^{\mathrm{M}}_{\mathrm{MH}_n\mathrm{L}}$ was obtained by means of successive approximation. Equation (7) involves N acid formation constants of protonated complexes, $K^{\mathrm{H}}_{\mathrm{MH}_i\mathrm{L}}$ ($i = 1, 2, \ldots, N$). For a set of assumed values for $K^{\mathrm{H}}_{\mathrm{MH}_i\mathrm{L}}$, the corresponding value for $K^{\mathrm{M}}_{\mathrm{MH}_n\mathrm{L}}$ was calculated for a point on the titration curve where the complex $\mathrm{MH}_n\mathrm{L}$ was assumed to predominate. The value for constant $K^{\mathrm{M}}_{\mathrm{MH}_n\mathrm{L}}$ was taken as that giving least deviation of the $K^{\mathrm{M}}_{\mathrm{MH}_n\mathrm{L}}$ values.

To determine the value of N, the average number ($\bar{n}_{\mathrm{H}}$) of hydrogen ions bound to complexes was calculated.[7,10]

$$\bar{n}_{\mathrm{H}} = \frac{\sum_{i=1}^{N} i[\mathrm{MH}_i\mathrm{L}]}{\sum_{i=0}^{N} [\mathrm{MH}_i\mathrm{L}]} \tag{8}$$

In a solution containing excess of metal ion the free ligand concentration may be neglected, and from equations (1) and (3), $\bar{n}_{\mathrm{H}}$ is given by

$$\bar{n}_{\mathrm{H}} = \frac{(4-a)T_{\mathrm{L}} - [\mathrm{H}] + [\mathrm{OH}]}{T_{\mathrm{L}}} \tag{9}$$

In a solution containing excess of ligand the free metal ion concentration may be neglected, and from equations (1)–(3), $\bar{n}_{\mathrm{H}}$ is given by

$$\bar{n}_{\mathrm{H}} = \frac{(4-a)T_{\mathrm{L}} - [\mathrm{H}] + [\mathrm{OH}] - P}{T_{\mathrm{M}}} \tag{10}$$

where P is the total concentration of hydrogen ions bound to the free ligand in all forms and is given by

$$P = \sum_{i=1}^{4} i[\mathrm{H}_i\mathrm{L}] = (T_{\mathrm{L}} - T_{\mathrm{M}}) \sum_{i=1}^{4} i[\mathrm{H}]^i K_i \Big/ \sum_{i=0}^{4} [\mathrm{H}]^i K_i$$

Formation constants of 1:2 *complex* ML_2

The extent of 1:2 complex formation can be characterized by the complex formation function or the average co-ordination number function ($\bar{n}_{\mathrm{OH}}$) introduced by Bjerrum.[11]

$$\bar{n}_{\mathrm{L}} = \frac{[\mathrm{ML}] + 2[\mathrm{ML}_2]}{[\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML}_2]} = \frac{K^{\mathrm{M}}_{\mathrm{ML}}[\mathrm{L}] + 2K^{\mathrm{M}}_{\mathrm{ML}_2}[\mathrm{L}]^2}{1 + K^{\mathrm{M}}_{\mathrm{ML}}[\mathrm{L}] + K^{\mathrm{M}}_{\mathrm{ML}_2}[\mathrm{L}]^2} \tag{11}$$

In a solution at high pH, protonated complexes can be ignored and the equations describing the total analytical concentration of ligand and metal ion, and electroneutrality, are

$$T_{\mathrm{L}} = X[\mathrm{L}] + [\mathrm{ML}] + 2[\mathrm{ML}_2] \tag{12}$$

$$T_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML}_2] \tag{13}$$

$$(4-a)T_{\mathrm{L}} = [\mathrm{H}] - [\mathrm{OH}] + Y[\mathrm{L}] \tag{14}$$

where $X = \sum_{i=0}^{4} [\mathrm{H}]^i K_i$, $Y = \sum_{i=1}^{4} i[\mathrm{H}]^i K_i$.

From equations (12)–(14) $\bar{n}_{\mathrm{L}}$ is given by

$$\bar{n}_{\mathrm{L}} = \frac{T_{\mathrm{L}} - X[\mathrm{L}]}{T_{\mathrm{M}}} \tag{15}$$

where $[\mathrm{L}] = \{(4-a)T_{\mathrm{L}} - [\mathrm{H}] + [\mathrm{OH}]\}/Y$.

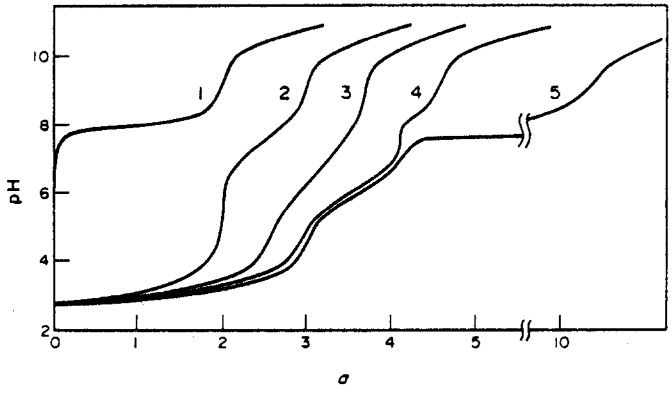

Fig. 1. Potentiometric titration curves of Zn(II)–SXO complexes at 25 ± 0·1°C in 50 ml of 0·1M KNO_3 solution with following molar ratios of metal ion to ligand: 1–Zn alone; 2-SXO alone; 3–Zn: SXO(1 : 2); 4–Zn: SXO(1 : 1); 5–Zn: SXO(4 : 1), a = number of moles of base added per mole of SXO.

T_M : *1*–9·68 × $10^{-4}M$; *3*–5·38 × $10^{-4}M$; *4*–1·07 × $10^{-3}M$; *5*–4·30 × $10^{-3}M$.
T_L : *2*–1·06 × $10^{-3}M$; *3*–9·72 × $10^{-4}M$; *4*–9·61 × $10^{-4}M$; *5*–9·54 × $10^{-4}M$.

For various points on the titration curve, the values for $\bar{n}_L$ are plotted against pL. Log $K^M_{ML_2}$ may be determined from the values of pL at an $\bar{n}_L$ value of 1·5.

RESULTS AND DISCUSSION

Determination of formation constants of the complexes from the pH titration curves

Potentiometric titration curves of zinc(II), SXO, and 1 : 2, 1 : 1 and 4 : 1 molar ratios of zinc(II) to SXO are presented in Fig. 1. The curve for SXO has two well-defined inflections, involving the dissociation of the acid species H_4L and H_3L^- between $a = 0$ and $a = 2$, H_2L^{2-} between $a = 2$ and $a = 3$, and HL^{3-} after $a = 3$.

At relatively low pH, all the curves for mixtures of the metal and ligand exhibit a buffer region, indicating the formation of a protonated metal chelate, which then dissociates at medium pH to a fully deprotonated species ML^{2-}. It is possible that more highly protonated species are also formed, especially in view of the lower pH of the buffer region when the molar ratio of metal to ligand is increased. The extent of the buffer region after the first inflection on curves 4 and 5 indicates that not more than one metal ion can combine with one SXO molecule when excess of zinc is present. Further addition of base after $a = 4$ results in formation of zinc hydroxide (*cf.* curve 1).

The average numbers ($\bar{n}_H$) of hydrogen ions bound to the complexes at various points on the titration curves, calculated from equations (9) and (10) were: 1·9 at the start of titration (I), 1·0 at the first inflection point (II), −0·2 at the second inflection point (III) for curve 3; 2·2 at point (I), 1·2 at point (II), 0·1 at point (III) for curve 4; 1·8 at point (I), 1·0 at point (II), −0·2 at point (III) for curve 5. The results indicate the presence of two protonated complexes, MH_2L and MHL^-, and a simple complex ML^{2-}. If only 1 : 1 complexes were formed, the $\bar{n}_H$ values at a given point should decrease when the molar ratio of metal ion increases. The average number ($\bar{n}_L$) of ligands bound per metal ion in the 1 : 2 mixture, calculated from equation (15), were 1·0 at pH 6·7, 1·25 at pH 9·0, 1·5 at pH 10·0. This indicates the presence of a 1 : 2 chelate $ML_2{}^{6-}$.

Table 1. Formation constants of zinc(II) complexes with SXO at 25 ± 0·1°C, $\mu = 0{\cdot}1$ (KNO_3)

Reaction	Log *K*
$M^{2+} + H_2L^{2-} \rightleftharpoons MH_2L$	$\log K^{M}_{MH_2L} = 2{\cdot}70$
$M^{2+} + HL^{3-} \rightleftharpoons MHL^{-}$	$\log K^{M}_{MHL} = 7{\cdot}13$
$M^{2+} + L^{4-} \rightleftharpoons ML^{2-}$	$\log K^{M}_{ML} = 11{\cdot}84$
$M^{2+} + 2L^{4-} \rightleftharpoons ML_2{}^{6-}$	$\log K^{M}_{ML_2} = 16{\cdot}60$*
$H^{+} + MHL^{-} \rightleftharpoons MH_2L$	$\log K^{H}_{MH_2L} = 2{\cdot}70$
$H^{+} + ML^{2-} \rightleftharpoons MHL^{-}$	$\log K^{H}_{MHL} = 6{\cdot}18$

* Data determined by Bjerrum's method, the rest by means of successive approximation.

The equilibria and the formation constants calculated from equations (7) and (15) are listed in Table 1. Table 2 shows the results of the successive approximations in which the deviations of each $K^{M}_{MH_nL}$ ($n = 0, 1, 2$) value were minimal at any point along the titration curve for the given set of values of $K^{H}_{MH_nL}$ ($n = 1, 2$).

The average number ($\bar{n}_{OH}$) of hydroxide ions bound to the complexes is given by[12]

$$\bar{n}_{OH} = \frac{(a-4)T_L - [OH] + [H] + S}{T_M}$$

$$= \frac{[M(OH)L] + 2[M(OH)_2L]}{[ML] + [M(OH)L] + [M(OH)_2L]}$$

Table 2. Formation constant values at points along titration curve*

pH	$\log K^{M}_{MH_2L}$	$\log K^{M}_{MHL}$	$\log K^{M}_{ML}$
2·971	2·68		
3·080	2·71		
3·171	2·72		
3·284	2·72		
3·400	2·70		
3·543	2·68		
4·394		7·18	11·90
4·458		7·18	11·90
4·590		7·14	11·86
4·739		7·11	11·83
4·897		7·09	11·80
5·189		7·08	11·80
5·376		7·09	11·81
5·475		7·08	11·78
5·579		7·08	11·78
5·670		7·11	11·82
5·760		7·12	11·84
5·837		7·10	11·81
5·997		7·12	11·83
av.	2·70 ± 0·02	7·13 ± 0·05	11·84 ± 0·06

* Assumed $K^{H}_{MH_nL}$ values: $\log K^{H}_{MH_2L} = 2{\cdot}70$; $\log K^{H}_{MHL} = 6{\cdot}18$. $T_M = 1{\cdot}07 \times 10^{-3}M$, $T_L = 9{\cdot}61 \times 10^{-4}M$.

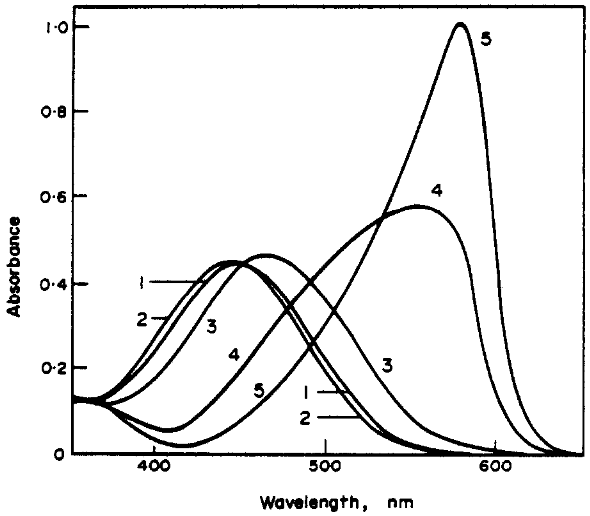

Fig. 2. Absorption spectra of Zn(II)–SXO complexes at different pH values.

$T_M = 4{\cdot}30 \times 10^{-5} M$; $T_L = 1{\cdot}92 \times 10^{-5} M$; pH: *1*–1·59; *2*–2·82; *3*–5·05; *4*–9·84; *5*–13·60.

where S is the concentration of hydrogen ions bound to the free ligand species and to the protonated complexes, and given by

$$S = \frac{\sum_{i=1}^{4} i[\mathrm{H}]^i K_i}{\sum_{i=0}^{4} [\mathrm{H}]^i K_i}(T_L - T_M) + \frac{\sum_{i=1}^{2} i[\mathrm{H}]^i K_i^1}{\sum_{i=0}^{2} [\mathrm{H}]^i K_i^1} T_M$$

Values of $\bar{n}_{OH}$ were about zero at any point along the 1:2 curve. This result indicates the absence of a hydroxo-complex in a solution of zinc(II) and SXO below pH 11·0.

Spectrophotometric investigation of the complexes

Absorption spectra of a solution containing zinc(II) and SXO at different pH values were measured between 350 nm and 650 nm (Fig. 2). With increase of pH, the absorption band first (pH 2·8) shifts slightly to shorter wavelength and then slightly shifts to longer wavelengths. The absorption spectra remained almost unchanged over the pH ranges 2·0–3·5, 4·5–5·5 and 8·0–11·0, the absorption maxima being at 445, 465 and 560 nm respectively. The mole-ratio method showed the combining ratios of zinc(II) and SXO to be 1:1 at pH 2·80 and 5·05, and 1:1 and 1:2 at pH 9·85. These results indicate the presence of four complexes MH_2L, MHL^-, ML^{2-} and ML_2^{6-}, in agreement with the potentiometric measurements. Spectra of the Zn(II) complex near pH 3·0, where MH_2L predominates, are nearly the same as those of SXO at pH 3·0–6·5 where H_2L^{2-} is formed by dissociation of the two carboxyl group protons. But it is supposition whether MH_2L is formed by displacement of a proton from each carboxyl group or one from one carboxyl group and the other from the quaternary ammonium group of the zwitterion. The conversion of MHL^- into ML^{2-} is accompanied by a change from yellow to red purple, due to dissociation of a proton from the phenol group.

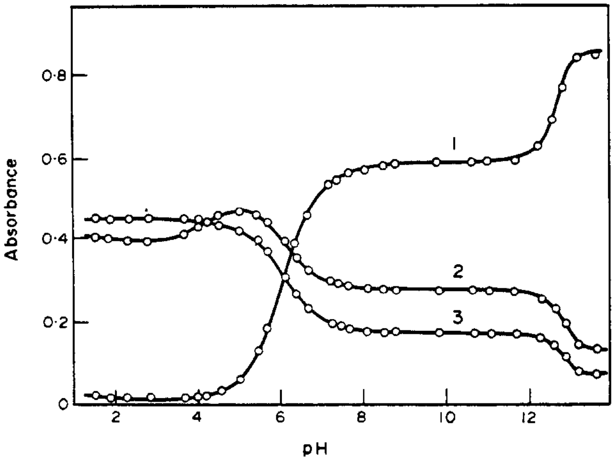

Fig. 3. Absorbance of Zn(II)–SXO complexes as a function of pH.
$T_M = 4{\cdot}30 \times 10^{-5}M$; $T_L = 1{\cdot}92 \times 10^{-5}M$; wavelength: *1*–561 nm; *2*–466 nm; *3*–445 nm.

Figure 3 shows the variation of absorbance at the absorption maximum for each complex species. The absorbance is almost constant over the pH range 8·5–11·5, indicating no hydroxo-complex is present. Figure 2 shows that at pH 12·5 a sharp and strong absorption band appears, with a maximum near 580 nm, and at pH > 13·5 the absorption band of the zinc(II)–SXO solution is identical to that of SXO alone. This shows that in a very alkaline medium the complexes dissociate to give $Zn(OH)_4^{2-}$ and L^{4-}.

From the spectra, the absorption maxima were found to be at 445 nm (MH_2L), 466 nm (MHL^-) and 561 nm (ML^{2-}), the molar absorptivities being $2{\cdot}34 \times 10^4$, $2{\cdot}42 \times 10^4$ and $3{\cdot}14 \times 10^4$ $l.mole^{-1}.cm^{-1}$ respectively.

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SHORT COMMUNICATIONS

SOLVENT EXTRACTION—SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTHS WITH CHLOROPHOSPHONAZO—III

(*Received* 12 *March* 1973. *Accepted* 3 *July* 1973)

The photometric reagent 2,7-bis-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxy-naphthalene-3,6-disulphonic acid (chlorophosphonazo III) is a derivative of chromotropic acid and has been used for determining calcium and magnesium[1] and rare earths[2] since Nemodruk *et al.*, reported its usefulness for determining uranium.[3] Buděšínský and Menclová reported the extractive photometric determination of rare earths with chlorophosphonazo DAL.[4] We have found that the rare-earth chlorophosphonazo III chelates are easily extracted from aqueous solution at low pH into n-butanol and the molar absorptivity of the chelate in the organic layer is higher than that in the aqueous layer and that of the chlorophosphonazo DAL chelate. In the present paper, we describe the solvent extraction-spectrophotometric determination of micro-amounts of rare earths with chlorophosphonazo III.

EXPERIMENTAL

Reagents

Rare-earth solutions. Standard solutions of lanthanum, praseodymium, samarium, gadolinium, dysprosium, erbium and lutetium chlorides were obtained by dissolving the 99·9% pure oxides in warm dilute hydrochloric acid and then evaporating the excess of acid. The solutions were standardized by EDTA titration with Xylenol Orange as indicator.

Chlorophosphonazo III stock solution, 0·02%. Prepared from commercial reagent (estimated purity–86%).

Butanol. n-Butanol was shaken with an equal volume of dilute hydrochloric acid (pH 1·1) and the butanol layer was used for extractions.

All other chemicals used were of analytical-reagent grade.

Procedure

A solution containing less than about 20 μg of rare earth ions was transferred into a beaker, 5 ml of chlorophosphonazo III solution were added, the pH was adjusted to 1·1–1·5 and the solution was transferred to a 20-ml volumetric flask and made up to volume with water. Ten ml of this solution were pipetted into a separatory funnel and extracted for 10 min with 10 ml of butanol. The butanol layer was transferred to a centrifuge tube and centrifuged to separate residual aqueous layer. The absorbance of the butanol solution was measured in a 1-cm cell at 668 nm against a reagent blank.

All experiments were done at about 25°.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the absorption spectra of chlorophosphonazo III in aqueous solution (pH 1·3) and in butanol solution after extraction from aqueous solution. The degree of extraction of the reagent was about 92%. It also shows the absorption spectra of gadolinium chlorophosphonazo III chelate in aqueous and butanol solution; the absorption maxima for the aqueous and butanol solutions are 674 and 668 nm, respectively. The chelate was almost completely extracted. The maximum absorbance in the butanol solution is about 3 times that in the aqueous solution.

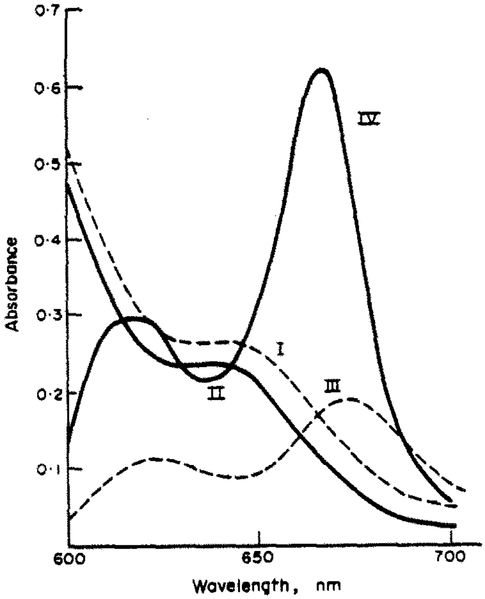

Fig. 1. Absorption spectra of chlorophosphonazo III and its gadolinium complex in aqueous and butanol solutions

I. Reagent in aqueous solution (pH 1·3) III. Complex in aqueous solution (pH 1·3)
II. Reagent in butanol solution IV. Complex in butanol solution
Chlorophosphonazo III—2·1 × 10^{-5} M; Gd^{3+}—0·49 μg/ml; III and IV—reagent blank as reference.

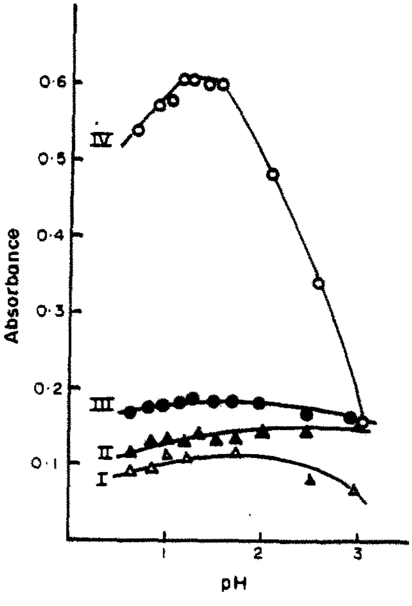

Fig. 2. Variation of absorbance of chlorophosphonazo III and its gadolinium chelate in aqueous and butanol solutions as a function of pH

I. Chlorophosphonazo III in aqueous solution
II. Chlorophosphonazo III in butanol solution
III. Gd-chlorophosphonazo III chelate in aqueous solution
IV. Gd-chlorophosphonazo III chelate in butanol solution
Chlorophosphazo III—2·1 × 10^{-5} M; Gd^{3+}—0·49 μg/ml; wavelength 668 nm.

Effect of pH

Figure 2 shows the variation of the maximum absorbance, for both the aqueous solution and the butanol extract, as a function of pH. The absorbance of the chelate in butanol solution is almost constant over the pH range from 1·1 to 1·5.

Effect of reagent concentration

The absorbance in aqueous and butanol solutions was studied as a function of the mole ratio of the reagent to gadolinium ion. The results are shown in Fig. 3. Constant absorbance is obtained with a 2 : 1 ratio of reagent to gadolinium in aqueous solution, and 8 : 1 if the extraction is used. At least a tenfold molar excess of reagent is therefore recommended.

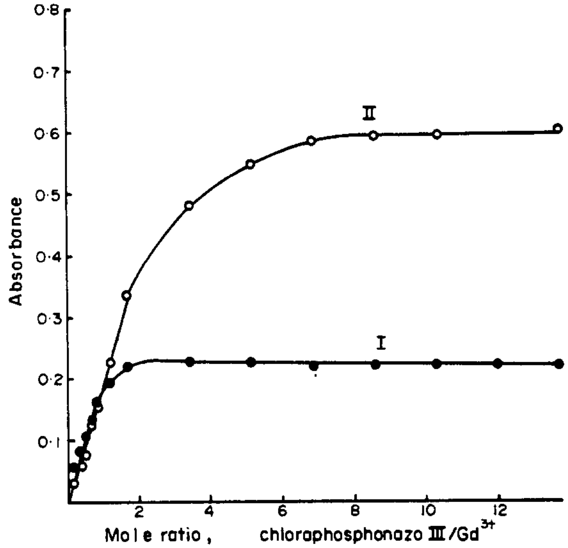

Fig. 3. Variation of absorbance of gadolinium chlorophosphonazo III chelate in aqueous and butanol solutions as a function of reagent concentration
I. In aqueous solution (pH 1·3)
II. in butanol solution
Gd^{3+} 0·49 μg/ml; wavelength 668 nm.

Beer's law

Beer's law is obeyed over a concentration range up to at least 0·73 μg/ml for both the aqueous and the butanol solutions, but the sensitivity is greater for the butanol system by a factor of three (implying that if a 1 : 1 complex is formed in aqueous medium,[2] a 1 : 3 complex is extracted into butanol, as would be expected for formation of a neutral species). The absorbance remains constant for at least 24 hr.

Effect of diverse ions

The effect of other ions on the determination is shown in Table 1. The presence of an equimolar ratio of uranyl or thorium ions, a tenfold mole-ratio of scandium or a hundredfold mole-ratio of iron(III) causes interference. However, hundredfold mole-ratios of sodium, potassium, magnesium, aluminium, phosphate, sulphate, acetate, citrate and EDTA do not interfere.

Behaviour of other rare earth chelates

Table 2 shows the wavelengths of the absorption maxima and the molar absorptivities of lanthanum, praseodymium, gadolinium, dysprosium, erbium and lutetium chelates in butanol and aqueous solution. Though the maximum of the absorption bands shifts from 677 to 673 nm with increasing atomic number, for aqueous solution, all the maxima are at 688 nm for butanol solution. In both cases, the molar absorptivities increase with atomic number from lanthanum to dysprosium and decrease from dysprosium to lutetium, and the complexes behave similarly to the gadolinium complex.

Table 1. Interferences in the determination of 0·49 μg of gadolinium in synthetic samples (measurement at 668 nm)

Other ion (M)	(M)/(Gd) mole ratio	Gd^{3+} found, μg	Other ion (M)	(M)/(Gd) mole ratio	Gd^{3+} found, μg
Mg^{2+}	100	0·48	Zr^{4+}	1	0·46
Ca^{2+}	10	0·53		10	0·48
	100	0·57	Th^{4+}	1	interference
Al^{3+}	1	0·49		10	serious interference
	100	0·47	SO_4^{2-}	10	0·51
Fe^{3+}	1	0·48		100	0·46
	10	0·54	PO_4^{3-}	1	0·49
	100	serious interference		100	0·46
Sc^{3+}	1	0·50		10	0·50
	10	interference	acetate	100	0·49
UO_2^{2+}	1	interference	citrate	100	0·46
	10	serious interference	EDTA	10	0·50
				100	0·46

Table 2. Maximum wavelengths of absorption bands and molar absorptivities of rare-earth chlorophosphonazo III chelates in aqueous and butanol solutions

	Maximum wavelength, *nm*		Molar absorptivities, *l.mole*$^{-1}$*cm*$^{-1}$	
	aqueous solution	butanol solution	aqueous solution	butanol solution
La	677	668	$5{\cdot}5 \times 10^{4}$	$1{\cdot}5 \times 10^{5}$
Pr	677	668	$5{\cdot}6 \times 10^{4}$	$1{\cdot}9 \times 10^{5}$
Sm	675	668	$6{\cdot}7 \times 10^{4}$	$2{\cdot}0 \times 10^{5}$
Gd	674	668	$7{\cdot}2 \times 10^{4}$	$1{\cdot}9 \times 10^{5}$
Dy	674	668	$8{\cdot}4 \times 10^{4}$	$2{\cdot}3 \times 10^{5}$
Er	674	668	$7{\cdot}6 \times 10^{4}$	$2{\cdot}0 \times 10^{5}$
Lu	673	668	$6{\cdot}0 \times 10^{4}$	$1{\cdot}7 \times 10^{5}$

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Summary—The rare-earth chlorophosphonazo III chelates are easily extracted from an aqueous solution (pH 1·1–1·5) into n-butanol. The absorbance at the absorption maximum (at 668 nm) is about 3 times that in aqueous solution. The spectrophotometric determination of rare earths has been investigated.

Zusammenfassung—Die Chelate der seltenen Erden mit Chlorphosphonazo III werden aus einer wäßrigen Lösung (pH 1,1–1,5) leicht in *n*-Butanol extrahiert. Die Extinktion am Absorptions maximum (bei 668 nm) ist etwa 3-mal so groß wie die in wäßriger Lösung. Die spektrophotometrische Bestimmung seltener Erden ist untersucht worden.

Résumé—Les chélates du chlorophosphonazo III avec les terres rares sont aisément extraits d'une solution aqueuse (pH 1,1–1,5) en *n*-butanol. L'absorbance au maximum d'absorption (à 668 nm) est environ 3 fois celle en solution aqueuse. On a étudié le dosage spectrophotométrique des terres rares.

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ADSORPTION OF CHLORINATED PESTICIDES FROM RIVER WATER WITH XAD-2 RESIN

(*Received* 26 *June* 1973. *Accepted* 3 *July* 1973)

Usually chlorinated pesticides are present in water in such small amounts that using a separatory funnel to carry out the extraction procedure is difficult because of the large volume of water needed to get meaningful data. For the determination of pesticides at lower concentrations two methods are usually used, continuous extraction with an organic solvent,[1] or adsorption on charcoal.[2, 3] These two methods are, however, rather time-consuming, requiring one hour to extract 0·5–1 litre of water in the continuous extraction procedure and up to 35 hr extraction with chloroform to recover the pesticide from the charcoal in the charcoal adsorption procedure. Recently several new absorbents have been proposed for the recovery of organics from water. A mixture of Carbowax 4000 monostearate and undecane on a Chromosorb W solid support has been used to recover chlorinated pesticides from water.[4] Amberlite XAD-2 resin has been used to concentrate dissolved organic materials from sea-water.[5] Polyurethane foam coated with a selective adsorbent has been used for the extraction of organochlorine pesticides from water.[6] Finally Amberlite XAD-2 resin has been used to recover trace organics from potable water.[7] Of these absorbents, Amberlite XAD-2 resins seemed to have the most potential and Amberlite XAD-2 was evaluated as an absorbent for concentration of trace organochlorine pesticides from river water.

EXPERIMENTAL

Apparatus

A Beckman GC-5 gas chromatograph equipped with a discharge electron-capture detector was used for the gas chromatography.

Column. A 2 × 20 cm glass tube was fitted with a Teflon stop-cock on one end and a Ŧ 24/40 outer joint on the other.

Reservoir. A 5-l. round-bottom flask was fitted with a Ŧ 24/40 inner joint on the bottom of the flask. A Teflon sleeve was used to seal the joint connecting the reservoir to the column.

Reagents

The XAD-2 resin was supplied by Rohm and Haas Co. The fine particles were removed from the resin by slurrying and decanting several times with water. The resin was filtered off and transferred to a Soxhlet extractor and extracted for 24 hr with pesticide-grade acetonitrile to remove impurities from the resin. The solvent was changed and extraction continued for another 24 hr with fresh solvent. The resin was washed free from acetonitrile with water and stored under water in a glass-stoppered bottle.

Procedure

A glass-wool plug was placed in the bottom of the column and 10 ml of resin were added to the column in a water slurry. A plug of glass wool was added to the top of the column and the reservoir connected to the top of the column. A 4-l. river-water sample was added to the reservoir and the flow-rate adjusted to approximately 50 ml/min. After the sample had passed through the column, 200 ml of hot acetonitrile were passed through the column at 50 ml/min and collected in a 1-l. separatory funnel. Water (700 ml) was

Zusammenfassung—Die Chelate der seltenen Erden mit Chlorphosphonazo III werden aus einer wäßrigen Lösung (pH 1,1–1,5) leicht in *n*-Butanol extrahiert. Die Extinktion am Absorptions maximum (bei 668 nm) ist etwa 3-mal so groß wie die in wäßriger Lösung. Die spektrophotometrische Bestimmung seltener Erden ist untersucht worden.

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The XAD-2 resin was supplied by Rohm and Haas Co. The fine particles were removed from the resin by slurrying and decanting several times with water. The resin was filtered off and transferred to a Soxhlet extractor and extracted for 24 hr with pesticide-grade acetonitrile to remove impurities from the resin. The solvent was changed and extraction continued for another 24 hr with fresh solvent. The resin was washed free from acetonitrile with water and stored under water in a glass-stoppered bottle.

Procedure

A glass-wool plug was placed in the bottom of the column and 10 ml of resin were added to the column in a water slurry. A plug of glass wool was added to the top of the column and the reservoir connected to the top of the column. A 4-l. river-water sample was added to the reservoir and the flow-rate adjusted to approximately 50 ml/min. After the sample had passed through the column, 200 ml of hot acetonitrile were passed through the column at 50 ml/min and collected in a 1-l. separatory funnel. Water (700 ml) was added to the separatory funnel and the aqueous acetonitrile was extracted with three 60-ml portions of pesticide-grade petroleum ether (b.p. 30–60°). The combined petroleum ether extracts were washed with two 15-ml portions of water, dried by passing through a column of sodium sulphate and concentrated to 1 ml with a Kuderna-Danish evaporation assembly and a 3-ball Snyder column. No "Florisil" clean-up of the petroleum ether extract was necessary before gas chromatographic analysis. For larger samples a bigger reservoir may be used, or several bottles of river water may be passed through the 5-l. reservoir in succession.

RESULTS AND DISCUSSION

Table 1 lists the results obtained for a series of weekly samples taken between January and June of 1973 from the Skunk River near Ames, Iowa. The XAD-2 results are the average of duplicate determinations which generally agreed within ±1 part per billion (10^{12}). Dieldrin was the only pesticide present in sufficient concentration to be monitored accurately with a 4-l. sample. During periods of high run-off or at other times with a larger sample, the following pesticides were detected but not quantitatively: *p,p'*–DDT, *p,p'*–DDE, *p,p'*–DDD, *o,p'*–DDT, heptachlor epoxide, lindane or atrazine or both, and several others yet to be characterized. The values obtained for dieldrin by using XAD-2 resin compare favourably with those from the regular extraction procedure.[8] The XAD-2 procedure is easier to use in that a 4-l. sample does not have to be manipulated several times.

Table 1. Comparison of dieldrin recovery from 4-l. river water samples by the XAD-2 procedure and the regular extraction procedure.[8] Results given in parts per billion (10^{12})

Date	XAD-2	Extraction	Date	XAD-2	Extraction
Jan. 8	9	6	April 5	4	4
Jan. 15	18	13	April 15	14	7
Jan. 24	4	4	April 22	4	4
Feb. 1	17	15	April 29	2	1
Feb. 4	16	16	May 6	5	3
Feb. 11	20	15	May 13	6	4
Feb. 19	5	3	May 20	4	3
March 19	5	2	May 28	9	9
March 24	8	6	June 3	6	5
March 30	5	4			

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Summary—Pesticides in river water at levels as low as parts per billion (10^{12}), can be recovered by sorption on a column of XAD-2 resin, followed by elution with acetonitrile. Water is added to the acetonitrile and the pesticides are extracted by petroleum ether and determined by gas chromatography. The new procedure is more convenient to use than the solvent extraction procedure and gives comparable results for dieldrin.

Zusammenfassung—Pestizide in Flußwasser können in ppb-Konzentrationen (10^{12}) erfaßt werden durch Sorption an einer Säule mit XAD-2-Harz und anschließender Elution mit Acetonitril. Zum Acetonitril wird Wasser gegeben, die Pestizide mit Petroläther extrahiert und durch Gaschromatographie bestimmt. Die neue Vorschrift ist bequemer als das Verfahren mit flüssig-flüssig-Extraktion und dibt bei Dieldrin vergleichbare Erfebnisse.

Résumé—On peut récupérer des pesticides dans l'eau de rivière à des teneurs aussi faibles que des parties par trillion (10^{12}) par sorption sur une colonne de résine XAD-2, suivie d'élution à l'acétonitrile. On ajoute de l'eau à l'acétonitrile et les pesticides sont extraits à l'éther de pétrole et déterminés par chromatographie en phase vapeur. La nouvelle technique est plus commode à utiliser que la technique d'extraction par solvant et donne des résultats comparables pour la dieldrine.

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM IN HIGH-PURITY INDIUM

(*Received* 19 *June* 1973. *Accepted* 28 *June* 1973)

An accurate determination of trace quantities of thallium in high-purity indium has great importance in the technology of semi-conductor materials. In the present paper a spectrophotometric method for determining 10^{-5}–10^{-6}% thallium in indium is described. High selectivity and sensitivity are attained by extractive separation of thallium from the matrix in hydrochloric acid medium,[1–5] and determination of thallium as the ion-association complex of $TlCl_4^-$ with Brilliant Green.[6–8]

EXPERIMENTAL

Reagents

Spectroscopically pure hydrochloric acid, analytical grade reagents and twice-distilled water were used throughout.

Standard thallium solution, 1 *mg/ml*. Thallium nitrate (1·3650 g) was dissolved in water containing 2 ml of conc. nitric acid and diluted to 1 l. with water. The solution was standardized by precipitation of Tl_2CrO_4. Working standards were prepared by dilution of this solution.

Brilliant Green, 0·01 % *solution*.

Phenol, 10% solution in glacial acetic acid.

Recommended procedure

Dissolve a sample of indium (1–5 g) in 25 ml of 6*M* hydrochloric acid. Add 0·2 g of copper wire and evaporate the solution to about 5 ml. Allow to cool and separate from the copper wire, add 5 ml of 6*M* hydrochloric acid and 5 drops of bromine water. Add 5 drops of phenol solution and extract thallium with di-isopropyl ether (shaking time 1 min). Wash the organic solution twice with 5-ml portions of 3*M* hydrochloric acid containing 1 drop of bromine water (shaking time 30 sec). Shake the ether extract for 30 sec with a mixture of 5 ml of 0·3*M* hydrochloric acid and 5 ml of Brilliant Green solution. Dilute the extract to volume with di-isopropyl ether in a volumetric flask, measure the absorbance against a blank solution at 630 nm and obtain the thallium concentration from a calibration curve.

RESULTS

Determination of thallium with Brilliant Green

Thallium complexes such as $TlCl_4^-$ or $TlBr_4^-$ and Brilliant Green form an ion-association complex,

Summary—Pesticides in river water at levels as low as parts per billion (10^{12}), can be recovered by sorption on a column of XAD-2 resin, followed by elution with acetonitrile. Water is added to the acetonitrile and the pesticides are extracted by petroleum ether and determined by gas chromatography. The new procedure is more convenient to use than the solvent extraction procedure and gives comparable results for dieldrin.

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RESULTS

Determination of thallium with Brilliant Green

Thallium complexes such as $TlCl_4^-$ or $TlBr_4^-$ and Brilliant Green form an ion-association complex, which can be extracted with organic solvents. The absorption spectrum of the $TlCl_4^-$ complex is shown in Fig. 1. The molar absorptivity in di-isopropyl ether is $1{\cdot}06 \times 10^5$ l. mole^{-1}· cm^{-1} at $\lambda_{max} = 630$ nm. Beer's law is obeyed for thallium concentrations up to 2 μg/ml and the colour is stable for at least 1 hr.

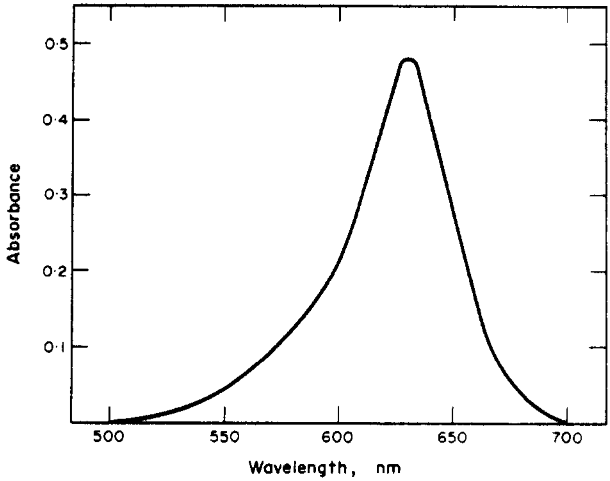

Fig. 1. Absorption spectrum of thallium–Brilliant Green complex in di-isopropyl ether medium. Thallium concentration 1·0 μg/ml, 10-mm cells.

Extraction of the complex is strongly dependent on the hydrochloric acid concentration in the aqueous phase (Fig. 2), the optimum hydrochloric acid concentration being 0·15*M*. For determination of thallium at least a 4-fold excess of Brilliant Green is necessary. Brilliant Green is not itself extracted into the organic phase. Under the conditions recommended for thallium determination a single extraction is sufficient. Equilibrium is attained in 30 sec of shaking.

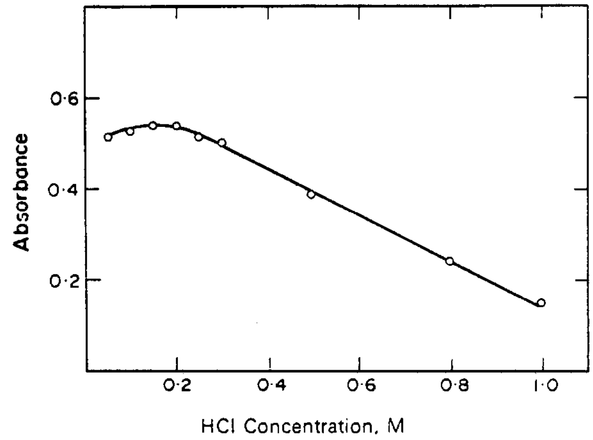

Fig. 2. Influence of hydrochloric acid concentration on thallium–Brilliant Green complex formation and on extraction into di-isopropyl ether.

Thallium(I) can be oxidized to Tl(III) with bromine water and the excess of bromine removed by addition of small amounts of phenol.

Extractive separation of thallium from indium

Because $InCl_4^-$ also forms a Brilliant Green complex a preliminary separation is necessary. This can be done by selective extraction of the chloride complex with oxygenated solvents. The influence of the hydrochloric acid concentration on extraction of thallium(III) and indium(III) with di-isopropyl ether is shown in Fig. 3. A 6*M* hydrochloric acid medium was chosen for separation of thallium from indium, and the efficiency of various extractants was examined (Table 1). Di-isopropyl ether gives relatively small values of the distribution coefficient for thallium but the best separation from indium.

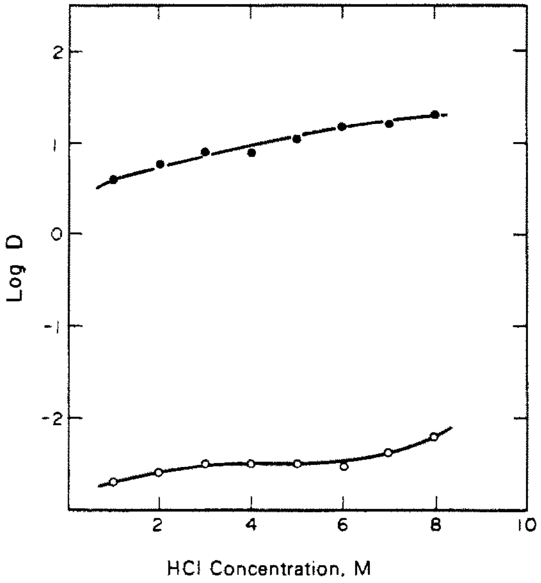

Fig. 3. Dependence of distribution coefficient of thallium (●) and indium (○) on hydrochloric acid concentration in extraction with di-isopropyl ether. Initial concentrations: thallium 100 μg/ml, indium 10 mg/ml.

Table 1. Distribution coefficients of thallium(III) and indium(III) between some organic solvents and 6*M* hydrochloric acid. Initial concentrations: $c_{Tl} = 10$ μg/ml, $c_{In} = 1$ mg/ml

Solvent	log D_{Tl}	log D_{In}	log $\frac{D_{Tl}}{D_{In}}$
di-isopropyl ether	1·2	−2·5	3·7
n-amyl acetate	1·4	−2·1	3.5
isoamyl alcohol	1·9	−1·3	3·2
methyl isobutyl ketone (MIBK)	2·3	−0·6	2·9

Interferences

From 6*M* hydrochloric acid medium, gold(III), antimony(V), iron(III), gallium(III), and partially indium(III) are extracted into di-isopropyl ether. These elements interfere in the thallium determination with Brilliant Green by giving similar colour reactions. However, washing the organic extract with 3*M* hydrochloric acid will remove iron(III), gallium and indium.

Interferences of gold(III) and antimony(V) can be eliminated by reduction of these elements with metallic copper[9] before extraction of the thallium. A tenfold amount of gold(III) and antimony(V) relative to thallium does not affect the results of thallium determination when the recommended procedure is applied.

Determination of thallium in high-purity indium

The method was applied to analysis of high-purity indium samples. The results presented in Table 2 show good precision and accuracy.

Table 2. Results of determination of thallium in high-purity indium metal samples

Sample weight, *g*	Tl found,* %	Standard deviation, %	Tl added, %	Total Tl found, %
5	3×10^{-6}	$0{\cdot}5 \times 10^{-6}$	10×10^{-6}	13×10^{-6} 14×10^{-6}
1	$6{\cdot}5 \times 10^{-5}$	$0{\cdot}37 \times 10^{-5}$	$5{\cdot}0 \times 10^{-5}$	11×10^{-5} 10×10^{-5}

* The average of 5 determinations.

DISCUSSION

Brilliant Green is a suitable reagent for the determination of thallium, the main advantages of this reagent being high sensitivity, stability of absorbance and absence of fluorescence (which occurs when Rhodamine B is used). The Brilliant Green itself is not extractable under the conditions used. The comparatively high molar absorptivity allows determination of trace amounts of thallium.

The preliminary extraction to separate thallium, followed by complex formation in the organic phase, is particularly convenient, since it avoids the need to strip the thallium or mineralize the extract, as done hitherto.

Other solvents (*e.g.*, MIBK) give more efficient thallium extraction than di-isopropyl ether but simultaneously increase the extraction of the matrix element unfavourably.

Indium, iron(III) and gallium are entirely removed by double washing of the ether phase with $3M$ hydrochloric acid. Any antimony(V) and gold(III) can be reduced with a little copper.

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Summary—Trace amounts of thallium in high-purity indium are separated from the matrix by extraction from $6M$ hydrochloric acid by di-isopropyl ether. On shaking the extract with Brilliant Green in $0{\cdot}15M$ hydrochloric acid, an ion-association complex is formed in the organic phase. Interference of other elements is removed by their reduction with metallic copper and scrubbing. The proposed method permits determination of 10^{-5}–10^{-6}% thallium in high-purity indium with good precision and accuracy.

Zusammenfassung—Spurenmengen Thallium in hochreinem Indium werden durch Extraktion mit Diisopropyläther aus 6 M Salzsäure von der Matrix getrennt. Schüttelt man den Extrakt mit Brillantgrün in 0,15 M Salzsäure, dann bildet sich in der organischen Phase ein Ionenassoziationskomplex. Die Störung durch andere Elemente wird durch Reduktion mit metallischem Kupfer und Auswaschen beseitigt. Das vorgeschlagene Verfahren erlaubt die Bestimmung von 10^{-5}–10^{-6}% Thallium in hochreinem Indium mit guter Genauigkeit und Richtigkeit.

Résumé—Des quantités de thallium à l'état de traces dans l'indium de haute pureté sont séparées de la matrice par extraction d'acide chlorhydrique 6*M* au moyen d'éther diisopropylique. En agitant l'extrait avec du Vert Brillant en acide chlorhydrique 0,15*M*, il se forme un complexe d'association ionique dans la phase organique. L'interférence d'autres éléments est éliminée par leur réduction avec du cuivre métallique et épuration. La méthode proposée permet le dosage de 10^{-5}–10^{-6}% de thallium dans l'indium de haute pureté avec de bonnes fidélité et précision.

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EVALUATION OF 1-(2-THIAZOLYLAZO)-2-HYDROXY-3-NAPHTHOIC ACID AS A METALLOCHROMIC INDICATOR

(*Recieved* 15 *May* 1973. *Accepted* 9 *June* 1973)

Many *o*-hydroxythiazolylazo compounds have been used as metallochromic indicators. Most cannot be used at a high pH because of the dissociation of the phenolic proton, but in 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid (TAHN)[1], the acidity of the phenolic proton is lessened by hydrogen-bonding with the carboxyl group.

The formation constants of TAHN chelates of copper, nickel and zinc and its value as an indicator are reported here.

EXPERIMENTAL

Reagents

TAHN The reagent was synthesized by the procedure reported previously.[1] It was used as a $10^{-3}M$ solution in dioxan.

Metal ion solutions. These were prepared by dissolving the reagent-grade metal nitrate in water.

NTA. This was recrystallized from distilled water.

Buffer solutions. Acetate and borate buffer solutions were used to adjust pH values.

Ionic strength. Sodium perchlorate prepared from sodium carbonate and perchloric acid was used to maintain the ionic strength at 0·1.

Solvent. Dioxan was purified by the method described previously.[2]

RESULTS AND DISCUSSIONS

Acid dissociation constants

The colour of strongly acidic aqueous solutions of TAHN changes with increasing pH from yellow to orange-yellow, to yellow, to rose owing to the dissociations of the thiazolinium ion, carboxyl group and hydroxy group respectively.

The dissociation constants of TAHN were determined in dioxan–water mixture by the Hildebrand–Reilley method.[3] The p*k* values are summarized in Table 1.

Table 1. Acid dissociation constants of TAHN ($\mu = 0{\cdot}1$, 25°C)

pk_{NH}	pk_{COOH}	pk_{OH}	Dioxan, %
0·68	3·45	9·83	5
0·5	3·68	10·4	20
	3·92	11·5	50

Zusammenfassung—Spurenmengen Thallium in hochreinem Indium werden durch Extraktion mit Diisopropyläther aus 6 M Salzsäure von der Matrix getrennt. Schüttelt man den Extrakt mit Brillantgrün in 0,15 M Salzsäure, dann bildet sich in der organischen Phase ein Ionenassoziationskomplex. Die Störung durch andere Elemente wird durch Reduktion mit metallischem Kupfer und Auswaschen beseitigt. Das vorgeschlagene Verfahren erlaubt die Bestimmung von 10^{-5}–10^{-6}% Thallium in hochreinem Indium mit guter Genauigkeit und Richtigkeit.

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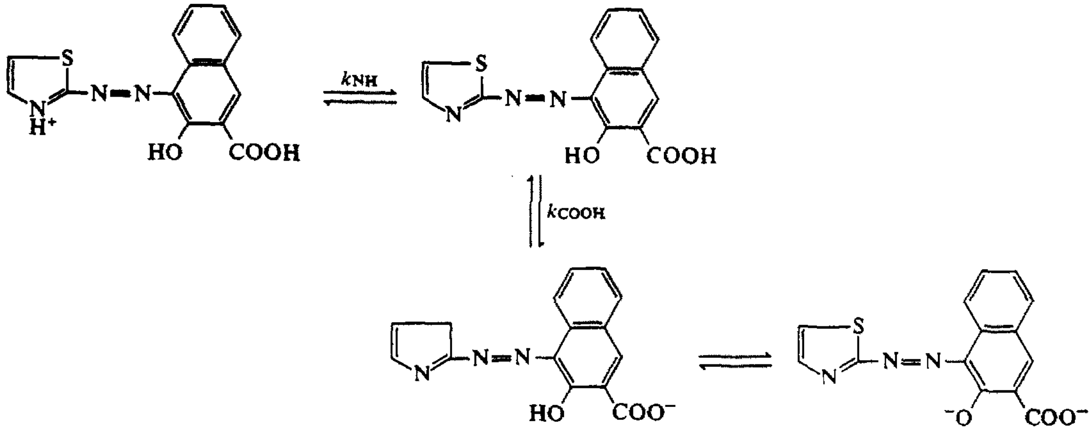

Formation of metal chelates

Copper. Copper(II) forms blue-violet chelates with TAHN at pH > 1·5. By the method of continuous variation, it was found that copper forms a 1:1 chelate up to pH 9. Figure 1*a* shows the absorption spectra of copper–TAHN chelates when copper is in excess. The presence of isosbestic points at 500 and 610 nm indicates the equilibrium $\mathrm{CuA} + \mathrm{H}^+ \rightleftharpoons \mathrm{CuHA}^+$. Since copper reacts with TAHN at very low pH and the spectral difference between CuA and CuHA^+ is very small, the formation constants of copper–TAHN chelates are determined by using a metal buffer solution consisting of copper and excess of nitrilotriacetic acid (NTA). The absorbances at 610 nm of 5% v/v dioxan–water solutions containing copper ($30{\cdot}9 \times 10^{-4}M$), NTA ($3{\cdot}90 \times 10^{-4}M$) and TAHN ($6{\cdot}00 \times 10^{-6}M$) were measured over the pH range 3–7 at 25° with a 5-cm cell.

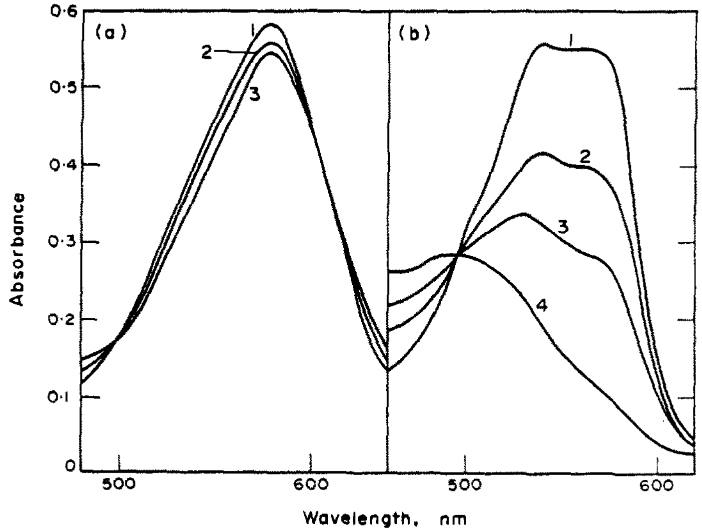

Fig. 1. Absorption spectra of Cu– and Zn–TAHN chelates (5% v/v dioxan–water, 5-cm cell)
Cu, Zn: $2 \times 10^{-4}M$, TAHN: $4 \times 10^{-6}M$
(*a*) Cu—1, pH 2·5–3; 2, pH 4·1; 3, pH > 5·5
(*b*) Zn—1, pH > 7; 2, pH 6·3; 3, pH 5·9; 4, pH 4·4

The conditional stability constant of copper–TAHN chelate is given by equation (1) (charges are omitted for simplicity):

$$K_{(\mathrm{CuA})'} = \frac{[(\mathrm{CuA})']}{[\mathrm{Cu}][\mathrm{A}]} = K_{\mathrm{CuA}}(1 + K^{\mathrm{H}}_{\mathrm{CuHA}}[\mathrm{H}]) \qquad (1)$$

where $[(\mathrm{CuA})']$ is the total concentration of CuA and CuHA^+ and

$$K_{\mathrm{CuA}} = \frac{[\mathrm{CuA}]}{[\mathrm{Cu}][\mathrm{A}]}, \quad K^{\mathrm{H}}_{\mathrm{CuHA}} = \frac{[\mathrm{CuHA}]}{[\mathrm{CuA}][\mathrm{H}]}$$

Since at 610 nm the absorbance of CuA is equal to that of CuHA and the absorbance of free TAHN is negligible, we have

$$[(\mathrm{CuA})'] = \frac{A}{\varepsilon} \tag{2}$$

where A and ε are the absorbance and the molar absorptivity respectively of the copper–TAHN chelate.

On the other hand [A] can be obtained from the total TAHN concentration C_{A}:

$$[\mathrm{A}] = \frac{[\mathrm{A}']}{\alpha_{\mathrm{A(H)}}} = \frac{C_{\mathrm{A}} - [(\mathrm{CuA})']}{\alpha_{\mathrm{A(H)}}} \tag{3}$$

where $\alpha_{\mathrm{A(H)}}$ is the side-reaction coefficient taking into account the acid dissociation of TAHN. Also [Cu] can be calculated from the composition of the metal buffer solution and its pH value:

$$[\mathrm{Cu}] = \frac{[\mathrm{CuX}]}{K_{\mathrm{CuA}}[\mathrm{X}]} = \frac{C_{\mathrm{Cu}}\alpha_{\mathrm{X(H)}}}{K_{\mathrm{CuA}}(C_{\mathrm{X}} - C_{\mathrm{Cu}})} \tag{4}$$

where C_{Cu} and C_{X} are the total concentrations of copper(II) and NTA, and $\alpha_{\mathrm{X(H)}}$ is the side-reaction coefficient taking into account the acid dissociation of NTA. Figure 2 shows a plot of $\log K_{(\mathrm{CuA})'}$ *vs.* pH. K_{CuA} and $K^{\mathrm{H}}_{\mathrm{CuHA}}$ were evaluated by a curve-fitting method.

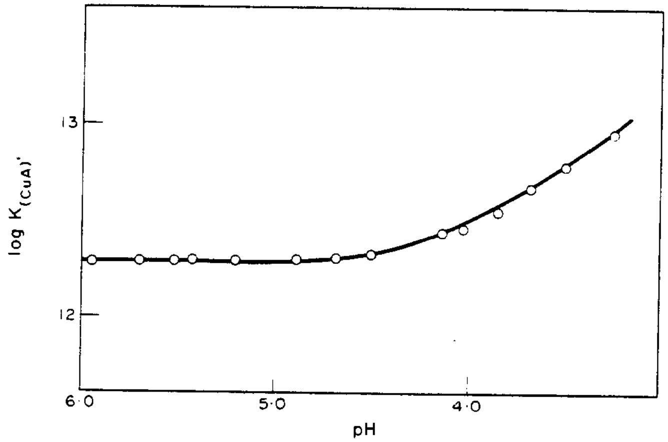

Fig. 2. Plot of $\log K_{(\mathrm{CuA})'}$ *vs.* pH.
Solid line is the theoretical curve.

Nickel. Nickel(II) forms red-violet chelates with TAHN at pH > 3, the molar ratio of nickel to TAHN being 1:1 at pH < 6, and 1:2 at higher pH. The formation of NiHA^+ is observed in the pH range between 3 and 5. As shown in Fig. 3 the absorption spectra of NiHA^+ and NiA are slightly different and show isosbestic points at 543, 550 and 578 nm. From the absorbances at 543 nm of the solutions containing TAHN and a 2–50-fold excess of nickel, the conditional stability constant of nickel–TAHN chelate, $K_{(\mathrm{NiA})'}$, was calculated, and K_{NiA} and $K^{\mathrm{H}}_{\mathrm{NiHA}}$ were obtained by the method described for copper.

The shape of the absorption spectrum of the 1:2 chelate is similar to that of the 1:1 chelate, but the molar absorptivity is twice as great .

The formation constant of $\mathrm{NiA_2}^{2-}$ is defined by equation (5).

$$\log K^{\mathrm{A}}_{\mathrm{NiA_2}} = \log \frac{[\mathrm{NiA_2}]}{[\mathrm{NiA}]} + \mathrm{pA} \tag{5}$$

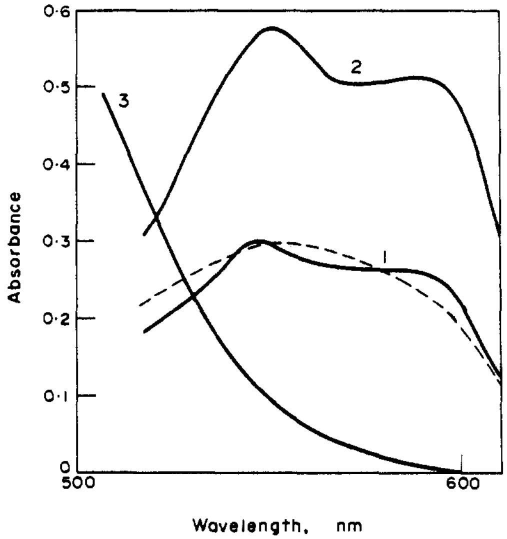

Fig. 3. Absorption spectra of Ni–TAHN chelates
(5% v/v dioxan–water, 5-cm cell)
1, Ni: $4 \times 10^{-5}M$, TAHN: $2 \times 10^{-6}M$ solid line: pH 6, dotted line: pH 4
2, Ni: $2 \times 10^{-6}M$, TAHN: $10^{-5}M$, pH 8 (against reagent blank)
3, TAHN: $10^{-5}M$, pH 8.

When the solution is $2 \times 10^{-6}M$ in nickel and contains a 5–10-fold excess of TAHN, and its pH is > 6, the concentration of nickel ion not combined with TAHN can be neglected. The ratio $[NiA_2]/[NiA]$ can be obtained from the absorbances at 580 nm, and equation (5) used to determine $K^{A}_{NiA_2}$.

Zinc. Zinc(II) forms a pink-red chelate with TAHN at pH > 6. Fig. 1*b* shows that the only chelate formed is ZnA and its stability constant was evaluated from the equilibrium constant K and k_{OH} (the dissociation constant for the phenolic proton):

$$K = \frac{[ZnA][H]}{[Zn][HA]} = \frac{K_{ZnA}}{k_{OH}} \tag{6}$$

$ZnA_2{}^{2-}$ does not form at pH less than 9.

The formation constants of copper, nickel and zinc are summarized in Table 2. Although the formation constants of 1:1 chelates of TAHN are almost of the same order as those of 1-(2-thiazolylazo)-2-naphthol (TAN), if the acid dissociations of TAHN and TAN are taken into account, the formation constants of 1:2 chelates of TAHN are much smaller than those of TAN (Fig. 4).

Table 2. Formation constants of TAHN chelates ($\mu = 0{\cdot}1$, 25°C, in 5% v/v dioxan–water)

	$\log K_{MA}$	$\log K^{H}_{MHA}$	$\log K^{A}_{MA_2}$
Cu(II)	12·29	3·82	
Ni(II)	9·70	4·90	8·0
Zn(II)	7·57		

Use as a metallochromic indicator

TAHN is a favourable metal indicator because the dissociation of a proton from the phenol group occurs at a higher pH and 1:2 chelates are leass easily formed than in the case of other *o*-hydroxythiazolylazo compounds. The second factor is advantageous in the case of nickel titration.

The optimum conditions for the EDTA titration of copper or nickel with TAHN as indicator are determined by the pM–pH diagrams (Fig. 5).[4,5] These results are confirmed by the photometric titrations. Copper

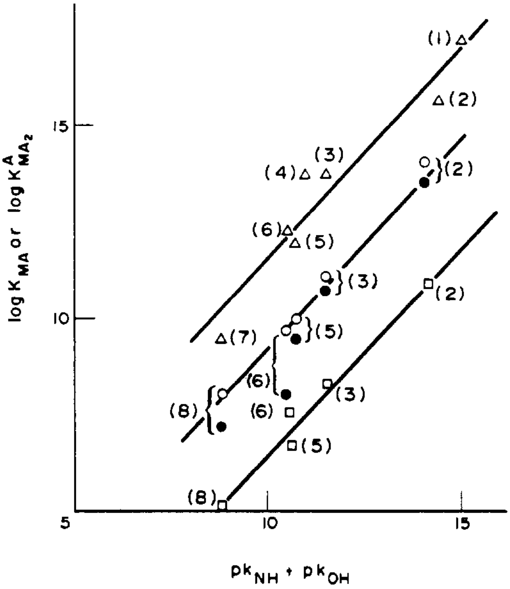

Fig. 4. The relation between the dissociation constants and the formation constants of metal chelates

△ $\log K_{CuA}$, ○ $\log K_{NiA}$, ● $\log K^{A}_{NiA_2}$, □ $\log K_{ZnA}$ (1) PAR [4-(2-pyridylazo)resorcinol], (2) PAN [1-(2-pyridylazo)-2-naphthol], (3) PAC [2-(2-pyridylazo)-4-methylphenol], (4) TAR [4-(2-thiazolylazo)resorcinol], (5) TAN, (6) TAHN, (7) TAC [2-(2-thiazolylazo)-4-methylphenol].

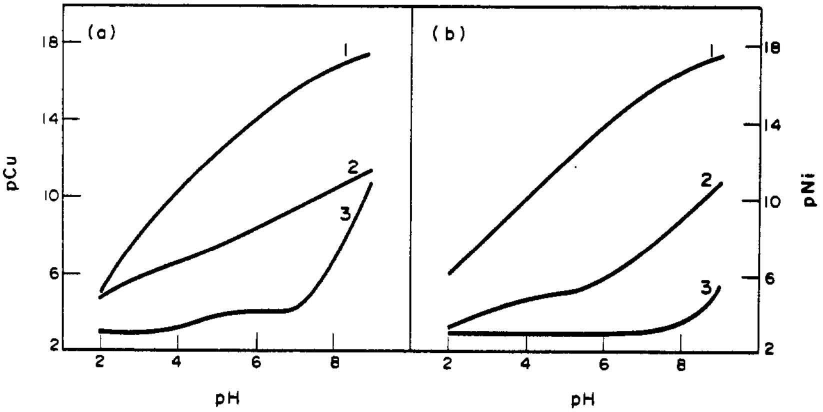

Fig. 5. pM *vs.* pH diagrams

1, pM for 100% excess of ligand; 2, pM for 50% colour change of indicator; 3, pM in absence of ligand.

(*a*) copper, (*b*) nickel.

Metal: $10^{-3}M$, TAHN: $10^{-5}M$

pH 2–7: 0·4M acetate buffer

pH 8–9: 0·2M ammonia buffer.

can be titrated in a pH range from 3 to 8 with a sharp colour change from blue-violet to yellow or orange-yellow at the equivalence point. In the case of nickel a sharp colour change can be obtained at the equivalence point in the pH range between 6 and 9. The addition of a small amount of blue dye ($10^{-5}M$) such as Methylene Blue or Bromocresol Green improves the contrast of colour change.

TAHN is recommended as an indicator in the titrations of copper and nickel.

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Summary—The acid dissociation constants of 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid (TAHN) and the formation constants of Cu(II), Ni(II) and Zn(II) chelates of this dye have been determined spectrophotometrically at 25° in a 5% v/v mixture of dioxan and water. The formation constants of the 1:2 chelates are smaller than those of other *o*-hydroxythiazolylazo compound chelates.TAHN is a satisfactory indicator for the titrations of Cu(II) and Ni(II) with EDTA.

Zusammenfassung—Die Säuredissoziationskonstanten von 1-(2-Thiazolylazo)-2-hydroxy-3-naphthoesäure (TAHN) und die Bildungskonstanten der Chelate dieses Farbstoffs mit Cu(II), Ni(II) und Zn(II) wurden bei 25° in einer 5% V/V-Mischung von Dioxan und Wasser spektrophotometrisch bestimmt. Die Bildungskonstanten der 1:2-Chelate sind kleiner als die anderer Chelate von o-Hydroxythiazolylazoverbindungen. TAHN ist ein zufriedenstellender Indikator für die Titration von Cu(II) und Ni(II) mit EDTA.

Résumé—On a déterminé spectrophotométriquement à 25° dans un mélange à 5% (v/v) de dioxane et d'eau les constantes de dissociation acide de l'acide 1-(2-thiazolylazo) 2-hydroxy 3-naphtoïque (TAHN) et les constantes de formation des chélates de Cu (II), Ni (II) et Zn (II) de ce colorant. Les constantes de formation des chélates 1:2 sont plus petites que celles de chélates d'autres *o*-hydroxythiazolylazo composés. Le TAHN est un indicateur satisfaisant pour le titrage de Cu (II) et Ni (II) à l'EDTA.

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COMPARISON OF THE ION-EXCHANGE BEHAVIOUR OF ZIRCONIUM, THORIUM, VANADIUM, URANIUM, STANNIC AND TITANIUM TUNGSTATES

(*Received* 20 *June* 1972. *Revised* 7 *May* 1973. *Accepted* 16 *May* 1973)

Titanium tungstate (TiW) and its ion-exchange properties have been described previously,[1–3] Amphlett[4] has observed that the composition and the ion-exchange properties of amorphous zirconium phosphate depend on the conditions of preparation. We have therefore synthesized zirconium, uranium, stannic, thorium and vanadium tungstates under conditions identical to those for titanium tungstate.[2] In this report we summarize their properties.

can be titrated in a pH range from 3 to 8 with a sharp colour change from blue-violet to yellow or orange-yellow at the equivalence point. In the case of nickel a sharp colour change can be obtained at the equivalence point in the pH range between 6 and 9. The addition of a small amount of blue dye ($10^{-5}M$) such as Methylene Blue or Bromocresol Green improves the contrast of colour change.

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Titanium tungstate (TiW) and its ion-exchange properties have been described previously,[1-3] Amphlett[4] has observed that the composition and the ion-exchange properties of amorphous zirconium phosphate depend on the conditions of preparation. We have therefore synthesized zirconium, uranium, stannic, thorium and vanadium tungstates under conditions identical to those for titanium tungstate.[2] In this report we summarize their properties.

EXPERIMENTAL

Preparation

The tungstates were synthesized under conditions given in Table 1. The reagents were mixed at room temperature with continuous stirring and were allowed to stand for 24 hr at room temperature. The supernatant liquid was decanted, the gel filtered off, and washed with distilled water. The product so obtained was dried at 80°. The dried product (~40 g) was immersed in 100 ml of $1{\cdot}0M$ nitric acid to remove the foreign ions adsorbed during the preparation. Very little of the compound dissolved during this process. Finally the exchangers were washed with demineralized water to remove the excess of acid and again dried at 80°.

Table 1. Conditions of preparation and some properties of zirconium, thorium, uranium, vanadium, stannic and titanium tungstates.

Ion-exchange material	Metal salt,* *M*	Sodium tungstate, *M*	Volume ratio	Precipitation pH	Chemical composition, W/M	Ion-exchange capacity, *meq/g*	Solubility *g/l.* Water M	Water W	6*M* HNO_3 M	6*M* HNO_3 W	Appearance of the dried material
Zirconium tungstate (ZrW)	0·3 ZrC	0·3	(1:1)	3·8	0·4	0·36	0·0	0·0	0·33	0·28	White opaque particles
Thorium (i) tungstate	0·3 ThN	0·3	(1:1)	0·8	—	—	—	—	—	—	Precipitate does not form
(Th-W) (ii)	0·3 ThN	0·3	(1:2)	3·4	—	0·0	—	—	—	—	White opaque particles
Vanadium tungstate (V-W)	0·3 VS	0·3	(1:1)	3·5	—	—	Dissolved completely		—	—	Brown-green opaque particles
Uranium tungstate (UW)	0·3 UN	0·3	(1:1)	2·8	1·1	0·82	0·0	0·0	0·25	0·010	Yellow opaque particles
Stannic tungstate (Sn(IV)W	0·3 Sn(IV)C	0·3	(1:1)	0·3	0·3	1·00	0·006	0·006	0·050	0·010	White shiny particles
Titanium tungstate (TiW)	0·3 Ti(IV)C	0·3	(1:1)	1·0	1·1	0·80	0·0	0·0	0·0	0·0	Lemon yellow shiny particles

* Zr = zirconyl; V = vanadyl; U = uranyl; C = chloride; S = sulphate and N = nitrate.

RESULTS

Physical properties

The properties of the ion-exchange materials are summarized in Table 1. The materials are stable in water and can be used in column operations.

Composition

A 100-mg portion of the exchanger was dissolved in 25 ml of concentrated sulphuric acid. Tungsten was separated from tin, zirconium or uranium with α-benzoinoxime and estimated.[1] Tin(IV) in the filtrate was determined volumetrically with dichromate.[5] Zirconium[6] and uranium[7] were determined gravimetrically. The results are summarized in Table 1.

The components of the ion-exchange materials dissolved by water and $6M$ nitric acid were determined by the methods used earlier.[2] Tin,[8], zirconium[9] and uranium[10] were estimated spectrophotometrically. The ion-exchange capacity of all the exchangers for potassium was determined as usual. The results are given in Table 1. The pH titrations were carried out by the method of Topp and Pepper,[11] 0·5 g of exchanger being taken in a 250-ml conical flask, treated with a total of 100 ml of $0{\cdot}1M$ sodium chloride and $0{\cdot}1M$ sodium hydroxide in varying ratios by shaking for 6 hr and the pH of the supernatant liquid then being measured. The pH decreases because the H^+ ions released by the Na^+ neutralize some of the sodium hydroxide. There is only one break in the titration curves so the exchangers are monofunctional.

Determination of distribution coefficients

Some distribution coefficients were determined by the method used before.[2] Al^{3+}, In^{3+} and Fe^{3+} were adsorbed completely on ZrW, UW and SnW but only negligibly on TiW. The results are summarized in Table 2.

Table 2. Distribution coefficients for some metal ions on various tungstates in water (pH 5·3)

Metal ion	$10^{-2} \times K_d$ value, *ml/g*			
	ZrW	UW	SnW	TiW
Mg^{2+}	3·0	3·0	7·0	0·66
Ca^{2+}	13·0	0·86	8·3	1·33
Sr^{2+}	7·0	1·00	7·0	6·0
Ba^{2+}	5·0	0·50	5·0	10·0
Zn^{2+}	2·5	1·12	264	3·5
Cd^{2+}	6·2	1·40	13·4	1·8

DISCUSSION

The thorium tungstate showed no ion-exchange behvaior and vanadyl tungstate dissolved when immersed in water, so only zirconium, uranium, stannic and titanium tungstates were examined in detail. The solubility in water and 6*M* nitric acid was found to increase with the difference in electronegativities between the two components of the exchanger.

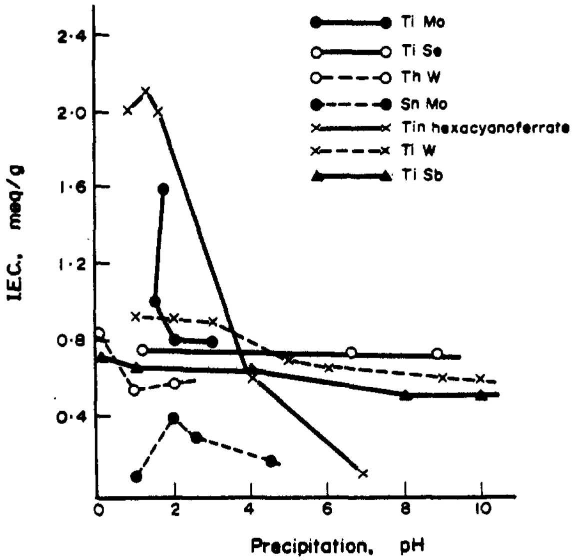

Fig. 1. Effect of precipitation pH on ion-exchange capacity.

Figure 1 shows the effect of precipitation pH on the ion-exchange capacity of numerous ion-exchangers synthesized in our laboratory, both in earlier studies[12–16] and the present work. The precipitation pH is the pH of the reagent mixture before precipitation starts. In our earlier studies it varied from 0 to 10, and was adjusted in the case of titanium molybdate by adding sulphuric acid, of thorium tungstate by adding nitric acid, of tin hexacyanoferrate by adding sodium hydroxide, and of titanium antimonate and tungstate by adding ammonia solution. The precipitation pH of ion-exchangers which were synthesized for this paper was 0–2·4, and was simply that of the mixture without further addition of acid or base. The amorphous gels obtained in this way do not show reproducible properties. It is therefore surprising that even so there is the general trend that ion-exchange capacity increases with decrease in precipitation pH, exceptions probably being due to the non-reproducible nature of the gels formed.

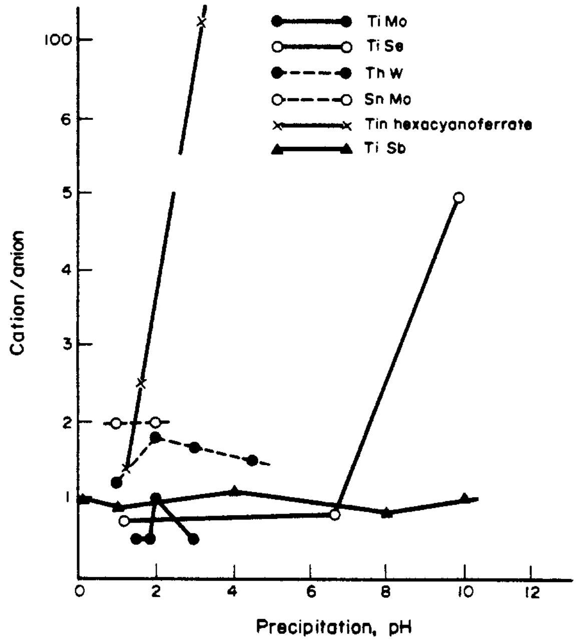

Fig. 2. Effect of precipitation pH on cation/anion ratio in the exchangers.

Figure 2 shows the effect of precipitation pH on the composition of the six exchangers. Only three of the 22 points plotted are against the general trend that as the precipitation pH increases the cation/anion ratio also increases. This appears understandable since at higher pH the cation is precipitated as a hydroxide while the anion remains in solution. The same explanation holds for solubility in nitric acid increasing with increase in precipitation pH. The solubility behaviour in water is different from that in nitric acid because hydrolysis becomes the predominant factor. The apparently anomalous behavior of titanium molybdate may be due to complex formation by titanium with the sulphuric acid used to adjust the pH.

An unusual and interesting feature of titanium tungstate is the negligible adsorption of tervalent ions such as Fe^{+3}, Al^{+3} and In^{+3}. Other tungstates show complete adsorption of these ions. In view of this characteristic property and its high stability it can be more useful than other tungstate ion-exchange materials for the separation of tervalent from univalent and bivalent ions. Stannic tungstate has a very high capacity for Zn and therefore it can be used to separate Zn from numerous metal ions.

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Summary—Zirconium, thorium, uranium, vanadium, stannic and titanium tungstates have been prepared and their properties such as ion-exchange capacity, K_d values of metal ions, chemical composition and stability have been compared. Titanium tungstate was found to be the most stable, and to have negligible capacity for tervalent cations.

Zusammenfassung—Die Wolframate von Zirkonium, Thorium, Uran, Vanadium, Zinn(IV) und Titan wurden hergestellt und ihre Eigenschaften, wie Ionenaustauschkapazität, K_d-Werte von Metallionen, chemische Zusammensetzung und Stabilität verglichen. Titanwolframat erwies sich als am stabilsten, und seine Kapazität für dreiwertige Kationen ist vernachlässigbar.

Résumé—On a préparé les tungstates de zironium, thorium, uranium, vanadium, étain stannique et titane et comparé leurs propriétés telles que la capacité d'échange d'ions, les valeurs K_d des ions métalliques, la composition chimique et la stabilité. On a trouvé que le tungstate de titane est le plus stable, et qu'il a une capacité négligeable pour les cations trivalents.

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RAPID EDTA DETERMINATION OF LEAD IN BINARY ALLOYS OF LEAD AND TIN

(*Received* 16 *February* 1973. *Accepted* 2 *May* 1973)

A wide variety of methods for the titrimetric determination of lead, in which EDTA is used as the titrant with varying results, appears in the chemical literature. Reilley and Barnard[1] list 58 different methods of which 37 are direct titration, and 5 are substitution titrations. Barnard[2] and Sriveeraraghavan[3] also list a variety of direct, back, and substitution titrations for lead.

Because of the large number of samples to be analysed in this study, it was considered much more desirable to be able to mask the tin than to carry out a separation. A variety of masking agents[1,2] for tin is listed in the literature. Sodium fluoride, triethanolamine, tartaric acid, and citric acid are but a few of those listed. None of these appeared to be particularly effective for tin(II), but worked with varied effectiveness for tin(IV).

The direct titration of lead at pH 5 with EDTA, with Xylenol Orange[1–7] as the indicator, was chosen because it offered the desired sharp end-point. The alloys were dissolved in a solution of sodium fluoride and nitric acid at room temperature. Under these conditions the sodium fluoride effectively masked the tin(IV).

The samples to be analysed resulted from composite eutectic alloy studies of binary alloys of lead and tin which were carried out in this laboratory. The samples were prepared in the form of small diameter rods which varied in composition along their length. In order to follow these changes in composition each rod was cut into several sections on a lathe. The lathe turnings from each cut, varying in weight from 15 to 750 mg, were used for chemical analysis, and the solid sections between the cuts were used for metallurgical studies. It was felt that in order to obtain representative analytical data each portion of turnings should be dissolved in its entirety. The method given below gave results quickly, simply and with good accuracy. The proper conditions for dissolution, masking and titration, and the effects of high salt concentration are discussed.

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RAPID EDTA DETERMINATION OF LEAD IN BINARY ALLOYS OF LEAD AND TIN

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A wide variety of methods for the titrimetric determination of lead, in which EDTA is used as the titrant with varying results, appears in the chemical literature. Reilley and Barnard[1] list 58 different methods of which 37 are direct titration, and 5 are substitution titrations. Barnard[2] and Sriveeraraghavan[3] also list a variety of direct, back, and substitution titrations for lead.

Because of the large number of samples to be analysed in this study, it was considered much more desirable to be able to mask the tin than to carry out a separation. A variety of masking agents[1,2] for tin is listed in the literature. Sodium fluoride, triethanolamine, tartaric acid, and citric acid are but a few of those listed. None of these appeared to be particularly effective for tin(II), but worked with varied effectiveness for tin(IV).

The direct titration of lead at pH 5 with EDTA, with Xylenol Orange[1–7] as the indicator, was chosen because it offered the desired sharp end-point. The alloys were dissolved in a solution of sodium fluoride and nitric acid at room temperature. Under these conditions the sodium fluoride effectively masked the tin(IV).

The samples to be analysed resulted from composite eutectic alloy studies of binary alloys of lead and tin which were carried out in this laboratory. The samples were prepared in the form of small diameter rods which varied in composition along their length. In order to follow these changes in composition each rod was cut into several sections on a lathe. The lathe turnings from each cut, varying in weight from 15 to 750 mg, were used for chemical analysis, and the solid sections between the cuts were used for metallurgical studies. It was felt that in order to obtain representative analytical data each portion of turnings should be dissolved in its entirety. The method given below gave results quickly, simply and with good accuracy. The proper conditions for dissolution, masking and titration, and the effects of high salt concentration are discussed.

EXPERIMENTAL

Reagents

Standard lead solution. Lead metal (99·99% purity), was dissolved in nitric acid (1 + 1). The solution was transferred to a 1-l. flask and diluted to volume with distilled water.

EDTA solution, 0·02*M*. The disodium salt of EDTA(14 g) was dissolved in 250 ml of water which contained 1–2 g of sodium hydroxide. When a clear solution was obtained the pH was adjusted to 6 with nitric acid and the solution was diluted to 2 l. with water. The solution was standardized against the standard lead solution, by the procedure described below for the determination of lead but omitting the addition of sodium fluoride and tartaric acid.

Dissolving solution. Sodium fluoride (10 g) was weighed into a 250-ml polypropylene beaker containing 100 ml of distilled water, to which was added concentrated nitric acid (100 ml).

Xylenol Orange indicator solution, 0·25%.

Dissolution

When the total sample size was 100 mg or less, the samples were weighed and transferred to 30-ml polypropylene beakers. Larger samples up to 750 mg in size were weighed and transferred to 100-ml polypropylene beakers. One ml of dissolving solution was added for each 20 mg of sample to be dissolved. Following addition of the dissolving solution the samples were allowed to stand at room temperature from half an hour to overnight to complete the dissolution. Samples containing 80% or more lead or those containing one large chunk of alloy tended to dissolve more slowly. A piece of clear plastic film was placed on each beaker and taped on to make a tight seal to prevent evaporation. Application of heat was avoided, to prevent the formation of insoluble metastannic acid. When dissolution was complete, the samples up to 100 mg in size were transferred to 150-ml glass beakers, diluted to 40 ml and titrated with 0·02*M* EDTA as described below. Samples larger than 100 mg were transferred to volumetric flasks and diluted to volume with water so that the fluoride concentration was 0·7% or less and appropriate aliquots were taken for the titration.

Lead titration

An aliquot containing 15–36 mg of lead was transferred by pipette into a 150-ml beaker. If the entire sample contained less than 15 mg of lead the entire sample was taken. Then 300–600 mg of tartaric acid, as needed to prevent the lead from precipitating as lead fluoride after pH adjustment, were added to those sample portions which contained 8 mg of lead or more. The volume was adjusted to 100 ml and 0·5–1·0 g of hexamine was added to buffer the solution. The pH was adjusted to 5·0 with concentrated ammonia solution and nitric acid (1 + 4). From 4 to 9 ml of 0·02*M* EDTA, dispensed from a 10-ml Class A burette, were required to titrate the recommended amount of lead. The titration was rapidly carried out, with Xylenol Orange as the indicator. A sharp colour change from red to yellow was observed and the point where no additional colour change took place was used as the end-point.

RESULTS AND DISCUSSION

The results of standardization and the final procedure are reported below. Useful hints and observations during development of the methods are discussed.

The EDTA was standardized against the standard lead solution. Eleven identical portions were taken containing 37·85 mg of lead and the buffer. Three portions contained 500 mg of tartaric acid, three portions contained 500 mg of tartaric acid and 500 mg of sodium fluoride and the other five portions contained only the lead and buffer. The mean found for the EDTA was 0·02059*M*, standard deviation $8 \times 10^{-6}M$.

Table 1 illustrates the results obtained when lead was titrated in the presence of tin. Pure lead and tin metal were individually weighed, mixed together in ratios ranging from approximately 1:4 to 4:1 to simulate the composition of the alloys likely to be encountered, and then dissolved according to the described procedure. The lead content varied from 5·32 to 41·72 mg within the ratio ranges. The mean absolute error for the 15 determinations was ±0·03 mg.

Both hexamine and sodium acetate were effective as buffers for the titration, but hexamine was chosen because a sharper end-point was obtained.

Tartaric acid was added to the sample solutions to prevent precipitation of the lead. In the absence of tartaric acid, lead, if present in large amounts, precipitated as the fluoride when the pH was raised.

Tin(IV) was effectively masked by fluoride in a nitrate medium if the fluoride was present as the alloy was being dissolved. Addition of fluoride following dissolution in hydrochloric acid or hydrobromic acid did not result in complete masking of the tin. For effective masking it proved necessary to oxidize the tin to the quadrivalent state.

A range of concentrations of sodium fluoride and nitric acid was used for dissolution of the lead–tin alloys. Ideally the lowest concentration of fluoride that maintains the tin in solution in the nitric acid medium should be chosen. A higher concentration of fluoride than necessary only tends to obscure the Xylenol

Table 1

Approximate ratio of lead to tin, *w/w*	Lead taken, *mg*	Lead found, *mg*
1:4	34·84	34·87
	26·13	26·17
	17·42	17·45
	8·71	8·70
2:3	31·91	31·94
	21·27	21·29
	10·64	10·66
	5·32	5·29
3:2	30·98	30·99
	23·24	23·33
	15·49	15·48
	7·75	7·74
4:1	41·73	41·82
	31·30	31·37
	20·87	20·90

Orange end-point. The concentration of fluoride and the ratio of fluoride to nitric acid used in the procedure were chosen to be useful over a wide range of tin and lead concentrations as illustrated by Table 1. With solutions of high salt concentration a sharper end-point was obtained by diluting the solutions to 120 ml before titration. In samples where less than 10 mg of lead was present the end-point was improved if the volume was kept to 40–50 ml during the titration. It was also possible to sharpen the end-point of the titration of those samples which contained only small amounts of lead by not adding tartaric acid. If any precipitation did then occur on pH adjustment, the pH was lowered to about 2 or until the precipitate redissolved. The 300–600 mg of tartaric acid were then added, the pH readjusted to 5·0 and the titration begun.

The dissolution of the sample is the only phase of the procedure which may consume a considerable amount of time. This depends, of course, on the sample composition, the physical form and the quantity of material involved. The method of dissolution has the advantage of requiring little or no attention and is ideally suited for working with a large number of samples at one time, thus the dissolution time per sample may also be minimal.

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Summary—Binary alloys of lead and tin were dissolved in nitric acid (1 + 1) containing 10% sodium fluoride. The tin(IV) was effectively masked by the fluoride. The lead was quickly and accurately titrated with EDTA in a hexamine-buffered solution, with Xylenol Orange as indicator.

Zusammenfassung—Binäre Legierungen aus Blei und Zinn wurden in Salpetersäure (1 + 1) gelöst, die 10% Natriumfluorid enthielt. Das Zinn(IV) wurde durch das Fluorid wirksam maskiert. Das Blei ließ sich mit EDTA in mit Urotropin gepufferter Lösung mit Xylenolorange als Indikator rasch und genau titrieren.

Résumé—On a dissous des alliages binaires de plomb et d'étain dans de l'acide nitrique (1 + 1) contenant 10% de fluorure de sodium. L'étain (IV) a été efficacement dissimulé par le fluorure. On a titré le plomb rapidement et avec précision par l'EDTA dans une solution tamponnée à l'hexamine, avec l'Orangé Xylénol comme indicateur.

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A NOTE ON THE DETERMINATION OF THORIUM IN THE PRESENCE OF SOME BIVALENT METAL IONS

(*Received* 20 *March* 1973. *Accepted* 25 *April* 1973)

Spinola Costa and Tavares[1] published a critical paper dealing with complexometric determination of thorium in the presence of lead, copper, nickel, mercury, bismuth and antimony. In contradiction of earlier work[2] they found that all these metals, even in 0·05 mmole amounts, interfere with determination of thorium at the optimal pH 2·4–2·8, with Methylthymol Blue as indicator. They also studied various masking agents such as BAL, thioglycollic acid, 3-mercaptopropionic acid, thiourea, thiosulphate, bis-(2-hydroxyethyl)-dithiocarbamate, for elimination of these interferences and found that none of them was able to mask properly all the elements mentioned.

Some years ago we published our experiences with the application of triethylenetetraminehexa-acetic acid (TTHA) in complexometry.[3] With TTHA it is possible to determine many bivalent metals and some tervalent metals as 2 : 1 (M_2L) complexes at pH 5–5·5 (hexamine buffer), using Xylenol Orange as indicator. On the other hand thorium, scandium, indium, bismuth, and rare earths form only 1 : 1 complexes. A number of papers have been published applying TTHA in complexometric determination of metal mixtures, which cannot be analysed by EDTA titration.[4–6]

We have now paid attention to the problem of how to determine thorium in the presence of bivalent metals, avoiding the use of any masking agents. Such a determination is based on a new principle. If we add thorium to a solution of Zn_2TTHA complex, then zinc is quantitatively displaced (changes are omitted):

$$\mathrm{Zn_2TTHA + Th = ThTTHA + 2\,Zn} \quad (1)$$

The zinc liberated can be determined by EDTA titration, with Xylenol Orange as indicator. Because 2 moles of EDTA are required per mole of thorium added, 1 ml of 0·05*M* EDTA corresponds to 5·80 mg of thorium. All bivalent heavy metals form 2 : 1 complexes with TTHA and displace zinc according to the equation

$$\mathrm{Zn_2TTHA + 2\,Me = Me_2TTHA + 2\,Zn} \quad (2)$$

and the consumption of EDTA is the same whether we determine these elements directly with EDTA or after the displacement reaction with Zn_2TTHA. The determination of thorium is now obvious. We determine the sum of the elements by DTPA titration of one aliquot, and in another aliquot the amount of zinc displaced according to equations (1) and (2). The difference between the two titrations gives the amount of thorium. We lose the advantage of the lower equivalent obtained in the determination of thorium in the absence of the other metals but we do not need any masking agents. This method cannot be used, of course for the determination of thorium in the presence of metals forming 1 : 1 TTHA complexes, because they also displace zinc from TTHA according to equation (1). On the other hand this reaction is very suitable for the determination of thorium after its separation from many other metals by precipitation with sodium hydroxide in the presence of triethanolamine.

EXPERIMENTAL

Reagents

EDTA, 0·05M. Standardized with lead nitrate, with Xylenol Orange as indicator.

DTPA, 0·05M. Prepared by dissolving 19·65 g of diethylenetriamine-*N,N,N′,N″,N″*, penta-acetic-acid in

Zusammenfassung—Binäre Legierungen aus Blei und Zinn wurden in Salpetersäure (1 + 1) gelöst, die 10% Natriumfluorid enthielt. Das Zinn(IV) wurde durch das Fluorid wirksam maskiert. Das Blei ließ sich mit EDTA in mit Urotropin gepufferter Lösung mit Xylenolorange als Indikator rasch und genau titrieren.

Résumé—On a dissous des alliages binaires de plomb et d'étain dans de l'acide nitrique (1 + 1) contenant 10% de fluorure de sodium. L'étain (IV) a été efficacement dissimulé par le fluorure. On a titré le plomb rapidement et avec précision par l'EDTA dans une solution tamponnée à l'hexamine, avec l'Orangé Xylénol comme indicateur.

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Some years ago we published our experiences with the application of triethylenetetraminehexa-acetic acid (TTHA) in complexometry.[3] With TTHA it is possible to determine many bivalent metals and some tervalent metals as 2 : 1 (M_2L) complexes at pH 5–5·5 (hexamine buffer), using Xylenol Orange as indicator. On the other hand thorium, scandium, indium, bismuth, and rare earths form only 1 : 1 complexes. A number of papers have been published applying TTHA in complexometric determination of metal mixtures, which cannot be analysed by EDTA titration.[4–6]

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and the consumption of EDTA is the same whether we determine these elements directly with EDTA or after the displacement reaction with Zn_2TTHA. The determination of thorium is now obvious. We determine the sum of the elements by DTPA titration of one aliquot, and in another aliquot the amount of zinc displaced according to equations (1) and (2). The difference between the two titrations gives the amount of thorium. We lose the advantage of the lower equivalent obtained in the determination of thorium in the absence of the other metals but we do not need any masking agents. This method cannot be used, of course for the determination of thorium in the presence of metals forming 1 : 1 TTHA complexes, because they also displace zinc from TTHA according to equation (1). On the other hand this reaction is very suitable for the determination of thorium after its separation from many other metals by precipitation with sodium hydroxide in the presence of triethanolamine.

EXPERIMENTAL

Reagents

EDTA, 0·05M. Standardized with lead nitrate, with Xylenol Orange as indicator.

DTPA, 0·05M. Prepared by dissolving 19·65 g of diethylenetriamine-*N,N,N′,N″,N″*, penta-acetic-acid in

130–150 ml of hot 1*M* sodium hydroxide and diluting to 1 litre with redistilled water, and standardized as for the EDTA.

Zinc chloride, 0·5M. Prepared by dissolving 16·15 g of pure zinc in the minimum necessary amount of hydrochloric acid and diluting to 500 ml with redistilled water. By appropriate dilution 0·1 and 0·05*M* solutions were prepared, and checked complexometrically.

Zn_2TTHA, 0·1M (0·2M in zinc). Prepared by dissolving 12·5 g of the free acid in 30 ml of water, neutralizing with 0·2*M* sodium hydroxide (total volume at this point must not exceed 100 ml) and adding the calculated amount of 0·5*M* zinc chloride and diluting to 250 ml. The necessary amount of zinc was determined by dissolving 0·25 g of TTHA in water and a few ml of 0·1–0·2*M* sodium hydroxide, diluting to 100–200 ml, slightly acidifying, adjusting the pH to 5–5·5 with solid hexamine, and titrating with 0·1*M* zinc chloride, using Xylenol Orange as indicator. From the amount of zinc solution consumed (about 20 ml) the necessary amount of 0·5*M* zinc chloride for (12·5 g) of TTHA is calculated (about 100 ml).

Solutions (0·05*M*) of thorium nitrate and other metal salts of zinc, lead, cadmium, cobalt, nickel *etc.* were prepared from reagent grade chemicals and their strength checked complexometrically.

Determination of thorium in pure solutions

Procedure. To the slightly acidic solution of thorium nitrate in a 250-ml titration flask add sufficient 0·1*M* Zn_2TTHA to give an excess. After 10 min add a few drops of Xylenol Orange and adjust the pH to 5–5·5 with hexamine. Titrate the solution with 0·05*M* EDTA from red-violet to lemon-yellow.

1 ml of 0·05*M* EDTA = 5·80 mg of thorium

The solution of thorium must be acid (pH 2–3), otherwise it hydrolyses and the reaction (1) is too slow or incomplete. The amount of Zn_2TTHA solution need not be measured precisely, but there must be an excess: 1 ml of 0·1*M* Zn_2TTHA is sufficient for 23·2 mg of thorium.

Determination of thorium and bivalent metals

For such determinations we need two aliquots of sample solution. In one we determine the sum of titratable metals, including thorium, with DTPA by direct or back-titration. In the second we determine with EDTA the zinc displaced from its TTHA complex. For the first titration we cannot use EDTA, because its complex with thorium gives a colour with the indicator and makes the determination impossible.

Procedure. To a slightly acidic sample aliquot add a small excess of 0·05*M* DTPA, dilute to 150–200 ml, adjust the pH to 5–5·5 with hexamine, add Xylenol Orange indicator and titrate with 0·05*M* zinc solution from yellow to red-violet.

To another aliquot (pH 1–2) add an excess of Zn_2TTHA solution and let stand for 10 min. Then dilute the solution to 150–200 ml, adjust the pH to 5–5·5 with hexamine, and after 2–3 min titrate slowly with 0·05*M* zinc chloride, using Xylenol Orange as indicator.

The difference between the titration values gives the amount of thorium: 1 ml of 0·05*M* EDTA = 11.60 mg of thorium. Some results are summarized in Table 1.

Table 1. Determination of thorium in the presence of some bivalent metals

Th taken, *mg*	Me taken, *mg*	Consumption of 0·05*M* DTPA, *ml*	0·1*M* Zn_2TTHA added, *ml*	Consumption of 0·05*M* EDTA, *ml*	Thorium Found, *mg*	Thorium Difference *mg*
11·98	—	—	2	2·10	12·2	+0·2
35·93	—	—	2	6·28	36·0	+1·0
119·76	—	—	7	20·69	120·0	+0·2
35·93	54 Pb	8·41	3	11·50	35·0	−0·0
11·98	15 Ni	6·16	3	7·16	11·6	−0·4
23·95	32 Zn	12·06	3	14·10	23·7	−0·3
11·98	108 Pb	11·54	7	12·57	12·0	−0·0
11·98	108 Pb	11·55	3	12·60	12·2	+0·2
11·98	3 Cu	2·10	3	3·11	11·7	−0·3
11·98	17 Cu	6·35	3	7·37	11·8	−0·2
59·88	3 Cu	6·25	5	11·43	60·1	+0·2
23·95	5 Cd	3·05	2	5·12	24·0	+0·1
35·93	58 Cd	13·35	5	16·45	36·0	+0·0
11·98	30 Co	11·55	5	12·59	12·1	+0·1
119·76	3 Co	11·40	10	21·65	118·9	−0·8

The method is suitable for up to 100 mg of thorium and up to 50 mg of nickel, copper, cadmium and zinc, and 100 mg of lead. The back-titration with zinc is more convenient as it avoids blocking of the indicator (in the presence of copper, nickel and cobalt) if reaction (2) does not proceed entirely quantitatively.

DISCUSSION

The mechanism of the displacement reaction can be explained as follows. The Zn_2TTHA added to the acidic solution of bivalent metals (pH 2–3) is more or less dissociated, according to its apparent stability constant. At this acidity all bivalent cations are more or less bound by the TTHA dissociated. Because they form more stable complexes than zinc with TTHA they are bound to TTHA quantitatively after adjustment of the pH to 5–5·5 with hexamine. For example, lead, after mixing with Zn_2TTHA, does not give a precipitate with sulphate. The displacement reaction with nickel is a little slow and traces of nickel can then block the indicator. For this reason the second determination is performed by addition of excess of EDTA and back-titration with zinc solution.

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Summary—A new method for complexometric determination of thorium in the presence of bivalent metals without their masking is presented. Two aliquots of metal solution are necessary. In one the sum of thorium and other metals is determined by DTPA titration. The second aliquot is treated with Zn_2TTHA complex. Only thorium, forming a 1 : 1 complex with TTHA, displaces twice its molar amount of zinc from the complex, while other elements displace only an equimolar amount of zinc. The amount of thorium corresponds to the difference of consumption in the two titrations.

Zusammenfassung—Es wird ein neues Verfahren zur komplexometrischen Bestimmung von Thorium in Gegenwart zweiwertiger Metalle ohne deren Maskierung angegeben. Es sind zwei abgemessene Teile der Metall-Lösung notwendig. In einem wird die Summe von Thorium und den anderen Metallen durch Titration mit DTTA bestimmt. Der zweite Teil wird mit dem Zn_2TTHA-Komplex behandelt. Nur Thorium, das mit TTHA einen 1:1–Komplex bildet, setzt aus dem Komplex das doppelte seiner molaren Menge an Zink frei, andere Elemente nur eine äquimolare Menge. Die Menge Thorium entspricht der Verbrauchsdifferenz bei den belden Titrationen.

Résumé—On présente une nouvelle méthode pour le dosage complexométrique du thorium en la présence de métaux bivalents sans leur dissimulation. Deux aliquotes de solution de métaux sont nécessaires. Dans l'une, on détermine la somme du thorium et des autres métaux par titrage au DTPA. La seconde aliquote est traitée par le complexe Zn_2TTHA. Seul le thorium, formant un complexe 1 : 1 avec le TTHA, déplace deux fois sa quantité molaire de zinc du complexe, tandis que les autres éléments déplacent seulement une quantité équimolaire de zinc. La quantité de thorium correspond à la différence de consommation dans les deux titrages.

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ANALYTICAL DATA

EXTRACTION OF METALS INTO CHLOROFORM WITH SOME DERIVATIVES OF PHENYLACETIC ACID

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In previous communications we have reported the extraction of some metal phenylacetates into chloroform,[1] and several applications.[2]

We have found that these extractions can be made still more selective. For example from acetate solutions only iron is extracted. In the presence of fluoride only copper is extracted. From solutions containing nitrilotriacetic acid only uranium is extracted.[4]

We considered that the extraction behavior of further derivatives of acetic acid might be interesting and further improve this type of separation. For this purpose we have used chloroform solutions of diphenylacetic acid, naphthylacetic acid and naphthoxyacetic acid.

EXPERIMENTAL

Reagents

Solutions (1*M*) of phenylacetic acid (PAA), diphenylacetic acid (DPAA) and naphthylacetic acid (NPAA) were prepared by dissolving 68·1, 106·2, and 93·1 g respectively of the compounds in 500 ml of pure chloroform. A 0.1*M* solution of 2-naphthoxyacetic acid was prepared by dissolving 10·1 g of the acid in 500 ml of chloroform. A 0·5*M* solution cannot be prepared, because of the low solubility of the acid in chloroform.

Solutions of various metal salts (0·05*M*) were prepared from reagent grade chemicals and standardized complexometrically.

Procedures

Metal solution (0·05*M*, 5 ml) was pipetted into a 150-ml separatory funnel and diluted to 10, 25 or 70 ml Then 10 ml of extractant were added with thorough stirring, and were followed by 10 ml of saturated hexamine solution. The mixture was shaken for 1 min. The chloroform phase was run off, and the aqueous phase was washed twice with 5 ml of pure chloroform. The metal left in the aqueous phase was determined complexometrically.

DISCUSSION

The results are summarized in Table 1. All the acids studied extract copper, iron and lead. For other cations the extractability increases roughly with increasing molecular weight of the acid but the selectivity decreases. The solubility in chloroform of some salts of these acids also decreases with increasing molecular weight of the acid.

Table 1. Extraction according to the described procedure.
Influence of dilution of aqueous phase

Aqueous phase						
Volume, *ml*	Concn., *M*	Metal	Phenyl-acetic acid	Diphenyl-acetic acid	Naphthyl-acetic acid	Naphthoxy-acetic acid
10	0·02	Cu	99%	100%	100%	100%
		Co	25	56	6	15
		Ni	18	67	50	70
		Pb	100	96	precip.[1]	precip.[1]
		Cd	83	79	61	69
		Zn	96	96	93	96
		Mn	0	31	2	precip.[1]
		Fe	100	precip.[1]	precip.[1]	100
		Al	precip.[4]	precip.[2]	precip.[1]	97
		In	precip.[4]	precip.[1]	100	100
		Ga	precip.[2]	93	precip.[2]	100[3]
25	0·001	Cu	100	100	100	100
		Co	7	18	0	14
		Ni	0	63	26	37
		Pb	96	100	precip.[1]	precip.[1]
		Cd	6	74	48	49
		Zn	5	94	82	precip.[1]
		Mn	0	14	0	precip.[1]
		Fe	100	precip.[1]	precip.[1]	100
		Al	precip.[2]	precip.[1]	precip.[1]	97
		In	100	precip.[1]	100	94
		Ga	precip.[4]	precip.[2]	precip.[3]	precip.[2]
70	$3{\cdot}5 \times 10^{-4}$	Cu	100	98	99	100
		Co	0	8	0	0
		Ni	0	29	3	3
		Pb	100	100	precip.[1]	precip.[1]
		Cd	0	0	47	6
		Zn	0	65	41	precip.[1]
		Mn	0	14	0	precip.[1]
		Fe	100	precip.[1]	precip.[1]	100
		Al	precip.	precip.[1]	precip.[1]	92
		In	100	precip.[1]	99	95
		Ga	100	precip.[2]	precip.[4]	precip.[2]

[1] Precipitate in both phases. Separation impossible.
[2] Partly extracted. Phase separation.
[3] Will dissolve after 5 min. Extract is clear.
[4] Quantitative extraction. Extract is cloudy.

From an analytical point of view phenylacetic acid is exceptionally good for separation of iron, copper and lead.

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Summary—A comparison has been made of phenylacetic, diphenylacetic, naphthylacetic and 2-naphthoxyacetic acids as extracting agents for metal ions. Phenylacetic acid is much superior to the others.

Zusammenfassung—Phenylessigsäure, Diphenylessigsäure, Naphthylessigsäure und 2-Naphthoxyessigsäure wurden als Extraktionsmittel für Metallionen verglichen. Phenylessigsäure ist den anderen weit überlegen.

Résumé—On a effectué une comparaison des acides phénylacétique, diphénylacétique, naphtylacétique et 2-naphtoxyacétique comme agents d'extraction pour les ions métalliques. L'acide phénylacétique est beaucoup supérior aux autres.

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ACID–BASE TITRATION CURVES FOR ACIDS WITH VERY SMALL RATIOS OF SUCCESSIVE DISSOCIATION CONSTANTS

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Summary—The shapes of the potentiometric acid–base titration curves obtained in the neutralizations of polyfunctional acids or bases for which each successive dissociation constant is smaller than the following one are examined. In the region $0 < f < 1$ (where f is the fraction of the equivalent volume of reagent that has been added) the slope of the titration curve decreases as the number i of acidic or basic sites increases. The difference between the pH-values at $f = 0{\cdot}75$ and $f = 0{\cdot}25$ has $(1/i)\log 9$ as the lower limit of its maximum value.

In the derivation of equations that describe potentiometric acid–base titration curves for polyfunctional acids, it is generally assumed that pK_{i+1} is larger than pK_i. There are a number of difunctional acids for which the ratio of the thermodynamic constants K_1/K_2 is very little larger than the "statistical" ratio of 4·00, and this has prompted some authors to consider the problem of distinguishing such acids from monofunctional ones. Sturrock[1] suggested a criterion based on the value of Δ(pH), which is defined as the difference between the values of pH at two points, one at 75% and the other at 25% of the way from the start of the titration to the single end-point that can be discerned. For a monofunctional acid $\Delta(\text{pH}) = \log 9 = 0{\cdot}954$ if both the acid and base are moderately concentrated[2] and if the acid is neither very strong nor very weak. If the solution is dilute, or if K_a is either very large or very small, $\Delta(\text{pH}) < 0{\cdot}954$ for a monofunctional acid or base. As is well known, the titration curve for a monofunctional acid is indistinguishable from that for a difunctional acid having $K_1/K_2 = 4{\cdot}00$. If K_1/K_2 is larger than 4·00, the value of Δ(pH) for a difunctional acid exceeds that for a monofunctional acid having $K_a = (K_1/K_2)^{\frac{1}{2}}$; if K_1/K_2 is smaller than 4·00, the value of Δ(pH) is less than that for such a monofunctional acid.

So far, acids for which K_1/K_2 is very much smaller than the statistical value have not been considered, and it is with these that this paper is concerned. The following derivation describes how Δ(pH) depends upon the number of acid sites and upon the magnitude of the difference between pK_{i+1} and pK_i.

Although very small values of K_i/K_{i+1} are unusual, two cases that could exhibit such behaviour are described here. Consider a molecule containing a fairly strongly acidic group so placed that it is folded into the centre of the molecule and thus unable to dissociate, and a weakly acidic functional group that is exposed to the solution and hence to dissociation and attack by a base. When this outer group is neutralized, the change in charge on the molecule might cause a change in convolution of the molecule, bringing the more strongly acidic group to the outside and rendering this acid group susceptible to dissociation and attack. In this case, it will be the order in which the two protons are removed that will dictate which of the dissociation constants is taken as K_1 and which as K_2, whereas in the ordinary case the order with time is the same as, and is governed by, the order of the equilibrium constants.

The second example would arise if addition of a proton yielded a protonated species that decomposed to form a base stronger than the original one. As will be shown later, the resulting equilibrium titration curve not only has just one end-point but is also abnormally flat around its mid-point. This is just the behaviour that is displayed by titration curves for dialkyldithiocarbamates.[3]

The graphs shown in Figs. 1, 2 and 3 were obtained by means of a Hewlett–Packard Model 9100A programmable calculator and a model 9125A plotter. The curves pertain

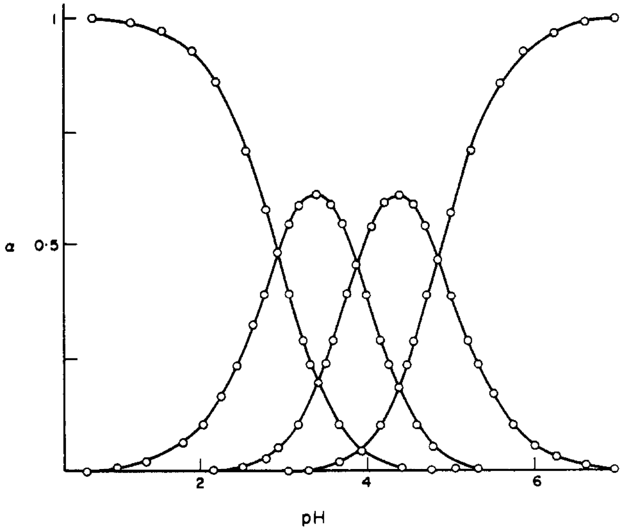

Fig. 1. Plot of fraction of species, α, *vs* pH for a trifunctional acid with $pK_1 = 3$, $pK_2 = 4$, $pK_3 = 5$.

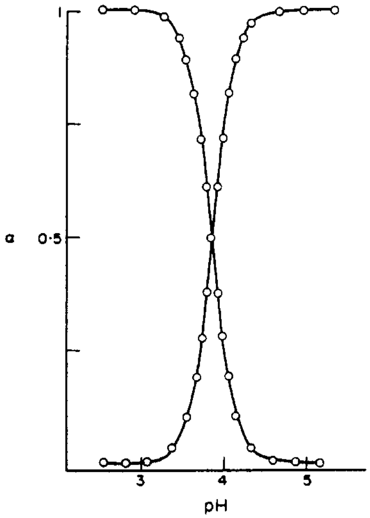

Fig. 2. Plot of fraction of species, α, *vs.* pH for a trifunctional acid with $pK_1 = 6$, $pK_2 = 4$, $pK_3 = 2$.

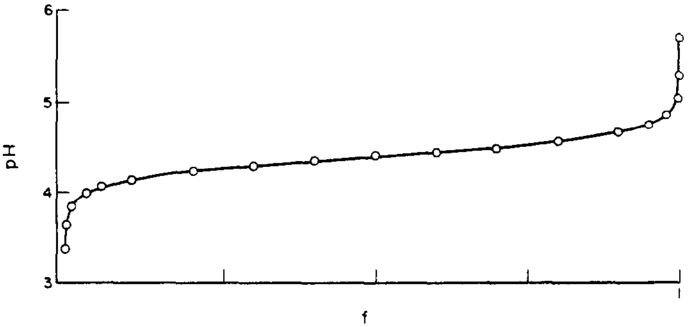

Fig. 3 Titration curve of a trifunctional acid with a monofunctional strong base. $pK_1 = 6$, $pK_2 = 4$, $pK_3 = 2$. $C_A^0 = 1M$, $r = 3$.

to a trifunctional acid. Although those in Fig. 2 have the same general shape as those for a monofunctional acid, they are much steeper in the vicinity of $f = 0{\cdot}5$, where pH $\sim$ pK_a for the monofunctional acid while pH $\sim 1/3\ [p(K_1K_2K_3)]$ for the trifunctional one. Because values of Δ(pH) taken from plotted titration curves, such as the one in Fig. 3, are subject to fairly large graphical errors, those quoted below were obtained from numerical calculations made with a digital computer.

The titration curve is described by the equation

$$f = \frac{(1/j)\left(\sum_{i=1}^{j} i\alpha_i\right) C_{\mathrm{H}_j\mathrm{A}} - [(\mathrm{H}^+) - (\mathrm{OH}^-)]}{C_{\mathrm{H}_j\mathrm{A}} + r\,[(\mathrm{H}^+) - (\mathrm{OH}^-)]}, \tag{1}$$

where f is proportional to the amount of titrant added and is equal to 1·00 at the last (jth) equivalence point, j is the number of acidic sites, $C_{\mathrm{H}_j\mathrm{A}}$ is the initial formal concentration of $\mathrm{H}_j\mathrm{A}$, r is the dilution parameter defined as the ratio of $C_{\mathrm{H}_j\mathrm{A}}$ to the formal concentration of the titrant (which is assumed to be monofunctional), and α_i is the fraction of the total A that is present as the ith species. Equation (1) is combined with the familiar expression for α_i

$$\alpha_i = \frac{i\text{th term}}{[\mathrm{H}^+]^j + [\mathrm{H}^+]^{j-1}K_1 + \ldots + K_1K_2\ldots K_j}, \tag{2}$$

to obtain an implicit relationship between $[\mathrm{H}^+]$ and f. This was solved at $f = 0{\cdot}25$ and 0·75 and Δ(pH) was obtained from the resulting values. Figures 4 and 5*b* are drawn for acids of different j but with $(K_1K_2\ldots K_j)^{1/j}$ always equal to 10^{-7}. For a monobasic acid this value would correspond to the maximum on a plot of Δ(pH) against pK_a[2,4]. As K_i/K_{i+1} decreases the titration curve becomes flatter and Δ(pH) decreases, but if K_i/K_{i+1} is as small as 10^{-2} a further decrease in it has no perceptible further effect on Δ(pH), which is also insensitive to variations of r in this range of acid strength. This limiting value of Δ(pH) is plotted against j in Fig. 4, and may be shown to be proportional to $1/j$. In the following paragraphs an algebraic proof of this proportionality is given. Figure 5 shows how the limiting value of Δ(pH) depends on $(1/j)\Sigma pK$, which is equal to the negative logarithm of the geometric mean dissociation constant, and on the concentration of the acid titrated.

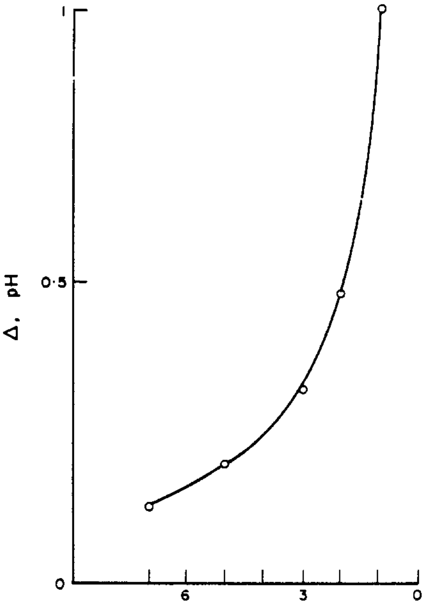

Fig. 4. Dependence of the limiting value (see text) of Δ(pH) on j for the titration of a polyfunctional acid with a monofunctional strong base with $(K_1K_2\ldots K_j)^{1/j} = 10^{-7}$. Values indistinguishable from those shown here are obtained whenever $C_A^0 \geq 10^{-3}M$ and $K_i/K_{i-1} \leq 10^{-2}$

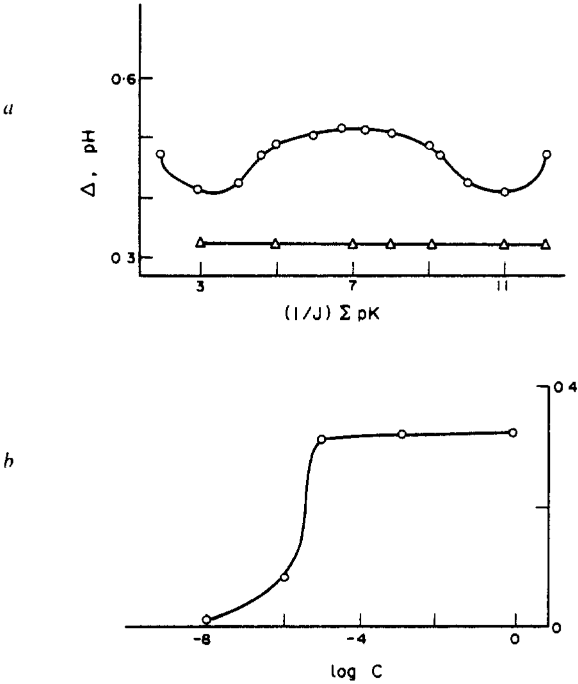

Fig. 5. Dependence of Δ(pH) on (*a*) $(1/j)\Sigma pK_i$ for (⊙) a difunctional acid with $K_1/K_2 = 10^{-2}$ and (△) a trifunctional acid with $K_1/K_2 = K_2/K_3 = 10^{-2}$, and (*b*) the concentration of a trifunctional acid with $pK_1 = 9$, $pK_2 = 7$, and $pK_3 = 5$, with $r = 2$.

If dilution, dissociation of H_jA, and dissociation of water are all neglected, equation (1) becomes

$$f = (1/j)\sum_{i=1}^{j} i\alpha_i. \tag{3}$$

We define a parameter m_i as equal to K_i/K_{i+1} and assume all the m_i to be very small; $\Delta(\text{pH})$ is then independent of m. Under these conditions only the species H_jA and A^{j-1} are important and therefore every α except α_0 and α_j is equal to zero. Of these, the former does not appear in equation (3) because the index has 1 rather than 0 as its smallest value. Hence every term in equation (3) is either zero or excluded, with the sole exception of α_j, and equation (3) can therefore be written as

$$f = \frac{1}{j}(j\alpha_j) = \alpha_j. \tag{4}$$

Since

$$\alpha_j = \frac{K_1K_2K_3\ldots K_j}{[\mathrm{H}^+]^j + K_1K_2K_3\ldots K_j}, \tag{5}$$

equation (4) may now be written as

$$f = \frac{K_1K_2K_3\ldots K_j}{[\mathrm{H}^+]^j + K_1K_2K_3\ldots K_j}, \tag{6}$$

From the definition above of m_i

$$K_2 = K_1/m_1 \tag{7}$$

$$K_3 = K_2/m_2 = K_1/(m_1m_2) \tag{8}$$

$$K_j = K_1\prod_{i=1}^{j-1}(1/m_i), \tag{9}$$

and, upon substitution into equation (6),

$$f = \frac{K_1\prod_{i=1}^{j-1} 1/m_i}{[\mathrm{H}^+]^j + K_1\prod_{i=1}^{j-1} 1/m_i}, \tag{10}$$

which can be solved for $[\mathrm{H}^+]$ giving

$$[\mathrm{H}^+]^j = K_1^j\left(\prod_{i=1}^{j-1} 1/m_i\right)(1-f)/f, \tag{11}$$

whence

$$\mathrm{pH} = \mathrm{p}K_1 - \frac{1}{j}\log[(1-f)/f] - (1/j)\log\left(\prod_{i=1}^{j-1} 1/m_i\right). \tag{12}$$

To examine the dependence of $\Delta(\text{pH})$ upon j, f can be set equal to 0·75 and then to 0·25. The difference between the resulting pH-values gives

$$\Delta(\text{pH}) = (1/j)\log 9 = 0{\cdot}954/j \tag{13}$$

The corresponding titration curve has only one point of maximum slope (see Fig. 3), no matter how many protons are on the original acid. In the region $0 < f < 1$ the curve is symmetrical around $f = 0{\cdot}5$ and in this interval the sign of the second derivative changes only once.

Because the value of $(\log 9)/j$ can be thought of as a limit of $\Delta(\mathrm{pH})$ as m goes to zero, it can also be used in general to aid in developing an empirical formulation of the dependence of $\Delta(\mathrm{pH})$ upon m. For a difunctional acid having $m < 5$, Meites[2] gave the empirical equation

$$\Delta(\mathrm{pH}) = 0{\cdot}478 + 0{\cdot}253\, m^{\frac{1}{2}} + 0{\cdot}0074\, m.$$

The intercept may be compared with the theoretical value of 0·4772. It is suggested that the general form for a j-functional acid is

$$\Delta(\mathrm{pH}) - (1/j)\log 9 = am^{\frac{1}{2}} + bm + \ldots,$$

and is valid as long as m is not too much greater than the statistical value.

It is not possible to apply a similar treatment to polyfunctional acids for which K_i is larger than K_{i+1}. This is because all the terms in α are then important and the resulting equations are impossible to solve in a closed form.

One last aspect of equation (13) is that acids of the type considered here could be used to prepare buffers of much higher buffer capacity than those that can be made from monofunctional ones or the familiar polyfunctional ones.

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Zusammenfassung—Die Form der potentiometrischen Säure-Basen-Titrationskurven bei der Neutralisation polyfunktioneller Säuren oder Basen, bei denen jede individuelle Dissoziationskonstante kleiner ist als die der nachfolgenden Stufe, wird untersucht. Im Bereich $0 < f < 1$ (wo f der zugegebene Bruchteil des äquivalenten Reagensvolumens ist) nimmt die Steigung der Titrationskurve ab, wenn die Anzahl j saurer oder basischer Funktionen zunimmt. Die untere Grenze für die Differenz der pH-Werte bei $f = 0{,}75$ und $f = 0{,}25$ beträgt $(1/j)\log 9$.

Résumé—On examine les formes des courbes de titrage potentiométrique acide–base dans les neutralisations d'acides ou bases polyfonctionnels pour lesquels chaque constante de dissociation successive est plus petite que la suivante. Dans la région $0 < f < 1$ (où f est la fraction du volume équivalent de réactif qui a été ajoutée), la pente de la courbe de titrage décroît quand le nombre j des positions acides ou basiques croît. La différence entre les valeurs de pH à $f = 0{,}75$ et $f = 0{,}25$ a $(1/j)\log 9$ pour limite inférieure.

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THE EFFECT OF HNO_3, HCl AND HBr ON THE FLUORESCENCE OF THE ALUMINIUM COMPLEX OF 1-(2-PYRIDYLAZO)-2-NAPHTHOL AND AN IMPROVED FLUOROMETRIC PROCEDURE FOR DETERMINATION OF ALUMINIUM

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Summary The fluorescence of the aluminium complex of 1-(2-pyridylazo)-2-naphthol (PAN) is both stabilized and enhanced by $10^{-3}M$ HNO_3, HCl or HBr. Other acids tested have no effect. An improved fluorometric procedure with a detection limit of 0·001 ppm, increased precision and reduced interferences over the existing Al–PAN method is described. It is satisfactory for the determination of aluminium in bronze when an ion-exchange separation is used, but is not suitable for the determination of aluminium in plants. The acidified Al–PAN is unsuitable for the determination of nickel(II) and fluoride by fluorescence quenching.

The fluorescence of the aluminium chelate of 1-(2-pyridylazo)-2-naphthol (PAN) was first reported by Surak *et al.* in 1964.[1] They described a direct fluorometric procedure for the determination of aluminium and applied it to the analysis of clays and mineral colloids. Schenk and Dilloway have employed the fluorescence of Al–PAN for the determination of nickel(II)[2] and fluoride[3] by fluorescence quenching. The determination of nickel relies on the fact that the stability constant of Ni–PAN is considerably higher than that for Al–PAN, so that nickel displaces aluminium from Al–PAN to form the non-fluorescent Ni–PAN complex. The quenching procedure for fluoride is based on the reaction

$$\underset{\text{Fluorescent}}{\text{Al–PAN}} + xF^- \rightarrow \underset{\text{Non-fluorescent.}}{AlF_x^{3-x}} + \text{PAN}$$

Several workers[2–4] have noted that both the stability and fluorescence of Al–PAN depend markedly on the amount of ethanol present in the solution containing the complex. In 95% ethanol fluorescence is low and the complex gradually decomposes over a period of 30 days or more. The use of absolute ethanol increases the intensity of fluorescence and improves the stability, although decomposition still occurs at a measurable rate, for at least 24 hr.

This paper describes how some acids enhance the fluorescence and improve the stability of Al–PAN. This has enabled an improved method for the fluorometric determination of aluminium to be developed. The suitability of acidified Al–PAN stock solution for the determination of nickel and fluoride by quenching procedures is also discussed.

EXPERIMENTAL

Reagents

Standard aluminium solutions. Pure (99·99%) aluminium was used to prepare aqueous solutions and analytical grade $Al(NO_3)_3 \cdot 9H_2O$ was used for ethanolic solutions. A 1000-ppm ethanolic solution of Al was prepared by dissolving 0·0138 g of the nitrate in 250 ml of absolute ethanol.

Ethanol. Commercial absolute ethanol doubly distilled and stored over a molecular sieve.

Hydrochloric acid. Analytical grade reagent doubly distilled.

PAN 10^{-3} *M solution.* Prepared by dissolving 0·0678 g of the Merck reagent in 250 ml of absolute ethanol.

Procedures

General. Wavelengths used for Al–PAN and acidified Al–PAN were 510 and 560 nm for excitation and emission, respectively. The excitation and emission spectra for Al–PAN were identical to those for acidified Al–PAN except for the height of the main fluorescence peak at 560 nm. These spectra are shown in Fig. 1. In all cases. 1-cm quartz cells were used to contain the solutions, and a Hitachi–Perkin-Elmer MPF-2A instrument was used.

To bring about equilibrium prepared solutions were allowed to stand at room temperature for 24 hr or were heated in a water-bath at 40° for 1 hr and then allowed to cool for 15 min.

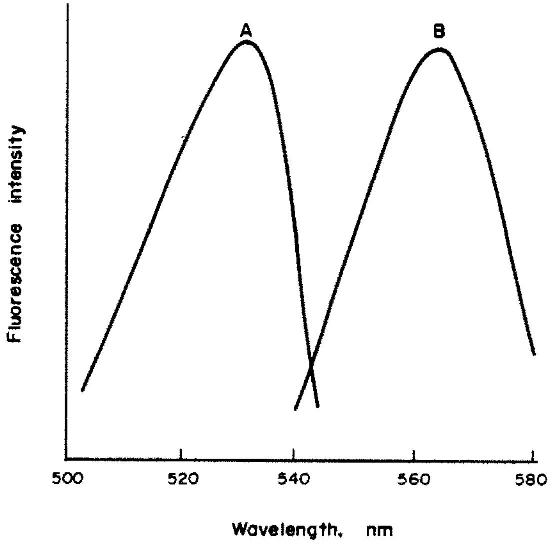

Fig. 1. Excitation and emission spectra for Al–PAN (and acidified Al–PAN).
A, Excitation spectrum. B, Emission spectrum.

Testing for effect of acids. First, water solutions of the acid to be tested were prepared in the concentration range 10^{-4}–1 *N* and 10^{-4} *M* solutions of Al^{3+} and PAN were made by dilution of the stock solutions. Then 1·0 ml of 10^{-4} *M* Al^{3+}, 0·25 ml of acid solution and 5·0 ml of 10^{-4} *M* PAN were added in turn to a 25-ml volumetric flask and the mixture made up to the mark with absolute alcohol. In this manner the percentage of ethanol was kept constant at 99% for each of the acid concentrations used. The solutions were then allowed to come to equilibrium.

Determination of aluminium. The stock solutions of Al and PAN were diluted to give the desired concentration level. Nitric acid, 10^{-3} *M*, was prepared and standardized against borax. This acid was used exclusively for all aluminium determinations.

Calibration curves covering several ranges were prepared, and the technique used is illustrated below by reference to a particular example. The procedure described can be adapted to other concentrations provided the Al:PAN ratio is kept at 1:5. The acid concentration used, however, was always 0·1*M* when a 100-fold dilution was used.

A calibration curve in the range 0–0·3 ppm Al^{3+} was prepared by adding 0–3·0 ml of 10^{-4} *M* aluminium, 0·25 ml of 0·1*M* nitric acid and 5·0 ml of 10^{-4}*M* PAN in turn to a 25-ml volumetric flask and diluting the contents to the mark with absolute ethanol. The solutions were then allowed to reach equilibrium. Unknown solutions were similarly treated.

Quenching procedures. The procedures of Schenk and Dilloway[2,3] for the determination of nickel(II) and fluoride were followed except that determinations were attempted at the $10^{-6}M$ level It should be noted that the Al–PAN stock solution used for the determination of nickel(II) is not suitable for the determination of fluoride because of the presence of excess of aluminium.

Analysis of samples Plant material was obtained predried and powdered. Samples (1 g) were placed in an air-oven at 90° for 18 hr in order to attain constant weight. This heating period was sufficient for all samples used.

The sample was transferred to a platinum crucible and gently heated over a microbunsen flame until emission of volatile components ceased. The crucible was then heated for 12 hr in a muffle furnace at 500 . Heating was continued after this period if any black specks of carbon remained. After cooling, the crucible was placed on a boiling water-bath and the ash digested with 5 ml of 10 *M* hydrochloric acid. For all samples analysed, complete dissolution of the ash was achieved. The digest was then allowed to cool.

The procedure for analysis of bronze samples was as follows. An amount of material corresponding to 40 μg of Al in the final solution (usually 0·01 g) was weighed out and the bronze dissolved in 2 or 3 drops of concentrated nitric acid. The solution was then gently heated on a hot-plate until all nitric acid had been removed and the residue was redissolved in 10 ml of 10 *M* hydrochloric acid. After the solution had been warmed slightly to ensure complete dissolution, it was allowed to cool.

An anion-exchange column was prepared as described by Lewis *et al.*,[4] except that Amberlite CG400 (100–200 mesh) resin and a column length of 15 cm were used. The column was pretreated by alternate washing with 100 ml of distilled water and 100 ml of 10 *M* hydrochloric acid, the process being repeated three times. The column was ready for ion-exchange separation after the final acid washing.

The 10*M* hydrochloric acid sample solution (ash digest or dissolved bronze) prepared as described above was added to the ion-exchange column and washed into the resin with 10–15 ml of 10*M* hydrochloric acid. The column was then eluted with 100 ml of 10*M* hydrochloric acid, the collection of eluate being commenced immediately after addition of the acid. Where several successive samples were being treated, the column was washed with 100 ml of distilled water followed by 100 ml of 10*M* hydrochloric acid before addition of the next sample

The eluate was placed in a beaker on a hot-plate and evaporated under moderate heat (below 140) to about 5 ml. Care was necessary to ensure that the temperature did not exceed 140 or that evaporation to dryness did not occur, because of potential losses of aluminium as the chloride. The pH of the solution was then adjusted to 1·3 with aqueous ammonia and the volume made up to 25·0 ml in a graduated flask with hydrochloric acid of pH 1·3 The pH-adjustment step was used so that further addition of acid was unnecessary. When a 50-fold dilution of the sample was used in the fluorometric stage, a pH of 1·3 in the sample digest produced the correct acid concentration in the final Al–PAN solution.

A 1·0-ml aliquot of the sample digest was transferred to a 50-ml volumetric flask containing 5 ml of $10^{-3}M$ PAN and made up to the mark with absolute ethanol. After a suitable development time, fluorescence measurements were made in the usual way.

RESULTS

Effect of acids on Al–PAN fluorescence

Acids tested were HNO_3, HCl, HBr, H_2SO_4, H_3PO_4 and CH_3COOH within the concentration range 10^{-6}–$10^{-2}N$. Of the acids examined, only nitric, hydrochloric and hydrobromic were found to affect the fluorescence intensity; the remaining acids had only the effect of added water. Figure 2 shows the way in which the fluorescence intensity varies with acid concentration. Log [acid] is used in preference to pH because of the difficulties associated with measuring pH in an alcoholic medium.

Identical enhancements were produced by these three acids with the maximum effect at a concentration of $10^{-3}M$. The anions NO_3^-, Cl^-, Br^- alone produced no enhancement. Similar graphs to Fig. 2 were prepared at lower concentrations of aluminium, but the position of the maximum remained unaltered. This led to the conclusion that the relevant criterion was the acid concentration and not the ratio of metal to acid. Hence it is not necessary to vary the acid concentration for different concentrations of aluminium.

Under the conditions described in the experimental section the fluorescence of acidified Al PAN was five times that of Al–PAN alone. This enhancement can be increased to a factor of ten if conditions are adjusted to provide a maximum percentage of alcohol while still maintaining an acid concentration of $10^{-3}M$.

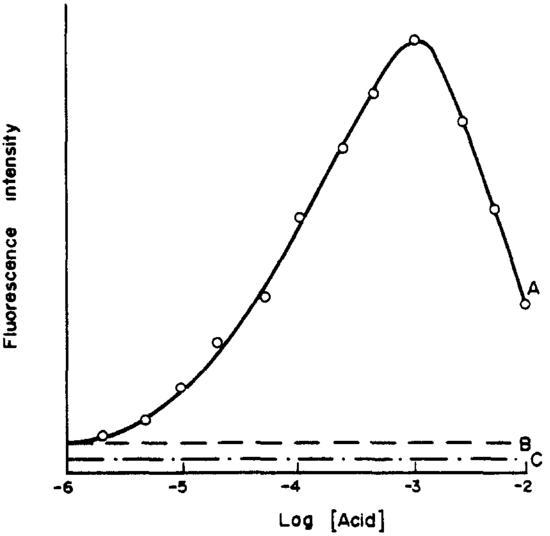

Fig. 2. Fluorescence of Al–PAN *vs.* acid concentration.
A, HNO_3, HCl, HBr. B, Al–PAN alone. C, H_2SO_4, H_3PO_4, CH_3COOH.

The order of addition of reagents affected the time taken for a stable fluorescence to be reached. The final intensity of the fluorescence, however, did not vary with the order of addition of reagents. The sequence Al^{3+} + acid + PAN resulted in a development time of 1 hr for heated solutions, whereas any other sequence gave development times in excess of 2 hr.

Effect of acids on stability of Al–PAN fluorescence

The instability of the Al–PAN fluorescence has been reported previously, a gradual decline in fluorescence intensity being noted.[2,3,5] This decline continues for 30 days in 95% ethanol medium and 24 hr in absolute ethanol.

The addition of nitric, hydrochloric or hydrobromic acid at a concentration of $10^{-3}M$ stabilized the fluorescence of Al–PAN and completely eliminated any decomposition. On addition of the acid, the fluorescence rose sharply for 40 min and then became stable for 10 days, after which time a gradual decline occurred.

The increased stability of the acidified Al–PAN solution allowed it to be prepared as a stock solution and stored unchanged for a period of 10 days.

Fluorometric procedure for determination of aluminium

The enhancement of the fluorescence and stability of Al–PAN has been applied to the development of an improved fluorometric procedure. Calibration curves were constructed over several concentration ranges of aluminium and the effect of nitric acid examined. A five-fold enhancement was produced with identical results being obtained from solutions left for 24 hr at room temperature and those heated at 40° for 1 hr. The calibration curve was reproducible for a period of 10 days, so it was not necessary to prepare fresh curves within this period.

The detection limit was 0·001 ppm Al. as compared with the limit of 0·027 ppm suggested by Surak *et al.*,[1,5] for the existing Al–PAN fluorometric procedure.

Table 1. Estimation of precision of Al–PAN and Al–PAN–HNO_3 methods

			Fluorescence		
$[Al^{3+}]$, *ppm*	Method used	Temp, °C	Mean	SD	RSD, %
0·3	PAN	15	59·3	10·0	17·0
0·3	PAN	40	60·9	10·0	16·5
0·1	PAN	15	56·4	9·9	17·7
0·1	PAN	40	60·8	11·7	19·3
0·3	PAN–HNO_3	15	49·2	1·3	2·6
0·3	PAN–HNO_3	40	51·4	1·5	2·9
0·1	PAN–HNO_3	15	53·7	6·4	12·0
0·1	PAN–HNO_3	40	48·5	5·4	11·2

Precision. The precision of the method was studied and compared with that of Surak's method. The relative standard deviation (RSD) of 10 replicates of the same concentration for two different concentrations (0·1 and 0·3 ppm) was calculated. Within each group of 10 replicates, the first solution was arbitrarily set to 50 units on the fluorometer scale and the remaining solutions compared with it. The results are shown in Table 1.

Table 1 shows that the RSD at the 0·3-ppm level for the acidified solutions was considerably less than for neutral solutions. This difference is not so marked at the 0·1-ppm level, although the RSD was lower for the acidified solutions. Similar values were obtained for the RSD regardless of the method used to bring the solutions to equilibrium.

These results indicate that precision is improved by addition of acid.

Interferences. Interferences in the Al–PAN fluorometric procedure have been reported previously.[2,3,5] The only other element which fluoresces with PAN is cobalt. Co(II) can be air-oxidized to Co(III) which is then able to form a diamagnetic fluorescent complex with PAN. Co–PAN does not represent an interference in the Al–PAN method because the emission wavelengths are well separated.

Of more importance, however, are ions which tend to quench the fluorescence of Al–PAN [such as F^- and Ni(II)]. Nitric acid suppressed the quenching effect of fluoride except when very large excesses of fluoride were present, and appreciably reduced the effect of nickel(II). Nickel does interfere, but the use of an excess of PAN permitted the method to be used in its presence provided that an Ni:Al ratio of 5:1 was not exceeded. Where appreciable amounts of nickel were present, the solution became red, owing to the red Ni–PAN complex. This red colour increased self-absorption effects and necessitated either further dilution or use of standard addition techniques, and this is recommended when the colour suggests the presence of nickel.

Other elements which form coloured complexes with PAN (*e.g.*, Cu, Zn, Fe) are potential interferents if present in sufficient concentration to cause absorption of the Al–PAN fluorescence. The critical concentrations of these elements depends on the solution matrix being used. In the analyses performed it was considered advisable to test this inner-filter effect by addition of a known small amount of aluminium and comparison with an interferent-free matrix. When the effect was observed, it was necessary to dilute the sample to decrease the absorption or to use standard addition procedures.

Apart from fluoride, no anions were found to interfere.

Fluorescence quenching procedures

The use of acidified Al–PAN as a stock solution for the determination of nickel and fluoride by quenching procedures was examined.

Since there was no observed quenching unless a large excess of fluoride was present the quenching procedure is not applicable to the determination of fluoride.

Nickel(II) gave rise to slight quenching, but this was not observed below $10^{-5}M$ concentrations, compared with levels of $10^{-9}M$ found to be feasible by Schenk and Dilloway.[2] The quenching was irregular and no satisfactory calibration curves could be prepared. This behaviour is attributed to the increased stability of Al–PAN when an appropriate acid is added.

Analysis of samples

. Dry-ashing of plant samples has been used previously in the determination of aluminium,[6] and is particularly suitable for such analyses because of the non-volatility of aluminium oxides. Provided procedural errors (such as allowing the sample to ignite) are avoided, there are no detectable losses of aluminium during dry-ashing at temperatures up to 500°.[6] In addition, dry-ashing has the advantage of allowing the sample to be taken up in concentrated hydrochloric acid, thereby facilitating the ion-exchange separation of aluminium.

Lewis *et al.* have described a selective ion-exchange procedure for aluminium.[4] The sample is dissolved in $10M$ hydrochloric acid and passed through an anion-exchange column, which takes up the many elements which form complex chloro-anions. Aluminium is not adsorbed. Of the potential interferents in the Al–PAN procedure, only nickel(II) is eluted with aluminium. Hence, this separation technique is particularly applicable to the analysis of aluminium bronzes where a large excess of copper and tin exists. The method also seemed relevant to plant samples, where aluminium is present in very small concentrations compared to other elements.

When a calibration curve was prepared by passing standard amounts of aluminium through the ion-exchange column, extremely high blank levels of aluminium were observed. The amount of aluminium in the resin was determined by three independent methods.

Table 2. Aluminium content of Amberlite CG400 (100–200 mesh) anion-exchange resin

Method	Value, *ppm*	Remarks
Emission spectrography	300	Qualitative estimate
Colorimetry[7]	120	2 samples
Fluorometry (Al–PAN)	104	1 sample

Very high values of aluminium were found (Table 2), and other batches of the resin gave rise to similar results. Blank values corresponding to 50–100 ppm Al were obtained in the effluent when the resin was left in contact with $10M$ hydrochloric acid for any appreciable time (> 1 day). These high values are attributed to the leaching effect of the acid. It is therefore important that the column is stored containing water only and is pretreated before use with several alternate washings with distilled water and $10M$ hydrochloric acid.

Recovery of added aluminium from the column was examined by performing the fluorometric determination of known amounts contained in a synthetic brass matrix. The results appear in Table 3.

Table 3 Recovery of added Al from a synthetic brass matrix

Al added, μg	Al found, μg	Recovery, %
1000	100·4	100·4
100	99·4	99·4
50	49·5	99·0
10	9·9	99·0

The sample matrix comprised 10 mg of Cu and 10 mg of Zn in 10 ml of 10 M HCl

Materials used for plant analysis consisted of two grass samples (of unknown Al content) and the standard kale material supplied by Bowen.[8] These samples were satisfactorily ashed and digested and were passed through the ion-exchange column without problems. However, heavy precipitates were formed when an aliquot of the aqueous sample solution was added to ethanolic PAN. This resulted in very low values for aluminium, probably because of its coprecipitation with the alcohol-insoluble chlorides present in the sample. Analysis of the precipitate showed it to contain mostly sodium, which is found in relatively high concentrations in plant material (standard kale contains 2594 ppm Na).[8] For this reason, the Al–PAN fluorometric procedure described in this paper was considered unsuitable for plant analysis.

Bronze samples analysed included three samples which had been analysed for aluminium gravimetrically with oxine, and a British Chemical Standard bronze (No. 304). Results for the analyses of these bronzes are shown in Table 4.

Table 4. Analysis of bronzes, by ion-exchange separation and use of acidified Al–PAN

Sample No.	Material		Al content (PAN method)		Previous Al analysis, %
	Description	Ni content, %	Mean, %	SD, %	
1	Al bronze	—	9·82 (7)*	0·021	9·87
2	Al bronze	3·8	2·17 (5)	0·12	1·8–2·2
3	Al bronze	—	0·87 (5)	0·004	0·5–1·0
4	BCS No. 304	4·75	9·85 (9)	0·052	9·82

* The figures in brackets are the number of determinations performed.

The precision of results for nickel-free samples was better than that for the two samples containing nickel. The reason for this was that greater dilutions and more manipulations were required for the latter. Despite this, precision for these samples was still acceptable and the method was considered suitable for the determination of aluminium in bronze.

CONCLUSION

The fluorescence of Al–PAN has been found to be both stabilized and enhanced by the presence of some inorganic acids. This observation has led to the development of a fluorometric method with improved sensitivity and precision over the existing Al–PAN method. The new method has proved satisfactory for the determination of aluminium in bronzes but is unsuitable for plant samples.

The acidified Al–PAN was found to be unsatisfactory for use as a stock solution for the determination of nickel(II) and fluoride by fluorescence quenching procedures.

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Zusammenfassung—Die Fluoreszenz des Aluminiumkomplexes von 1-(2-Pyridylazo)-2-naphthol (PAN) wird durch $10^{-3}M$ HNO_3, HCl oder HBr sowohl stabilisiert als auch verstärkt. Andere untersuchte Säuren haben keinen Effekt. Es wird ein verbessertes fluorometrisches Verfahren mit einer Nachweisgrenze von 0,001 ppm, erhöhter Genauigkeit und verminderten Störungen gegenüber der vorhandenen Al-PAN-Methode beschrieben. Es reicht für die Bestimmung von Aluminium in Bronze aus, wenn man eine Ionenaustausch-Abtrennung verwendet, aber zur Bestimmung von Aluminium ist es nicht geeignet. Die angesäuerte Al-PAN-Lösung eignet sich nicht zur Bestimmung von Nickel(II) und Fluorid durch Fluoreszenzlöschung.

Résumé—La fluorescence du complexe de l'aluminium avec le 1-(2-pyridylazo) 2-naphtol (PAN) est à la fois stabilisée et exaltée par HNO_3, HCl ou HBr 10^{-3} M. Les autres acides essayés n'ont pas d'influence. On décrit une technique fluorimétrique améliorée avec une limite de détection de 0,001 ppm, une précision accrue et des interférences réduites par rapport à la méthode Al-PAN existante. Elle est satisfaisante pour le dosage de l' aluminium dans le bronze quand on utilise une séparation par échange d'ions, mais ne convient pas au dosage de l'aluminium dans plante. L'Al-PAN est impropre au dosage du nickel(II) et du fluorure par extinction de fluorescence.

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NON-ISOTHERMAL THERMAL ANALYSIS: A CRITICAL EXAMINATION OF SOME RECENT THEORIES

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Summary—A critical examination is made of the theories and recommendations of MacCallum and Tanner, Prime, Draper, and Ingraham and Marier concerning the applicability of the Arrhenius equation to the kinetic analysis of data obtained by non-isothermal thermal analysis. Except for the last mentioned these theories are found to be of questionable validity. It is suggested that a number of factors related to the experimental procedure and the assumptions made about the decomposition processes studied, require more extensive investigation before the theoretical limitations of the Arrhenius equation can be adequately assessed.

The validity of the Arrhenius-type representation of data obtained by non-isothermal thermogravimetry (TG) and related techniques, *e.g.*, DTG, DTA and DSC, has frequently been debated over the past few years.

The equations normally utilized in the kinetic analysis of thermoanalytical data are:

$$\frac{dx}{dt} = Ae^{-E/RT}\cdot f(x)\,, \tag{1}$$

$$\frac{dx}{dT} = \frac{A}{a}\,e^{-E/RT}\cdot f(x), \tag{2}$$

where x is the degree of conversion, t the time, A the pre-exponential factor, E the activation energy, R the gas constant, T the absolute temperature, and a the linear rate of heating, and evaluation methods based on these equations have been reviewed widely.[1–5]

It has been found that, even with the same experimental data, different evaluation methods may result in different values for kinetic parameters such as activation energy, pre-exponential factor and reaction order.[2,4,5] The parameters have also been observed to change with changes in the applied heating rate,[6,7,8] and parameters calculated from data obtained in non-isothermal experiments have been found to differ from those obtained under isothermal conditions with the same type of sample.[5,9]

These discrepancies have often been attributed to inadequacies of the Arrhenius-type representation given in equations (1) and (2). Modified equations and new theories have emerged in attempts to create consistency between theory and the actual phenomena.

In this critical examination, the theories and modifications proposed by Ingraham and Marier,[10] Draper,[11] MacCallum and Tanner[12,13] and Prime[9] are discussed at length, and an attempt is made to assess their validity.

Ingraham and Marier[10] have proposed a modified kinetic equation:

$$\frac{dx}{dt} = A'Te^{-E/RT} \cdot f(x), \tag{3}$$

which takes into consideration the temperature-dependence of the pre-exponential factor. This can be represented by:

$$A = \frac{\mathbf{k}}{\mathbf{h}} e^{S/R} \cdot T = A'T, \tag{4}$$

where **k** is the Boltzmann constant and **h** the Planck constant. Compared to the corresponding parameters obtained by using equation (1), the activation energy is slightly smaller, and the pre-exponential factor at normal temperatures is up to about three orders of magnitude smaller, when equation (3) is used for the calculation.

Draper[11] considered the Arrhenius equation [equation (1)] to be applicable only to isothermal processes and proposed that it should be represented with the dx/dt term as a partial derivative:

$$\left(\frac{\partial x}{\partial t}\right)_T = Ae^{-E/RT} \cdot f(x). \tag{5}$$

He suggested that the introduction of the linear heating rate, a, into equation (1) to obtain equation (2) was mathematically incorrect because the time term used in the expression for the linear heating rate was fundamentally different from the corresponding time term of equation (5). He regarded the latter as "isothermal time", t_I, and the former as "temperature-variation time", t_T, and proposed that the total differential of the conversion should be written as

$$dx = \left(\frac{\partial x}{\partial t_I}\right)_{t_T} dt_I + \left(\frac{\partial x}{\partial t_T}\right)_{t_I} dt_T. \tag{6}$$

In isothermal processes t_T is constant and the second term is zero, while in non-isothermal processes t_I remains unchanged and the first term is zero. According to Draper, in order to obtain correct results from non-isothermal analysis it is necessary to carry out the analysis in such a way that t_I remains constant.

Draper and George[14] identified the t_I variable and found that to keep it constant a hyperbolic heating rate, θ, is required, where θ is defined by

$$\theta = \frac{d(1/T)}{dt}. \tag{7}$$

It can be shown that in this case

$$\int_0^x \frac{dx}{f(x)} = F(x) = \int_x^{1/T} Ae^{-E/RT} \cdot \frac{1}{\theta} d\left(\frac{1}{T}\right) = Ae^{-E/RT} \cdot t_I, \tag{8}$$

where

$$t_I = -\frac{R}{E\theta}. \tag{9}$$

Values for the rate constant at different temperatures can be obtained from equation (8), and with these data the activation energy and pre-exponential factor can easily be calculated.

MacCallum and Tanner[12,13] expressed a perference for isothermal procedures. They set out to show that the original Arrhenius equation is not applicable to non-isothermal processes. On the basis of Kissinger's formulation:

$$x = f(T,t), \tag{10}$$

they reason as follows. The derivative of the conversion function [equation (10)] is

$$\mathrm{d}x = \left(\frac{\partial x}{\partial t}\right)_T \mathrm{d}t + \left(\frac{\partial x}{\partial T}\right)_t \mathrm{d}T, \tag{11}$$

and hence the reaction rate

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{12}$$

From equations (1) and (5) it follows that

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{-E/RT}\cdot f(x) + \left(\frac{\partial x}{\partial T}\right)_t a, \tag{13}$$

i.e.,

$$\frac{\mathrm{d}x}{\mathrm{d}t} \neq \left(\frac{\partial x}{\partial t}\right)_T. \tag{14}$$

Thus the Arrhenius equation is not applicable to the non-isothermal processes in which the term $(\partial x/\partial T)_t$ has a value other than zero.

Prime[9] has used the same line of reasoning as MacCallum and Tanner and has, further, attempted to identify the $(\partial x/\partial T)_t$ term of equation (13). By integrating equation (5) and differentiating with respect to the time and temperature he obtained the relationship

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Z\left(\frac{\partial x}{\partial t}\right)_T, \tag{15}$$

where

$$Z = \left(1 + \frac{tE}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\right) = \left(1 + \frac{E\Delta T}{RT^2}\right), \tag{16}$$

ΔT is the difference between the temperature at a particular time and the temperature at which the reaction started: $\Delta T = T - T_i$.

Substitution for Z and $(\partial x/\partial t)_T$ into equation (15) gives

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(1 + \frac{E\Delta T}{RT^2}\right) Ae^{-E/RT}\cdot f(x), \tag{17}$$

and, with this equation, one can obtain values for A and E/R by plotting $\ln(\mathrm{d}x/\mathrm{d}t)/Zf(x)$ against $1/T$.

The suggestions above for achieving consistency reflect markedly different opinions concerning the nature and origin of the discrepancies. We have considered these theories, and find that apart from that of Ingraham and Marier they are of doubtful validity.

Draper's theory was developed to satisfy a requirement that experimental data from non-isothermal and isothermal processes should be the same. When this is so, an integral of the form shown in equation (8) can be used for the evaluation, which may be carried out in a simple manner by plotting the data in the logarithmic form:

$$\ln F(x) - \ln t = \ln A - \frac{E}{RT} = \ln k(T), \tag{18}$$

where k is the rate coefficient. The experimental data required from non-isothermal experiments when Draper's concept is applied lie on lines parallel to the ordinate in Fig. 1.

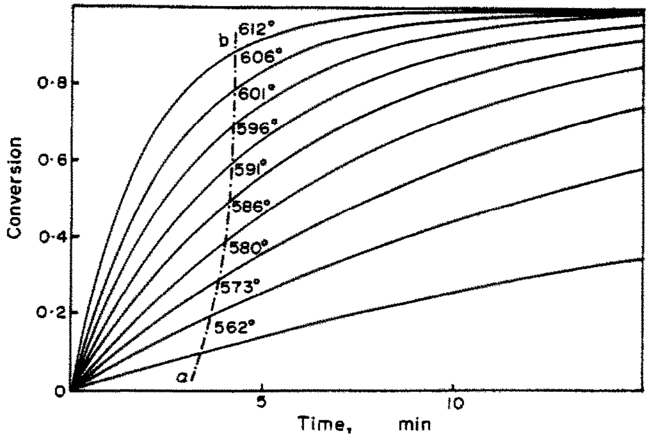

Fig. 1. Isothermal and non-isothermal reaction routes. The a–b line corresponds to a thermogravimetric trace characterized by the following variables: $E = 40$ kcal/mole; $A = 10^{14}$ min^{-1}; $n = 1$; $a = 4$ deg/min. The isotherms have been calculated for the same kinetic parameters and for temperatures belonging to degrees of conversion 0·1, 0·2, ..., 0·9 on the non-isothermal curve.

Although, in calculations based on isothermal measurements, the constancy of time is convenient, if one wishes to compare various isotherms, it is not altogether necessary. The kinetic constants can be determined from data obtained in other ways, including data obtained by using linear temperature programming. A practical example of this situation is marked by the line a–b in Fig. 1. It should be noted that the time scale on the abscissa of Fig. 1 applies only to the isothermal x–t functions which are indicated by continuous lines. The condition that the x–T data pairs obtained by non-isothermal experiments should also be obtainable by isothermal processes should be considered as fulfilled. From Fig. 1 it can be seen that a series of stepwise isothermal processes will be equivalent to a single non-isothermal procedure. The physical meaning of equation (6) is that any Δx–ΔT change in an experimental conversion–temperature (x–T) function can be achieved with a suitable combination of isothermal and hyperbolically-programmed steps; thus any conceivable reaction route should be considered as "legitimate". The same conclusion has been arrived at by Simmons and Wendlandt.[16]

If equation (1), which describes only a momentum of the x–t–T function, is integrated with strict regard to the nature of the time–temperature relationship, at each step of the reaction path the derivation remains true. This means that it is not necessary to introduce two different time scales.

If equation (1) is integrated for a hyperbolic heating rate [equation (7)] we obtain equation (8) regardless of the possibility of different time scales. Such integration is the usual practice for producing equations for non-isothermal evaluation purposes. Thus, if we use a linear heating rate, equation (2) is integrated in the following form:

$$\int_0^x \frac{dx}{f(x)} = \frac{A}{a}\int_0^T e^{-E/RT}\cdot dT. \tag{19}$$

The main advantage of using hyperbolic heating rates is that equation (1) can then be directly integrated, whereas with linear programming the calculations are more complicated and, if approximations are involved, not completely accurate. Hyperbolic and exponential temperature programming have been reported by Farre-Rius and his co-workers.[18]

In line with Kissinger's earlier suggestion[15] both MacCallum and Prime assume that the conversion is a state function of two independent variables, namely the time and temperature. Some problems regarding derivations based on Kissinger's formulation [equation (10)] have already been considered in detail elsewhere.[17] In particular it has been noted that partial differentiation cannot be applied to this expression, since the above-mentioned assumption is not valid.

If one substitutes data into equation (15) it can be seen that Prime's approach can lead to surprising results. Thus, if the values of Z corresponding to an activation energy of 13 kcal/mole and an initial decomposition temperature (T_i) of 55° are substituted into equation (15) then the calculated reaction rate at 100° is almost six times larger, and the reaction rate at 200 is almost eleven times larger, than the reaction rate under normal isothermal conditions at the same degree of conversion.[9] The explanation for these unlikely results lies in the mathematical treatment employed. The procedure,[9] however, has not been described in detail, although a reference was made to a future publication which we have not been able to find.

On the outline of the derivation given by Prime,[9] at least two procedures can be devised to obtain expressions that might lead to equations (15) and (16). However, in both derivations, it is necessary to make incorrect assumptions in order to arrive at Prime's equations.

Consider, for example, the more demonstrative of the two procedures mentioned above. From the isothermal equation

$$\left(\frac{dx}{dt}\right)_T = Ae^{-E/RT}\cdot f(x), \tag{i}$$

we obtain by integration:

$$\int_0^x \frac{dx}{f(x)} = \int_0^t Ae^{-E/RT}\cdot dt = Ae^{-E/RT}\cdot t, \tag{ii}$$

and by subsequent differentiation:

$$d\int_0^x \frac{dx}{f(x)} = d(Ae^{-E/RT}\cdot t),$$

i.e.,

$$dF(x) = Ae^{-E/RT}\left(\frac{E}{RT^2}t\cdot dT + dt\right). \tag{iii}$$

where the right-hand side of equation (iii) is a total differential. From (iii):

$$\mathrm{d}F(x) = Ae^{-E/RT}\left(\frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\cdot t + 1\right)\mathrm{d}t, \tag{iv}$$

and hence:

$$\int_0^{F(x)} \mathrm{d}F(x) = \int_0^t Ae^{-E/RT}\left(\frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\cdot t + 1\right)\mathrm{d}t,$$

i.e.,

$$F(x) = \int_0^x \frac{\mathrm{d}x}{f(x)} = \int_0^t Ae^{-E/RT}\left(\frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\cdot t + 1\right)\mathrm{d}t. \tag{v}$$

Thus

$$\frac{\mathrm{d}x}{f(x)} = Ae^{-E/RT}\left(\frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\cdot t + 1\right)\mathrm{d}t, \tag{vi}$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{-E/RT}\left(\frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\cdot t + 1\right)f(x), \tag{vii}$$

i.e., we obtain equation (17).

If the $\mathrm{d}T/\mathrm{d}t$ term in equation (iv) and in the subsequent derivation is regarded as some sort of heating rate a very serious error is committed. Equation (iii) is an expression describing only some properties of the *x–T–t isothermal* reaction surfaces, and is limited by the $x = 0$ and $t = 0$ lower integration boundaries.

Its application to actual isothermal reactions gives the obvious result:

$$F(x) = \int_0^t Ae^{-E/RT}\cdot\mathrm{d}t\,, \tag{viii}$$

since the term containing $\mathrm{d}T$ must be zero.

Equation (iii) cannot generally be applied to non-isothermal processes since, according to the original assumption, its time parameter is the time spent in a reaction proceeding from $x = 0$ to x isothermally at a constant temperature (T). There is, however, one exception to this limitation. If Draper's[11] assumptions of two different time scales are applied to equation (iii) one obtains:

$$\mathrm{d}F(x) = Ae^{-E/RT}\left(\frac{E}{RT^2}\,t_{\mathrm{I}}\,\mathrm{d}T + \mathrm{d}t_{\mathrm{I}}\right). \tag{iiia}$$

Equation (iii*a*) can be applied to non-isothermal reactions proceeding through hyperbolically-programmed and isothermal steps. The conditions $\mathrm{d}t_{\mathrm{I}} = 0$ and $\mathrm{d}T = 0$ lead to equations (8) and (viii) respectively.

The incorporation of a generally-expressed heating rate in equation (iii) leads to the expression:

$$\mathrm{d}F(x) = Ae^{-E/RT}\left(\frac{E}{RT^2}\,t_{\mathrm{I}}\,\frac{\mathrm{d}T}{\mathrm{d}t_{\mathrm{T}}} + \frac{\mathrm{d}t_{\mathrm{I}}}{\mathrm{d}t_{\mathrm{T}}}\right)\mathrm{d}t_{\mathrm{T}}\,. \tag{iva}$$

Since t_I in this equation can only be interpreted in terms of a constant hyperbolic heating rate and for this condition $\mathrm{d}t_\mathrm{I}/\mathrm{d}t_\mathrm{T} = 0$, we obtain:

$$\mathrm{d}F(x) = A\,e^{-E/RT}\cdot \mathrm{d}t_\mathrm{T}, \tag{viii$a$}$$

which is again equivalent to equation (1).

Some results from a DSC study on the curing of an epoxy resin given by Prime[9] appear to justify his theoretical treatment. From measurements at different heating rates he obtained values for the activation energy and pre-exponential factor by using equations (1) and (17). He compared these two sets of results and values obtained from isothermal measurements and calculated by using equation (1). The results from equation (17) are, indeed, in better agreement with the isothermal ones than those calculated by using non-isothermal data in equation (1). However, it was surprising to find that results calculated from non-isothermal measurements on the basis of equation (1) were in better and better agreement with those obtained from isothermal ones as the heating rate increased.

This phenomenon would suggest a highly exothermic reaction, where in some cases the spontaneous temperature rise in the sample might exceed that from the applied heating rate. Thus the actual sample temperature might be consistently higher than that assumed. The larger the difference between the real and assumed temperatures, the larger would be the activation energy calculated on the basis of equation (1), since the preset linear heating rate and thus the assumed temperatures are generally used in the evaluation procedure. For such behaviour, however, the measuring routine employed, and not equation (1), must surely be held responsible.

The introduction of a temperature-dependent term in equation (1) must, naturally, modify the calculated activation energy values.

To ascertain the basis of the difference in the values of the kinetic constants calculated from equations (1), (3) and (17), we need first to define the quantity "experimental activation energy", E_exp. This is given by the relationship:

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E_\mathrm{exp}}{RT^2}, \tag{20}$$

because it is determined by studying the temperature dependence of the rate constant.

From equation (3) we can derive the expression

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T} + \frac{E}{RT^2} = \frac{RT+E}{RT^2}, \tag{21}$$

and from equations (20) and (21) we obtain

$$E_\mathrm{exp} = RT + E. \tag{22}$$

Thus E_exp increases linearly with the temperature as RT increases, from 0·6 to 2 kcal/mole, over the temperature range from 300 to 800 K. From equation (17) the rate constant, k, can be expressed as $AZe^{-E/RT}$, hence:

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\mathrm{d}\ln Z}{\mathrm{d}T} + \frac{E}{RT^2}. \tag{23}$$

We have found that the particular function in the published experiment could be approximated as:

$$Z \sim C(T - T_{\mathrm{i}})^{1/2}, \tag{24}$$

where C is a constant.

Using this expression for Z, we obtain from equation (23):

$$\frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{1}{Z\Delta T} + \frac{E}{RT^2}\,. \tag{25}$$

From equations (25) and (20) a new expression for E_{exp} is now derived:

$$E_{\mathrm{exp}} = \frac{RT^2}{2\Delta T} + E. \tag{26}$$

The $1/2RT^2/\Delta T$ term could be expressed in an approximate form. Thus, using the published data:[9]

$$E_{\mathrm{exp}} \sim 33T^{-0{\cdot}64} + E. \tag{27}$$

According to equation (27), E_{exp}, *i.e.*, the E values calculated without using the Z-value correction, should decrease with increasing temperature. The value of the $33T^{-0{\cdot}64}$ term ranges from about 10 to about 1·5 kcal/mole as the temperature rises from 50 to 200°, and the higher the average temperature of the reaction the smaller the difference between the average values of E_{exp} and E. It should be noted that the average reaction temperature increases with increasing heating rate, and this is why the published activation energies move closer to one another and the differences between the corrected and uncorrected values also decrease with increasing heating rates. Thus in Prime's treatment the errors attributed to the use of equation (1) appear to have been overcome by the use of equation (17). In fact, in this instance, we have one of those rare occasions when an incorrect theory is applied to a suitable set of data to yield acceptable results.

Some authors[6,7,8] have reported that kinetic parameter values obtained by non-isothermal thermoanalytical methods change with changing degrees of conversion and/or changing heating rates. They find that values for the activation energy usually increase with decreasing heating rates, approaching the isothermally-obtained value.

The changes in heating rate and degree of conversion usually correspond to changes in temperature, but the effects of these changes on the calculated E values are more dramatic than the increase expressed by equation (22). In such cases the theory of Ingraham and Marier[10] is not of practical value. However, this theory appears to be acceptable theoretically, unlike the other three.

The lack of agreement amongst practical results may be attributed to many factors, such as differing assumptions about the reaction mechanism, inadequate heating rates, too large a sample-size, and uncontrolled thermal behaviour.

These practical and procedural factors may have an over-riding effect on the data obtained from thermoanalytical measurements of any type. If such effects are not eliminated or taken carefully into consideration, the results obtained from different experimental conditions will obviously disagree.

There seems to be no fundamental reason why the non-isothermal nature of measurements should be responsible for disagreement between isothermally and non-isothermally obtained results. If the reaction mechanism remains unchanged as the reaction proceeds, these results can, indeed, be in good agreement.[19] We think that further work is required on the influences of the above-mentioned factors and similar phenomena on the experimental data and/or the results of particular procedures of evaluation. Only when satisfactory procedures have been established for obtaining the appropriate data can it be decided whether or not the underlying theory, *i.e.*, the Arrhenius-type representation of the kinetic processes, requires modification.

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Zusammenfassung—Die Theorien und Empfehlungen von MacCallum und Tanner, Prime, Draper und Ingraham und Marier bezuglich der Anwendbarkeit der Arrhenius-Gleichung auf die kinetische Analyse von Daten aus der nichtisothermen Analyse wurden kritisch überprüft. Außer der zuletzt erwähnten erweisen sich diese Theorien als von fraglicher Gültigkeit. Es wird angedeutet, daß eine Anzahl von Faktoren, die mit dem Versuchsverlauf zu tun haben, und die über die untersuchten Zersetzungsprozesse gemachten Annahmen noch ausführlicher untersucht werden müssen, ehe die theoretischen Begrenzungen der Arrhenius-Gleichung hinreichend abgeschätzt werden können

Résumé—On fait un examen critique des théories et recommandations de MacCallum et Tanner, Prime, Draper et Ingraham et Marier concernant la possibilité d'application de l'équation d'Arrhenius à l'analyse cinétique des données obtenues par l'analyse non-isothermique. A l'exception de le dernière mentionnée, on a trouvé que ces théories sont de validité douteuse. On suggère qu'un certain nombre de facteurs relatifs à la technique expérimentale et les hypothèses faites sur les processus de décomposition étudiés exigent une recherche plus développée avant que les limitations theoriques de l'equation d'Arrhenius puissent être appréciees convenablement.

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NEW APPROACHES TO GEOCHEMICAL ANALYSIS AND SAMPLING

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Summary Methods are now being devised for the design of sampling schemes and for data evaluation promise to increase the certainty with which large, inhomogeneous, and segregated masses of material (mountains) may be analysed for interesting constituents. These methods are directed toward the integration of work originating within several disciplines, and utilize different kinds of sampling constant to control error.

Griffiths[1] has remarked that no organized attempt has been made to resolve the problem of sampling in the mineral industries (or the geosciences). This is not the overstatement it may at first appear. Algorithms for solution of the problem have not been used. This is probably due to a lack of liaison between disciplines. Miesch[2] has identified part of the problem: "Analytical errors include errors due to crushing, splitting, homogenization, laboratory subsampling, procedures at bench or instrument, and even recording and typing the lab report. The analyst has to be concerned with these sources of analytical error, but from the geologist's standpoint, it's the total analytical error that's important."

Most investigations of the geochemical sampling problem, with some notable exceptions, have been directed toward devising sampling patterns. The principles of field sampling design has been treated in depth: see, for example, the references cited by Griffiths.[1] This aspect of geochemical sampling is outside the scope of this paper, which emphasizes problems arising after the field sampling pattern has been established.

These problems have all been more or less thoroughly treated in their parts: this paper suggests integration of these parts as a first try at the "organized attempt" mentioned by Griffiths.

The key to the overall sampling problem may lie in the fact that analysts are seldom able to control error incurred during preparation of the sample presented for analysis. At best, they have the possibility of measuring the sampleability of material received, and of giving warning of potential difficulties at other levels of sample treatment. Even this possibility does not occur routinely.

When submitted samples are inhomogeneous or non-uniform, they are apt to be unrepresentative of the field samples from which they were prepared. Evaluation of the results is in consequence doubly frustrated; analyses are not reproducible, and also do not represent what they are supposed to. This frustration is often attributed to analytical error or to poor analytical discrimination.[3] Sometimes investigators are led to manipulate such results statistically, and censor those which do not fit a preconceived model.

It has been observed[4] that many data sets which do not fit a normal (Gaussian) distribution may be transformed[5,6] into new data sets which will fit this distribution, by conversion of the individual values into logarithms and addition of suitable constants. Mathematical devices are used[7–9] to establish that part of the log-normal distribution which is beyond the reach of an analytical method because of lack of sensitivity. Rules of varying complexity have been proposed for eliminating "outliers". One of the more trivial of these, which has the virtue of being easily understood, is that "bad" analyses should be repeated in the hope of a "better" result. This rule is based on the empirical observation that enough "repeats" will usually generate a value compatible with any desired model.

The manipulation of data to fit a normal, a log-normal, or some other ideal distribution is sometimes productive. More often, what is needed is a technique for adjusting available models to fit the data. To this end, the properties of non-Gaussian distributions are receiving attention.[10–12] An effort is developing to overcome difficulties induced through indiscriminate use of the Gaussian approximation and the log-normal empiricism, and to avoid extrapolation of observed variance beyond the process step in which it originates.

THE SAMPLING OF MOUNTAINS

Why do we wish to sample a mountain? For the purpose of this article, we wish to discover not only how much of valuable element X it contains, but also to find the distribution of this element within the mountain. To do this, samples must be taken, they must be reduced in size to a few grams, and they must be analysed.

A distinction between "samples" and "subsamples" is worth while. A sample of a mountain is not necessarily a representative sample of the mountain. The composition of a mountain with respect to the element X is only found through analysis of many samples, none of which can reasonably be expected to be individually representative. The overall concentration of X in the mountain could best be found by taking as many samples as possible, reducing them properly, mixing them and finally making one analysis by the most accurate method available. This would, however, tell nothing of the way in which the element X is distributed throughout the mountain, and would provide the mining engineer with only a preliminary overall grade estimate.

A subsample is a split of a sample, prepared in such a way that there is some confidence in its having the same concentration of X as the sample from which it originated. Between samples of the mountain, one expects there to be differences in X-content; indeed, such differences provide a picture of the distribution of X in the mountain. Between subsamples of the same sample, one hopes that there will be no difference in X-content.

The process of reducing a sample (which may weigh many pounds or even tons) to a laboratory subsample (which may weigh a few grams or less) may have to be different for every constituent. A thoroughly adequate reduction scheme for constituent X may be inadequate for constituent Y. For example, molybdenum may be present in veins or large rosettes, while tin or gold may be evenly distributed in minute grains of cassiterite or native metal. Each of these mineral species carries its own comminution characteristics. Zinc may be concentrated in one part of the mountain, and lead in another. If more than one element is of interest, two or more different, overlapping, and co-ordinated sampling and subsampling schemes may have to be devised. Of course, an adequate sampling scheme for one element may result in oversampling for another; this obviously does no harm.

There are many sources of error in the sampling and reduction process, and for success *all* of these must be considered. The information chain leads from the mountain to the balance pan through sample collection and reduction. It then leads back to the mountain *via* chemical or instrumental analysis and evaluation of results. This chain is no stronger than its weakest link. Efforts directed toward strengthening any other link are wasted.

One must first discover which link is the weakest, and, since all data originate at the analytical link, this link should be examined first. A primary analytical requirement is the capability to analyse homogeneous samples for the element X with the required accuracy, precision, speed, and confidence. When the measured concentration of X in successive subsamples shows an unacceptable variance, it is necessary to discover how much of this variance is due to analytical error, and how much to subsampling error.

Sometimes it is difficult to isolate and clearly define analytical error; nevertheless, its definition is an *essential first step* toward control of the overall information-gathering process. If, by definition, analytical error is to include crushing, splitting, homogenization, and subsampling error, there will be no possibility of isolating and defining it. It will remain the catch-all for geochemical confusion.

There are several methods by which analytical and subsampling errors may be separated. To measure analytical error, repetitive analyses of samples of known uniformity is the most straightforward method. If such samples are not available, as is often the case, comparisons of method performance by use of different sample weights may be useful, or repetitive analyses of selected samples before and after grinding to a finer grain-size may yield the required information. The difference in variance of results on fine and coarse samples, or on small and large samples, provides an estimate of both subsampling and analytical variances, and permits their separation.

When confidence in analytical methods has been established by such means, it is possible to investigate the sampling and subsampling characteristics of the material in the "mountain." This investigation must take place in three or more overlapping stages. The problems at each stage are conveniently defined in terms of sampling constants.

SAMPLING CONSTANTS

We define three types of sampling constant.

1. A laboratory sampling constant,[12] useful in describing the subsampling characteristics of laboratory samples and submitted samples.
2. Gy's sampling constant,[13–15] useful in controlling the reduction of field samples to laboratory size.
3. Visman sampling constants,[16–19] useful during the design of field sampling procedure.

Of these sampling constants, those of Gy and Visman have unquestioned claim to priority. Each reflects basic sampling principles; they differ only in emphasis and field of applicability. If Griffiths' challenge is to be eventually met, they will all be combined into a truly general sampling theory.

The laboratory sampling constant K_s

The homogeneity or uniformity, and hence the subsampling characteristics, of a well-mixed laboratory sample or submitted sample may be defined, with respect to the element X, by a laboratory sampling constant

$$K_s = R^2 w, \qquad (1)$$

where R is the relative subsampling error incurred by using subsamples of weight w. R may be estimated from the coefficient of variation of a series of N analytical results for subsample weight w:

$$R = 100\, s/\bar{X} = \sqrt{K_s/w}, \qquad (2)$$

where s is the estimated standard deviation and $\bar{x}$ is the mean of N analytical results by a precise analytical method. The distribution of the N analytical results must be approximately Gaussian, or they must be randomly grouped (according to the central limit theorem) to yield such a distribution. Other methods of estimating K_s have been suggested.[12] These include physical measurements of various kinds. Like Gy's constant (see below), K_s is descriptive of the material, is independent of sample or subsample size, and has no relation to analytical error.

In using the method of repetitive determination to estimate K_s, it is very important that N be large enough to permit estimation of the frequency of occurrence of isolated high-X mineral grains. Principles governing the selection of N are the same as those used by Visman and Gy (see below) except in circumstances where the distribution of analytical results does not follow a Gaussian pattern, and calculations based on the Gaussian approximation do not apply. Such circumstances arise far more frequently at the laboratory subsampling level than at other levels in the sampling process.

When samples or subsamples are small and the overall concentration of X is low, it is always possible that none of N samples or subsamples will contain a grain of high-X mineral. For example, a 100-mg subsample of a 200-mesh rock powder containing 20 ppm SnO_2 may carry only one grain of cassiterite. Several 10-mg subsamples of this rock powder may show no grain of cassiterite. The occasional 10-mg subsample which does carry a grain of cassiterite will show about 200 ppm SnO_2. It is impossible, in this example, for any single 10-mg subsample to show the true overall concentration of SnO_2. If the sample is 100-mesh instead of 200-mesh, 160 ppm SnO_2 might be missed entirely if 10-mg subsamples are taken. If the 100-mesh sample contains 1600 ppm (0·16%) SnO_2, an average 100-mg subsample will contain 10 grains of cassiterite, and successive 100-mg subsamples will generate results of high variance, because each subsample will contain a randomly varying number of cassiterite grains. The results will show a Poisson distribution in which successive results differ by multiples of about 160 ppm, and with a standard deviation of $\sqrt{10} \times 160$, or about 500 ppm. If this distribution should be attributed to analytical error, or if it were extrapolated to supposed field relationships, false conclusions might be drawn.

At the field sampling level, a similar situation may prevail. For example, one 3-mesh grain of MoS_2 in a 36-kg sample contributes about 0·04% Mo to a 2-kg split of that sample. See the example given at the end of this article.

Because of such considerations, it is of importance to consider carefully the subsample weights required by various analytical methods, and to relate those requirements to particle size and other characteristics of the submitted samples being examined. This is most easily done through use of the laboratory sampling constant K_s.

Defining K_s in terms of relative sampling error, instead of in terms of variance or standard deviation, has several advantages. It is the weight in grams needed to ensure (68% confidence) a result which differs from the mean by no more than 1%. The square root of the sampling constant is numerically equal to the coefficient of variation of a set of results obtained from 1-g subsamples by a precise analytical method. In the construction of a calibration curve for an analytical method, the length of error bars may be calculated from K_s values of the respective samples and calibrating standards without reference to the concentrations of X in either, if a blank measurement establishes the intercept on the ordinate.

Only after laboratory subsampling error has been brought under control is it possible to begin evaluation of processes by which submitted samples are prepared from field samples.

Gy's sampling constant. C

The principles which ought to guide bulk sample reduction have been thoroughly developed by Gy.[13–15] Gy's sampling constant is defined in his basic sampling equation

$$C = Ms_R^2/d^3 = fglm, \tag{3}$$

where M is the weight of sample required to attain a relative sampling variance s_R^2, and d is the linear dimension of the largest pieces in the lot to be sampled. The sampling constant C is the product of several factors—a shape factor f, a particle-size distribution factor g, a liberation factor l, which approaches zero for completely homogeneous material and unity for completely heterogeneous material, and a mineralogical composition factor

$$m = (1 - a)(r - ar + at)/a, \tag{4}$$

where r and t are the densities of the ore mineral and the gangue respectively, and a is the average ore-mineral content expressed as a fraction of the whole. Gy's sampling slide-rule[15] permits quick calculations using these principles. The slide-rule carries a table giving corresponding values of l and d/L, the ratio of biggest particle size to liberation size (*i.e.*, largest particle size of the component of interest).

A simpler principle, which must, however, be applied with caution, involves use of the Tyler screen scale.[20] Very often, if a sample is reduced to pass the next finer screen on the $\sqrt{2}$ scale, one-half of it may be split out without loss of information, and the split remains representative of the whole. Obviously, the grains of high-X mineral must be reduced in size during crushing for this rule to be valid. Mere breaking up of aggregates or reduction of gangue minerals will not have the desired effect. The several factors and devices described by Gy must remain in consideration if sampling mistakes are to be avoided.

However the field samples are treated during preparation, it is necessary to monitor reduction errors, because no reduction theory can be exactly applied. Replicate submitted samples should be prepared in sufficient number for sure detection of inadequacies in the reduction process; this should be done as early in an exploration as possible, to avoid generation of meaningless data. Gy's sampling constant and its associated arguments provide the best available means for controlling and strengthening the third essential link in the information chain.

Visman sampling constants A *and* B

Any field sampling operation involves two essential steps, the devising of a sampling pattern (which must always fit circumstances dictated by Nature), and the physical process of collection (which is often similarly restricted). These steps may well be guided by the "General Sampling Theory" of Visman.[16–19]

Visman's theory, as applied to the analysis of unknown materials which are both inhomogeneous and segregated, requires the collection of two series of samples, one series of small samples and one series of large samples. The members of each series are reduced and analysed, care being taken that variance in the results does not originate from errors of sample reduction, from laboratory subsampling error, or from analytical error. The importance of controlling reduction error, using Gy's principles or their equivalent, and of minimizing laboratory subsampling and analytical errors, is obvious. If any of these is out of control, the variances which are important to the application of Visman's theory may represent, not the sampling characteristics of the mountain, but a jumble of mixed errors.

Visman sampling constants are calculated from the formulae

$$A = w_1 w_2 (s_1^2 - s_2^2)/(w_2 - w_1), \tag{5}$$

$$B = s_2^2 - A/w_2, \tag{6}$$

where A is a homogeneity constant, B is a segregation constant, s_1^2 is the small-sample variance, s_2^2 is the large-sample variance, w_1 is the small-sample weight, and w_2 is the large-sample weight.

The constants A and B having been determined, the expected variance in the combined results for N samples, each of weight w, is given by

$$S^2 = A/W + B/N, \tag{7}$$

where $W = Nw$, the total weight of samples of weight w. Note that as the segregation constant B increases, the number N of samples taken assumes greater importance. If the ore body, shipment, or mountain is not at all segregated, B is zero, and it makes no difference into how many increments the total weight of samples W is divided. With segregated materials, there is evidently an optimum field sampling weight w_{opt} which will yield a most precise estimate of the X-content of the mountain for any given total weight W of field samples. By differentiating (7) with respect to w and equating to zero, this optimum weight is found to be

$$w_{\text{opt}} = A/B = W/N. \tag{8}$$

As data accumulate during an exploration, or during a mining operation, increasingly accurate estimates of A and B will permit adjustment of field sample weights so as to obtain the most information at the lowest cost.

Visman's sampling theory was developed semi-empirically. Duncan,[17] Visman *et al.*,[18] Visman,[19] and Switzer[21] have examined it critically in the light of statistical theory, and its validity in several respects has been established. However, some of its approximations may not be tolerable in real circumstances when segregation is extreme. A major approximation is the assumption of a linear relationship between segregation-induced variance and sample size. By taking three or more (instead of two) series of samples of differing size, it is possible to establish a size–variance curve more accurately,[18,19] and thereby avoid approximations which may not be valid in a particular case.

An important practical fact which may influence selection of field sample weights is that subsampling errors (as distinct from sampling errors) are likely to be small for small samples, maximum with medium-size samples, and to diminish as samples become very large (always supposing that sound reduction procedures are followed). For example, a 4-in. length of drill core can be completely ground to pass a 100- or 200-mesh sieve, and will exhibit negligible subsampling error in comparison with the very large difference which may be expected between samples. With very large samples (over 100 kg), reduction errors and sampling aberrations are likely to cancel in any well-devised and well-directed reduction process. It is with medium-size (1–10 kg) samples that such accidents as the loss or gain of rich ore or nuggets is most likely. Should it turn out that the optimum field sample weight is close to that at which mistakes and accidents are more likely, sample weight adjustment may be desirable. Generally, if the calculated optimum field sample weight is very large or very small, practical considerations may override it. It nevertheless remains an important guide to efficient sampling procedure.

Because of these interrelated considerations, it is probably not possible to write general definitive directions for arriving at an optimum field sampling weight. Such directions must be derived for each particular case, following a careful assessment of practical problems and a knowledgeable application of appropriate statistical principles.

USEFUL RELATIONSHIPS

Several useful relationships, based on statistical principles, have been developed by Engels and Ingamells[22] and Ingamells and Switzer.[12]

$$R = 100 \times (H - L)\sqrt{pq}/K\sqrt{n}, \tag{7}$$

$$R_{\max} = 50 \times (2p - 1)/\sqrt{n(p - p^2)}, \tag{8}$$

$$c = s^2/(K - L), \tag{9}$$

$$z = (K - L)^2/s^2, \tag{10}$$

$$n = H/c - L/c, \tag{11}$$

$$u^3 = w/\mathbf{d}n, \tag{12}$$

$$P = 1 - (1 - e^{-z})^N, \tag{13}$$

$$K_s = 10^4 \times (K - L)(H - L)u^3\mathbf{d}/K^2, \tag{14*}$$

where

R = relative subsampling error in analyses of a two-component mixture of uniform grain size, in %.

H = the X-content of the high-X mineral, in %.

L = the X-content of the low-X mineral, in %.

K = the overall concentration of X, in %.

$R_{\max}$ = the maximum possible value of R for a mixture of two minerals of the same density

n = the effective number of grains in a subsample of w g.

$p = 1 - q$ = the proportion of the low-X mineral.

$q = 1 - p$ = the proportion of the high-X mineral.

c = the contribution of a single grain of high-X mineral to a single analytical result on a w-g subsample.

z = the average number of grains of high-X mineral in a single subsample of w g.

s^2 = the variance in a set of N analytical results.

u = the effective linear mesh size, in cm.

P = the probability that at least one of N subsamples is free from high-X mineral grains, *i.e.*, that the lowest in a series of N results represents the X-content of the low-X mineral or gangue.

$\mathbf{d}$ = a function of mineral densities, usually closely approximated by the density of the high-X mineral.

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* A derivation of (14) is given in the appendix

CORRELATION OF THE VARIOUS SAMPLING CONSTANTS

The three types of sampling constant may be compared by placing them in similar format.

Visman

$$s^2 = A/w + B = NS^2, \tag{15}$$

Gy

$$s^2 = CK^2d^3/w \quad (B = 0), \tag{16}$$

Ingamells and Switzer

$$s^2 = 10^{-4} \times K_sK^2/w \quad (B = 0). \tag{17}$$

Only the formulation by Visman includes a segregation constant. The three homogeneity constants are related as follows, by inspection of equations (15) and (16) and from equation (14):

$$A = CK^2d^3 = K_sK^2 \times 10^{-4} = (K - L)(H - L)u^3\mathbf{d}. \tag{18}$$

The usefulness of sampling constants can be enhanced by employing one or more of the relationships in (18). For example, if C can be estimated by using the processes described by Gy, A can be found from (18), avoiding the necessity for two series of results called for by (5) and (6). Equation (6) can then be used directly to find B.

With well-mixed samples, B is zero, and the relationships in (18) may be used to find, for example, the effective grain size of an ore mineral or the concentration of X in the gangue.

APPLICATION

The exploration of a mountain (or other inhomogeneous and segregated mass of material) for the element X should be pursued according to a flexible but well-defined plan, which is revised continuously as the data accumulate.

Initial samples may be small and should be collected as inexpensively as possible. Sometimes a few expertly collected hand-samples will suffice for preliminary work. These should be used to investigate the mineralogy of the deposit, to evaluate subsampling problems in a preliminary way, to develop analytical methods, and to establish laboratory procedures appropriate to the investigation. Initial samples will likely not be representative in the sense that they contain the same proportion of X as the whole mountain, but they may be used to generate several "standard" or "reference" samples which will permit calibration and control of routine analytical methods. Several such standards should be prepared, repetitively analysed by a rapid and precise method to establish sampling constants for the element X, and then by primary (usually classical) methods to determine their exact composition. Appropriate secondary methods should be selected and developed. Subsampling problems, characteristic of the material in the mountain, will be noted. If small subsamples are to be used in analytical work, the distributions of the results may be non-Gaussian.

After such preliminaries have been completed, and a sampling pattern has been devised, suites of samples of differing size will be collected, and Visman constants calculated from the results. Estimates of the optimum field sampling weight will be continually reviewed as exploration proceeds. A size-variance curve, characteristic of the mountain, will be constructed.

All sample reductions will be made, of course, according to Gy's principles, the relevant constants being progressively revised. Analytical methods and subsampling procedures will be altered as necessary, in conformance with changing estimates of sampling constants.

Initial analytical work may often be performed by rapid approximate methods, using as controls the reference samples referred to above. As exploration proceeds, it may become necessary to use fewer, larger samples and more accurate analytical methods to define the ore body adequately. For example, d.c. arc spectroscopy, invaluable in preliminary surveys, may not be capable of the necessary precision and accuracy simply because the analytical subsamples it demands are too small; fewer determinations by another method using larger subsamples may be more useful.

The calculated field sample weight may vary from a few grams to many tons. The number of field samples needed for the required overall precision may vary from a few dozen to many hundreds. Often, some informed subjective judgement must be applied, and theoretically optimum procedures must be modified to conform to such practical realities as cost and the law of diminishing returns. One cannot avoid a basic principle of sampling, that a 10-fold increase in precision for a given procedure requires a 100-fold increase in total weight of sample. Obviously, the greatest gain lies in the optimization of sampling and subsampling procedures, and not in the blind accumulation of vast quantities of data.

EXAMPLES

Many examples of actual application of the principles outlined above are given in the references cited.[12,13,16,18,22] Summaries of two of these and two original examples follow.

Use of the laboratory sampling constant K_s

In K–Ar and ^{39}Ar–^{40}Ar dating of minerals, samples of known age are essential for calibration and control. Several such reference samples are widely distributed among practising geochronologists. Sampling constants K_s for potassium in several of these have been determined[12] by repetitive determination and by physical examination and microprobe analysis. Table 1 shows some of these values. Knowing the sampling constant for potassium or for radiogenic argon for a reference sample, a geochronologist can readily calculate the probable error introduced by using this sample as a calibrating standard. If he wishes to establish the precision of an analytical method, he may make repetitive determinations

Table 1. Sampling constants for potassium in K-Ar reference samples

Sample	Description	$\%K_2O$	K_s, g	$\sqrt{K_s}$	w^*, g
Bern 4M	Muscovite	10·40	0·020	0·14	0·18
Bern 4B	Biotite	9·47	0·012	0·11	0·11
USGS P-207	Muscovite	10·4	0·168	0·41	1·5
Mica = Mg	Phlogopite	10·18	0·000	0·00	0·00x
LP-6 Bio 40–60 #	Biotite	10·03	0·005	0·07	0·045
PSU Or-1	Orthoclase	14·92	0·000	0·00	0·00x
MIT B-3203	Biotite	9·05	0·19	0·44	1·7

* Subsample weight necessary to ensure a relative standard deviation due to subsampling of less than 1% with 98% confidence. K_s is the subsample weight necessary for a relative standard deviation of 1% with 68% confidence. $\sqrt{K_s}$ is numerically equal to the coefficient of variation expected in a series of repetitive determinations using 1-g subsamples. Mica-Mg and PSU Or-1 have never shown any measurable subsampling error for potassium.

on the reference sample, and attribute observed variance above that predicted by the sampling constant to error in the analytical method. In some instances, the sampling constant for radiogenic argon may be the same as that for potassium; this will be true if the reference sample is geochronologically homogeneous; it will not be true if the sample contains two or more generations of potassium-bearing mineral. Little work has been done on estimation of sampling constants for radiogenic argon in geochronological standards. Preliminary work with LP-6 Bio 40–60# indicates that its sampling constant for radiogenic argon may be higher than that for potassium. This makes it less desirable as a ^{39}Ar–^{40}Ar standard than, for example, the Bern biotite 4B.

Early K–Ar standards such as the MIT biotite B-3203 and the USGS muscovite P-207, prepared before the importance of mineral purity was fully recognized, have proven inadequate as either reference materials or calibrating standards. This is reflected in high values of K_s for potassium (Table 1).

Suppose a geochronologist uses his method for potassium to make eight determinations of K_2O on LP-6 Bio 40–60#. The subsample weight is 0·02 g, and the average of the eight determinations is 10·11% K_2O, with an estimated standard deviation of 0·30%. The relative standard deviation is 3·0%. The relative standard deviation due to subsampling error, calculated from $\sqrt{K_s} = 0{\cdot}07$, is $\sqrt{K_s/w} = 0{\cdot}07/\sqrt{0{\cdot}02} = 0{\cdot}49\%$. The investigator can be sure that the variance in his results is mostly due to analytical error, and can apply himself to its correction. Had he used, instead, the reference sample P-207, interpretation of similar results would be very different. With P-207, the relative error due to subsampling, calculated from $\sqrt{K_s} = 0{\cdot}41$, is $0{\cdot}41/\sqrt{0{\cdot}02} = 2{\cdot}9\%$. Most of the observed error derives, not from the analytical method, but from the essential non-uniformity of the reference sample.

Use of Gy's sampling constant, C

This example is borrowed from a pamphlet on Gy's sampling slide-rule, distributed by D. J. Ottley, Cerro Corporation, New York.[15]

The assay error in a zinc ore of top size about 2 cm and a practical liberation size of about 0·2 mm, and which contains 6·6% Zn as ZnS, is calculated from $d/L =$ top particle size/liberation size $= 100$; whence l, the liberation factor, is 0·05. For a 10-kg sample, estimating the shape factor f at 0·5, the particle-size distribution factor g at 0·25, and a mineralogical composition factor $m = 43\ \mathrm{g/cm^3}$, yields a sampling constant $C = 0{\cdot}27\ \mathrm{g/cm^3}$. Finally, $s_R^2 = Cd^3/M = 0{\cdot}00022$, and $s_R = 0{\cdot}015$. Out of 100 samples, 95 would assay 6·6 ± 0·2% Zn (if 10-kg ore samples were taken, and they were properly reduced and subsampled for analysis). If the top particle size were 4 in. (10 cm) instead of 2 cm, the sampling constant C would be about 0·11 g/cm^3, and about 2 tons of sample would be required to ensure (95% confidence) that an assay would yield the true Zn content within 0·1%.

This example may serve to emphasize the intractability of real-life sampling problems. The 2 tons of sample called for in the example having been collected, it must, in practice, be reduced, without change in composition, to a few grams for analysis. Often, the largest error is incurred at this stage.

Use of Visman's sampling constants A *and* B

In the examination of a molybdenum ore body, three sets of samples were collected from drill cores: 100 4-in. core sections, 100 10-ft core sections, and 100 50-ft core sections. Molybdenum determinations on the three sets of samples yielded standard deviations of

0·838%, 0·245% and 0·181%. Using core lengths instead of sample weights, Visman constants A and B were calculated from the 4-in. and 10-ft lengths, the 4-in. and 50-ft lengths, and the 10-ft and 50-ft lengths, using equations (5) and (6). Sampling constants so obtained were $A = 0·221$, $B = 0·038$ for the first pair, $A = 0·225$, $B = 0·028$ for the second pair, and $A = 0·343$, $B = 0·026$ for the third. The optimum core-length lies somewhere between 5 and 15 ft, and 5000 10-ft core lengths will establish the overall Mo concentration in the ore body to within ± 5% relative error (68% confidence).

One other example will be given. This example demonstrates the important fact that variance in analytical results may be generated at any level of the sampling–analysis structure, in any link of the chain which leads from the mountain to the balance pan, and should not be extrapolated past that link.

Thirty molybdenum determinations on 2-kg splits of 3-mesh (0·67 cm) 36-kg ore samples showed values ranging from 0·172 to 0·321% Mo, with a mean of 0·220% and a standard deviation of 0·0349%. The 2-kg splits were reduced to 10-mesh (0·2 cm) and about 100 g of each were ground to 150-mesh for analysis. Analytical subsamples were 2 g in weight.

Calculation of c and z from equations (9) and (10), assuming $L = 0·172$ [the probability of this is 0·99 from equation (13)] shows that the distribution is skewed and approximately Poisson with interval $c = 0·0253$ and an average effective number of large high-Mo grains per subsample, $z = 1·91$. It is possible to calculate the mesh size at which this distribution is generated, by using equations (11) and (12).

Table 2. Molybdenum values on three separate 36-kg samples

	A		*B*		*C*	
Weight of 3-mesh (0·67 cm) ground to 10-mesh (0·20 cm)	1100 *g*		36 *kg*		80 *g*	
Weight of 10-mesh (0·20 cm) ground to 150-mesh (0·0105 cm)	100 *g*		1100 *g*		80 *g*	
	Mo. % (2-*g* analytical subsamples)					
(Separate 10-mesh samples, ground to 150-mesh for analysis).	0·279	0·273	0·300	0·298	0·332	0·333
	0·310	0·299	0·318	0·318	0·293	0·289
	0·255	0·252	0·285	0·284	0·275	0·278
	0·257	0·250	0·299	0·299	0·302	0·303
	0·253	0·274	0·318	0·317	0·310	0·313
	0·279	0·273	0·302	0·306	0·313	0·319
	0·334	0·324	0·307	0·306	0·347	0·350
	0·269	0·264	0·274	0·275	0·375	0·376
	0·356	0·343	0·306	0·305	0·245	0·244
	0·290	0·280	0 283	0·285	0·329	0·323
$\bar{x}$	0·2867		0 2994		0·3125	
s	0·0317		0·0142		0·0370	
c	0·0303		0·0081		0·0202	
z	1·10		3·07		3·37	
R	11·1%		4·7%		11·9%	

Analysts—B Rowles, C Gray, Climax Molybdenum Corp.

Corresponding values of mesh size and sample weight for the observed value of c are as follows

3 mesh (0·67 cm)	3486 g
10 mesh (0·20 cm)	91 g
150 mesh (0·0105 cm)	0·013 g

Since the analytical method uses a 2-g subsample, and since 2-kg samples of the 3-mesh (0·67 cm) material were taken for grinding to 10-mesh, the skewness of the distribution must have been largely generated at the 10-mesh level; it does not, therefore, necessarily reflect either analytical error or the distribution of Mo in the ore body.

To help confirm this deduction, three of the 36-kg 3-mesh samples were treated in different ways, which are summarized in Table 2. Analytical error, measured by differences between duplicates, is less than a third of the sampling error, and is therefore inconsequential.[23] As before, the data exhibit an approximately Poisson distribution, indicating the occasional presence of ore-mineral grains. The effective sample weights at the 10-mesh level are known, and the mesh size of the particles responsible for the variance in the results can be estimated as before, from (11) and (12). These particles are about 10-mesh. The relative standard deviation for the three sets of results varies closely with the square root of the weight of 10-mesh material which was reduced to 150-mesh. This confirms that the observed variance was generated at the 10-mesh level. Further confirmation is provided by the fact that sample B shows an improvement in sampling precision not much greater than is generated by the increase in the amount of 10-mesh material which was reduced to 150-mesh. The reduction in relative deviation from about 12% to about 4% is mostly due to increased sample (not subsample) size at the 150-mesh level. The duplicate determinations show that negligible subsampling error is generated at the 150-mesh level.

Another approach using the data in Table 2 yields essentially the same conclusion. A maximum subsampling error may be calculated from (8). The data show that the ore approximates to the maximum error case at the 10-mesh level of sampling. Since variance

Table 3. Molybdenum determinations on 2-kg splits of a single 36-kg sample

Subsample	Mo, % (2-g analytical subsample)		Analytical error Mo, %
1	0·265	0·260	0·005
2	0·273	0·271	0·002
3	0·250	0·247	0·003
4	0·259	0·259	0·000
5	0·260	0·259	0·001
6	0·297	0·297	0·000
7	0·253	0·252	0·001
8	0·255	0·255	0·000
$\bar{x}$	0·264	0·263	
s	0·0152	0·0156	0·001
	Omitting outliers (subsamples No. 6) (see text)		
$\bar{x}$	0·259	0·258	
s	0·0078	0·0075	
R	3%	3%	($R_{\max} = 4\%$)

Analyst—C. Gray, Climax Molybdenum Corp.

at the 10-mesh level is high, it is not possible to obtain from the data any good estimate of sampling characteristics at coarser sampling levels. However, some distortion of the Poisson distribution suggests that there may be occasional grains of high-Mo mineral, much larger than 10-mesh, which contribute a few "outlying" or "anomalous" values.

To confirm these deductions, eight 2-kg splits were taken from a single 3-mesh 36-kg sample. Each was ground to pass 150-mesh, the whole 2 kg being put through the screen, and 2·5-g subsamples were analysed for Mo. Results are shown in Table 3. One of the eight samples shows an anomalously high value, indicating the presence of a single large grain of high-Mo mineral in that split. The difference between the anomalous value and the average of the other seven is 0·035% Mo. If this difference is due to a single grain of high-Mo mineral, the linear dimension of such a grain is about 0·5 cm.

The conclusion is that the 3-mesh ore contains sparsely distributed grains of high-Mo mineral, a few of which are as large as 0·5 cm, but most of which are about 10-mesh (0·2 cm). When only 2 kg of the 36-kg samples are reduced to an analytical sample, there is almost no possibility that the analytical results will accurately reflect either the Mo content or the distribution of Mo in the mountain. Methods of data evaluation which attempt to associate observed variance in this example with field relationships are likely to yield false conclusions.

CONCLUSION

The processes of sampling a mountain (or other inhomogeneous and segregated mass of material), analysing the samples, and interpreting the results are subject to many errors. The use of three types of sampling constant permits estimation and control of these errors. Non-Gaussian statistics may often best describe the distribution of analytical results. There is a possibility of determining the origin of observed variance and skewness and thereby avoiding the extrapolation of such variance beyond the process link in which it originates.

The information chain which leads from the mountain to the balance-pan *via* sample reduction and subsampling and then to analysis and data evaluation is no stronger than its weakest link. Efforts to strengthen any other link are wasted.

APPENDIX

The derivation of (14) may be of interest.
By definition,

$$K_s = R^2 w. \tag{1A}$$

The weight of a subsample, w, is the sum of the weights of two constituent minerals:

$$w = w_L + w_H. \tag{2A}$$

For uniform grain size u, the number of particles in weight w is

$$n = w_L/d_L u^3 + w_H/d_H u^3, \tag{3A}$$

where d_L and d_H are the densities of the low-X and the high-X minerals respectively. Let the number of grains of high-X mineral per subsample be z; then the number of grains of low-X mineral is $n - z$. From (2A) and (3A)

$$w = z d_H u^3 + (n - z) d_L u^3. \tag{4A}$$

For a two-mineral mixture in which the high-X mineral is a minor constituent (the common case in mining exploration), Poisson statistics apply, and the standard deviation in a set of results is

$$s = c\sqrt{z}, \tag{5A}$$

where c is the contribution of a single grain of high-X mineral to an analytical result. Also, the overall X-concentration in the average subsample is the sum of the gangue contribution and the contribution of z grains of high-X mineral:

$$K = L + cz. \tag{6A}$$

Eliminating c from (5A) and (6A) gives

$$s^2 = (K - L)^2/z. \tag{7A}$$

Also, by definition and from (7A),

$$R^2 = 10^4 s^2/K^2 = 10^4 (K - L)^2/K^2 z. \tag{8A}$$

Substituting (4A) and (8A) in (1A) gives

$$K_s = \frac{10^4(K - L)^2 u^3}{K^2}\left[d_H - d_L + \frac{n}{z} d_L\right]. \tag{9A}$$

From

$$K = (1 - q_w)L + q_w H, \tag{10A}$$

where q_w is the weight proportion of high-X mineral,

$$q_w = (K - L)/(H - L). \tag{11A}$$

The volume proportion of the high-X mineral is

$$q = z/n. \tag{12A}$$

The relation between q and q_w is

$$q = \frac{z}{n} = \frac{d_L q_w}{d_H(1 - q_w) + d_L q_w}. \tag{13A}$$

Substituting (11A) in (13A) gives

$$q = \frac{z}{n} = \frac{d_L(K - L)}{d_H(H - K) + d_L(K - L)}. \tag{14A}$$

Substituting (14A) in (9A) gives

$$\begin{aligned} K_s &= \frac{10^4(K - L)^2 u^3}{K^2}\left[d_H - d_L + \frac{d_L(K - L) + d_H(H - K)}{d_L(K - L)} . d_L\right] . \\ &= 10^4 \times (K - L)(H - L)u^3\mathbf{d}/K^2 \end{aligned}$$

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Zusammenfassung—Zur Zeit im Planungsstadium befindliche Verfahren zum Entwurf von Probenahme-Schemata und zur Auswertung von Daten versprechen, die Sicherheit zu erhöhen, mit der große, inhomogene und entmischte Materialmengen (Berge) auf interessante Bestandteile analysiert werden können. Die Verfahren zielen auf das Zusammenwirken von Arbeitsmethoden, die ihren Ursprung in verschiedenen Fachgebieten haben, und verwenden verschiedene Arten von Probenahmekonstanten, um den Fehler zu kontrollieren.

Résumé—Les méthodes qui sont maintenant élaborées pour l'étude de schémas d'échantillonnage et pour l'évaluation de données promettent d'accroître la certitude avec laquelle des masses de matière grandes, non homogènes et divisées (montagnes) peuvent être analysées pour les constituants intéressants. Ces méthodes sont dirigées vers l'intégration du travail provenant de plusieurs disciplines, et utilisent différentes sortes de constantes d'échantillonnage pour contrôler l'erreur.

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THE OXIDATION OF ORGANIC SUBSTANCES BY COMPOUNDS OF TERVALENT MANGANESE—I

OXIDATION OF MANDELIC ACID, ETHYLENE GLYCOL, GLYCEROL AND D-MANNITOL BY THE PYROPHOSPHATE COMPLEX OF MANGANESE(III) AND BY MANGANESE(III) SULPHATE

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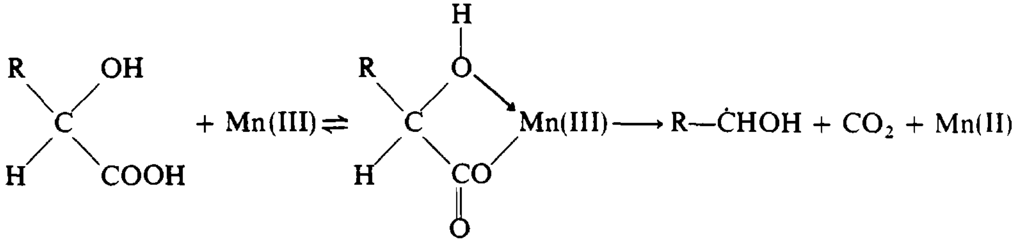
Summary—The oxidation of mandelic acid, ethylene glycol, glycerol and D-mannitol by the pyrophosphate complex of manganese(III) and with manganese(III) sulphate was studied. It was shown that benzaldehyde is formed by oxidation of mandelic acid, which undergoes no further oxidation. In the case of ethylene glycol, glycerol and D-mannitol the reactions do not follow a simple course and therefore are not of analytical utility. The effect of acidity and time on the course of the reactions was found and a procedure for the indirect titrimetric determination of mandelic acid with both reagents proposed.

Compounds of tervalent manganese are strong oxidants, with formal redox potentials and stability in solution which depend upon the acidity and the presence of complexing agents, *e.g.*, fluoride, phosphate or pyrophosphate.[1] Complexing agents increase the stability of solutions of manganese(III); however, they decrease the value of the corresponding formal redox potential as well as the reactivity of manganese(III). The use of these species in titrimetric analysis has been reviewed.[1]

In the reactions of organic compounds with manganese(III) compounds, a certain selectivity can be traced.[2] The pyrophosphate complex of manganese(III) does not oxidize simple alcohols and simple and unsaturated carboxylic acids; in contrast, it readily reacts with pinacol and other 1,2-glycols. Further, this reagent does not oxidize formaldehyde and trichloroacetaldehyde, whereas other substances of aldehyde character are oxidized further than to the corresponding carboxylic compounds. This fact is explained by the assumption that the first step of the reaction is a slow acid-catalysed enolization and only the enol formed is further oxidized. Manganese(III) in the form of manganese(III) sulphate is less stable but more reactive than the pyrophosphate complex.

Detailed information on the reactions of manganese(III) compounds with organic compounds is contained in the review by Waters[3] and in a recent monograph.[4]

In the present paper, the oxidation of mandelic acid, ethylene glycol, glycerol, and D-mannitol by the pyrophosphate complex of manganese(III) and with manganese(III) sulphate was studied from the viewpoint of analytical utilization of these reactions. Kemp and Waters proposed the following mechanism for the oxidation of α-hydroxycarboxylic acids.[5]



$$R\text{—}\dot{C}HOH + Mn(III) \longrightarrow RCHO + Mn(II) + H^+$$

For mandelic acid it could thus be assumed that benzaldehyde would be the product of its oxidation, and this cannot form an enol and therefore cannot be oxidized further. The analytical use of this reaction (in contrast to the oxidation of the polyalcohols studied) follows from the results given in the experimental part of the paper.

EXPERIMENTAL

Reagents

Potassium permanganate, 0·1*N* (0·02*M*).

Potassium dichromate, 0·1, 0·05, 0·02 and 0·01*N*.

Ferrous sulphate, 0·1, 0·05, 0·02 and 0·01*N* in 0·5*N* sulphuric acid. Standardized daily by potentiometric titration with standard potassium dichromate solution.

Sodium pyrophosphate, saturated solution.

Manganese(II) sulphate, 0·5*M*.

Sulphuric acid, 2, 4, 8, 12 and 16*N*.

2,4-Dinitrophenylhydrazine. Saturated solution in 2*M* hydrochloric acid.

Mandelic acid, 0·01, 0·02, 0·03, 0·001, 0·002 and 0·003*M*. Prepared by dissolving an accurately weighed amount of the pure substance and diluting to 1 litre.

The other chemicals used were of *p.a.* purity.

Manganese(III) pyrophosphate solution. This reagent was prepared for each experiment by adding 5·0 ml of 0·5*M* manganese(II) sulphate to 10·00 ml of 0·1*N* potassium permanganate and dissolving the manganese dioxide formed in 45 ml of a freshly prepared mixture of a saturated solution of sodium pyrophosphate, 4*N* sulphuric acid and 0·5*M* manganese(II) sulphate in a 30:5:10 ratio.[6]

Manganese(III) sulphate solutions. These solutions were prepared by electrochemical oxidation of manganese(II) at a platinum electrode with an area of 1 cm^2, at a current density of 20 mA/cm^2. As the base electrolyte, 0·25*M* manganese(II) sulphate in 6*M* sulphuric acid was employed.[7] The auxiliary electrode was separated by a frit. The titre was determined by potentiometric titration with ferrous sulphate.

Procedures and results

Oxidation of mandelic acid with the pyrophosphate complex of manganese(III). The dependence of the oxidation rate on the sulphuric acid concentration was first measured, under otherwise constant conditions. To the reagent solution, 70 ml of sulphuric acid of appropriate normality were added and, after thorough mixing, the solution was placed in the thermostat, in which it was maintained at 20 for 30 min. Then 10·00 ml of 0·02*M* mandelic acid were added, the solution was mixed carefully, and placed in the thermostat again. After another 30 min, the unconsumed manganese(III) complex was determined by potentiometric titration with 0·1*N* ferrous sulphate. The stabilization of potentials during the titration is too slow in 8*N* sulphuric acid medium[8] and therefore it was necessary to decrease the acidity by the addition of 50 ml of distilled water before the back-titration. Any possible change in the reagent titre was compensated by a parallel blank determination. The results obtained are given in Table 1. All results given in this and other tables are the average of three measurements.

Table 1. Consumption of manganese(III) pyrophosphate complex by mandelic acid, as a function of sulphuric acid concentration; temperature 20°, time 30 min

H_2SO_4, *N*	1	2	4	6	8
Reagent consumption, *equiv/mole*	0·33	0·47	0·84	1·25	1·66

From the results it appears that two equivalents of reagent per mole of mandelic acid, corresponding to its quantitative oxidation to benzaldehyde and carbon dioxide, might be consumed in an analytically acceptable time in 4*N* sulphuric acid medium. The rate of reaction in this medium was therefore examined (Table 2).

Table 2. Rate of oxidation of mandelic acid with manganese(III) pyrophosphate complex (4*N* H_2SO_4 medium at 20°)

Time, *hr*	0·5	1	2	4	6	8	10	12	24
Reagent consumption, *equiv/mole*	0·84	1·22	1·67	1·91	2·01	1·99	2·00	1·99	2·00

That benzaldehyde is formed was proved by forming the 2,4-dinitrophenylhydrazone, and comparing its m.p. and infrared spectrum with those of an authentic specimen.

Oxidation of mandelic acid with manganese(III) sulphate. First, the dependence of the oxidation rate on the sulphuric acid concentration was measured, by adding 30 ml of sulphuric acid of the required normality to 10·00 ml of 0·01 *N* manganese(III) sulphate, mixing thoroughly, placing the solution in the thermostat at 20° for 30 min, adding 10·00 ml of 0·0025*M* mandelic acid, mixing and again placing in the thermostat, then after 5 min titrating the unreacted manganese(III) potentiometrically with 0·01*N* ferrous sulphate. A blank determination was again performed The results obtained are given in Table 3.

Table 3. Consumption of manganese(III) sulphate by mandelic acid, as a function of sulphuric acid concentration; temperature 20°, time 5 min

H_2SO_4, *N*	2	4	6	8
Reagent consumption, *equiv/mole*	1·55	1·18	1·06	0·99

The time dependence of the oxidation in 2*N* sulphuric acid medium was measured at 20 . It is not suitable to work at a lower acidity, because of the decreasing reagent stability with decreasing sulphuric acid concentration The results are given in Table 4

Table 4. Rate of oxidation of mandelic acid with manganese(III) sulphate (2*N* H_2SO_4 medium at 20°)

Time, *min*	5	10	15	30	60	90	120	240
Reagent consumption, *equiv/mole*	1·55	1·80	1·92	1·99	2·00	2·00	2·00	2·00

The formation of benzaldehyde was established as above.

Recommended procedures

With the pyrophosphate complex. Add 70 ml of 8*N* sulphuric acid and 10·00 ml of 0·01–0·03*M* mandelic acid to the manganese(III) pyrophosphate solution prepared by the procedure given above. Mix, set aside for 12 hr at laboratory temperature, and then titrate the unconsumed manganese(III) potentiometrically with 0·1*N* ferrous sulphate. Run a blank determination. Calculate the amount of mandelic acid from the difference between the values for the blank and the determination (1 ml of 0·1*N* ferrous sulphate corresponds to 7·607 mg of mandelic acid)

With manganese(III) sulphate. Add 40 ml of distilled water and 10·00 ml of 0·001–0·003*M* mandelic acid to 10·00 ml of 0·01*N* manganese(III) sulphate in 6*M* sulphuric acid, mix carefully, let stand for 2 hr at laboratory temperature, then titrate the unconsumed manganese(III) potentiometrically with 0·01*N* ferrous sulphate. Run a blank and calculate as before (1 ml of 0·01*N* ferrous sulphate corresponds to 0·7607 mg of mandelic acid). The results obtained are given in Table 5. The standard deviations were calculated from 10 determinations.

Oxidation of ethylene glycol, glycerol, and D*-mannitol*

With polyhydroxy compounds of the $CH_2OH(CHOH)_nCH_2OH$ type it would be expected that the products of their oxidation with compounds of tervalent manganese would be formaldehyde and formic acid; these substances should not be appreciably further oxidized.[2]

Although this basic assumption was verified, it was found that these reactions are not of analytically utility, because their rate is too low at laboratory temperature and at 50° the formaldehyde and formic acid formed are further oxidized[9, 10]

Table 5. Determination of mandelic acid

Mandelic acid taken, *mg*	Mandelic acid found, *mg*	Standard deviation, *mg*
	Oxidation with manganese(III) pyrophosphate complex	
15·21	15·25	0·18
30·43	30·40	0·14
45·64	45·66	0·14
	Oxidation with manganese(III) sulphate	
1·521	1·519	0·014
3·043	3·038	0·017
4·564	4·561	0·019

DISCUSSION

The advantages of the proposed procedure follow from its comparison with other methods of oxidation of the substance to be determined. The method using the oxidation of mandelic acid with excess of zinc manganate(IV)[11] is performed at 100° and the benzaldehyde formed is immediately distilled from the reaction mixture in order to prevent its further oxidation. Another method is based on the oxidation of mandelic acid with excess of potassium periodate at the boiling point in a special apparatus; the carbon dioxide formed is then determined.[12] Our method is simpler and does not require any special apparatus. The simplicity of the method is comparable to that of the method using oxidation of mandelic acid with lead tetra-acetate;[13] the drawback of the latter method is that the reagent preparation is somewhat more complicated.

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Zusammenfassung—Die Oxidation von Mandelsäure, Äthylenglykol, Glycerin und D-Mannit mit dem Pyrophosphatkomplex von Mangan(III) und mit Mangan(III) sulfat wurde untersucht. Es wurde gezeigt, daß durch Oxidation von Mandelsäure Benzaldehyd gebildet wird; dieser wird nicht weiter oxidiert. Im Falle von Äthylenglykol, Glycerin und D-Mannit verlaufen die Reaktionen kompliziert und besitzen daher keinen analytischen Nutzen. Der Einfluß der Aciditat und der Zeit auf den Verlauf der Reaktion wurde verfolgt und ein Verfahren zur indirekten titrimetrischen Bestimmung von Mandelsäure mit beiden Reagentien vorgeschlagen.

Résumé—On a étudié l'oxydation de l'acide mandélique, de l'éthylèneglycol, du glycérol et du D-mannitol par le complexe pyrophosphate du manganèse(III) et avec le sulfate de manganèse(III). On a montré que par oxydation de l'acide mandélique, il se forme du benzaldéhyde qui ne subit pas d'oxydation ultérieure. Dans le cas de l'éthylèneglycol, du glycérol et du D-mannitol, les réactions ne suivent pas un cours simple, et ne sont pas par conséquent d'utilité analytique. On a trouvé l'influence de l'acidité et du temps sur le cours des réactions, et l'on propose une technique pour le dosage titrimétrique indirect de l'acide mandélique avec les deux réactifs.

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SHORT COMMUNICATIONS

POTENTIOMETRIC DETERMINATION OF AUTOPROTOLYSIS CONSTANTS OF SOLVENTS

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Most of the methods for the determination of the ionic product of water are also used for the determination of autoprotolysis constants of non-aqueous amphiprotic solvents. The older methods and results are summarized by Beans and Oakes[1] and the recent ones by Clever [2] In all potentiometric versions of the method it is essential to have a strong acid and a strong base. For many non-aqueous solvents, however, this condition is difficult to achieve, mainly because of the lack of strong bases. This obstacle is usually overcome by combining the potentiometric method with some other method—very often with conductimetry.[3] Unfortunately the results so obtained sometimes show a difference of several logarithmic units and even in the opinion of the authors themselves[4] cannot be considered as definitive.

We therefore present an independent potentiometric method for the determination of autoprotolysis constants, which does not require both a strong acid and a strong base. To simplify the treatment, the present work deals with a system in which the activity coefficients are kept constant.

THEORY

Suppose we have a solvent SH in which a weak base B is titrated with a strong acid HA. The following proton transfer equilibria are established·

$$\begin{array}{r} B + H^+ \rightleftharpoons BH^+ \\ SH + H^+ \rightleftharpoons SH_2^+ \\ HA \rightleftharpoons A^- + H^+ \\ SH \rightleftharpoons S^- + H^+ \end{array} \qquad (1)$$

According to the electroneutrality rule

$$[S^-] + [A^-] = [BH^+] + [SH_2^+]. \qquad (2)$$

Since $[A^-] = [HA]_{tot}$ in the alkaline region, $pcH = -\log[SH_2^+]$ and $K_{BH^+} = [B][SH_2^+]/[BH^+]$, after some rearrangement we obtain:

$$[S^-] = [B]_{tot}/(1 + 10^{pcH-pK_{BH^+}}) - [HA]_{tot} + 10^{-pcH}. \qquad (3)$$

$[B]_{tot}$ and $[HA]_{tot}$ are the total molar concentrations of the base and the acid in the titrated solution. Inserting (3) into the Nernst equation $E = E_B^{0'} - k\log[S^-]$ we obtain the equation

$$E = E_B^{0'} - k\log\{[B]_{tot}/(1 + 10^{pcH-pK_{BH^+}}) - [HA]_{tot} + 10^{-pcH}\}, \qquad (4)$$

from which the constant $E_B^{0'}$—the standard potential of the cell in the alkaline region—can be computed. For this purpose the pK_{BH^+} value and the pcH values at each point of titration must be known. This requirement is easily fulfilled since the acid is strong and the value of $E_A^{0'}$—the standard potential of the cell in the acid region—can easily be found after the equivalence point by means of the equation:

$$E_A^{0'} = E - k\log\{[HA]_{tot} - [B]_{tot}\}. \qquad (5)$$

Then pcH is calculated from the well-known relationship $pcH = (E_A^{0'} - E)/k$. The value of K_{BH^+} is calculated from the relationships:

$$K_{BH^+} = \frac{[SH_2^+](1 - \bar{n}_H)}{\bar{n}_H}, \qquad (6)$$

$$\bar{n}_H = \frac{[HA]_{tot} - [SH_2^+] + K_{SH}/[SH_2^+]}{[B]_{tot}}. \qquad (7)$$

In equations (6) and (7) there are two unknowns—K_{BH^+} and the autoprotolysis constant K_{SH}. The problem is solved by means of a successive approximation procedure in which first a rough value of K_{BH^+} is found by neglecting the value of K_{SH} in equation (7). Then a rough value of K_{SH} by means of (4) and $pK_{SH} = (E_A^{0'} - E_B^{0'})/k$ is found and the calculations are repeated until convergence is obtained.

When a weak acid is titrated with a strong base, similar equations can be derived:

$$E_B^{0'} = E + k\log\{[B]_{tot} - [HA]_{tot}\}, \tag{8}$$

$$E = E_A^{0'} + k\log\{[HA]_{tot}/(1 + 10^{pS-pK_{A^-}}) - [B]_{tot} + 10^{-pS}\}, \tag{9}$$

where $pS = -\log[S^-]$ and K_A is the dissociation constant of the conjugate base of the acid HA.

$$K_{A^-} = \frac{[S^-](1 - \bar{n}_B)}{\bar{n}_B}, \tag{10}$$

$$\bar{n}_B = \frac{[B]_{tot} - [S^-] + K_{SH}/[S^-]}{[HA]_{tot}}. \tag{11}$$

To prove the validity of the proposed method, some experiments were performed as described in the experimental part below. It was essential, however, to choose an appropriate solvent, for which the magnitude of the autoprotolysis constant is quite certain. It is evident why the first step was the determination of the autoprotolysis constant of water.

EXPERIMENTAL

Reagents

Twice-distilled water was used. Ethylene glycol (EG) was distilled *in vacuo* (10 mmHg) over dried sodium sulphate. Potassium chloride, *p.a.*, was recrystallized from water and dried at 105°. Hydrochloric acid solutions were prepared by saturation of the solvent with dry hydrogen chloride. The sodium hydroxide solution was free from carbonate. Diphenylguanidine (DFG) was recrystallized from benzene and dried *in vacuo*. Triethylamine (TEA) and monochloroacetic acid (MCA), *p.a.*, were used without further purification.

Measurements

The potentiometric measurements (±0.2 mV) were carried out at 25.0 ± 0.1° with a Radiometer pH-meter type PHM-4. A single glass electrode (Radiometer type G 202 B) and a silver-silver chloride reference electrode were used for all potentiometric measurements.

Table 1. The primary data of the potentiometric titrations

Series I		Series II		Series III		Series IV	
HCl, *ml*	*E, mV*	HCl, *ml*	*E, mV*	NaOH, *ml*	*E, mV*	HCl, *ml*	*E, mV*
0·0	+285·6	0·0	−313·2	0·0	+233·9	0·0	−250·0
5·0	+276·3	0·2	−310·7	0·3	+230·2	0·5	−234·3
10·0	+264·3	0·4	−308·3	0·5	+227·9	1·0	−220·2
12·0	+258·1	0·6	−306·0	0·7	+225·5	1·5	−207·7
14·0	+249·8	0·8	−303·5	1·0	+221·7	2·0	−196·3
16·0	+238·4	1·0	−301·0	1·5	+214·7	2·5	−185·3
18·0	+219·3	1·4	−295·9	2·0	+207·2	3·0	−173·8
18·5	+210·6	2·0	−288·0	2·5	+198·2	3·5	−161·5
19·0	+198·6	2·4	−282·3	3·0	+188·0	4·0	−144·0
19·5	+176·4	3·2	−270·0	3·5	+174·5	4·5	−114·0
20·0	−216·0	4·0	−254·8	4·0	+152·9	5·0	+285·7
20·5	−254·1	4·4	−244·9	4·4	+103·2	5·5	+337·3
21·0	−269·1	4·8	−231·2	4·8	−259·8	6·0	+353·0
22·0	−285·2	5·4	−182·8	5·2	−290·3	6·5	+362·5
23·0	−294·4	5·7	+156·5	6·0	−312·0	7·0	+369·3
25·0	−306·8	6·0	+200·5	6·5	−319·3	8·0	+378·9
28·0	−317·7	6·5	+221·2	7·0	−325·0	9·0	+385·4
31·0	−324·9	7·5	+239·8	8·0	−333·0	10·0	+390·3
35·0	−331·5	8·0	+245·2	9·0	−338·8		
40·0	−338·0	9·0	+259·5	10·0	−343·0		

Conditions: I—50 ml of H_2O + 20 ml of 0·0921*M* NaOH titrated with 0·0906*M* HCl; $\mu = 1$ (KCl). II—15 ml of H_2O + 5 ml of 0·1005*M* TEA titrated with 0·0905*M* HCl; $\mu = 1$ (KCl). III—15 ml of H_2O + 5 ml of 0·1060*M* MCA titrated with 0·1147*M* NaOH; $\mu = 1$ (KCl). IV—20 ml of 0·0237*M* DFG titrated with 0·1*M* HCl in EG; $\mu = 0·1$ (KCl).

Table 2. Calculation of $E_A^{0'}$, pcH values and pK_{BH^+} for the titration of TEA with hydrochloric acid in aqueous medium. The pK_{BH^+} values are found after the first step of the applied successive approximation procedure

HCl added, *ml*	E_{meas}, *mV*	$pH = (E_A^{0'} + E_{meas})/k$	HA_{tot} *mmole*	$\bar{n}_H = HA_{tot}/B_{tot}$	$pK_{BH^+} = -\log(h - \bar{n}_H/\bar{n}_H)$
0·00	−313·3	11·552	0·0000		
0·20	−310·7	11·510	0·0181	0·0360	10·082
0·40	−308·3	11·469	0·0362	0·0720	10·359
0·60	−306·0	11·431	0·0543	0·1081	10·514
0·80	−303·5	11·388	0·0724	0·1441	10·615
1·00	−301·0	11·346	0·0905	0·1801	10·688
1·20	−298·4	11,302	0·1086	0·2161	10·743
1·40	−295·9	11·260	0 1267	0·2521	10·788
1·70	−291·9	11·191	0·1538	0·3062	10·837
2·00	−288·0	11·126	0·1810	0·3602	10·877
2·40	−282·3	11·030	0·2172	0·4322	10·911
2·80	−276·6	10·934	0·2834	0·5043	10·941
3·20	−270·0	10·822	0·2896	0·5763	10·956
3·60	−262·4	10·700	0·3258	0·6484	10·966
4·00	−254·8	10·565	0·3620	0·7204	10·976
4·40	−244·9	10·398	0·3982	0·7924	10·980
4·80	−231·2	10·166	0·4344	0·8645	10·971
5·10	−217·0	9·933	0·4615	0·9185	10·985

HCl added *ml*	E_{meas} *mV*	*ml* HCl after EP	$[HA]_{tot}$(*mole/l.*) after EP (= *h*)	$-k.\log h$	$E_A^{0'} = E_{meas} - k\log h$
5·70	+156·5	0·09	$3{\cdot}169 . 10^{-4}$	207·0	363·5
6·00	+200·5	0·39	$1{\cdot}357 . 10^{-3}$	169·6	370·1
6·50	+221 2	0·89	$3{\cdot}039 . 10^{-3}$	148·9	370·1
7·00	+232·2	1·39	$4{\cdot}659 . 10^{-3}$	137·9	370·1
7·50	+239·8	1·89	$6{\cdot}220 . 10^{-3}$	130·5	370·3
8·00	+245·2	2·39	$7{\cdot}725 . 10^{-3}$	124·9	370·1
9·00	+253·4	3·39	$1{\cdot}058 . 10^{-2}$	116·9	370·2
10·00	+259·5	4·39	$1{\cdot}324 . 10^{-2}$	111·1	370·4

Conditions 15 ml H_2O + 5 ml 0·1005*M* TEA titrated with 0·0905*M* HCl; B_{tot} = 0·5025 mmole; $\mu = 1$ (KCl), the equivalence point (EP) is at 5·61 ml

RESULTS

Determination of the autoprotolysis constant of water

The titrations were performed in a cell with liquid junction, at constant ionic strength $\mu = 1$ (KCl). This ionic strength was chosen because some recent determinations[5,6] of the autoprotolysis constant of water were performed at this ionic strength, and showed a low scatter. A plot of $E_{meas} - k\log[H^+]$ as a function of $[H^+]$[7] showed that the liquid junction potential had a low value and could be neglected.

Three types of titration were performed: (*i*) strong base (sodium hydroxide) with strong acid (hydrochloric acid), (*ii*) weak base (triethylamine) with strong acid (hydrochloric acid) and (*iii*) weak acid (monochloroacetic acid) with strong base (sodium hydroxide). The aim of the first titration was check the response of the electrodes. The primary data results are shown in Table 1. The determination of the ionic product of water by means of the proposed method was performed in the same cell with the second and third type of titration. The primary results for the latter are shown in Table 1. For the sake of brevity only the titration of triethylamine (TEA) with hydrochloric acid will be discussed. The equivalent point after neutralization of TEA was found by means of a Gran plot [8] The known excess of hydrochloric acid was used to find $E_A^{0'}$. The calculations performed are shown in Table 2 The pcH values for each titration point were calculated and rough pK_{BH^+} values were found (see Table 2) Because of the use of approximation in equation (7), the values for pK_{BH} showed scatter Then the value of pK_{BH^+} was used in equation (4) to find the constant E_B^0. The calculation of the rough value of pK_w is shown in Table 3 Once the value of pK_w was known, the whole calculation was repeated with exact solution of (7), until convergence was obtained The values of pK_{BH^+} and pK_w and their approximations to a constant value

Table 3. Calculation of pK_w values after the first step of the applied successive approximation procedure

pH	pH − pK_{BH^+}	$\frac{B_{tot}(mmole)}{\text{antilog}(pH - pK_{BH^+}) + 1} = b$	OH(*mmole*) = $b - HA_{tot}$(*mmole*)	[OH⁻].10³ *mole/l.*	$E_B^{0'}$ = −*k*.log[OH⁻] + E_{meas}	pK_w
11·552	0·699	0·0837	0·0837	4·183	−453·9	13·93
11·510	0·657	0·0907	0·0726	3·593	−455·3	13·95
11·469	0·617	0·0978	0·0616	3·021	−457·4	13·99
11·431	0·578	0·1050	0·0508	2·464	−460·3	14·04
11·388	0·535	0·1138	0·0410	1·970	−463·5	14·09
11.346	0·493	0·1221	0·0316	1·505	−468·0	14·17
11·302	0·449	0·1317	0·0231	1·092	−473·6	14·26
11·260	0·407	0·1414	0·0147	0·686	−483·0	14·42
11·192	0·339	0·1578	0·0039	0·181	−513·3	14·93
11·126	0·273	0·1747				

Conditions: 15 ml H_2O + 5 ml 0·1005*M* TEA titrated with 0·0905*M* HCl; B_{tot} = 0·5025 mmole; ionic strength μ = 1 (KCl).

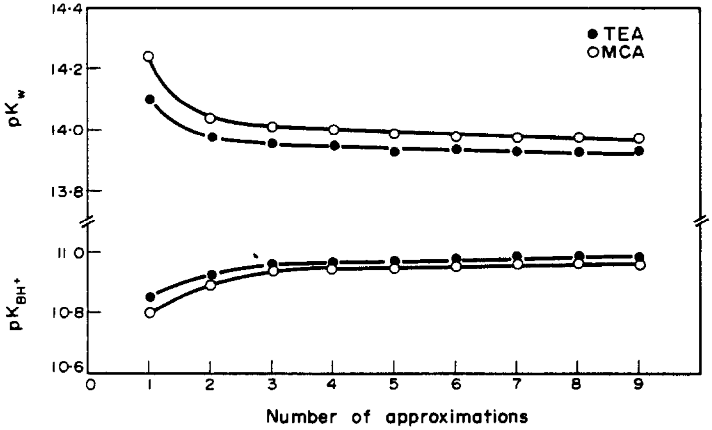

Fig 1. Plot of pK_{BH^+} and pK_w values *vs.* the number of approximations in the course of the calculations.

in the course of the calculations are shown in Fig. 1. The same figure shows the results of the third experiment. It can be seen that the value of the constants pK_{BH^+} and pK_w became convergent after the fifth or sixth iteration.

The final values for pK_w are in fairly good agreement for all three titrations (13.90 ± 0.005, 13.97 ± 0.08 and 13.93 ± 0.1) and with the reported values (13.80)[5] and (13.96)[6] at this ionic strength.

Determination of autoprotolysis constant of ethylene glycol (EG)

A cell without liquid junction, at constant ionic strength $\mu = 0.1$ (KCl) was used for titration of the weak base DFG with hydrochloric acid (Table 1). The complete dissociation of the latter was proved in a preliminary experiment. The experimental data were treated as described above. The autoprotolysis constant found for EG was $pK_{EG} = 15.4 \pm 0.2$, in good agreement with the only reported[9] value for pK_{EG}, 15.6 at 30° and ionic strength $\mu = 0$

DISCUSSION

The weaker the base (or acid) is, the greater the uncertainty in the constant obtained, because the term $pcH - pK_{BH^+}$ in equation (4) [see also (9)] begins to be very small compared to the error of pcH determination. The error depends on the accuracy of the potentiometric measurements, but an upper limit of 3–4 logarithmic units difference between the dissociation constant of the weak base (or acid) and K_{SH} could be set as a restriction on the applicability of the method. It is clear, however, that the stronger the base (or acid) is, the more precise the results.

As mentioned above, the other requirement of the method is the presence of at least one strong protolyte, acid or base, which is necessary to define the $pcSH_2^+$ or the pcS^- scale in the solvent. Bjerrum deduced that ion-pair formation occurs to a considerable degree in solvents which have dielectric constant lower than 40, and this is to some extent true for acids and bases. It follows that it will be difficult to apply the proposed method in such solvents.

A further restriction on the method is the maintenance of a constant ionic strength. For solvents with dielectric constants 35–40 and higher, this requirement can still be fulfilled It is not difficult, however, to derive equations taking into consideration the activity factors by means of the Debye Hückel law

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Summary—A new method is proposed for determination of autoprotolysis constants by titration of a weak acid with strong base or strong acid with weak base, and applied to water and ethylene glycol (EG). The constants found were $pK_w = 13{\cdot}90–13{\cdot}97$, and $pK_{EG} = 15{\cdot}4 \pm 0{\cdot}2$.

Zusammenfassung—Ein neues Verfahren zur Bestimmung von Autoprotolysekonstanten durch Titration einer schwachen Säure mit einer starken Base oder einer starken Säure mit einer schwachen Base wird vorgeschlagen; es wurde auf Wasser und Äthylenglykol (EG) angewandt. Die gefundenen Konstanten sind $pK_W = 13.90$, $pK_{EG} = 15.4 \pm 0.2$.

Résumé—On propose une nouvelle méthode pour la détermination des constantes d'autoprotolyse par titrage d'un acide faible avec une base forte ou d'un acide fort avec une base faible, et l'applique à l'eau et à l'éthylèneglycol (EG). Les constantes trouvées sont $pK_w = 13{,}90–13{,}97$ et $pK_{EG} = 15{,}4 \pm 0{,}2$.

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OXIDIMETRIC DETERMINATION OF THIOUREA, THIOSULPHATE AND SULPHITE WITH THALLIC PERCHLORATE IN ACID MEDIUM

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The use of thallium (III) as an analytical reagent has not received much attention,[1] although kinetic studies[2] have been made. Thallium (III) is a mild oxidizing agent but the redox process in some cases is very fast. The oxidation of thiourea, thiosulphate and sulphite is almost instantaneous and these species can be determined either indirectly by reaction with excess of thallium (III) and iodometric back-titration or by direct titration with *p*-ethoxychrysoidine as indicator. The earlier methods[3–11] for the determination of thiourea are indirect and not always quick. Several methods[6–11] exist for the determination of thiosulphate, but are complicated or require critical conditions, except iodimetry.[12] Similarly, various indirect methods[6,10,13,17] have been reported for the determination of sulphite. Permanganate[18] has been employed for the direct titration of sulphite in the presence of iodine monochloride. The main difficulty in a direct titration of sulphite has been the formation of dithionate[19] which is not oxidized by the permanganate.

Thallic perchlorate reacts rapidly according to the equations

$$\mathrm{Tl(III)} + 2\mathrm{CS_2(NH_2)_2} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H^+} + (\mathrm{H_2NCSNH})_2, \tag{1}$$

$$\mathrm{Tl(III)} + \mathrm{SO_3^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H^+} + \mathrm{SO_4^{2-}}, \tag{2}$$

$$\mathrm{Tl(III)} + 2\mathrm{S_2O_3^{2-}} \rightarrow \mathrm{Tl(I)} + \mathrm{S_4O_6^{2-}}. \tag{3}$$

The advantage of using thallium (III) perchlorate as a reagent is that it is stable, unaffected by air and light and is non-hygroscopic.

EXPERIMENTAL

Reagents

Thallic perchlorate solution. Prepared by dissolving thallic oxide in 60% perchloric acid, and standardized iodometrically.[20] The acidity is checked by titration. Some potassium bromide is also added to reduce the hydrolysis of Tl(III) at high pH.

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Summary—A new method is proposed for determination of autoprotolysis constants by titration of a weak acid with strong base or strong acid with weak base, and applied to water and ethylene glycol (EG). The constants found were $pK_w = 13{\cdot}90–13{\cdot}97$, and $pK_{EG} = 15{\cdot}4 \pm 0{\cdot}2$.

Zusammenfassung—Ein neues Verfahren zur Bestimmung von Autoprotolysekonstanten durch Titration einer schwachen Säure mit einer starken Base oder einer starken Säure mit einer schwachen Base wird vorgeschlagen; es wurde auf Wasser und Äthylenglykol (EG) angewandt. Die gefundenen Konstanten sind $pK_W = 13.90$, $pK_{EG} = 15.4 \pm 0.2$.

Résumé—On propose une nouvelle méthode pour la détermination des constantes d'autoprotolyse par titrage d'un acide faible avec une base forte ou d'un acide fort avec une base faible, et l'applique à l'eau et à l'éthylèneglycol (EG). Les constantes trouvées sont $pK_w = 13{,}90–13{,}97$ et $pK_{EG} = 15{,}4 \pm 0{,}2$.

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OXIDIMETRIC DETERMINATION OF THIOUREA, THIOSULPHATE AND SULPHITE WITH THALLIC PERCHLORATE IN ACID MEDIUM

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The use of thallium (III) as an analytical reagent has not received much attention,[1] although kinetic studies[2] have been made. Thallium (III) is a mild oxidizing agent but the redox process in some cases is very fast. The oxidation of thiourea, thiosulphate and sulphite is almost instantaneous and these species can be determined either indirectly by reaction with excess of thallium (III) and iodometric back-titration or by direct titration with *p*-ethoxychrysoidine as indicator. The earlier methods[3–11] for the determination of thiourea are indirect and not always quick. Several methods[6–11] exist for the determination of thiosulphate, but are complicated or require critical conditions, except iodimetry.[12] Similarly, various indirect methods[6,10,13,17] have been reported for the determination of sulphite. Permanganate[18] has been employed for the direct titration of sulphite in the presence of iodine monochloride. The main difficulty in a direct titration of sulphite has been the formation of dithionate[19] which is not oxidized by the permanganate.

Thallic perchlorate reacts rapidly according to the equations

$$\mathrm{Tl(III)} + 2\mathrm{CS_2(NH_2)_2} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H^+} + \mathrm{(H_2NCSNH)_2}, \tag{1}$$

$$\mathrm{Tl(III)} + \mathrm{SO_3^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H^+} + \mathrm{SO_4^{2-}}, \tag{2}$$

$$\mathrm{Tl(III)} + 2\mathrm{S_2O_3^{2-}} \rightarrow \mathrm{Tl(I)} + \mathrm{S_4O_6^{2-}}. \tag{3}$$

The advantage of using thallium (III) perchlorate as a reagent is that it is stable, unaffected by air and light and is non-hygroscopic.

EXPERIMENTAL

Reagents

Thallic perchlorate solution. Prepared by dissolving thallic oxide in 60% perchloric acid, and standardized iodometrically.[20] The acidity is checked by titration. Some potassium bromide is also added to reduce the hydrolysis of Tl(III) at high pH.

Table 1. Titrimetric estimation of thiourea with thallic perchlorate

Amount of thiourea, *mg*			
Direct titration		Indirect titration	
Taken	Found	Taken	Found
0·76	0·76	1·52	1·52
1·52	1·53	2·66	2·66
2·18	2·19	3·04	3·05
2·28	2·29	4·56	4·57
3·04	3·05	5·32	5·3
3·80	3·80	6·08	6·09
4·56	4·55	7·98	7·98
5·38	5·39	9·12	9·13
6·84	6·86	10·64	10·65
9·12	9·10	18·6	18·6
13·68	13·70		
15·2	15·25		
19·0	19·05		
22·8	22·75		
26·6	26·5		

Table 2 Titrimetric estimation of thiosulphate with thallic perchlorate

Amount of thiosulphate, *mg*			
Direct titration		Indirect titration	
Taken	Found	Taken	Found
2·48	2·48	1·24	1·24
2·96	2·96	2·48	2·48
7·45	7·47	3·72	3·72
9·93	9·94	6·21	6·20
12·41	12·42	8·67	8·07
14·88	14·89	8·69	8·69
22·32	22·32	9·30	9·30
24·82	24·80	10·55	10·55
27·28	27·29		
49·64	40·65		
55·85	55·84		
74·46	74·45		

Table 3. Titrimetric estimation of sulphite with thallic perchlorate

Amount of sulphite, *mg*			
Direct titration		Indirect titration	
Taken	Found	Taken	Found
1·26	1·26	0·63	0·63
2·52	2·50	1·26	1·27
6·30	6·30	2·52	2·53
7·56	7·57	2·84	2·83
12·6	12·6	3·47	3·46
17·6	17·6	4·73	4·72
18·9	18·8	5·36	5·36
25·2	25·3	7·56	7·55
31·5	31·4	10·08	10·07
44·1	44·2		
50·4	50·5		
63·0	63·0		

Thiourea, sulphite and thiosulphate solutions. Standardized iodometrically.[21]
p-Ethoxychrysodine, 0·2% *alcoholic solution.*

Procedure

A known volume of thiourea, thiosulphate or sulphite solution was taken in a 50-ml flask and sufficient sulphuric or perchloric acid added for the acidity not to be less than 0·5 *M* during the titration. A drop of indicator was added. The solution was vigorously swirled after each addition of Tl(III), and towards the end, the titrant was added dropwise at intervals of 10–15 sec. The end-point was marked by disappearance of the pink colour. Since thiosulphate decomposes in acid solutions,[22] the acid concentration should not be more than 1·0 *M*.

For the indirect determination a known excess of thallic perchlorate was added and the surplus back-titrated iodometrically.

The results are given in Tables 1, 2 and 3.

Interferences

Zn^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}· Ba^{2+}, SO_4^{2+} and NO_3^- have no effect in the direct determination but Cl^- and Br^- interfere by forming strong complexes with Tl(III)[23–25] which are not reactive and hence prevent oxidation by the Tl(III). The inhibition by chloride has already been reported.[26,27] Cu^{2+} and Fe^{2+} interfere in the indirect determination, but chloride and bromide do not.

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Summary—Conditions have been established for the titrimetric estimation of thiourea, thiosulphate and sulphite with thallic perchlorate, with visual end-points, in perchloric and sulphuric acid medium. In the direct determination, chloride and bromide interfere. In the indirect iodometric determination, Cu^{2+} and Fe^{2+} interfere, but chloride and bromide do not.

Zusammenfassung—Die Bedingungen zur titrimetrischen Bestimmung von Thioharnstoff. Thiosulfat und Sulfit mit Thallium (III)-perchlorat in überchlorsaurer oder schwefelsaurer Lösung mit visueller Endpunktsbestimmung wurden festgelegt Bei der direkten Bestimmung stören Chlorid und Bromid. Bei der indirekten jodometrischen Bestimmung stören Cu^{2+} und Fe^{2+}, nicht jedoch Chlorid und Bromid.

Résumé—On a établi les conditions du dosage titrimétrique de la thiourée, du thiosulfate et du sulfite avec le perchlorate thallique, avec points de fin de dosage visuels, en milieu acides perchlorique et sulfurique. Dans le dosage direct, le chlorure et le bromure gênent. Dans le dosage iodométrique indirect, Cu^{2+} et Fe^{2+} gênent, mais pas le chlorure et le bromure.

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SIMULTANEOUS ION-BEAM COLLECTION FOR PRECISE MEASUREMENT OF NUCLIDIC ION-CURRENT RATIOS IN SPARK-SOURCE MASS SPECTROMETRY

(*Received* 19 *June* 1973. *Accepted* 4 *September* 1973)

Simultaneous ion-beam collection has been employed for many years for precise measurement of isotopic ratios in mass spectrometers employing electron bombardment or surface ionization ion-sources.[1] Although this technique was also used with the spark-source mass spectrometer as early as 1941,[2] it has not been used in recent developments[3] concerned with electrical ion-detection. This note describes a simultaneous beam-collector system and its application to analytical problems in spark-source mass spectrometry.

Figure 1 illustrates the Mattauch-Herzog ion-optical system used with the radiofrequency (rf) spark ion-source.[4] Photographic ion-detection, used for most studies with the spark ion-source,[5] is accompanied by positioning a photoplate along the focal plane. Electrical ion-detection has also been successfully applied in recent years and is accomplished by making two concurrent measurements involving the electrical signal from the total beam monitor and the signal from the particular ion focused at the collector in the focal plane. This type of reference to the total ion-beam is necessary because of the erratic nature of the ion-currents produced in the rf spark ion-source. Such ion-current intensity measurements are generally satisfactory when homogeneous samples are sparked and form both electrodes. However, for many studies, heterogeneous samples or dissimilar sparking electrodes must be used and the total ion-beam no longer serves as an accurate reference for specific ion-currents

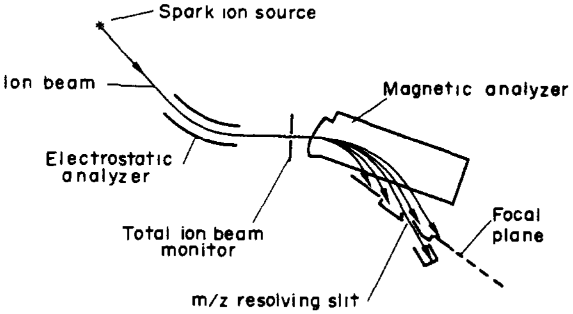

Fig. 1. Schematic drawing of special collector used with a spark-source mass spectrograph ion-optical system

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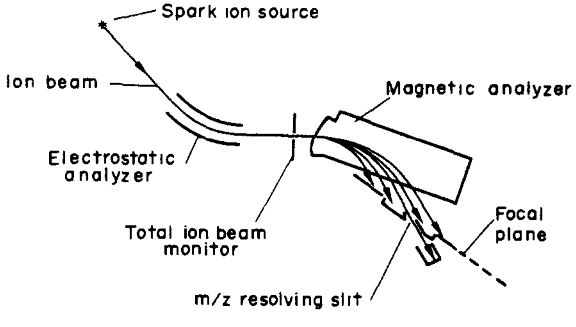

Fig. 1. Schematic drawing of special collector used with a spark-source mass spectrograph ion-optical system

Simultaneous ion-beam collector

If a portion of the grounded plate which lies along the focal plane (see Fig. 1) is replaced by a suitably sized Faraday collector, then two or more ion-currents which are mass-resolved along the focal plane can be measured simultaneously. The ratios of these signals can be measured independent of variations of ion-current signals in other portions of the spectrum. Figure 2 is a schematic drawing of such an ion-beam collector. The defining slit-width is set by adjusting the distance between the two trough-like Faraday collectors. The ion-beam enters the focal plane at an angle of about 45°. The ends of the Faraday troughs are therefore tapered to permit particular *m/z* ions to pass through the slit without touching any surfaces and be detected by either a second Faraday collector or an electron-multiplier. A collector assembly based upon this scheme was constructed which allowed all ions within a mass range, Δm, corresponding to $\pm 15\%$ of the *m/z* focused at the slit, to be collected. Any desired mass range could be accommodated by altering the length of the assembly.

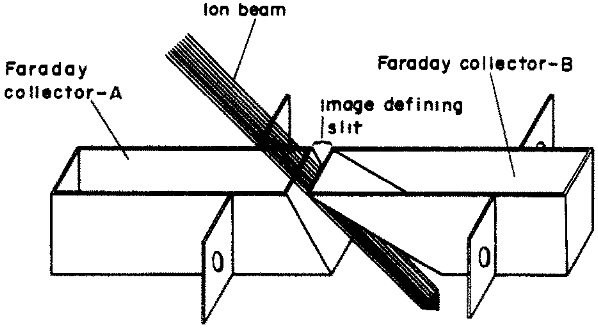

Fig. 2. Spark-source mass spectrograph special ion-beam collector. (A and B are connected electrically.)

The advantage of this collector when used with heterogeneous Nd_2O_3-graphite pelleted samples is illustrated in Fig. 3. In the experiment the $^{142}Nd^+$ ion-current was focused at the collector slit. This ion-current was then alternately referenced to the special collector ion-current signal due to all of the other Nd^+ ion-currents and to the total beam monitor signal. Each data point in the figure represents the ratio of integrated ion-current signals obtained during 10 sec. The larger fluctuations noted for total beam monitor referencing are attributed to variations in the concentrations of major ions in the total beam (*i.e.*, Nd^+, Nd^{2+}, C^+, O^+, and CO^+). The special collector obviates these variations and only the ratio of $^{142}Nd^+$ to the remaining ion-currents due to singly-charged neodymium ions is measured.

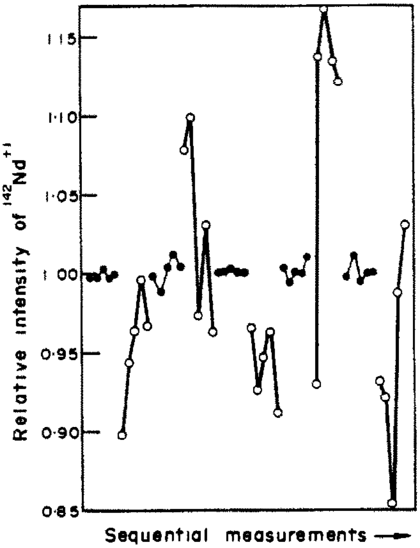

Fig. 3. Improvement in measuring precision of $^{142}Nd^+$ from a Nd_2O_3-graphite pellet sample. (Ion beam referencing by two different techniques: data in solid circles, with collector shown in Fig. 1; data in open circles, with conventional total ion-beam monitor

Application

A successful application of this collector has been in the routine monitoring of other rare-earth impurities in rare-earth oxides. This technique utilizes the higher detection sensitivity of electrical detection in mass-spectral regions near large matrix ion-currents, for the determination of trace-level impurities at spectrum positions adjacent to that for the matrix rare earth.

A second application involves measuring relative isotopic abundances in oxide–graphite pellet samples. Table 1 gives some results for the dysprosium isotopic relative abundances for three separate sample pellet loadings. Each measurement is the result of eighteen 10-sec observations

Table 2 shows some results for titanium nuclides observed for three TiO_2–graphite pellet loadings The cause of the large measurement bias for all the isotopes and the higher standard deviation for $^{48}Ti^+$ has not been found although the results suggest a possible systematic error. The $^{46}Ti^+$ signal decreases down the table and the cause for this systematic deviation, not present in measurements of $^{47}Ti^+$, $^{49}Ti^+$ and $^{50}Ti^+$, is also unknown at present The measurements for $^{47}Ti^+$, $^{49}Ti^+$, and $^{50}Ti^+$ show precisions comparable to those obtained for the dysprosium nuclides

A third application of the special collector has been in the determination of concentration profiles of trace amounts of Ni, Fe, Cr, Ti and Nb in vanadium diffusion couples One sparking electrode is a rod (2·5 × 25 mm) constituting the vanadium diffusion couple and the other is a 0·0075-in diameter pure gold wire Although V^+, V^{2+}, Au^+, and Au^{2+} all contribute significant and varying amounts to the total ion-current, the special collector detects only the V^+ ion-signal which serves as a better ion-beam reference for the analytical measurements than that from the total beam monitor The results for iron, obtained by referencing to the monitor and the special collector, are shown in Fig 4. Fourteen samplings, separated by approximately 0·9 mm, were made along the

Table 1. Spark-source mass spectrometric measurement of relative isotopic abundances for Dy in a Dy_2O_3–graphite pellet sample electrical detection

				Abundance, %		
	Trial	^{164}Dy	^{163}Dy	^{162}Dy	^{161}Dy	^{160}Dy
Loading I	1	33·49	24·59	23·98	16·20	1·73
	2	33·80	24·04	24·17	16·23	1·76
	3	33·59	24·32	24·12	16·23	1·75
	4	33·67	24·22	24·18	16·14	1·78
	5	33·62	24·29	24·20	16·13	1·76
	6	33·73	24·23	23·93	16·35	1·75
	Av	33·65	24·28	24·10	16·22	1·76
Loading II	1	33·52	24·18	24·26	16·30	1·74
	2	33·83	24·21	23·98	16·21	1·77
	3	33·30*	24·24	24·40*	16·30	1·77
	4	33·49	24·47	24·21	16·07	1·75
	5	33·68	24·04	24·19	16·34	1·76
	6	33·80	23·82*	24·58*	16·10	1·69*
	Av	33·60	24·16	24·27	16·22	1·75
Loading III	1	33·87	24·08	24·01	16·30	1·74
	2	33·65	24·46	24·02	16·11	1·76
	3	33·77	24·24	24·09	16·15	1·76
	4	34·07*	24·25	23·94	15·99	1·76
	5	33·61	24·40	24·11	16·13	1·75
	6	33·83	24·20	23·99	16·23	1·75
	7	33·89	24·13	24·02	16·21	1·75
	Av	33·82	24·25	24·02	16·16	1·75
	Overall av	33·70	24·23	24·12	16·20	1·75
	Std. devn	0·18	0·18	0·17	0·10	0·019

* If these values are rejected according to the 95% Student *t*-test, the results become,

	Av	33·70	24·24	24·08	16·20	1·76
	Std devn	0·13	0·13	0·11	0·10	0·012

Table 2. Measurement of Ti relative isotopic abundances for Ti in a TiO_2–graphite pellet sample

				Abundance		
	Trial	^{46}Ti	^{47}Ti	^{48}Ti	^{49}Ti	^{50}Ti
Loading I	1	2171	1922	63331	1534*	1473
	2	2165	1901	64078	1567	1501
	3	2172	1923	64042	1564	1496
	4	2155	1909	62416	1558	1492
	5	2151	1900	61641	1556	1486
	Av	2163	1911	63102	1556	1490
Loading II	1	2156	1917	63411	1562	1508
	2	2150	1894	61538	1570	1495
	3	2151	1925	61698	1559	1502
	4	2145	1892	61063	1563	1491
	5	2134	1911	61529	1560	1497
	Av	2147	1908	61848	1563	1499
Loading III	1	2140	1905	64945	1563	1491
	2	2124	1892	66404	1570	1500
	3	2123	1896	66732	1566	1481
	4	2118	1916	65459	1560	1483
	5	2110	1902	63530	1558	1494
	Av	2123	1902	65414	1563	1490
	Overall av	2144	1907	63454	1561	1493
	Std. devn.	19·0	12·0	1832	9·00	9·00
	Rel. std. devn., %	0·9	0·6	2·9	0·6	0·6

* If this value is rejected according to the 95% Student *t*-test, the standard deviation becomes 4 and the relative standard deviation 0·3%.

vanadium bar with each sampling consisting of nine readings 10 sec in duration. The precision is given in the upper portion of the figure and shows that beam referencing with the special collector yields deviations only about one half as great as those when the conventional total beam monitor is used.

Conclusion

Simultaneous ion-beam collection has been shown to improve the precision of electrical ion-detection measurements in the analysis of heterogeneous samples by spark-source mass spectrometry. This improvement results from the use of a specific matrix ion-current signal as the reference rather than the ion-current signal from the conventional total ion-beam monitor. The general utility of the spark-source mass spectrometer is considerably broadened by this easily installed ion-detector. The ion-collector described here is limited in mass range because only one signal at a time can be detected with an electron-multiplier or second Faraday collector. However, simultaneous multiple ion-beam collection can be adapted advantageously to other analytical problems by altering the design of the collector.

Acknowledgements—The authors acknowledge the aid of Mr. Clarence Ness who operated the mass spectrometer and the work of Mr. Gary Wells who made the collector.

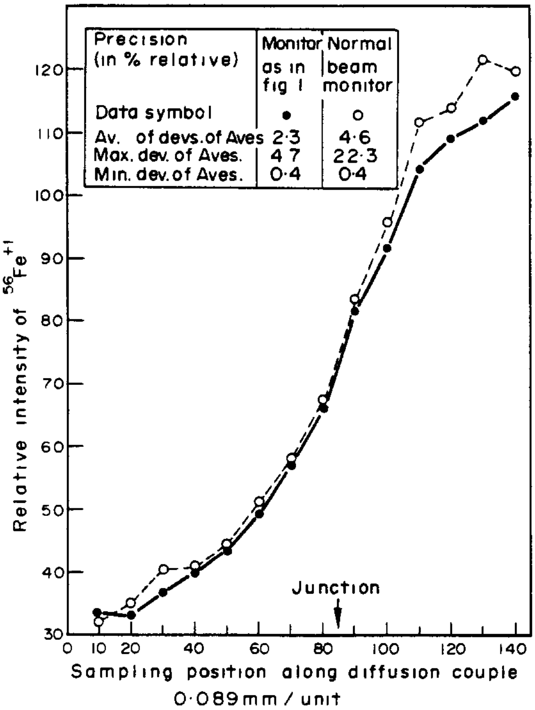

Fig 4. Scan of Fe$^+$ along a vanadium diffusion couple with a pure gold wire counter-electrode. (Ion beam referencing by two different techniques: data in solid circles with collector shown in Fig. 1. *i.e.*, V$^+$, data in open circles with conventional total beam monitor, *i.e.*, sum of Au$^+$, Au^{2+}, V$^+$, V^{2+} intensities.)

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Summary—Simultaneous ion-beam collection techniques make significant improvement possible in the precision of measurements when electrical ion-detection is used with the spark ion-source. The advantage of reference of specific ion-current signals only to those from desired regions of the mass spectrum is that reproducible measurements may be made on heterogeneous samples such as oxide–graphite pellets. For example, isotopic ratio measurements from separate samplings of an oxide (pelleted with graphite) are reproducible to better than ±0·5%. The technique is also advantageous when sparking dissimilar electrodes, such as a gold probe and a metal bar.

Zusammenfassung—Simultane Ionenstrahl-Auffangtechniken ermöglichen wesentliche Verbesserungen in der Meßgenauigkeit, wenn mit der Funken-Ionenquelle der elektrische Ionennachweis verwendet wird. Der Vorteil, spezifische Ionenstromsignale nur auf solche aus erwünschten Gegenden des Massenspektrums zu beziehen, liegt darin, daß man an heterogenen Proben wie etwa Oxid Graphit-Tabletten reproduzierbare Messungen machen kann. Zum Beispiel sind Messungen der Isotepenverhältnisse an separaten Proben eines mit Graphit verpreßten Oxids besser als auf ±0.5% reproduzierbar. Das Verfahren ist auch van Vorteil, wenn man unterschiedliche Elektroden abfunkt, etwa eine Goldsonde und einen Metallstab.

Résumé—Les techniques de collection simultanée de faisceaux d'ions rendent possible une amélioration importante dans la precision des mesures quand on utilise la détection d'ions électrique avec la source d'ions à étincelles. L'avantage qu'il y a à rapporter des signaux ion-courant spécifiques seulement à ceux des régions désirées du spectre de masse est que des mesures reproductibles peuvent être effectuées sur des échantillons hétérogènes tels que des pastilles oxyde–graphite. Par exemple, des mesures de rapport isotopique d'échantillonnages séparés d'un oxyde (en pastilles avec du graphite) sont reproductibles à mieux que ±0·5%. La méthode est aussi avantageuse quand on fait jaillir les étincelles entre des électrodes dissemblables, comme une sonde d'or et une barre métallique.

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THE DECOMPOSITION AND SUBSEQUENT ANALYSIS OF Rh-Fe FOR IRON

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Little information is available about the analysis of rhodium alloyed with base metals. Typical problems arise in the decomposition of these alloys, as some of them behave more nobly than pure rhodium itself. Alloys in which Rh predominates are not attacked by acids and bases. Mixtures of molten salts are also unsuitable for decomposition of these alloys. Finely powdered Fe–Rh (50 at.%) can be dissolved in a mixture of sodium and potassium persulphate (1 : 1), but it is a rather time-consuming procedure.

Beamish and co-workers[1,2] examined the general behaviour of platinum metals in an atmosphere of chlorine and found that pure rhodium can be quantitatively converted into $RhCl_3$ in a stream of chlorine at about 700 Intermetallic FeRh, however, behaves more nobly towards chlorine than pure Rh does. We have found that it can be decomposed by the dry chlorination procedure if the temperature is increased to 900°. At about 1000° the decomposition rate is 20 mg/hr in a gas stream of 50 ml/min.

The apparatus used is shown in Fig. 1. A 5–10-mg sample is placed in a quartz tube (*A*) which is heated in the electric furnace (*B*). The chlorine, which is passed through sulphuric acid in order to control conveniently the gas flow at 1 bubble/sec, is led over the sample. Both rhodium trichloride and iron trichloride sublime. The salts partially condense on the wall of the quartz tube outside the oven and partially form a cloud of particles which precipitate in the container *D*; the particles act as condensation nuclei for the chlorine gas which condenses in *D* as the container is cooled by liquid nitrogen in the Dewar *E*.

The Pyrex container is in open connection with the air. A slow stream of air enters the container when *D* is cooled. This counter-flow prevents a loss of dust during the decomposition. When the container is brought to room temperature the condensed water prevents an escape of chloride. A quartz–Pyrex graded seal (*F*) is used between the quartz tube and Pyrex container; with a joint irregular results were found. The apparatus is opened near *G* by cutting the glass.

$FeCl_3$ is hygroscopic. $RhCl_3$ formed in this way is completely insoluble in aqueous media. The apparatus is washed with 10-ml portions of 0·1*M* hydrochloric acid. The collected washings are filtered to remove $RhCl_3$, boiled

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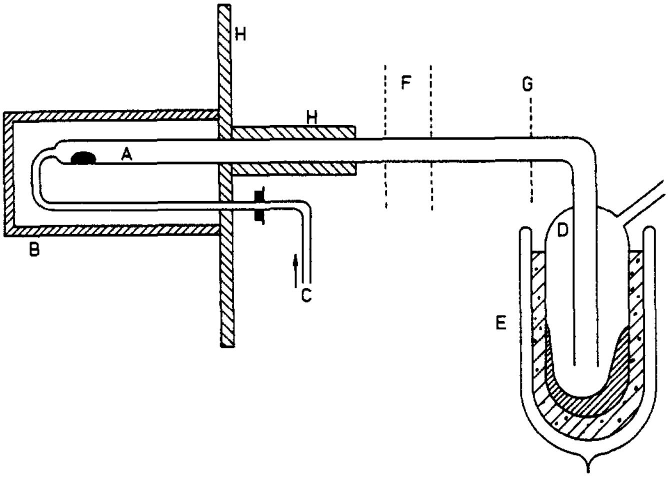

Fig 1 The apparatus for chlorination of Fe–Rh.
A: quartz tube (diameter 20 mm). *B*: electric oven at 1000 *C*: Pyrex inlet tube (diameter 6–8 mm) *D*: Pyrex container in open connection with the air. *E*: Dewar with liquid nitrogen. *F*: glass–quartz graded seal. *G*· place where apparatus is cut. *H*· Al_2O_3 heat-shield and tube insulation.

to expel chlorine, and made up to 250 ml. Then 5-ml portions containing about 1·5 μmole of Fe(III) are used for the titrations

The iron content is determined complexometrically by photometric titration Excess of EDTA is added and back-titrated with Ce^{3+}, Xylenol Orange being used as indicator (pH 5·5, hexamine buffer). The wavelength for maximum Ce–XO absorption is 575 nm.

The method has been tested with Fe alone, with seperate pieces of Fe and Rh and finally with Rh–Fe samples (50 at.%) which had shown no loss of weight when manufactured.

Some of the results (means of five titrations) are shown in Table 1

Table 1.

Taken in tube	Fe found
8·87 mg Fe	8·83 mg 8·84 mg
2·61 mg Fe + 5·04 mg Rh	2·62^4 mg
3·08 mg Fe + 10·2 mg Rh	3·06 mg
5·64 mg FeRh (50 at %)	50·5 at %
6·31 mg FeRh (50 at %)	50·2 at %
10·13 mg FeRh (50 at %)	49·9 at %
9·82 mg FeRh (50 at %)	49·8 at %
16·32 mg FeRh (50 at %)	50·5 at %
12·24 mg FeRh (50 at %)	49·8 at %
20·2 mg FeRh (50 at %)	50·0 at %

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Summary—Rhodium alloyed with base metals can be decomposed by dry chlorination at 1000°. The reaction product sublimes and can be freed from the insoluble rhodium trichloride by filtration after the apparatus has been washed out. The condensation of the excess of chlorine in a liquid-nitrogen trap was found very effective for the prevention of sample loss during decomposition stage.

Zusammenfassung—Mit unedlen Metallen legiertes Rhodium kann durch trockene Chlorierung bei 1000° aufgeschlossen werden. Das Reaktionsprodukt sublimiert und kann nach dem Auswaschen des Apparats durch Filtration von dem unlöslichen Rhodiumtrichlorid befreit werden. Zur Vermeidung eines Verlustes an Probe während des Aufschlusses erwies sich die Kondensation des überschüssigen Chlors in einer mit flüssigem Stickstoff gekühlten Falle als sehr wirkungsvoll.

Résumé—Le rhodium allié à des métaux de base peut être décomposé par chloration sèche à 1000°. Le produit de réaction se sublime et peut être libéré du trichlorure de rhodium insoluble par filtration après que l'appareil ait été lavé. On a trouvé que la condensation de l'excès de chlore dans un piège à l'azote liquide est très efficace pour empêcher une perte d'échantillon pendant le stade de décomposition.

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DETERMINATION OF YTTRIUM IN ROCKS BY NEUTRON ACTIVATION AND A SIMPLE GROUP SEPARATION

(*Received* 11 *July* 1973. *Accepted* 31 *August* 1973)

Yttrium in rocks is most often determined by optical emission spectrography, and in recent years also by X-ray fluorescence spectrometry. The applications of neutron-activation analysis have been few, mainly because the only yttrium isotope exhibiting sufficiently high sensitivity, 64-hr ^{90}Y, is a pure β-emitter. In addition, yttrium is not easily separated from the rare-earth group, which includes a number of nuclides with far higher activation cross-sections than that of ^{89}Y. This apparently makes the determination of yttrium by neutron activation almost impossible unless elaborate chromatographic separations are carried out. The previously reported methods for yttrium in rocks by neutron activation have all involved some kind of group separation followed by separation of the individual rare-earth elements on ion-exchange columns.[1–4] More recent neutron-activation methods for rare-earth determination[5–8] are based on Ge(Li) γ-spectrometry directly on the rock samples or on group-separated fractions, thus leaving yttrium undetermined.

The use of β-counting in activation analysis is usually assumed to require a sample of high radionuclide purity in order to work satisfactorily. In the cases of some nuclides with high-energy β-emission, however, this simple counting technique may be useful even when rather complicated radionuclide mixtures are concerned. It has been shown to be feasible to determine potassium[9] as well as phosphorus[10] in rock samples without use of radiochemical separations. This seemed to indicate that yttrium might be determined by a β-counting method, if the rare-earth group could be separated from other activities.

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EXPERIMENTAL

Preliminary experiments

On neutron activation, all 14 stable members of the lanthanide group give rise to activities of sufficiently long half-life to interfere with the measurement of ^{90}Y. The contribution from some of these nuclides may be eliminated by suitable use of absorbers, while in other cases, such as ^{140}La, ^{142}Pr, ^{152}Eu and ^{166}Ho, β-particles of very high energy are associated with the decay. In addition, other types of radiation such as X-rays and soft γ-rays may interfere. The nuclides of potential interest in this connection are listed in Table 1.

The standard procedure used when the activity of a nuclide emitting high-energy β-rays is to be measured in the presence of a complex mixture of interfering activities, is to count the sample through two different absorbers, the thickness of which is selected so that one eliminates conversion electrons and low-energy β-particles, while the other is sufficiently thick to discriminate against the β-rays of the nuclide to be determined, thus transmitting only γ-rays and to some extent X-rays. The difference between the two observed count-rates will mainly represent contribution from high-energy β-emitters.

In order to decide whether yttrium could be determined according to such a procedure in the presence of rare earths with natural distributions, the following experiments were carried out.

Standard solutions of yttrium and the 14 rare earths, made by dissolving weighed amounts of the spectroscopically pure oxides in nitric acid and diluting to appropriate concentrations with water, were irradiated in sealed polyethylene tubes for 1 hr in the JEEP II reactor (Kjeller, Norway). The thermal-neutron flux was about $1{\cdot}5 \times 10^{13}$ n. cm^{-2}. sec^{-1} and the cadmium ratio of gold about 3·0 in the irradiation position. Aliquots (100 μl) of the irradiated solutions were adsorbed on separate circular pieces of filter paper placed in small circular aluminium cups (20 mm dia.) for activity measurements. The samples were counted 4, 7, 10 and 13 days after the irradiation. A Geiger-Müller counter with conventional shelf arrangement was used. The window thickness of the tube was 10 mg/cm^2, and the effective diameter was 28 mm. The samples were counted with three different aluminium absorbers, namely 210 mg/cm^2 (activity A_1), 350 mg/cm^2 (activity A_2) and 1280 mg/cm^2 (activity A_3), discriminating β-particles of maximum energy 0·61, 0·90 and 2·5 MeV respectively. The differences A_1-A_3 and A_2-A_3 were calculated for each sample and divided by the weight of element present. These specific activity values were divided by the corresponding value for yttrium, and the "relative interference factors" thus obtained are listed in Table 1.

From these observations it is evident that the elements Ce, Pr, Nd, Gd, Dy, Er and Lu do not represent any significant interference in the analysis of samples with natural distributions of the rare-earth elements, provided that the measurements are postponed to 13 days after the end of the irradiation. If absorber 2 is chosen rather than absorber 1, the Tm interference also becomes almost insignificant. Furthermore, the elements Sm, Tb and Yb are also of relatively little importance in this respect. Of the remaining elements La, Eu and Ho, lanthanum will be the major interference in most rock samples, owing to a higher abundance than the other two elements. The relative interference from La could be further reduced by increasing the decay time, but this would result in considerably more difficulties with Eu, Tb and Tm, which involve long-lived nuclides. A decay time of 13 days and the use of absorbers 2 and 3 therefore seemed to be a good compromise for application to geological materials.

It appears that the elements yielding significant interference in the determination of yttrium, and the content of which must therefore be known, namely La, Sm, Eu, Tb, Ho and Yb, can be readily determined by neutron activation followed by a group separation of the rare earths and subsequent Ge(Li) γ-spectrometry. The preliminary results therefore indicated that a determination of yttrium might well be combined with such a procedure provided that the sample is prepared in a form suitable for β-counting with an end-window tube.

Application to silicate rocks

As test material for this investigation, five U.S. Geological Survey standard rocks with considerably different rare-earth distribution patterns were selected. As the content of most rare earths in these rocks was well known from previous work in the author's group and elsewhere, a new determination of the elements expected to interfere with the measurements of yttrium was not carried out. The following procedure was applied.

Samples of about 100 mg, packaged in aluminium foil, were irradiated for 20 hr as described above, together with an yttrium standard solution sealed in a quartz ampoule. After 12 days' delay, the samples were transferred to nickel crucibles containing carriers of Y (20 mg), La (1 mg), Eu (0·1 mg) and Dy (0·1 mg) and fused with 2 g of sodium hydroxide pellets, in an electrothermal burner. The fusion cake was removed by centrifuging, washed with water and then dissolved in 25 ml of 9*M* hydrochloric acid. Solvent extraction with 25 ml of 50% tri-n-butyl phosphate in toluene was then performed, and the rare-earth elements were subsequently precipitated from the acid phase by addition of a few ml of concentrated hydrofluoric acid. The fluoride precipitate was centrifuged, washed with water, filtered off on a membrane filter and then mounted on a cardboard sample holder for β-counting. Aliquots (100 μl) of the Y standard solution were processed in the same manner as the rock samples.

The TBP extraction step was introduced in order to remove ^{46}Sc (and ^{47}Sc from Ca). More than 98% of the scandium is extracted into the TBP phase, while less than 5% of the heavy and less than 2% of the light rare earths are extracted

Table 1. "Relative interference factors" for rare earths estimated to interfere with the determination of yttrium by neutron activation and β-counting of ^{90}Y (irradiation 1 hr)

Element	Radioactive isotope (half-life)	Maximum β-energy MeV	Other radiation types	(Specific activity)$_{\text{element}}$/(Specific activity)$_{\text{Y}}$ 4 d A_1–A_3	4 d A_2–A_3	7 d A_1–A_3	7 d A_2–A_3	10 d A_1–A_3	10 d A_2–A_3	13 d A_1–A_3	13 d A_2–A_3
Y	^{90}Y (64 hr)	2·27		1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00
La	^{140}La (40 hr)	2·18	γ	1·21	0·62	0·79	0·41	0·55	0·28	0·35	0·17
Ce	^{141}Ce (32 d) + ^{143}Pr (14 d)	0·93 (^{143}Pr)	X, γ, e^-	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
Pr	^{142}Pr (19 hr)	2·16	(γ)	1·51	1·38	0·25	0·23	0·04	0·04	<0·01	<0·01
Nd	^{147}Nd (11 d) + ^{149}Pm (53 hr)	1·07 (^{149}Pm)	X, γ, e^-	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
Sm	^{153}Sm (47 hr)	0·80	X, γ, e	0·14	0·11	0·11	0·09	0·08	0·06	0·06	0·05
Eu	^{152}Eu (12 y) + ^{154}Eu (14 y)	1·88 (^{152}Eu)	X, γ	3·95	2·68	0·25	0·14	0·38	0·23	0·83	0·49
Gd	^{153}Gd (242 d) + ^{159}Gd (19 hr)	0·95 (^{159}Gd)	X, γ, e^-	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
Tb	^{160}Tb (72 d)	0·86	X, γ, e^-	0·03	0·02	0·07	0·04	0·14	0·09	0·29	0·18
Dy	^{159}Dy (144 d)		X, γ, e	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
Ho	^{166}Ho (27 hr)	1·84	X, γ, e	11·4	7·33	4·30	2·62	1·44	0·82	0·45	0·26
Er	^{169}Er (9·5 d)	0·34	X, γ, e	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
Tm	^{170}Tm (130 d)	0·97	X, γ, e^-	0·30	0·01	0·58	0·02	1·14	0·03	2·45	0·06
Yb	^{169}Yb (32 d) + ^{175}Yb (4·2 d)	0·50 (^{175}Yb)	X, γ, e	<0·01	<0·01	<0·01	<0·01	0·01	0·01	0·02	0·02
Lu	^{177}Lu (6·8 d)	0·50	γ	0·01	0·01	0·02	0·01	0·03	0·02	0·04	0·03

Table 2. Yttrium content (*ppm*) of five standard rocks. Comparison of data from the present work with values of other workers

	AGV-1	BCR-1	G-2	GSP-1	W-1
Present method	24·7 (24·8, 24·5)	44·3 (43·9, 44·6)	7·9 (8·5, 7·3)	22·8 (21·2, 24·4)	28·0 (28·2, 27·8)
Fleischer,[15] recommended value					25
Flanagan,[16] average value	25·3	46·2	12·2	36·6	
Literature neutron-activation values		36·5[4]	9·5[4]		23·8[1], 27·1[2], 28·0[2], 25·2[17]

The β-activity measurements were performed on the following day according to the procedure described above. After the counting, chemical yields were determined by re-activation. The precipitates were removed from the sample holders and activated for 10 sec, and after a 2-hr delay subjected to γ-spectrometry with a Ge(Li) detector system for the measurement of ^{165}Dy, ^{152m}Eu and ^{140}La The ^{140}La activity was recorded through a 2-mm lead absorber. The yield for Y was assumed to be the same as that for Dy. In all cases the difference in yield for the three elements investigated was less than 10%. No corrections for differences in chemical yield were therefore introduced in the calculation of interferences.

The differences in count-rates obtained with the two absorbers were corrected for contributions from lanthanide activities by applying the empirical correction factors of Table 1 (13 days' delay) adjusted to 20 hours' irradiation, and available literature data for La,[11] Sm,[12] Eu,[1,13] Tb,[14] Yb[15] and Lu[15] in the U.S.G.S. standard rocks. For Ho and Tm, in which cases no data seemed to be available except for W-1, the contents were estimated on the basis of values for the neighbouring elements and general knowledge on rare-earth distributions in rocks.

RESULTS AND DISCUSSION

The results obtained for the yttrium content of the five U.S.G.S. standard rocks after appropriate corrections, are given in Table 2 and compared with data by other workers. Each sample was run in duplicate, and the agreement observed indicates that a very good precision may be obtained by the present method down to low yttrium levels.

The accuracy of the results is mainly dependent on the accuracy with which the correction factors, as well as the concentrations of the rare earths in question, are known. The magnitude of the correction in the case of a sample enriched in the "cerium-group" of rare earths as compared to one more abundant in the members of the "yttrium-group" may be demonstrated by giving figures for the per cent contribution of elements to the observed count rate in the case of a G-2 and a BCR-1 sample:

G-2: Y, 41·6; La, 49·2; Sm, 1·6; Eu, 6·3; Tb, 0·8; Ho, 0·3; Tm, 0·1; Yb, 0·1.

BCR-1: Y, 89·3; La, 5·3; Sm, 0·5; Eu, 3·6; Tb, 0·8; Ho, 0·2; Tm, 0·1; Yb, 0·2.

This would indicate that in the case of samples with rare-earth distributions not deviating too much from that of chondritic meteorites, the exact knowledge of rare-earth concentration is not critical for the present method. The results obtained for BCR-1 and W-1 should therefore presumably be fairly accurate. For samples with a distinct enrichment in the lighter rare earths, however, accurate data become important, especially for lanthanum. An error of 10% in the La value for G-2 would yield a corresponding error of about 12% in the result for Y, which indicates that the results obtained in the present work for G-2 and GSP-1 are probably less accurate than the others.

A comparison with the available literature data seems to support the conclusions already drawn. The present values for AGV-1, BCR-1 and W-1 are in good agreement with Flanagan's average values[16] and Fleischer's recommended value[15] respectively For W-1, the agreement with previous neutron-activation work also appears satisfactory. In the case of G-2 and GSP-1, the present results are considerably lower than Flanagan's averages. This might indicate systematic errors in the method. The data upon which Flanagan's average values have been calculated, however, show a rather large spread, and additional work seems to be necessary before a firmer conclusion can be drawn on this point. It should be noted that Rey *et al.* have also obtained a low value for Y in G-2 by neutron activation.

If nuclides other than those belonging to the rare-earth group are carried through the radiochemical separation procedure, additional systematic errors may occur. From previous work by the author[10] it appears that none of the major long-lived contributors to high-energy β-radiation from irradiated rocks (*i.e.*, ^{32}P, ^{86}Rb, $^{122-124}$Sb) except the rare-earth group are likely to interfere appreciably In samples with high concentration of uranium, the possibility of interference from fission-product activities in the rare-earth region should not be overlooked.

The present method, although perhaps not especially attractive for routine determination of yttrium alone, should provide a valuable supplement to activation analyses where a number of rare earths are determined by group separation and Ge(Li) γ-spectrometry, enabling yttrium to be included among the elements to be determined, without any significant increase in work load. It would be necessary, however, to determine a set of correction factors specially for the β-counting system to be used.

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Summary—A neutron-activation method is proposed for the determination of yttrium in rocks by separation of the rare-earth group and β-counting. Interferences from rare-earth nuclides and the necessary corrections are discussed, and results for some standard rocks are presented. The method is suitable for combination with rare-earth determinations by group separation and Ge(Li) γ-spectrometry.

Zusammenfassung—Ein Neutronenaktivierungsverfahren zur Bestimmung von Yttrium in Gesteinen durch Abtrennung der Gruppe der seltenen Erden und β-Zählung wird vorgeschlagen. Die Störungen durch Nuklide der seltenen Erden und die notwendigen Korrekturen werden diskutiert und Ergebnisse für einige Standardgesteine angegeben. Das Verfahren eignet sich zur Kombination mit Bestimmungen seltener Erden durch Gruppenabtrennung und Ge(Li)-γ-Spektrometrie.

Résumé—On propose une méthode par activation de neutrons pour le dosage de l'yttrium dans les roches par séparation du groupe des terres rares et comptage β. On discute des interférences des nuclides des terres rares et des corrections nécessaires, et présente des résultats pour quelques roches étalons. La méthode est convenable pour une combinaison avec les dosages de terres rares par séparation de groupe et spectrométrie γ Ge (Li).

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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH FERRON AND A QUATERNARY AMMONIUM SALT

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(*Received* 3 *May* 1973 *Accepted* 15 *June* 1973)

Summary—The reproducibility of the ferron method for aluminium has been greatly improved by the addition of cetyltrimethylammonium chloride (CTMAC) The improvement is attributed to reduction of the reagent blank and increased stability of Al(ferron)$_3^{3-}$ The aluminium–ferron complex formed in the presence of CTMAC has an absorption peak at 385 nm The interference from iron can be eliminated by application of a correction based on measurement at two wavelengths

A number of reagents have been proposed for the spectrophotometric determination of aluminium Most have distinct disadvantages, the reagent blank is usually high and varies with pH and with some of the reagents, Beer's law is not obeyed even if the pH and other variables are controlled with extreme care

Of the numerous reagents proposed, 8-quinolinol (8-hydroxyquinoline or oxine) seems to give the most reliable results[1–3] However, 8-quinolinol forms an insoluble complex with aluminium which has to be extracted into an organic solvent before the spectrophotometric measurements

An attempt was made to eliminate the extraction step by using ferron, the 7-iodo-5-sulphonic acid derivative of 8-quinolinol, but it became apparent that in spite of its rather wide use,[4–7] reproducible results are not obtained unless extreme care is taken to control the pH and other variables In addition, the calibration curve is non-linear at higher concentrations of aluminium It was found that the difficulties associated with the use of ferron can be eliminated by addition of a cationic surfactant

EXPERIMENTAL

Reagents

Ferron solution Dissolve 0 8 g of ferron in 100 ml of 40% v/v aqueous *N*,*N*-dimethylformamide

CTMAC–KCl solution Dissolve 20 g of cetyltrimethylammonium chloride (CTMAC) in 800 ml of water Add 150 g of potassium chloride and dilute to 1 litre

Buffer solution (*pH* 5) Dissolve 327 g of sodium acetate trihydrate in water, add 34 ml of glacial acetic acid and dilute to 1 litre

Standard aluminium solution, 50 *ppm* Dissolve 0 8792 g of aluminium potassium sulphate, $AlK(SO_4)_2)12H_2O$, in a small volume of water containing 1 ml of concentrated hydrochloric acid and dilute to 1 litre with water

Recommended procedure

Place an aliquot of sample containing not more than 60 μg of aluminium in a 25-ml volumetric flask, add 2 ml of ferron solution 3 ml of buffer and 5 ml of CTMAC–KCl solution Dilute to volume and measure the absorbance at 385 nm against a reagent blank

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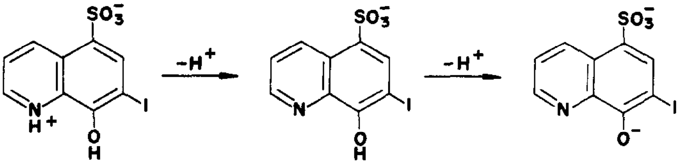
DISCUSSION

Ferron dissociates in two steps[8]



$pK_1 = 2{\cdot}50$; $pK_2 = 7{\cdot}11$ ($0{\cdot}1M$ KCl)

It is believed that the doubly charged species (designated hereafter as ferron^{2-}) combines with aluminium through the N and O atoms

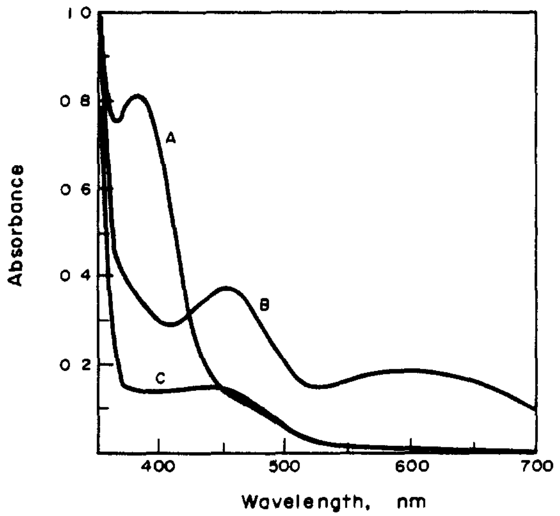


Fig 1 Absorption spectra (1-cm cell, against distilled water)
A 50 μg Al/25 ml final volume, *B* 50 μg Fe/25 ml final volume, *C* reagent blank

Figure 1 shows the absorption spectra of the ferron complexes of aluminium and iron formed in the presence of CTMAC, and that of the reagent blank The absorption peak of the Al–ferron complex is moved to 370–385 nm by the addition of CTMAC The iron complex has an absorption spectrum which is quite different in shape from that of the aluminium complex. Both iron(II) and iron(III) give rise to virtually the same absorption spectrum, indicating the oxidation of iron(II) during complex formation

The addition of cetyltrimethylammonium chloride brought about many advantages over the usual spectrophotometric procedure Tetradecyldimethylbenzylammonium chloride (Zephiramine) and cetylpyridinium chloride can be used in place of CTMAC, but with ferron these surfactants sometimes form precipitates which dissolve in excess of the surfactant.

One of the advantages of the addition of CTMAC is the much lower reagent blank (Fig 2). This permits a higher concentration of ferron to be used. This is especially advantageous when iron is present in the solution because iron reduces the concentration of ferron available for complex formation with aluminium

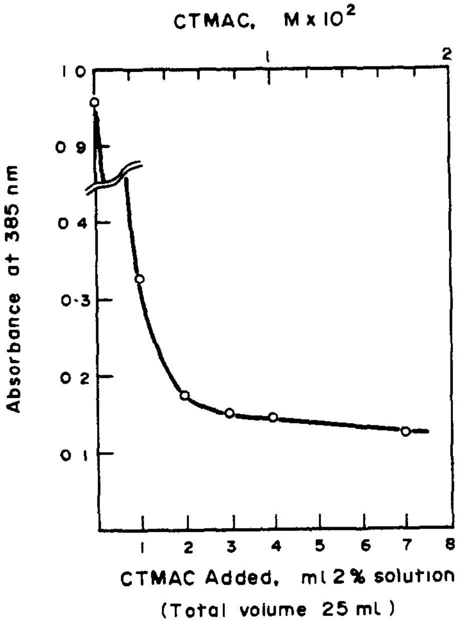


Fig 2 Effect of CTMAC on reagent blank

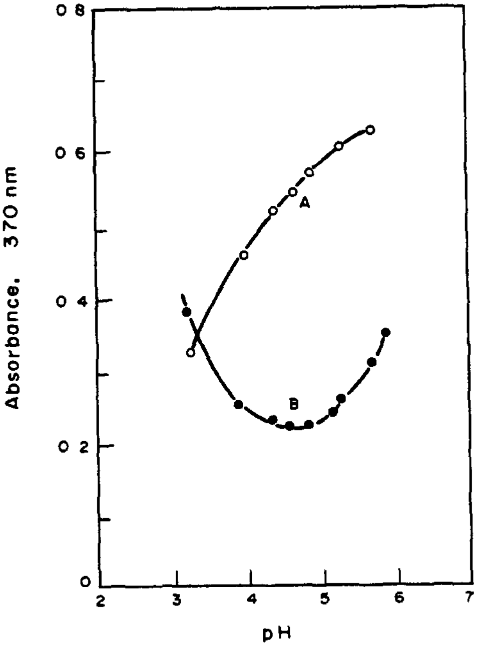


Fig 3 Effect of pH in the absence of CTMAC

A 60 μg Al against reagent blank, *B* reagent blank against water Total ferron 5 7 × 10^{-4} *M*

In the absence of CTMAC, the reagent blank varies with pH (Fig. 3). In addition, the formation of the aluminium–ferron complex is not complete at pH values where the reagent blank is low. In the presence of CTMAC, on the other hand, the formation of the aluminium complex is complete over the pH range 4–6, where the reagent blank is low and less susceptible to pH changes (Fig 4)

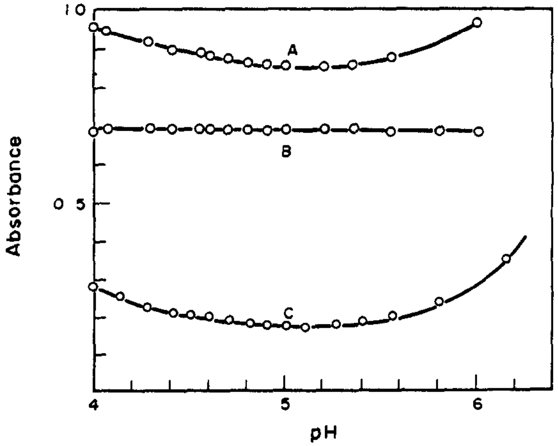


Fig 4 Effect of pH on the formation of Al-ferron complex in the presence of CTMAC Ferron 1 8 × $10^{-3}M$, CTMAC 0 4% (1 25 × $10^{-2}M$), total acetate 0 36M, KCl 0 4M *A* 50 µg Al/25 ml against water, *B* 50 µg Al/25 ml against reagent blank, *C* reagent blank

The calibration curve is linear in the presence of CTMAC but not in its absence. Beer's law is obeyed when a sufficient quantity of CTMAC is present, but deviations occur when it is not.

As shown above, formation of the aluminium–ferron complex is complete over a wide range of pH in the presence of CTMAC, but it is recommended that the pH be adjusted to within ±0·2 because the reagent blank changes slightly with pH

Another problem is that the reagent blank changes with the ionic strength, but this can be overcome by the addition of sufficient potassium chloride.

The error due to the pH and ionic strength effects on the reagent blank can be reduced by using smaller ferron concentrations The ferron concentration could be reduced to one fourth that given in the recommended procedure, if aluminium is the only cation present which combines with ferron.

Iron interferes strongly by forming an intensely coloured complex with ferron, but the error due to iron can easily be corrected by determining the absorbance at two wavelengths Simultaneous determination of aluminium and iron is also possible by this technique. For determination of only the aluminium, however, it is more convenient to make the measurements at two wavelengths at which the iron complex has the same absorptivity, so that the absorbance due to the iron is self-compensating (Fig 5)[9,10] Suitable wavelengths are 385 and 455 nm Table 1 shows that when this method is used, iron can be tolerated in amounts up to 25 times that of the aluminium present (w/w).

Calcium, magnesium, sulphate and chloride ions have no effect on the determination of aluminium, but zinc, copper, cadmium and manganese interfere by forming complexes with similar absorption spectra. Of these metal ions, however, only aluminium is masked by addition of 1 ml of 0 5 M sodium fluoride per 25 ml final volume It is therefore possible to determine the concentration of aluminium by measuring the difference between the absorbances obtained in the presence and absence of sodium fluoride

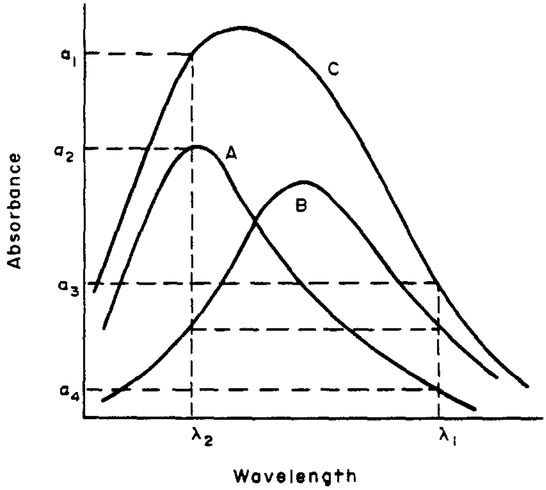


Fig 5 Principle of two-wavelength spectrophotometry
In normal spectrophotometry, species A is determined from the absorbance at wavelength λ_2 The error introduced by the presence of B is $\epsilon_{\lambda_2,A}(a_1 - a_2)$ In two-wavelength spectroscopy, the difference between the absorbances at λ_2 and λ_1, $(a_1 - a_3)$, is measured on a two-wavelength spectrophotometer If λ_2 is selected so that $\epsilon_{\lambda_2,B} = \epsilon_{\lambda_1,B}$ then $a_1 - a_3 = a_2 - a_4 = (\epsilon_{\lambda_2,A} - \epsilon_{\lambda_1,A})[A]$ and is independent of [B]

Table 1 The effect of iron on the two-wavelength spectrophotometric determination of 20 μg of aluminium (total vol 25 ml)

Fe added, μg	Al found μg
0	20 0
200	19 0
300	20 0
500	19 3

The use of cationic surfactants in the spectrophotometric determination of metal ions with anionic dyes has been reviewed by Kohara and Ishibashi[11] and by Ueno[12] Some of these ternary systems have been applied to the determination of aluminium[13–16]

The roles of cationic surfactants in these applications have been discussed by many investigators, including Bailey *et al*[17] Kohara *et al*[18] and Shijo and Takeuchi[19] It is generally accepted that the cationic surfactant shifts the absorption peak of a metal-dye complex to a longer wavelength A considerable increase in sensitivity is often achieved by addition of a surfactant, this is considered to be partly due to the enhancement of dissociation of acid groups on the dye molecule, which favours the formation of higher complexes with greater absorptivity

However the sensitivity of the ferron–aluminium system is not greatly enhanced by the addition of CTMAC An enhanced dissociation of the OH group of ferron is observed only at low ionic strengths and CTMAC seems to have little effect on the dissociation constant at higher ionic strengths. Nevertheless, better reproducibility was achieved by the addition of CTMAC even in the presence of large quantities of potassium chloride. It is apparent therefore that some other factors are responsible for the improvement.

The poor adherence to Beer's law of the usual ferron method may be attributed to the simultaneous formation of two or more complexes between aluminium and ferron. Figure 6 shows the distribution of aluminium between various ferron complexes as a function of free ferron^{2-} concentration. The distribution was calculated from the stability constants reported by Langmyhr and Storm.[8] It shows that at free ferron^{2-} concentrations lower than $10^{-4}M$, considerable quantities of $Al(ferron)_2^-$ exist in equilibrium with $Al(ferron)_3^{3-}$ and that the ratio of these two aluminium–ferron complexes to each other varies with ferron^{2-} concentration. Even if the pH and the total ferron concentration are strictly adjusted to constant values, the concentration of free ferron^{2-} will vary with the total concentration of aluminium. Therefore, the ratio of $Al(ferron)_3^{3-}$ to $Al(ferron)_2^-$ may vary with the concentration of aluminium, leading to deviations from Beer's law. Although it is expected that Beer's law is strictly obeyed at ferron^{2-} concentrations higher than $10^{-4}M$, a high ferron^{2-} concentration should be avoided because the ferron^{2-} ion has a high molar absorptivity near the absorption maximum of the $Al(ferron)_3^{3-}$

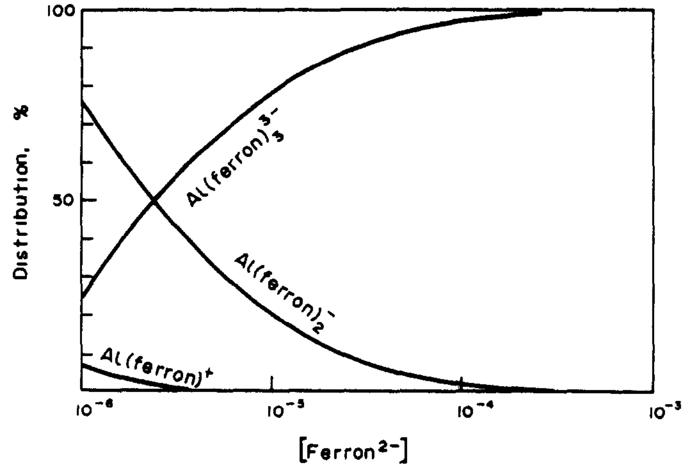


Fig. 6. Distribution of various Al–ferron species as a function of free ferron^{2-} concentration. Calculated from stability constant data reported by Langmyhr and Storm[8] (log K's 7·6, 7·1 and 5·6 in 0·1M KCl)

Figure 7 shows the average number of moles of ferron bound per mole of aluminium, as a function of ferron^{2-} concentration, as calculated from a potentiometric titration curve. In the absence of CTMAC, it increases gradually as the ferron^{2-} concentration increases, indicating the successive formation of 1:1, 1:2 and 1:3 (aluminium.ferron) complexes. In the presence of CTMAC, on the other hand, the average number of moles of ferron bound per mole of aluminium increases very steeply as the ferron concentration reaches a critical level, and approaches 3 at a lower ferron^{2-} concentration than in the absence of CTMAC. There was no indication of the formation of 1:1 and 1:2 complexes. It is therefore concluded that CTMAC increases the stability of the 1:3 complex, relative to that of the 1:1 and 1:2 complexes. This is easily understood if it is considered that the

1 3 complex has the highest negative charge and will be the most stabilized by the positively-charged micelles of quaternary ammonium cations

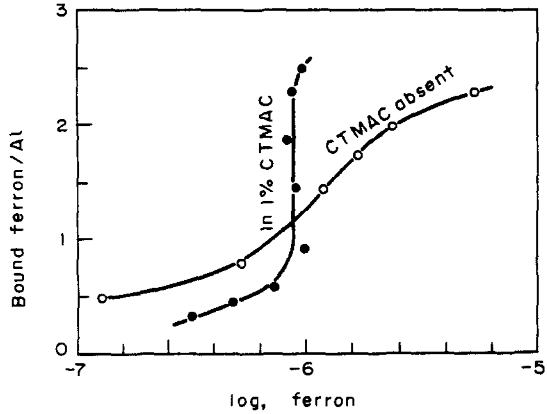


Fig 7 Average number of moles of ferron bound per mole of aluminium as a function of ferron^{2-} concentration (1 M KCl present)

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Resume—La reproductibilite de la methode au ferron pour l'aluminium a ete grandement amelioree par l'addition de chlorure de cetylmethylammonium (CTMAC) L'amélioration est attribuée a une reduction du temoin du reactif et a une stabilité accrue de Al(ferron)$_3^{3-}$ Le complexe aluminium-ferron forme en la presence de CTMAC a un pic d'absorption a 385 nm L'interférence du fer peut être éliminee par l'application d'une correction basee sur la mesure à deux longueurs d'onde

Zusammenfassung—Die Reproduzierbarkeit des Ferronverfahrens zur Aluminiumbestimmung wurde durch Zugabe von Cetyltrimethylammoniumchlorid (CTMAC) stark verbessert Die Verbesserung wird auf die Verkleinerung des Blindwertes und auf erhohte Stabilitat von Al(ferron)$_3^{3-}$ zuruckgefuhrt Der in Gegenwart von CTMAC gebildete Aluminium-Ferron-Komplex hat ein Absorptionsmaximum bei 385 nm Die Storung durch Eisen kann vermieden werden indem man eine Korrektur anbringt die auf der Messung bei zwei Wellenlangen beruht

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DETECTION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH DIMEDONE DIOXIME

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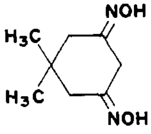
Summary—Dimedone dioxime forms coloured complexes only with cobalt, nickel and copper ions in alkaline solution Acidification and solvent extraction enables cobalt (1–50 μg) to be determined spectrophotometrically without interference A specific spot test for cobalt is based on the same reaction

Compounds with the 1,2-dioxime grouping have received a great deal of attention as analytical reagents The mechanism of their reactions with metal ions has been studied in detail Compounds with the 1,3-dioxime grouping, however, have received very little attention, probably because the dioxime groups are too far apart to form chelates with metal ions It should be appreciated, however, that although the formation of a chelate ring confers added stability on a complex, complexes that do not contain chelate rings are not necessarily unstable, and may also possess many other desirable analytical qualities, such as high molar absorptivity, rapid and selective formation, and solubility in water or organic solvents



(I)

Dimedone (5,5-dimethylcyclohexane-1,3-dione) is readily oximated to give a 1,3-dioxime (I) This paper describes the synthesis of the dioxime, the investigation of its reactions with metal ions and the consequent development of specific and sensitive methods for the detection and spectrophotometric determination of cobalt, and shows that a 1,3-dioxime is a useful chromogenic reagent

Reagent

Dimedone dioxime is a white, crystalline compound, m.p 170°, readily soluble in most organic solvents, including alcohols and chloroform, it is also soluble in alkaline aqueous solutions, but is sparingly soluble in water

Reactions with metal ions

The reagent was tested for reactions with 19 metal ions Mg^{2+}, Co^{2+}, UO_2^{2+}, Al^{3+}, Ni^{2+}, Ba^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Sn^{4+}, Pb^{2+}, Cd^{2+}, Th^{4+}, Pd^{2+}, Be^{2+}, Ti^{4+}

or Ag^+ (500 μg) were mixed with 2 ml of sodium acetate buffer solutions over a pH range of 4–9 and 2 ml of an 0·5% ethanolic solution of dimedone dioxime. After the mixtures had stood for half an hour, cobalt had formed an intense yellow colour, nickel a green colour and copper a pale green colour in solutions at pH 8 and 9 No other metal ions gave a visible reaction with the reagent, and no reactions were observed at lower pH values. Subsequent experiments showed that the nickel and copper reactions could easily be suppressed, so methods for the specific determination and detection of cobalt could be developed.

Development of a quantitative spectrophotometric method for cobalt

The absorption spectra of the reagent and its cobalt and nickel complexes are shown in Fig. 1. The cobalt complex has an absorbance maximum of 400 nm; that of the nickel complex is at 385 nm, whereas that of the reagent is in the ultraviolet and ends at 450 nm

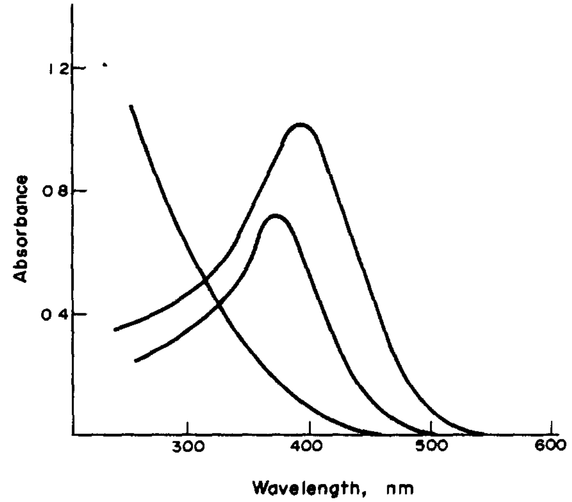


Fig 1 Absorption spectra of alkaline solutions of (*a*) Co^{2+} (50 μg), (*b*) Ni^{2+} (50 μg), obtained under the optimal conditions, after 30 min, (*c*) dimedone dioxime, (*d*) Co^{2+} (50 μg) after extraction

The absorbance given by the cobalt and nickel complexes increased with increasing pH This is illustrated in Fig. 2 Maximal colour development for cobalt is achieved at pH 9–9·5, which is obtained when 0·2 ml of 0·05 *M* sodium hydroxide solution is added to a very dilute aqueous solution of cobalt nitrate.

The reaction between cobalt or nickel and the reagent occurred slowly, 45 min being necessary for complete colour development in a solution containing 5 ppm of cobalt at the optimal alkalinity The colour remained stable for at least another 20 min In all subsequent experiments, therefore, the reaction mixture was allowed to stand for an hour The amount of reagent added also affected the degree of colour development for cobalt As shown in Table 1, a final reagent concentration of at least 0·2% is necessary for almost complete colour development.

On the basis of these results, it was possible to devise a procedure for the determination of cobalt in aqueous solution When measured at 400 nm, a linear calibration graph is obtained up to 50 μg of cobalt per 10 ml, but there is a positive intercept on the absorbance axis A rectilinear calibration graph, of only half the sensitivity but passing through the origin, is obtained by measuring the absorbance at 450 nm. The molar absorptivity is $2·30 \times 10^4$ l mole^{-1} cm^{-1} at 400 nm and $1·10 \times 10^4$ l.mole^{-1}.cm^{-1} at 450 nm in alkaline aqueous solution The sensitivity at 400 nm according to Sandell[1] is 0·0023 μg/cm^2

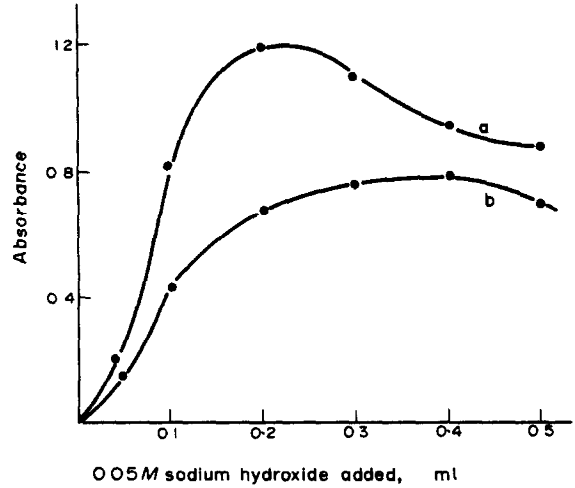


Fig 2 The effect of sodium hydroxide addition on the absorbance of aqueous solutions (pH 4) containing 50 μg of (*a*) cobalt, (*b*) nickel, final volume 10 ml

In the procedure developed for cobalt, ppm of nickel and copper give chromogenic reactions and therefore interfere It was found, however, that acidification of the solution of the coloured complexes immediately destroyed the nickel and copper complexes, but not that of cobalt A similar phenomenon is reported to occur with the nickel, copper and cobalt complexes of nitroso-R salt on addition of mineral acids[1] Addition of 0·2 ml of 0·1 *M* hydrochloric acid completely decolourized a 10-ml alkaline solution containing 50 μg of nickel as its dimedone dioxime complex, prepared by the recommended procedure. The cobalt complex was slowly destroyed (Table 2). There was also a marked immediate initial decrease in the absorbance of the cobalt complex and a shift in the absorbance maximum to 350–380 nm

Although the addition of hydrochloric acid removes the interference of nickel, the slow decomposition of the cobalt complex precludes precise measurement of the absorbance. Solvent extraction was investigated, therefore, as a means of stabilizing the cobalt complex The cobalt and nickel complexes were not extracted from the alkaline solution by chloroform, isoamyl alcohol or methyl isobutyl ketone, but the cobalt complex could be extracted into these solvents from an acidified solution The nickel complex could also be extracted from suitably dilute acidic solutions The effect of various concentrations of hydrochloric acid on the absorbance of the extract is shown in Fig 3. It shows that some extraction of the nickel complex occurs at low acidity, but the effect of nickel is completely

Table 1 Effect of reagent concentration on the absorbance of the cobalt complex at 400 nm

Reagent, *ml**	0·0	0·1	0·2	0·4	0·8	1·0	1·5	2·0	4·0
Absorbance	0·00	0·40	0·82	1·20	1·60	1·65	1·70	1·75	1·80

* In 10 ml of solution containing 50 μg of cobalt and 0·2 ml of 0·5 *M* sodium hydroxide

Table 2 Effect of time on the absorbance of an acidified solution of the cobalt complex

Time, *min*	0·0	10	20	30	40	60	80
Absorbance* at 370 nm	0·66†	0·46	0·40	0·35	0·34	0·30	0·28

* Absorbance of 50 μg of cobalt after addition of 0·2 ml of 0·1 *M* hydrochloric acid to the alkaline test solution prepared according to the recommended procedure

† Absorbance before acidification = 1·65

eliminated by addition of sufficient acid. The molar absorptivity of the cobalt complex is similar to that measured initially in the acidified solution The absorbance maximum in methyl isobutyl ketone is at 370–380 nm (Fig. 1). On the basis of these results a procedure was developed for the determination of 1–50 μg of cobalt by use of acidification and solvent extraction. The molar absorptivity is 1·13 × 10^4 l mole^{-1} cm^{-1} and the Sandell sensitivity 0·0057 $\mu g/cm^2$

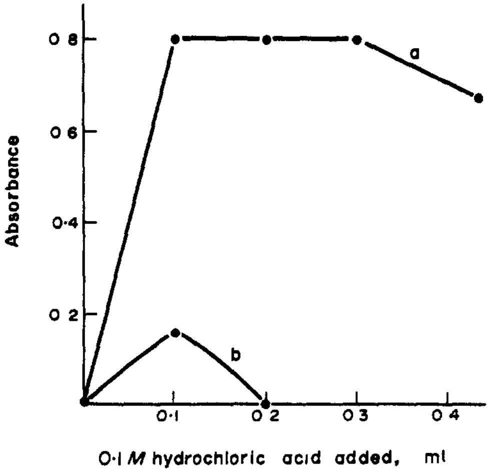


Fig. 3 The effect of hydrochloric acid addition on the absorbance of (*a*) Co^{2+}, (*b*) Ni^{2+} complexes in methyl isobutyl ketone

The effect of nickel on the absorbance of the cobalt complex when the extraction procedure is used is shown in Table 3 At least 50 μg of nickel are without effect. Analysis of synthetic cobalt and nickel mixtures confirms these results (Table 4)

There was no interference from 50 μg of the following species on the determination of 25 μg of cobalt: Cu^{2+}, Mg^{2+}, UO_2^{2+}, Ca^{2+}, V(V), Zn^{2+}, Cd^{2+} and Fe^{2+}, but when metals that combine with hydroxyl ions are present, care should be taken that more alkali is

Table 3 Effect of nickel on the cobalt absorbance (extraction procedure)

Nickel conc *µg/10 ml*	Absorbance of 10 *µg* Co	25 *µg* Co
0·0	0·185	0·425
10	0·184	0·425
30	0·186	0·430
50	0·190	0·431

added to raise the pH to 9 0–9 5. Similarly, precautions must be taken with hydrogen phosphate and other protonated anions Tartrate (0 5 mg), citrate (0·3 mg), nitrate (0 2 mg), acetate (0·15 mg), sulphate (0 25 mg) and phosphate (0 5 mg) ions did not interfere in the determination of 50 μg of cobalt, but 100 μg of cyanide ions almost completely destroyed the cobalt complex

Table 4 Determination of cobalt in the presence of nickel

Taken, μg		Co found,
Co	Ni	μg
30 0	30	30 0
10 0	40	10 3
20 0	50	20 0
25 0	30	25 3
15 0	40	15 3
5 0	50	5 0

Development of a specific spot test for cobalt

The reaction between cobalt and dimedone dioxime can be used to provide a rapid, sensitive and specific test for cobalt Although the cobalt complex forms slowly at room temperature, formation is almost complete within 1 min if the solution is heated to 60° The interferences of nickel and copper may again be removed by acidifying the solution after complex formation The nickel and copper complexes are destroyed immediately, but the cobalt complex dissociates only slowly; its colour persists for at least 2 hr. If the cobalt complex is extracted from the acidic solution into methyl isobutyl ketone, the complex is even more stable

The behaviour of numerous ions was investigated, using the test procedure described below. The ions investigated were those studied in the preliminary tests (above) and Cr^{3+}, Zr^{4+}, Hf^{4+}, In^{3+}, NH_4^+, phosphate, citrate, tartrate and acetate The only visible reactions in the alkaline solution were that cobalt gave a yellow colour and nickel and copper gave green colours; only the cobalt complex remained on acidification and no other colour developed The tolerance of the test procedure to other ions is summarized in Table 5

Table 5 Tolerance of cobalt test to other ions

Cobalt μg	Other ion, μg	Cobalt μg	Other ion, μg
50	Ni^{2+}(100)	10	Zn^{2+} (100)†
50	Ni^{2+}(500)*	10	. V(V) (100)†
50	NH_4^+(500)	10	$H_2PO_4^-$(500)
20	Cu^{2+}(50)†	5	Mg^{2+}(100)
20	Al^{3+}(100)†	5	Cd^{2+}(50)†
10	Ca^{2+}(200)	5	citrate (500)
10	Ni^{2+}(100)*	5	tartrate (500)
10	Fe^{2+}(50)†	5	acetate (500)

* On addition of 0 8 ml of 0 1 *M* hydrochloric acid

† 6–10 drops of the sodium hydroxide solution required to bring the pH to 9

Larger amounts of hydrolysable ions can also be tolerated if more alkali is added to raise the pH to above 9.

Nature of the complex

The cobalt:ligand ratio in alkaline solution was measured by Job's[2,3] method and the mole ratio method.[4] Job's method indicated the formation of 1:1 and 1.6 cobalt:ligand complexes (Fig. 4). The mole ratio plot showed the formation of only a 1.6 complex. When in sufficiently high concentration, therefore, dimedone dioxime (HL) must act as a unidentate ligand. As complex formation occurs only in alkaline solution, the oxime anion L^- is probably the binding species. Thus in alkaline solution the complex is probably (CoL_6^{4-}). The anionic nature of the complex precludes extraction from alkaline solution

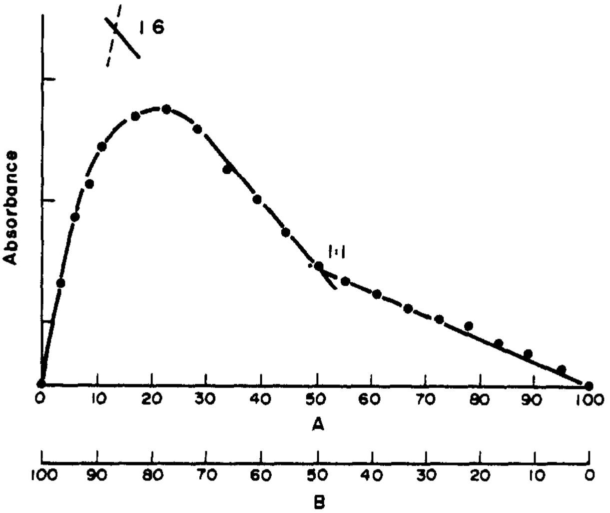


Fig 4 Job plot for the cobalt complex, measured at 400 nm and corrected for reagent absorbance A = ml of $10^{-3}M$ Co^{2+}, B = ml of $10^{-3}M$ reagent

Acidification immediately decreases the absorbance to 36% of its initial value (Table 2). An extractable, and therefore uncharged, species is formed. The two-thirds reduction in absorbance roughly indicates the loss of four ligands, so that the uncharged complex could be CoL_2. Prolonged contact with the acid causes further, slow, breakdown of the complex:

$$CoL_2 + 2H^+ \rightarrow Co^{2+} + 2HL$$

Conclusion

The method proposed is highly selective for cobalt. It is sensitive, and the reagent, although not yet commercially available, is easy to synthesize from simple chemicals. A comparison with some other reagents is included (Table 6). Nitroso-R salt is the most sensitive reagent, but is experimentally difficult to use in that it needs accurately controlled heating to achieve reproducible complex formation

The spot test is sensitive and is specific for cobalt. It uses a simple reagent, can be carried out rapidly, and is unaffected by much larger amounts of most ions. Few other tests for cobalt have the advantages of the present one. The common tests[5] with α-nitroso-β-naphthol, thiocyanate and rubeanic acid lack specificity, and only the rather time-consuming

Table 6 Comparison of dimedone dioxime with some other spectrophotometric reagents for cobalt

Reagent	Wavelength *nm*	Molar absorptivity *l mole⁻¹ cm⁻¹*	Sandell sensitivity *µg/cm²*	Interferences	Refs
Nitroso-R	420	3.40×10^4	0.0019	—	1
salt	520	1.40×10^4	0.0042	—	1
2-Nitroso- 1-naphthol	530	1.40×10^4	0.0042	Pb^{2+}, Fe^{2+}	1
Thiocyanate ion	620	1.00×10^3	0.055	Cu^{2+}, Bi^{3+}, Cr^{3+} Ni^{2+}, Fe^{3+}	1
Isonitroso- dimedone	374	1.97×10^4	0.0030	Fe^{2+} Cu^{2+}, Cr^{3+} Ni^{2+}	8
Furil α-dioxime	350	1.86×10^4	0.0032	Cu^{2+}, Ni^{2+}, Fe^{2+} Pb^{2+}, Ag^{+}	9
2,2′-Dipyridyl ketoxime	388	1.95×10^4	0.0030	Fe^{2+}, Fe^{3+}, Cu^{2+} Pb^{2+}	10
Dimedone	400	2.30×10^4†	0.0023	Cu^{2+}, Ni^{2+}	
dioxime*	380	1.13×10^4‡	0.0057	—	

* Present work
† Alkaline solution
‡ Solvent extraction procedure

test with nitroso-R salt in an ion-exchange resin[5] will detect smaller concentrations of cobalt. The *p*-nitrophenylhydrazone of diacetylmonoxime[6] provides a selective but less sensitive test for cobalt but the same derivative of 3-isonitrosopentane-2-one[7] gives a specific reaction as sensitive as the present test. The reagent, however, is more difficult to prepare.

EXPERIMENTAL

Synthesis of dimedone dioxime

Dimedone (20 g) was dissolved in ethyl alcohol (100 ml) in a round-bottomed flask. A solution of hydroxylammonium chloride (20 g) in 15 ml of water was adjusted to pH 6.5–7.5 with sodium carbonate, and mixed with the dimedone solution. The mixture was heated under reflux on a boiling water-bath for about 2 hr. Sufficient water was then added to dissolve the sodium chloride formed and the mixture was evaporated to 50–60 ml. The solution was left overnight to allow complete crystallization. The crystals were filtered off, washed with water and dried under vacuum on a hot-plate at 60°. The product was recrystallized twice from 50% aqueous ethyl alcohol. The crystals were small white needles (m.p. 170°). Analysis: found C, 56.6%, H, 8.0%, N, 16.3%, calculated for $C_8H_{14}N_2O_2$: C 56.4%, H, 8.2%, N 16.4%.

Dimedone dioxime is readily soluble in alcohols, chloroform and alkaline aqueous solutions, but is sparingly soluble in water.

Determination of cobalt

In alkaline solution. To a 10-ml volumetric flask add an appropriate amount (<5 ml) of test solution containing 0–50 µg of cobalt followed by 4 ml of 0.5% dimedone dioxime solution in ethyl alcohol and 0.20 ml of 0.05*M* sodium hydroxide and dilute to 10 ml with distilled water. Allow the solution to stand for 1 hr and measure its absorbance at 400 nm in 1-cm cells against a similar solution to which no cobalt has been added. Prepare a calibration graph in a similar manner from solutions containing 2.5–50 µg of cobalt.

By solvent extraction To a 100-ml separating funnel add an appropriate amount ($\leqslant 5$ ml) of test solution containing 1–50 μg of cobalt, followed by 4 ml of 0 5% dimedone dioxime solution and 0 2 ml of 0 05*M* sodium hydroxide solution. Make up to 10 ml with water, and allow to stand for an hour Add 4 ml of methyl isobutyl ketone and 0 2 ml of 0 1*M* hydrochloric acid, and shake well for 1 min to extract the cobalt complex After removal of the organic layer, add another 4 ml of the organic solvent, shake again for 1 min and remove the organic layer Combine the extracts, and make up to 10 ml with the same solvent Measure the absorbance at 380 nm in 1-cm cells against a similar extract of a solution to which no cobalt had been added Prepare a calibration graph in a similar manner

Detection of cobalt

Treat successively in a semimicro test-tube a few drops of the test solution with a few drops of a saturated solution of the reagent in ethyl alcohol Add a few drops of water followed by 2 or 3 drops of 0 05*M* sodium hydroxide and heat for 0 5 min in hot water (60°) Add six drops of methyl isobutyl ketone followed by four drops of 0 1 *M* hydrochloric acid and shake the mixture well A yellow extract indicates cobalt A green colour formed in the aqueous alkaline solution but destroyed on acidification indicates copper or nickel

Identification limit 0·5 μg of cobalt.

Dilution limit. 1 2 $\times 10^6$

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Résumé—La dioxime de la dimedone forme des complexes colores seulement avec les ions cobalt, nickel et cuivre en solution alcaline L'acidification et l'extraction par solvant rend possible la détermination spectrophotométrique du cobalt (1–50 μg) sans interférence Un essai à la touche spécifique du cobalt est basé sur la même reaction

Zusammenfassung—Dimedondioxim bildet nur mit Kobalt-, Nickel- und Kupferionen in alkalischer Losung farbige Komplexe Ansauern und Extraktion erlauben eine storungsfreie spektrophotometrische Bestimmung von 1–50 μg Kobalt. Auf der selben Reaktion beruht eine spezifische Tupfelprobe fur Kobalt

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ACID EQUILIBRIA OF SEMI-METHYLTHYMOL BLUE AND FORMATION CONSTANTS OF COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES WITH SEMI-METHYLTHYMOL BLUE

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Summary—Potentiometric and spectrophotometric studies on Semi-Methylthymol Blue (SMTB or H_4L) have been performed. The acid–base and Co(II), Ni(II), Cu(II) and Zn(II)–ligand reaction stoichiometries were determined, and the formation constants of the corresponding proton and metal complexes, and the molar absorptivities were calculated. Evidence was found for the formation of 1:1 Co(II), Ni(II) and Cu(II) complexes, and 1:1 and 1:2 Zn(II) complexes. Cu(II) formed the hydroxo-complex, $Cu(OH)L^{3-}$ but no hydroxo-complexes of the other metal ions were observed. Suggestions are made concerning the probable structure of the complexes.

The mono-substituted product Semi-Methylthymol Blue, 3[*N*,*N*′-di(carboxymethyl)-aminomethyl]thymolsulphonphthalein (SMTB)[1,2] is also synthesized when Methylthymol Blue, 3,3′-bis[*N*,*N*′-di(carboxymethyl)aminomethyl]thymolsulphonphthalein (MTB)[1] is prepared. Earlier,[2] we separated SMTB from MTB, and pointed out its utility as a complexometric reagent and photometric indicator for the determination of a number of metal ions.

Although there have been many investigations of MTB and its metal complexes, we have not found accounts of the dissociation equilibria of SMTB and of its metal complexes. The present work remedies this lack of information.

EXPERIMENTAL

The procedures, apparatus and reagent solutions were those used previously,[3] together with SMTB which was purified[2] by cellulose column chromatography and ion-exchange by the batch method. The product was the free acid form of SMTB [m.p. 198–199° (decomp.), found C, 61.1%, H, 6.4%, N 2.1%, calculated for $C_{32}H_{37}O_9NS \cdot H_2O$: C 61.04%, H 6.24%, N, 2.22%]. The purity of the SMTB, determined by potentiometric titration, was nearly 100%.

RESULTS AND DISCUSSION

Formation constants of SMTB

Absorption spectra of SMTB (H_4L) at differing pH values are shown in Fig. 1 and the potentiometric titration of SMTB is shown in Fig. 2. Two protons per ligand molecule may dissociate between $a = 0$ and $a = 2$ (where a = moles of base added per mole of ligand). At higher pH region two more protons may dissociate, one between $a = 2$ and $a = 3$, and the other above $a = 3$. Between pH 2·5 and 6·6, the absorption curves are almost identical, indicating dissociation of two protons from the carboxyl groups. In alkaline medium the equilibrium between the yellow and the purple blue SMTB corresponds to dissociation of a proton from the phenol group. Above pH 10, the colour changes from

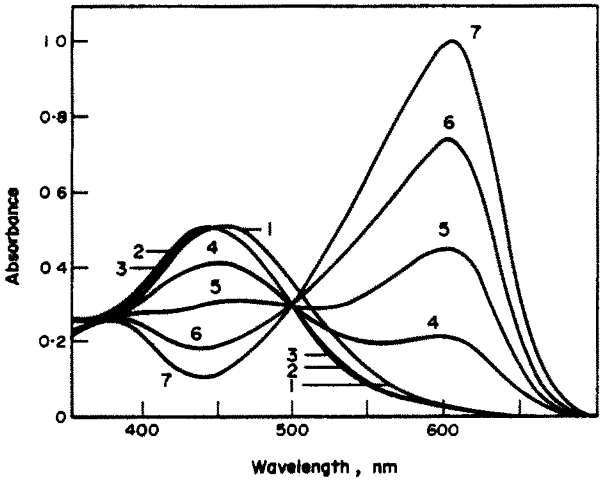


Fig. 1 Absorption spectra of SMTB at different pH values
$T_L = 2\ 83 \times 10^{-5}\ M$, pH. *1*—1 84, *2*—2 81, *3*—5 09, *4*—7 71, *5*—10 17, *6*—12 33, *7*—13 52

light blue to deep blue, but that of Thymol Blue does not, so this involves the dissociation of the proton of the quaternary iminodiacetate group (derived by proton transfer from the sulphonic acid group).

The four acid formation constants and the molar absorptivities are calculated by means of the methods given previously,[4] and are tabulated in Table 1

Potentiometric investigations of metal complexes

Potentiometric titration of each metal, SMTB, and 1.2, 1:1 and 2 1 molar ratios of each metal to SMTB were performed. The results for the 1·1 molar ratio of Co(II), Ni(II), Cu(II) and Zn(II) to SMTB are presented in Fig. 2.

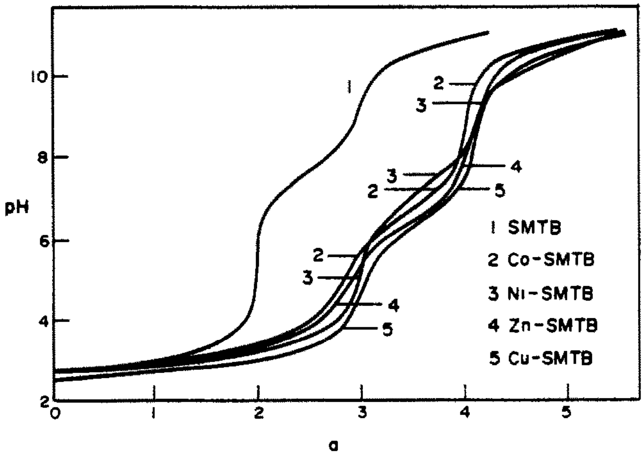


Fig 2 Potentiometric titration curves of SMTB in the presence of the following metal ions at 25 ± 0 1°C in 0 1 *M* KNO_3 solutions, *1*—SMTB alone, *2*—Co(II) SMTB (1 1), *3*—Ni(II) SMTB (1 1), *4*—Zn(II) SMTB (1 1), *5*—Cu(II) SMTB (1 1)
a = number of moles of base added per mole of SMTB T_L *1*—9 90 × 10^{-4} *M*, *2*—9 91 × 10^{-4} *M*, *3*—9·25 × 10^{-4} *M*, *4*—9 43 × 10^{-4} *M*, *5*—9 29 × 10^{-4} *M*, T_M *2*—9 09 × 10^{-4} *M*, *3*—8 39 × 10^{-4} *M*, *4*—1 07 × 10^{-3} *M*, *5*—9 62 × 10^{-4} *M*

Table 1 Acid formation constants, wavelengths of absorption maxima and molar absorptivities of SMTB

Ion	Wavelength λ_{max}, *nm*	Absorptivity, 10^4 *l mole*$^{-1}$ *cm*$^{-1}$	Equilibrium constant, log *k*
H_4L	452	1.79	
			2.0*
H_3L^-	452	1.79	
			2.81*
H_2L^{2-}	447	1.77	
			7.61* 7.60
HL^{3-}	603	1.64	
			12.12
L^{4-}	607	3.65	

* Data measured by means of pH titration at 25 ± 0.1°C, $\mu = 0.1$ (KNO_3), the rest by means of spectrophotometry at room temperature, $\mu = 0.1$ (KNO_3)

Each curve consists of two well-defined buffer regions, a long one terminated by a sharp inflection at $a = 3$ and the other between $a = 3$ and $a = 4$, indicating the formation of a reasonably stable monoprotonated metal chelate species.

For the 2:1 metal ligand system, hydrolysis of free metal ion takes place beyond $a = 4$, corresponding to the pH region where each metal hydroxide precipitates. The extent of the buffer region for the hydrolysis of the free metal ion indicates that not more than one ion can combine with one SMTB molecule.

The average numbers of proton,[5,6] ligand[7] and hydroxyl ions[8] bound to the complexes were evaluated from potentiometric data as described previously.[3] The results suggested the presence of three complex species, MH_2L, MHL^- and ML^{2-}, for Co(II) and Ni(II), of four species, MH_2L, MHL^-, ML^{2-} and ML_2^{6-}, for Zn(II) and of three species, MHL^-, ML^{2-} and $M(OH)L^{3-}$, for Cu(II).

The formation constants of these metal complexes were calculated from mass balances and electroneutrality, utilizing the successive approximation method described in detail previously[3] and are listed in Table 2.

Spectrophotometric investigations of complexes

The absorption spectra of SMTB solutions containing 2:1 mole ratio of Co(II), Ni(II), Cu(II) and Zn(II) to SMTB at different pH values were measured between 350 and 700 nm.

Table 2 Formation constants of zinc(II), copper(II), nickel(II) and cobalt(II) complexes with SMTB at 25 ± 0.1°C $\mu = 0.1$ (KNO_3)

Reaction		Log *k* Co(II)	Ni(II)	Cu(II)	Zn(II)
$M^{2+} + L^4 \rightleftharpoons ML^{2-}$	K^M_{ML}	12.75	12.37	13.5	12.92
$M^{2+} + HL^{3-} \rightleftharpoons MHL^-$	K^M_{MHL}	7.16	7.26	7.7	6.99
$M^{2+} + H_2L^{2-} \rightleftharpoons MH_2L$	$K^M_{MH_2L}$	2.52	2.14		3.03
$M^{2+} + 2L^{4-} \rightleftharpoons ML_2^{6-}$	$K^M_{ML_2}$				19.94*
$ML^{2-} + OH^- \rightleftharpoons M(OH)L^{3-}$	$K^{OH}_{M(OH)L}$			3.6†	
$MHL^- \rightleftharpoons ML^{2-} + H^+$	K^H_{MHL}	6.53	7.00	6.3	6.20
$MH_2L \rightleftharpoons MHL^- + H^+$	$K^H_{MH_2L}$	2.90	2.48		3.24

* Data measured by Bjerrum's method

† Data determined by means of spectrophotometry at room temperature

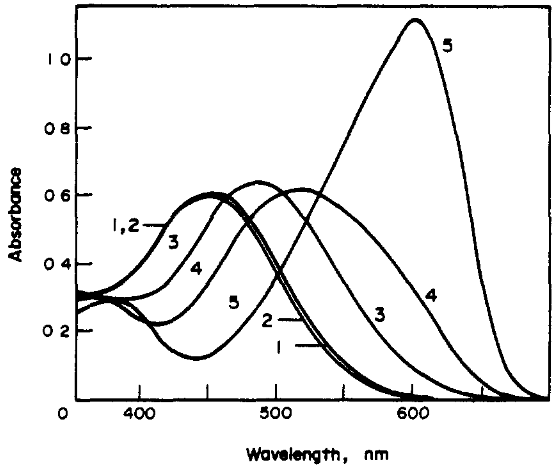


Fig 3 Absorption spectra of Zn(II)-SMTB complexes at different pH values T_{Zn} = 8 60 × 10^{-5} *M*, T_L = 3 84 × 10^{-5} *M* pH *1*—1 83, *2*—3 09, *3*—5 57, *4*—9 10, *5*—13 57

Among these metals, Zn(II), Co(II) and Ni(II) behave similarly and Cu(II) differently. The results for Zn(II) and Cu(II) are compared in Figs. 3 and 4.

Zn(II), Co(II) and Ni(II) complexes Below pH 12, the Zn(II), Co(II) and Ni(II) complexes show similar patterns of the absorption spectra The pH ranges and the wavelengths at the absorption maximum for the respective spectrum bands are presented in Table 3, together with the complex species which are discussed below. In the case of Zn(II), the changes in the absorbances at the maximum wavelengths of 448, 485 and 517 nm are plotted against pH in Fig. 5 The mole-ratio methods were used to investigate the composition of the metal complexes formed in the pH ranges tabulated in Table 3 The combining molar ratios for each metal ion are 1:1 at each pH, except for Zn(II) at pH 10·0 (1.1 and 1:2) These facts may indicate the presence of four Zn(II) complexes, MH_2L, MHL^-, ML^{2-} and ML_2^{6-}, and that of three Co(II) and Ni(II) complexes, MH_2L, MHL^- and ML^{2-}, below pH 12.

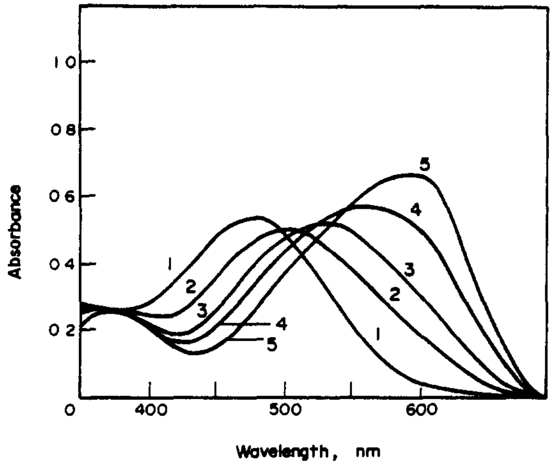


Fig 4 Absorption spectra of Cu(II)-SMTB complexes at different pH values T_{Cu} = 6 93 × 10^{-5} *M*, T_L = 2 64 × 10^{-5} *M*, pH *1*—4 00, *2*—6 55, *3*—8 98, *4*—12 13, *5*—13 55

Table 3 pH range of existence, wavelength maximum and absorptivity of each species of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes with SMTB

	pH range of existence				Wavelength λ_{max}, *nm*				Absorptivity, 10^4 *l mole*$^{-1}$ *cm*$^{-1}$			
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
MH_2L	2.5–3.5	2.0–3.2		2.7–3.6	447	451		448	1.60	1.81		1.59
MHL^-	5.0–6.2	4.0–6.2	2.2–5.4	5.1–6.3	477	480	475	485	1.62	2.10	2.04	1.69
ML^{2-}	8.3–12.0	8.2–12.2	7.6–10.0	8.0–12.0	590	598	525	517	2.23	3.07	2.03	1.62
$M(OH)L^{3-}$			10.0–11.0				558				2.14	

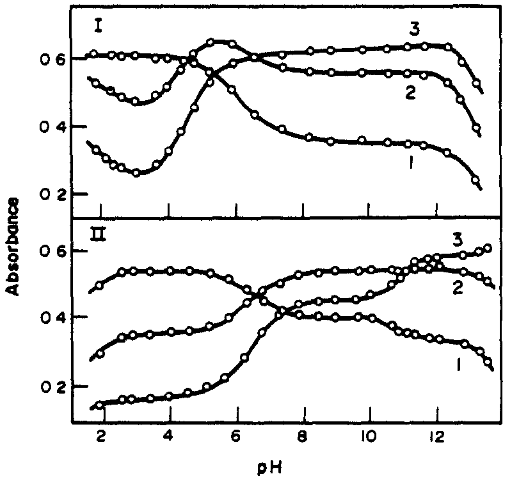


Fig 5 Absorbance of Zn(II), Cu(II)-SMTB complexes as function of pH
I Wavelength *1*—448 nm, *2*—485 nm, *3*—517 nm, $T_{Zn} = 8\,60 \times 10^{-5}\,M$, $T_L = 3\,84 \times 10^{-5}\,M$ II Wavelength *1*—475 nm, *2*—525 nm, *3*—558 nm, $T_{Cu} = 6\,93 \times 10^{-5}\,M$, $T_L = 2\,64 \times 10^{-5}\,M$

Below pH 3·0 the absorption band for Zn(II) shifts slightly to shorter wavelength with increasing pH as shown in Fig. 3. The bands for Co(II) and for Ni(II) also shift, below pH 2·8 and 2 5 respectively. Moreover, the spectra for these pH ranges are similar to those of SMTB solutions at pH 4–6·5 where the acid species H_2L^{2-}, which is formed by dissociating two protons from carboxyl groups, predominates. It may be suggested that the initial displacement of the two protons to form the complex MH_2L involves the removal of two protons from the carboxyl groups, and these metal ions combine with the oxygen atoms of these groups. Accordingly the spectra would not change greatly.

With increase of pH from the value stated above for each metal, the spectrum band shifts to longer wavelength and the solution colour changes from yellow to orange, and the absorption of the Zn(II) complex at 485 nm becomes maximum at pH 5·57 as shown in Fig. 5. The absorption of Ni(II) at 480 nm becomes maximum at pH 5 05, and that of Co(II) (at 477 nm) at pH 5·01 These pH values correspond to those at the first inflection points, which are at $a = 3$ in the potentiometric titration curves shown in Fig. 2. These changes of the spectra may therefore indicate that the dissociation of a proton from the complex MH_2L and the formation of the complex MHL^- is complete at the pH values stated The small change in colour of the solution may lead to the assumption that the conversion from MH_2L to MHL^- is accompanied by the dissociation of the proton which bonds to the nitrogen atom of the iminodiacetate group, and that the metal combines with the nitrogen atom. This assumption may be supported by the facts that the formation constants of the SMTB complexes MHL^- for Co(II) and Zn(II) are almost the same as the corresponding values for iminodiacetic acid,[9] even though the values for Ni(II) are slightly different, as shown in Table 4.

Above about pH 5, new bands appear near 520 nm for Zn(II), and the absorbance increases with increase of pH and remains constant about pH 8–12 as shown in Fig. 5 Also, bands occur at 590 and 600 nm for Co(II) and Ni(II) respectively, and these metal complexes behave like the Zn(II) complex. Each solution is red-purple near pH 6, and purple-blue above pH 7 It seems obvious that a proton of the phenol group dissociates, to yield the complex ML^{2-}, the metal ion combining with the oxygen atom of the phenol group Above pH 8, formation of the complex ML^{2-} is complete and no new complex species form up to pH 12

Cu(II) complexes Below pH 13, the Cu(II) complexes show similar patterns of absorbance change, and the maximum wavelengths and pH ranges are listed in Table 3 The mole-ratio method shows that the Cu(II)–SMTB complexes formed in the pH ranges listed in Table 3 are all 1 · 1

Although the other three metal ions show two patterns of absorbance change, the Cu(II) complex shows only one and the curve shifts slightly to longer wavelength with increase of pH from 2 to 5. The solution is orange It may be considered that the diprotonated complex is not formed and the initial complex formed is MHL^-

Above pH 5 the band shifts to longer wavelengths and the spectrum becomes broad as shown in Fig 4; the absorbance at 525 nm increases with increase of pH as shown in Fig. 5 The colour of the solution changes from orange to red-purple This change may correspond to the conversion from MHL^- to ML^{2-} Above pH 8 the spectrum changes very little The behaviour of the spectrum indicates the same type of MHL^- and ML^{2-} complexes for Cu(II) as for the other three metal ions

With increase of pH above 10, the spectrum band becomes broader and the absorbance at 558 nm increases (Figs 4 and 5) up to pH 11·5 and then becomes almost constant. This behaviour is not observed with the other three metal ions The formation of a new complex species may be considered, shown by the mole-ratio method to be 1.1 The equilibrium for the formation of this complex may be represented by

$$\mathrm{CuL}^{2-} + n\mathrm{OH}^- \rightleftharpoons \mathrm{Cu(OH)}_n\mathrm{L}^{(2+n)-}, \quad K^{\mathrm{OH}}_{\mathrm{Cu(OH)}_n\mathrm{L}} = \frac{[\mathrm{Cu(OH)}_n\mathrm{L}]}{[\mathrm{CuL}]\,[\mathrm{OH}]^n}$$

The plot of $\log[\mathrm{Cu(OH)}_n\mathrm{L}]/[\mathrm{CuL}]$ *vs* pOH gave a straight line with slope $n = 1$ and $K^{\mathrm{OH}}_{\mathrm{Cu(OH)L}}$ was evaluated graphically from the pOH value obtained when the log term was equal to zero[10]

As the pH is increased above pH 13, the spectrum for each metal ion complex becomes almost the same as that of SMTB, which indicates that in strongly alkaline medium the complexes are unstable and dissociate to give the metal hydroxide and L^{4-}

From the absorption spectra, the absorption maxima and the molar absorptivities were obtained and are tabulated in Table 3

Stabilities and geometrical configurations of the complexes

SMTB is a branched quadridentate ligand centred on the iminodiacetate nitrogen atom The stability constants of the Co(II), Ni(II), Cu(II) and Zn(II) complexes MHL^- and ML^{2-} for SMTB are listed in Table 4, together with the corresponding values for nitrilotriacetic acid (NTA),[11, 12] aminoethyliminodiacetic acid (AEIDA),[13] and 2,2′,2″-triaminotriethylamine (TREN)[14] which are branched quadridentate ligands of a type similar to SMTB

The trend of the metal co-ordination ability is NTA < SMTB(ML) ~ AEIDA < TREN The SMTB complex stabilities are roughly the same as those for AEIDA, though differences arise from metal to metal The difference in structure between SMTB and AEIDA is that the aminoethyl group of AEIDA is substituted by the sulphophthalein group Accordingly, the phenol oxygen atom may have almost the same affinity for metal

Table 4 Formation constants of transition metal complexes

Ligand (L)	Log K Cu(II)	Ni(II)	Zn(II)	Co(II)
IDA*	10.55	8.30	7.02	7.01
SMTB(MHL)†	7.7	7.26	6.99	7.16
NTA*	13.16	11.54	10.66	10.4
SMTB(ML)†	13.5	12.37	12.92	12.75
AMIDA§	15.90	13.73	11.93	11.78
TREN§	18.8	14.8	12.8	14.65

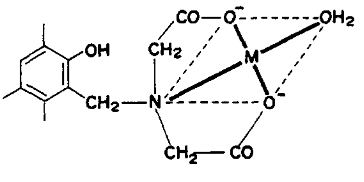
* $\mu = 0.1$, 30°
† $\mu = 0.1$, 25°
§ $\mu = 0.1$, 20°

ions as the aminoethyl nitrogen atom of AEIDA, that is, as an amino group of a polyamine, and this is a larger affinity than expected.

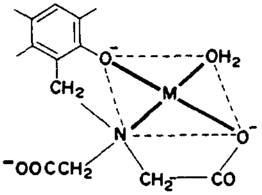
It is of interest that both the MHL^- and ML^{2-} SMTB complexes differ less in stability from metal to metal than those of the other chelating agents. Also, the stability order for ML^{2-} is Cu(II) > Zn(II) > Co(II) > Ni(II), but that for MHL^- is Cu(II) > Ni(II) > Co(II) > Zn(II). This is not the normal trend expected for the other ligands. These and some other properties of the complexes may be explained if the steric configurations and the co-ordination numbers of the metal ions are considered.

Figure 6 shows the variation of the absorbance of each metal–SMTB complex over the pH region in which the complex MHL^- may predominate. From it, the pH values can be obtained at which the complex MHL^- is formed and then by dissociation of a proton is converted into ML^{2-}. The Cu(II) complex MHL^- may be present over the widest pH range, the ranges being in the order Cu(II) > Ni(II) > Co(II) > Zn(II). This behaviour is that expected from the potentiometric titrations. The first inflections of the curves for Cu(II) and Ni(II) are sharper than those for Co(II) and Zn(II), as shown in Fig. 2. This may suggest that the sharper the inflection of the curve, the more stable the complex (MHL^-) and the wider the pH range in which it exists.

From the properties discussed above, Cu(II) and Ni(II) may take a planar configuration as in **I** and **II**.



CuHL⁻ or NiHL⁻ (I)



CuL²⁻ or NiL²⁻ (II)

It may be sterically impossible for the oxygen atom of the phenol group in **I** to be brought into a position *trans* to the nitrogen atom, because of being so far away from it. The result may be that one of the positions *cis* to the nitrogen atom is occupied by the phenol oxygen atom. Accordingly the conversion from MHL^- to ML^{2-} would be difficult to perform, and the complex MHL^- exist over a wide pH range. In the arrangement assumed, one of the carboxyl groups may remain unco-ordinated and SMTB func-

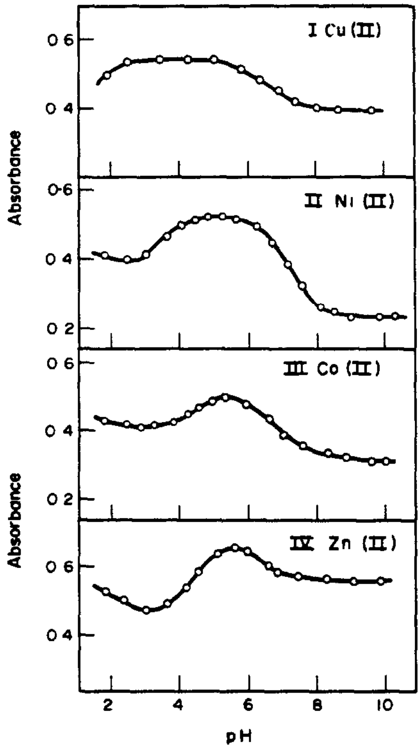
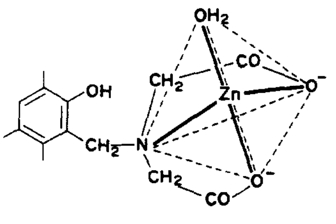


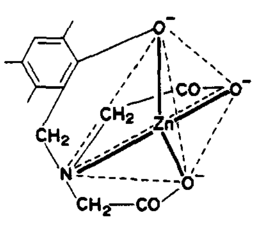
Fig 6 Absorbance of Co(II) Ni(II), Cu(II), Zn(II)-SMTB complexes as function of pH Wavelength I—475 nm, II—480 nm, III—477 nm, IV—485 nm T_L I—2.64 × 10^{-5} *M*, II—2.48 × 10^{-5} *M*, III—3.06 × 10^{-5} *M*, IV—3.84 × 10^{-5} *M* T_M I—6.93 × 10^{-5} *M*, II—5.27 × 10^{-5} *M*, III—6.43 × 10^{-5} *M*, IV—8.60 × 10^{-5} *M*

tion as a terdentate ligand, so that the stability constant of the ML^{2-} complex for Cu(II) and Ni(II) may not be as large as expected

For the structure of the quadridentate SMTB molecule, the most stable geometrical arrangement seems to be tetrahedral, in which one phenol oxygen atom and two carboxyl oxygen atoms co-ordinate without strain *cis* to the nitrogen atom and all available sites on the metal ion are occupied by the four groups of SMTB. The relatively high stability of the Zn(II) complex ZnL^{2-} and the narrow pH range where $ZnHL^-$ is predominant, may be attributed to the tetrahedral bonding as shown in **III** and **IV**. As seen in **III** the phenol oxygen atom of $ZnHL^-$ co-ordinates at an unoccupied site *cis* to the nitrogen atom without difficulty, to form ZnL^{2-} as shown in IV

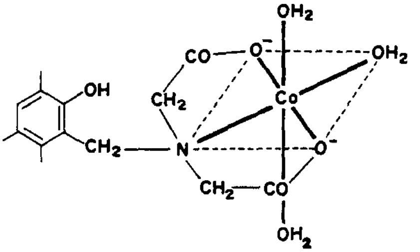


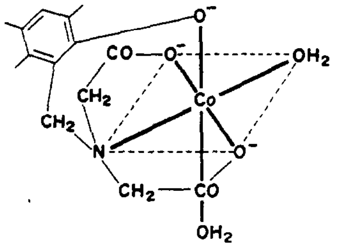
ZnHL⁻ (III)



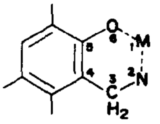
ZnL²⁻ (IV)

Co(II) may take an octahedral arrangement, which is normal for it, as shown in V and VI for the complexes $CoHL^-$ and CoL^{2-}, respectively.


$CoHL^-$ (V)


CoL^{2-} (VI)

The six-membered chelate ring, which involves the phenol oxygen atom, metal ion and nitrogen atom in the complex ML^{2-}, may be the most stable sterically when each bonding angle is 120° as shown in VII. For the octahedral CoL^{2-}, the positions 2 and 6 are oriented at angles of 90° to the central metal ion. The formation of the chelate ring may cause distortion of the octahedral configuration and reduce the stability On the other hand, a tetrahedral structure cannot arise without serious strain, because of the 109°28′ angles required For these reasons, the stability of ZnL^{2-} is slightly larger than that of CoL^{2-}, though that of $ZnHL^-$ is not



(VII)

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Résumé—On a effectue des études potentiometriques et spectrophotometriques sur le Bleu de Semi-Methylthymol (SMTB ou H_4L) On a détermine les stoechiometries de reaction acide-base et Co(II), Ni(II), Cu(II) et Zn(II)-coordinat et calculé les constantes de formation des complexes proton et metal correspondants, et les absorptivites molaires On a trouve des preuves en faveur de la formation de complexes 1 1 Co(II), Ni(II) et Cu(II), et de complexes 1 1 et 1 2 Zn(II) Cu(II) forme l'hydroxo-complexe, $Cu(OH)L^{3-}$ mais on n'a pas observe d'hydroxo-complexes des autres ions metalliques On fait des suggestions concernant la structure probable des complexes

Zusammenfassung—Semimethylthymolblau (SMTB oder H_4L) wurde potentiometrisch und spektrophotometrisch untersucht Die Stochiometrien der Reaktionen mit Sauren, Basen, Co(II), Ni(II), Cu(II) und Zn(II) wurde ermittelt und die Bildungskonstanten der entsprechenden Protonen- und Metallkomplexe sowie die molaren Extinktionskoeffizienten berechnet Es wurden Beweis fur die Bildung von 1 1-Komplexen mit Co(II), Ni(II) und Cu(II) sowie von 1 1- und 1 2-Komplexen mit Zn(II) gefunden Cu(II) bildete den Hydroxokomplex $Cu(OH)L^{3-}$, bei den anderen Metallionen wurden keine Hydroxokomplexe beobachtet Fur die wahrscheinliche Struktur der Komplexe werden Vorschlage gemacht

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ACID EQUILIBRIA OF METHYLTHYMOL BLUE AND FORMATION CONSTANTS OF COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES WITH METHYLTHYMOL BLUE

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Summary—Potentiometric and spectrophotometric studies on acid equilibria and reactions with Co(II) Ni(II) Cu(II) and Zn(II) for Methylthymol Blue (MTB) are described The equilibrium constants have been calculated MTB has been found to form 1 1 and 2 1 (mole ratio of metal to ligand) complexes, including protonated ones The probable configuration of the complexes and the effects on the stabilities have been discussed

Methylthymol Blue, 3,3′-bis[*N*,*N*′-di(carboxymethyl)aminomethyl] thymolsulphonphthalein (MTB or H_6L) was first introduced and purified by Korbl [1] MTB reacts with metal ions, and forms deep blue complexes It is an excellent metallochromic and photometric indicator for a number of metal ions in acid and alkaline solutions.

The acid dissociation constants of MTB have been reported by Korbl[2] and other workers,[3 4] but the MTB was not completely pure MTB purified according to Korbl's method contains some mono-substituted product SMTB,[5] 3-[*N*,*N*′-di(carboxymethyl)-aminomethyl] thymolsulphonphthalein MTB differs from SMTB in two important ways (*i*) the buffer region between the first and second inflection points on the potentiometric titration curve of MTB is at lower pH than that of SMTB[6] (pH at mid-point of the buffer region is 7·0 for MTB, 7·4 for SMTB), (*ii*) in alkaline solution, the wavelength of the absorption maximum of MTB is longer than that for SMTB[6] (617 nm for MTB, 601 nm for SMTB at pH 13 51) The titration curve of MTB (purified by the Korbl method[1]) showed a buffer region at higher pH than that for our MTB (mid-region pH about 7·4). Moreover, the earlier value of the wavelength at the absorption maximum of MTB in alkaline solution differs from ours (about 604 nm at pH 13·5) These facts suggest that the MTB purified by Korbl contained small amounts of SMTB and other impurities

Metal complexes with MTB have been studied by many investigators. Tikhonov[7] has reported that Co(II), Ni(II), Cu(II) and Zn(II) form 1 1 complexes with MTB, and Tataev[8] has reported the spectrophotometric properties of these metal complexes

In the previous work,[5] the separation and purification of MTB was reported In the present work, the acid equilibria of MTB and the reaction of four metal ions, Co(II), Ni(II), Cu(II) and Zn(II), and MTB in aqueous solutions from pH 1 5–14 are studied potentiometrically and photometrically The mechanism of the complex formation has been elucidated and the formation constants of the complexes are evaluated

EXPERIMENTAL

Reagents

MTB The reagent was synthesized and purified by means of cellulose column chromatography and batch ion-exchange.[5] Column ion-exchange results in adsorption of MTB on the resin. The purity of the product was established by elemental analysis, potentiometric titration, paper chromatography, and the absorption spectrum. The product was the free acid form of MTB [m.p. 252–256°(decomp.), found C, 56.0%, H, 6.1%, N, 3.5%. Calculated for $C_{37}H_{44}O_{13}N_2S \cdot 2H_2O$, C, 56.05%, H, 6.10%, N, 3.53%.] The purity, determined by potentiometric titration,[5] was 99.7%.

Stock solutions of metal ions, 0.01 *M*. Standardized with EDTA.

Buffers Standard solutions[9] were used. All reagents were analytical grade materials.

Procedure

Potentiometric and photometric measurements were performed as described previously.[9] The acid formation constants of MTB were calculated as in previous work.[10]

The formation constants of the metal complexes were calculated in two steps. In the first, it was assumed that only 1:1 complex species exist if the mole ratio of metal to ligand is 1:1 and the mixture is titrated with alkali, and that 2:1 complexes can be neglected, the formation constants of the 1:1 complexes were calculated from the "1:1" titration curve, and were then used to calculate the formation constants of the 2:1 complexes from a "2:1" titration curve. In the second step, both 1:1 and 1:2 complexes were taken into account in the "1:1" curve and the constants for the 1:1 complexes were corrected by using those of the 2:1 complexes, and these new values were used to calculate those of the 2:1 complexes from the "2:1" titration curve. These two steps were repeated until the no further change in the constants occurred.

The calculation was done with a modification of Schwarzenbach's[11] and Martell's[12,13] methods. In the mathematical treatment, T_L = total analytical concentration of ligand in all forms, T_M = total analytical concentration of metal ion in all forms, a = number of moles of base added per mole of ligand, k_i = formation constant of ligand, $k_i = [H_iL]/[H_{i-1}L][H]$, $K^M_{M_iH_jL}$ = successive formation constant of complex M_iH_jL, $K^M_{M_iH_jL} = [M_iH_jL]/[M][M_{i-1}H_jL]$, $K^H_{M_iH_jL}$ = formation constant of protonated complex M_iH_jL, $K^H_{M_iH_jL} = [M_iH_jL]/[M_iH_{j-1}L][H]$.

The formation constants of the 1:1 complexes were calculated from the mass balances and electroneutrality, utilizing the successive approximation method which was described in detail previously.[9]

For the system of ligand H_6L and metal ion M, in which the 1:1 complexes MH_iL ($i = 0, 1, \ldots, N$) and the 2:1 complexes M_2H_iL ($i = 0, 1, \ldots, M$) are formed, the analytical concentrations of ligand and of metal ion can be represented by equations (1) and (2), and electroneutrality gives equation (3)

$$T_L = \sum_{i=0}^{6} [H_iL] + \sum_{i=0}^{N} [MH_iL] + \sum_{i=0}^{M} [M_2H_iL] \tag{1}$$

$$T_M = [M] + \sum_{i=0}^{N} [MH_iL] + 2\sum_{i=0}^{M} [M_2H_iL] \tag{2}$$

$$(6 - a)T_L = [H] - [OH] + \sum_{i=1}^{6} i[H_iL] + \sum_{i=1}^{N} i[MH_iL] + \sum_{i=1}^{M} i[M_2H_iL] \tag{3}$$

Equations (1), (2) and (3) can be written in terms of [M], $[MH_nL]$ and $[M_2H_nL]$ as follows.

$$T_L = U_n[MH_nL]/[M] + V_n[MH_nL] + W_n[M_2H_nL] \tag{4}$$

$$T_M = [M] + V_n[MH_nL] + 2W_n[M_2H_nL] \tag{5}$$

$$T_H = X_n[MH_nL]/[M] + Y_n[MH_nL] + Z_n[M_2H_nL] \tag{6}$$

where

$$U_n = \sum_{i=0}^{6} [H]^i K_i/[H]^n K_n K^M_{MH_nL}, \quad V_n = \sum_{i=0}^{N} [H]^i K_i^1/[H]^n K_n^1$$

$$W_n = \sum_{i=0}^{M} [H]^i K_i^2/[H]^n K_n^2, \quad X_n = \sum_{i=1}^{6} i[H]^i K_i/[H]^n K_n K^M_{MH_nL}$$

$$Y_n = \sum_{i=1}^{N} i[H]^i K_i^1/[H]^n K_n^1, \quad Z_n = \sum_{i=1}^{M} i[H]^i K_i^2/[H]^n K_n^2$$

$$K_i = k_1 k_2 \quad k_i (K_0 = 1), \quad T_H = (6 - a) T_L - [H] + [OH]$$

$$K_i^1 = K^H_{MHL} K^H_{MH_2L} \quad K^H_{MH_iL} (K_0^1 = 1)$$

$$K_i^2 = K^H_{M_2HL} K^H_{M_2H_2L} \quad K^H_{M_2H_iL} (K_0^2 = 1)$$

The simultaneous equations (4), (5) and (6) are solved in the usual way for [M], [MH_nL] and [M_2H_nL], and the successive formation constant of the complex M_2H_nL is then given by

$$K^M_{M_2H_nL} = [M_2H_nL]/[M]\,[MH_nL] \; (n = 0\ 1 \qquad , M) \tag{7}$$

The value of $K^M_{M_2H_nL}$ was obtained by means of successive approximation The values of k_i, $K^M_{MH_iL}$ and $K^H_{MH_iL}$ obtained by the methods mentioned above were used to calculate the value of $K^M_{M_2H_nl}$ Equation (7) involves M formation constants of protonated complexes $K^H_{M_2H_iL}$ (i = 1, 2, , M) For a set of values assumed for $K^H_{M_2H_iL}$ the corresponding value of $K^M_{M_2H_nL}$ was calculated at points on the titration curve in a certain range of a values over which the complex M_2H_nL was assumed to be predominant The values for $K^H_{M_2H_iL}$ were varied and the set that gave minimum variation for $K^M_{M_2H_nL}$ was taken as correct and so was that value of $K^M_{M_2H_nL}$

In the second step the simultaneous equations (1), (2) and (3) were solved for [M] [H_nL] and [MH_nL] in the same way as for the complex M_2H_nL, and the formation constant of the complex MH_nL is given by

$$K^M_{MH_nL} = [MH_nL]/[M]\,[H_nL] \; (n = 0, 1, \qquad , N) \tag{8}$$

As for correction of $K^M_{MH_nL}$ by utilizing $K^M_{M_2H_iL}$ and $K^H_{M_2H_iL}$ obtained in the first step, a corrected value of $K^M_{MH_nL}$ was obtained from equation (8) by variation of the values for $K^H_{MH_iL}$ Then a corrected value of $K^M_{M_2H_nL}$ was calculated from equation (7), by utilizing the correct values of $K^M_{MH_iL}$ and $K^H_{MH_iL}$ These calculations were repeated until no further correction for each constant was obtained

To determine the value of M the average number[11] of hydrogen ions bound to the 2 1 complexes was calculated

$$\bar{n}_H = \sum_{i=1}^{M} i[M_2H_iL] / \sum_{i=0}^{M} [M_2H_iL] \tag{9}$$

In a solution containing excess of metal ion, it may be assumed that only 2 1 complexes predominate and free ligand species and 1 1 complexes are negligible From equations (1) and (3), $\bar{n}_H$ is given by

$$\bar{n}_H = \{(6 - a)T_L - [H] + [OH]\}\; T_L \tag{10}$$

RESULTS AND DISCUSSION

Acid equilibria and formation constants of MTB

Absorption spectra of MTB at different pH values are shown in Fig 1 and the potentiometric titration of MTB is shown in Fig 2 Three protons dissociate between $a = 0$ and $a = 3$ (where a = moles of base added per mole of ligand). At high pH three more protons dissociate, one between $a = 3$ and $a = 4$, and the other two above $a = 4$ At pH from 1 8 to 5 4, MTB has almost identical absorption curves with absorption maxima at 435 nm, although three protons are dissociated according to the potentiometric titration In this pH range, two protons, one from the sulphonic group and the other from one of the four carboxyl groups, may be transferred to both imino nitrogen atoms Only a small change in the spectrum may be expected from dissociation of three protons from the carboxyl groups

Above pH 5·4, new bands appear near 600 nm, and with increase of pH the solutions change colour from yellow to purple blue, possibly because of proton dissociation from the phenol group With increase of pH from 11·0 to 12 5 the absorption maximum shifts to slightly shorter wavelength, the absorptivity decreases and the colour becomes grey Above pH 12 5 the absorptivity gradually increases and the colour changes from grey to deep blue This behaviour at pH above 11·0 is not observed for Thymol Blue, so it presumably involves the dissociation of an amino-group proton of each iminodiacetate group

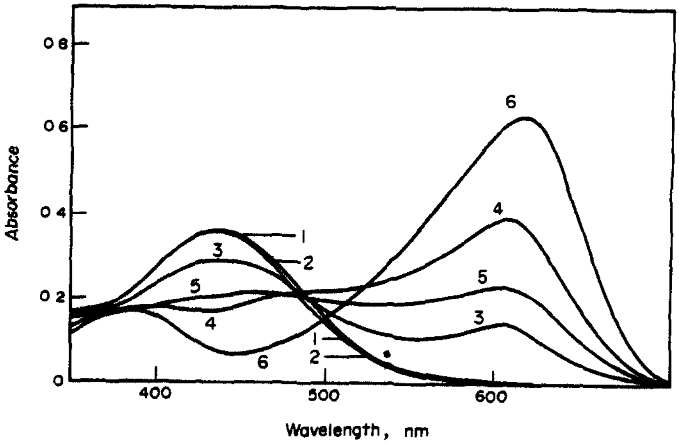


Fig 1 Absorption spectra of MTB at different pH values
T_L = 1 99 × 10^{-5} *M*, pH 1—1 82, 2—5 08, 3—6 66, 4—8 70, 5—11 51, 6—31 52

Six acid formation constants of MTB and the molar absorptivities were calculated, and are tabulated in Table 1 The p*K* values for MTB obtained by Korbl and Kakáč[2] are higher than ours, and the differences cannot be accounted for by the difference in ionic strengths used. This fact supports the points above about the relative purity of our samples.

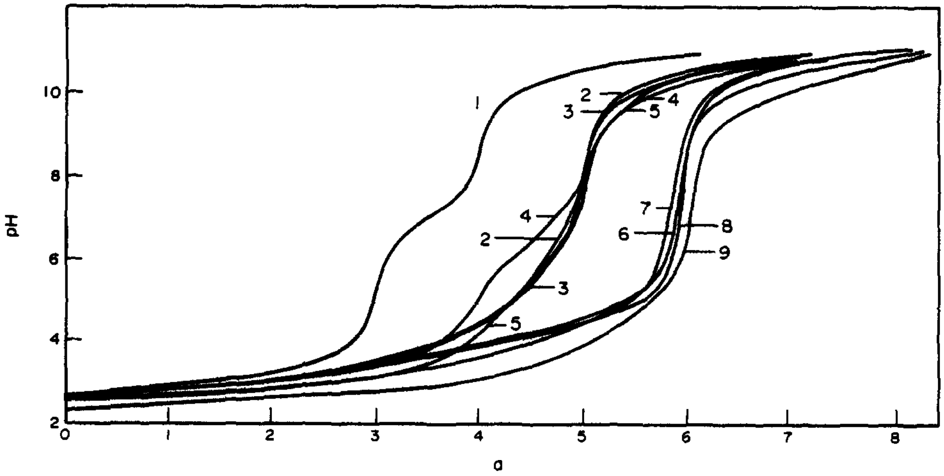


Fig 2 Potentiometric titration curves of Co(II), Ni(II), Cu(II), Zn(II)–MTB complexes at 25 ± 0 1°C in 0·1 *M* KNO_3 solutions with following molar ratios of metal ion to ligand 1—MTB alone, 2—Co(II) MTB (1 1), 3—Zn(II) MTB (1 1), 4—Ni(II) MTB (1 1), 5—Cu(II) MTB (1 1), 6—Co(II) MTB (2 1), 7—Ni(II).MTB (2 1), 8—Zn(II) MTB (2 1), 9—Cu(II) MTB (2 1), *a* = number of moles of base added per mole of MTB T_L 1—1 01 × 10^{-3} *M*, 2-9—1 00 × 10^{-3} *M* T_M 2—1 01 × 10^{-3} *M*, 3—9 89 × 10^{-4} *M*, 4—9·98 × 10^{-4} *M*, 5—1 00 × 10^{-3} *M*, 6 and 7—1 92 × 10^{-3} *M*, 8—1 91 × 10^{-3} *M*, 9—1 90 × 10^{-3} *M*

Table 1. Acid formation constants, wavelengths of absorption maxima and molar absorptivities of MTB

Ion	Wavelength λ_{max}, *nm*	Absorptivity 10^4 *l mole*$^{-1}$ *cm*$^{-1}$	Equilibrium constant log *k*
H_6L	435	1.89	1.8*
H_5L^-	435	1.89	2.0*
H_4L^{2-}	435	1.89	3.04*
H_3L^{3-}	435	1.89	6.85*, 6.91
H_2L^{4-}	607	2.15	
HL^{5-}	458	1.2	11.14
L^{6-}	617	4.27	12.94

* Data measured by means of pH titration at 25 ± 0.1°C, $\mu = 0.1$(KNO$_3$), the rest by means of spectrophotometry at room temperature $\mu = 0.1$(KNO$_3$).

Potentiometric investigation of complexes

Potentiometric titrations of MTB solutions containing 1:2, 1:1, 2:1 and 3:1 molar ratios of Co(II), Ni(II), Cu(II) and Zn(II) to MTB were performed, and Fig. 2 shows the results for the 1:1 and 2:1 mole ratios as to each metal. All four metal ions behave similarly.

At medium pH, each 1:1 (molar ratio of metal to ligand) curve exhibits a buffer region over an interval which corresponds to 1 mole of base per mole of ligand and is terminated by a sharp inflection at $a = 5$, indicating the formation of a stable diprotonated complex MH_2L^{2-} which has dissociated completely to a monoprotonated complex MHL^{3-} at $a = 5$. The dissociation of a proton from the complex MHL^{3-} and the formation of a simple complex ML^{4-} occur at $a > 5$. In more acidic media, more highly protonated species may be formed. For 2:1 or 3:1 metal:ligand molar ratios, all of the available protons of the ligand are neutralized in a single step, with the formation of binuclear complexes. On the "3:1" curve, beyond $a = 6$, there is a long buffer region on the alkaline side, corresponding to hydrolysis of free metal ion. This buffer region is similar to the pH region where metal hydroxide precipitates, and its extent over two units of a indicates that there is one mole of free metal ion per mole of ligand, and that not more than two metal ions can combine with one MTB molecule.

The average numbers of hydrogen ions bound to the metal complexes were calculated, those for the 1:1 complexes from the "1:1" curve as previously[9] and those for the 2:1 complexes from the "2:1" and "3:1" curves by equation (10). The results suggested the presence of the four complex species, MH_3L^-, MH_2L^{2-}, MHL^{3-} and ML^{4-} with the exception of MH_3L^- for Cu(II), in the "1:1" solutions. They also suggested the existence of two binuclear complexes M_2HL^- and M_2L^{2-} in the "2:1" or "3:1" solutions for each metal.

These formation constants were calculated by means of the methods stated above, and are listed in Table 2.

Spectrophotometric investigation of complexes

The absorption spectra of MTB solutions containing 1:1 and 2:1 mole-ratios of metal ion to ligand at different pH values were measured between 350 and 700 nm, and the variation of absorbance with pH was studied. All the complexes behaved similarly at pH-values <9.5 but differently at higher pH.

Table 2 Formation constants of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with MTB at 25 ± 0 1 C $\mu = 0{\cdot}1(KNO_3)$

Reaction		Log K			
		Co(II)	Ni(II)	Cu(II)	Zn(II)
$M^{2+} + L^{6-} \rightleftharpoons ML^{4-}$	K^{M}_{ML}	12 69	12 66	14 05	13 31
$M^{2+} + HL^{5-} \rightleftharpoons MHL^{3-}$	K^{M}_{MHL}	10·59	10 29	11 29	10 93
$M^{2+} + H_2L^{4-} \rightleftharpoons MH_2L^{2-}$	$K^{M}_{MH_2L}$	6 55	7 38	8 11	6 56
$M^{2+} + H_3L^{3-} \rightleftharpoons MH_3L^{-}$	$K^{M}_{MH_3L}$	1 78	2 29		2 30
$M^{2+} + ML^{4-} \rightleftharpoons M_2L^{2-}$	$K^{M}_{M_2L}$	11 0	11 26	12 4	11 1
$M^{2+} + MHL^{3-} \rightleftharpoons M_2HL^{-}$	$K^{M}_{M_2HL}$	3 9	4 28	4 6	3 8
$M_2L^{2-} + 2OH^{-} \rightleftharpoons M_2(OH)_2L^{4-}$	$K^{OH}_{M_2(OH)_2L}$			2 9*	
$MHL^{3-} \rightleftharpoons ML^{4-} + H^{+}$	K^{H}_{MHL}	10 84	10 56	10 18	10 56
$MH_2L^{2-} \rightleftharpoons MHL^{3-} + H^{+}$	$K^{H}_{MH_2L}$	6 33	6 59	6 08	6 11
$MH_3L^{-} \rightleftharpoons MH_2L^{2-} + H^{+}$	$K^{H}_{MH_3L}$	2 10	1 78		2 30
$M_2HL^{-} \rightleftharpoons M_2L^{2-} + H^{+}$	$K^{H}_{M_2HL}$	3 8	3 51	2 2	3 3

* Data determined by means of spectrophotometry, $\mu = 0\ 1(KNO_3)$

The absorption spectra of the "1:1" solutions for Ni(II) and Cu(II) are shown in Figs 3 and 4. Figure 5 shows the variation of absorbance with pH for Ni(II) all the whole pH range investigated, and Fig. 6 that for Co(II), Cu(II) and Zn(II) at pH above 9. Table 3 shows the pH range, wavelength of maximum absorbance and molar absorptivity for each metal complex.

Metal complexes at low pH. The absorption spectra of the "1.1" solutions for Co(II), Ni(II) and Zn(II) were almost identical to that of MTB at pH below 3, with a shift to slightly longer wavelength [maximum absorbances at (435, 438 440 and 443 nm for MTB, Co(II), Ni(II) and Zn(II), respectively] From these results and the potentiometric data, the initial complex formed may be MH_3L^-. Since the absorbances are not so different from that of MTB, the initial three protons may be released from the carboxyl groups The metal ion may combine with two carboxyl groups attached to one of the imino nitrogen atoms.

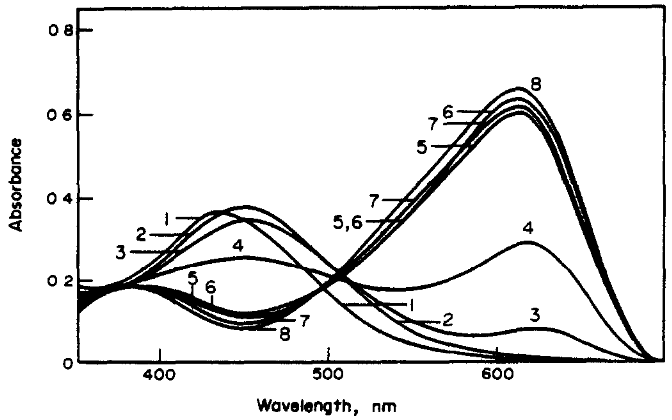


Fig 3 Absorption spectra of MTB solutions containing 1 mole of Ni(II) per mole of MTB at different pH values
$T_M = 2\ 00 \times 10^{-5}\ M, T_L = 2\ 00 \times 10^{-5}\ M$ pH 1—2 78, 2—4 03, 3—4 13, 4—5 63, 5—8 13, 6—10 07, 7—12 20, 8—13 44

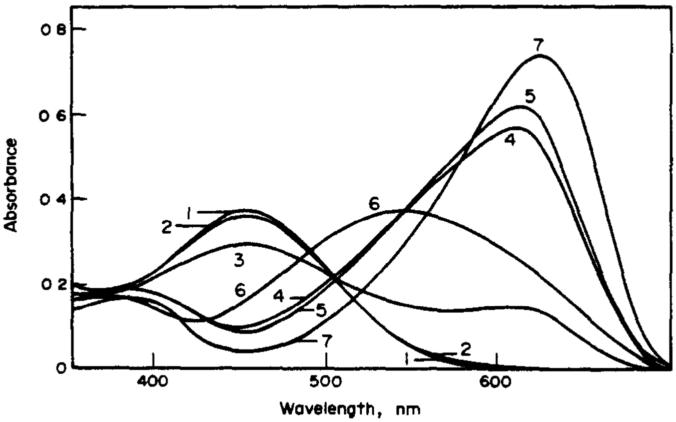


Fig 4 Absorption spectra of MTB solutions containing 2 moles of Cu(II) per mole of MTB at different pH values

$T_M = 4.01 \times 10^{-5} M$, $T_L = 1.98 \times 10^{-5} M$ pH 1—1.91, 2—2.79, 3—4.27, 4—9.40, 5—12.22, 6—0.4 M NaOH, 7—4.0 M NaOH

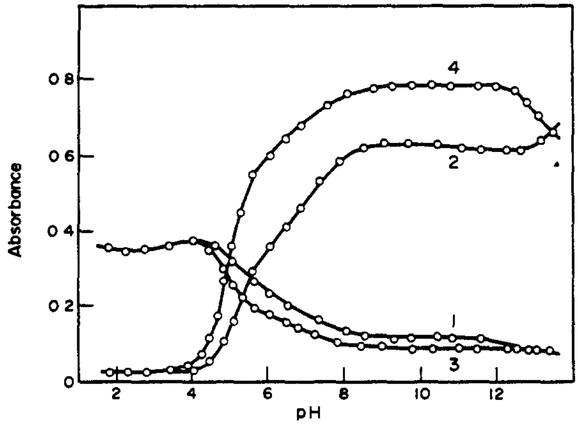


Fig 5 Absorbances of Ni(II)-MTB complexes as functions of pH

$T_L = 2.00 \times 10^{-5} M$ T_M 1 and 2—2.00 × $10^{-5} M$, 3 and 4—3.99 × $10^{-5} M$ wavelength 1—453 nm, 2—614 nm, 3—455 nm, 4—618 nm

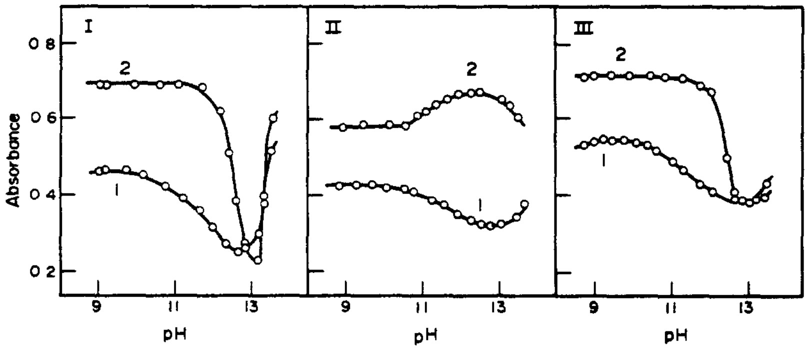


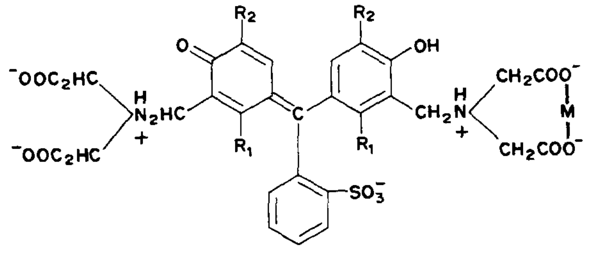
Fig 6 Absorbances of Co(II), Cu(II), Zn(II)-MTB complexes as functions of pH

I $T_L = 2.03 \times 10^{-5} M$, T_{Zn} 1—2.03 × $10^{-5} M$ 2—4.01 × $10^{-5} M$, wavelength 1—598 nm, 2—608 nm II $T_L = 1.98 \times 10^{-5} M$, T_{Cu} 1—1.96 × $10^{-5} M$, 2—3.99 × $10^{-5} M$, wavelength 1—583 nm 2—611 nm III $T_L = 2.00 \times 10^{-5} M$, T_{Co} 1—2.01 × $10^{-5} M$ 2—4.00 × $10^{-5} M$, wavelength 1—611 nm 2—618 nm

Table 3 pH range of existence, wavelength and absorptivity of each species of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with MTB

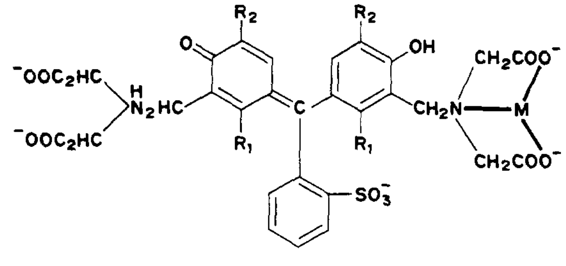
	pH range of existence				Absorptivity $10^4\ l\ mole^{-1}\ cm^{-1}$				Wavelength λ_{max} nm			
Species	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
MH_3L^-	3.5-3.8	3.3-4.4		3.4-4.0	1.73	1.72		1.73	438	440		443
MH_2L^{2-}	4.2-5.5	4.5-5.5	2.0-4.2	4.3-5.6	1.76	1.87	1.88	1.76	440	453	450	445
MHL^{3-}	6.0-9.1	6.2-8.4	5.5-8.6	6.0-9.0	2.70	3.19	2.15	2.27	611	614	583	598
ML^{4-}	9.5-12.6	9.0-12.2	8.8-12.4	9.2-12.6	2.08	3.09	1.88	1.76	584	615	538	540
M_2HL^-	3.2-4.0	3.6-4.6	2.0-3.0	3.0-4.0	1.79	1.86	1.87	1.86	440	455	445	442
M_2L^{2-}	6.0-11.8	5.5-12.1	5.5-10.0	5.4-11.3	3.57	4.75	2.93	3.39	618	618	611	608
$M_2(OH)_2L^{4-}$			10.5-12.5				3.04				615	

as shown in **I**, because the steric hindrance of the bulky sulphonphthalein group might make it impossible for the remaining carboxyl groups co-ordinate to the same metal ion



MH_3L^- (I)

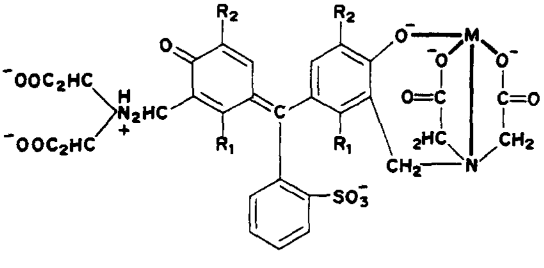
With increase of pH, the absorbance maxima for Co(II), Ni(II) and Zn(II) gradually shift to slightly longer wavelength as shown in Fig. 3. Between pH 3 and 5 the colour of each solution changes from yellow to blue–yellow. This may suggest dissociation of the proton bound to the nitrogen of the iminodiacetate group co-ordinating to the metal ion in the complex MH_3L^- and formation of the diprotonated complex MH_2L^{2-} with the nitrogen co-ordinating to the metal ion as shown in **II**.



MH_2L^{2-} (II)

On the other hand, the behaviour with Cu(II) is different below pH 5. At pH 1·8 the absorption bands of Cu(II)–MTB "1:1" solutions are at longer wavelengths than those for the other metals, and the absorbance decreases with increase of pH. At pH between 3·4 and 5·0, the absorbance is constant with maximum absorbance at 450 nm and these curves are similar to those of the other metals at pH about 4 where the complex MH_2L^{2-} is predominant [curve 3 in Fig. 4 for Cu(II), curve 3 in Fig 3 for Ni(II)]. The colour changes from yellow to purple–yellow. This fact probably indicates that the complex MH_3L^- is not formed, and that the initial complex formed as MH_2L^{2-}, the MTB releasing four protons from the carboxyl groups and from one of the imino nitrogen atoms, and that the formula is given by **II**.

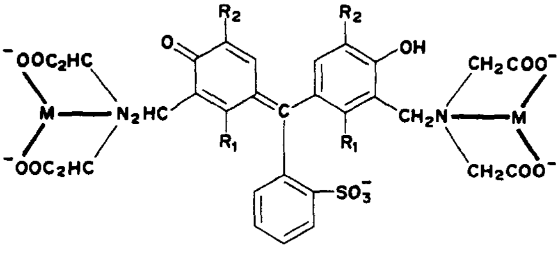
At pH about 5–9·5, all four metal ions behave similarly. New bands appear near 600 nm, the absorbances at this wavelength increase with increase of pH, and the colours of the solutions change to blue for Co(II), green–blue for Ni(II), blue–purple for Cu(II), and purple–blue for Zn(II). These changes may correspond to the conversion from MH_2L^{2-} to MHL^{3-}. The strong colour changes suggest change of the electronic structure of the sulphonphthalein group, so the dissociated proton is probably from the phenol group, and the metal ion combines further with the oxygen atom of this group and the formula of the complex MHL^{3-} is given by **III**. At pH about 9–10, depending on the metal, the absorbance remains almost constant, indicating complete formation of MHL^{3-}.



MHL^{3-} (III)

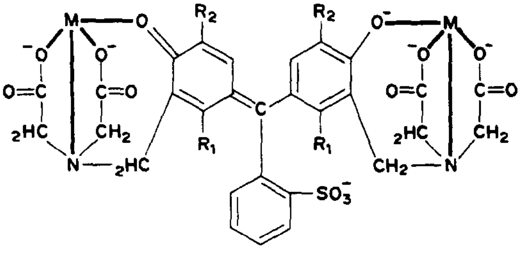
In the case of the "2:1" solutions for Co(II), Ni(II) and Zn(II), the behaviour of the absorbance is similar to that of the corresponding "1:1" solutions below pH 3. The mole-ratio method showed that the combining mole ratio of metal to ligand is 1:1 for each metal. The formation of the binuclear complex is not considered in this pH range. Between pH 3 and 4, although the absorbance maxima are at almost the same wavelengths as those for the corresponding "1.1" solutions, the absorptivities differ, as shown for Ni(II) in Fig 5. The results of the mole-ratio method clearly show the formation of binuclear complexes. On the other hand, for Cu(II)–MTB "2:1" solutions, the wavelength of the maximum is slightly different from that of the "1·1" solution (450 nm for the "1:1", 445 nm for the "2.1" at pH 1·8) and the absorptivity becomes clearly different from that of the "1.1" above pH 2·5. This shows that Cu(II) forms the binuclear complex at lower pH than the other metals.

In the corresponding pH ranges the diprotonated complex MH_2L^{2-} is predominant in each "1:1" solution, and considering the results of the potentiometric titrations, the following is assumed. The initial binuclear complex is M_2HL^-. The small changes in the spectra may indicate that the second metal ion combines with the carboxyl oxygen atoms and the imino nitrogen atom which are unco-ordinated to the first metal ion (see **II**), and that the proton attached to this nitrogen atom is released, the arrangement of the complex M_2HL^- being given by **IV**.



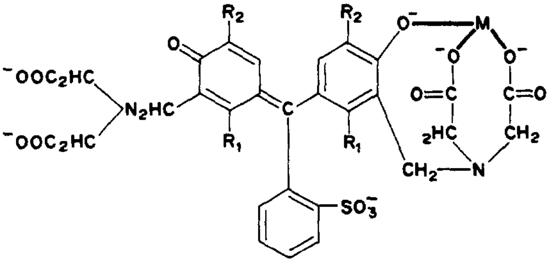
M_2HL^- (IV)

Above pH 4, the absorbances of all four "2:1" solutions near 450 nm decrease and new bands appear near 610 nm, and with increase of pH the colours change from yellow to deep blue for Co(II) and Ni(II), and to deep purple–blue for Cu(II) and Zn(II), which may indicate dissociation of the phenol proton in the complex M_2HL^- and the formation of the complex M_2L^{2-} by the co-ordination of each phenol oxygen atom to a metal ion as shown in V



M_2L^{2-} (V)

Metal complexes at high pH The absorbances for all metal·ligand "1.1" solutions behave similarly above pH about 9. The intensities and the maximum wavelengths are constant, indicating complete formation of the complex MHL^{3-}. With increase of pH from about 10, depending on the metal, the absorption maxima shift to shorter wavelength and the intensities decrease as shown in Figs 5 and 6, and there are strong colour changes. The change is slight for Ni(II) as shown in Fig 3, and great for Co(II), Cu(II) and Zn(II) as shown for Cu(II) in Fig 4 The changes become minimal at pH 13. The maximum absorbances are at 584, 615, 538 and 540 nm for Co(II), Ni(II), Cu(II) and Zn(II), respectively at pH 13, and the solutions are purple, blue, purple–red and red–purple, respectively From these facts and the log K^{H}_{MHL} values (Table 2), the reactions may involve the dissociation of the proton attached to the unco-ordinated imino nitrogen atom (see **III**) and the formation of the complex ML^{4-} as shown in **VI**



ML^{4-} (VI)

Above pH 13 for each "1 1" solution, the absorbance increases and the maxima shift to longer wavelength, the spectra becoming similar to that of MTB It may be considered that each metal complex ML^{4-} is unstable in strongly alkaine medium and dissociates to form the corresponding metal hydroxide and L^{6-}

The absorbances of ("2 1" solutions for Co(II), Ni(II) and Zn(II) are almost constant from pH 9 to 11 5, indicating formation of the complex M_2L^{2-} and no further formation of the hydroxo complex With increase of pH from 11·5, the absorbances decrease abruptly and the maxima shift to shorter wavelength, although this change is slight for Ni(II). At pH about 13, the spectra and the colours are similar to those of the "1:1" solutions, and the mole-ratio method shows the combining mole ratios are 1 · 1 With further increase of pH, sharp and strong bands appear which are similar to those of MTB This may show that the

Co(II), Ni(II) and Zn(II) M_2L^{2-} complexes are unstable in strongly alkaline medium and dissociate in two steps, first by dissociation of M_2L^{2-} to the metal hydroxide and ML^{4-}, and secondly of ML^{4-} to the hydroxide and L^{6-}.

On the other hand, the intensity of "2:1" Cu(II) solutions increases and the absorbance maximum shifts slightly to longer wavelength, and the mole-ratio indicates a 2:1 compound. The formation of the hydroxo-complex $M_2(OH)_nL^{(2+n)-}$ may occur, and the complex equilibrium be represented by

$$Cu_2L^{2-} + nOH^- \rightleftharpoons Cu_2(OH)_nL^{(2+n)-}; \quad K^{OH}_{Cu_2(OH)_nL} = \frac{[Cu_2(OH)_nL]}{[Cu_2L][OH]^n}$$

The plot of log $[Cu_2(OH)_nL]/[Cu_2L]$ *vs* pOH gave a straight line with slope $n = 2$ and $K^{OH}_{Cu_2(OH)_2L}$ was evaluated graphically from the pOH value obtained when the log term was equal to zero;[14] the value obtained was $10^{2\cdot9}$.

Above pH 12·4 the intensity decreases and the absorbance maximum shifts to shorter wavelength, and the spectrum and the colour of the "2:1" solution in 0·4 *M* sodium hydroxide are similar to those of the "1:1" solution. In much more alkaline medium a sharp and strong absorption band appears, identical to that of MTB. This may show that the binuclear hydroxo complex for Cu(II) is also unstable in strongly alkaline medium and dissociates to metal hydroxide and L^{6-} in two steps as the other three metals do.

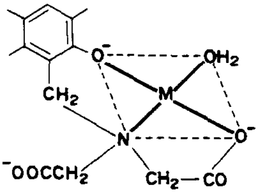
Stabilities of complexes

The formation constants of the metal–MTB complexes are summarized in Table 4, together with those for SMTB.[6] The stabilities for MTB complexes are consistent with the trends shown by the potentiometric titration curves.

Table 4. Formation constants of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with MTB and SMTB at 25 ± 0·1°C, $\mu = 0\cdot1(KNO_3)$

		Log *K*							
		Co(II)		Ni(II)		Cu(II)		Zn(II)	
SMTB	MTB	SMTB	MTB	SMTB	MTB	SMTB	MTB	SMTB	MTB
$K^M_{MH_2L}$	$K^M_{MH_3L}$	2·52	1·78	2·14	2·29			3·03	2·30
K^M_{MHL}	$K^M_{MH_2L}$	7·16	6·55	7·26	7·38	7·7	8·11	6·99	6·56
K^M_{ML}	K^M_{MHL}	12·75	10·59	12·37	10·29	13·5	11·92	12·92	10·93
	K^M_{ML}		12·69		12·66		14·05		13·31
	$K^M_{M_2HL}$		3·9		4·28		4·6		3·8
	$K^M_{M_2L}$		11·0		11·26		12·4		11·1

The stability constants for the MH_3L, MH_2L and M_2HL complexes follow the Irving–Williams order, but those for MHL, ML and M_2L do not, those for Cu(II) and Ni(II) being lower than expected. Cu(II) and Ni(II) may take a planar configuration and one of the carboxyl groups may remain unco-ordinated, resulting in decrease of the stability. For the complexes MHL^{3-}, ML^{4-} and M_2L^{2-} for Cu(II) and Ni(II), it may be more correct to show two chelate rings as in **VII** instead of the three chelate rings shown in **III**, **VI** and **V**



(VII)

The 1 1 complexes MHL, MH_2L and MH_3L for MTB have the same co-ordination configuration as the complexes ML, MHL and MH_2L for SMTB,[6] if the other *N*-methyliminodiacetate group of MTB is regarded as unco-ordinated However, the stabilities of the MTB complexes are lower than the corresponding SMTB complexes except for the MHL (SMTB) and MH_2L (MTB) complexes with Cu(II) This general effect may be due to the unco-ordinated *N*-methyliminodiacetate group acting as an electron-acceptor, and reducing the electron densities both in the sulphonphthalein rings and the co-ordinated iminodiacetate group

The dissociation of the MTB complex MHL results in the great increase in the stability of the complex ML, although the configuration of the chelate rings does not change, and the greater stability than that of the SMTB complex ML This may be due to the lone-pair of electrons on the unco-ordinated and unprotonated imino nitrogen atom, acting as an electron-donor

The dissociation of a proton from the MTB complex M_2HL greatly increases the stability of the complex M_2L This may be explained by a change in the chelate rings, that is, in the complex M_2L both the phenolic oxygen atoms, which have a large affinity for metal ions (almost the same as that of an amino group of a polyamine),[6] are co-ordinated to a metal ion, whereas, in the complex M_2HL they are not, as seen in **V** and **IV** respectively

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Resume— On decrit des etudes potentiometriques et spectrophotometriques sur les equilibres acides et les reactions avec Co(II) Ni(II) Cu(II) et Zn(II) pour le Bleu de Methylthymol (MTB) On a calcule les constantes d'equilibre On a trouvé que le MTB forme des complexes 1 1 et 2 1 (rapport molaire du metal au coordinat) incluant les complexes protones On discute de la configuration probable des complexes et des influences sur les stabilites

Zusammenfassung—Potentiometrische und spektrophotometrische Untersuchungen über die Säure-Basen-Gleichgewichte und die Reaktionen von Methylthymolblau (MTB) mit Co(II), Ni(II), Cu(II) und Zn(II) werden beschrieben. Die Gleichgewichtskonstanten wurden berechnet. Es wurde gefunden, daß MTB 1:1- und 2:1-Komplexe (Molverhältnisse Metall:Ligand) sowie protonierte Komplexe bildet. Die wahrscheinliche Konfiguration der Komplexe und die Einflüsse auf ihre Stabilität werden diskutiert.

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THE ERROR IN ABSORPTION MEASUREMENTS, CAUSED BY THE USE OF NON-MONOCHROMATIC LIGHT—II

GAUSSIAN FUNCTIONS

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Summary—The errors in absorption measurements in spectrophotometry, caused by the use of non-monochromatic light have been calculated Gaussian functions have been assumed for the wavelength-dependence of the intensity of the incident light falling on the cell and the absorbance of the compound measured Results found are similar to those found with parabolic functions. Experiments have been made to compare the results of the calculations with experimental values The agreement is fairly good in most cases

In the first paper[1] errors in absorption measurements caused by the use of non-monochromatic light were calculated for the case that absorbance wavelength and light-intensity *vs* wavelength curves were both parabolic in nature. This assumption seems reasonable, but is arbitrary. Therefore similar calculations have been performed on the assumption that both curves are Gaussian, which also seems reasonable The assumptions have been compared with each other, and with some experiments.

DERIVATION OF EQUATIONS

Assumptions

For convenience the wavelength λ at the absorption maximum of the component measured (Fig 1) is taken as reference and assigned the value zero The absorbance at this value $\lambda = 0$ is E_0, at other wavelengths E_λ is often given in fair approximation by

$$E_\lambda = E_0 \; e^{-1/2(\lambda/\beta)^2} \tag{1}$$

The half-bandwidth is defined in the usual way as the wavelength region where E_λ varies between $1/2E_0$ and E_0 The value of the half-bandwidth is $2\beta\sqrt{2 \ln 2}$ (see Fig 1).

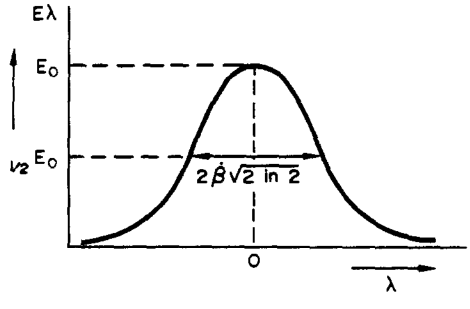

Fig 1 Absorbance E_λ as a function of wavelength λ

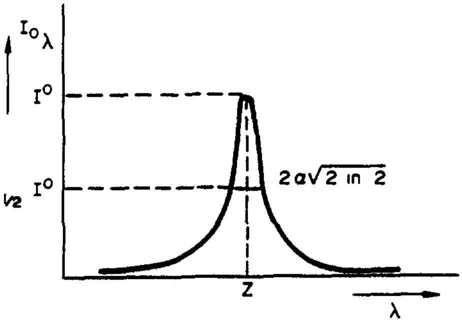

Fig 2 Intensity of incident light I^0_λ as a function of wavelength

For the intensity of the light falling on the cell, I^0_λ (Fig. 2), the function

$$I^0_\lambda = I^0 e^{-1/2\{(\lambda - z)/\alpha\}^2} \tag{2}$$

is assumed, where I^0 is the maximum light-intensity falling on the cell, z is the difference in wavelength units between the maximum of the light-intensity curve (Fig. 2) and the maximum of the absorption curve (Fig. 1) Here the half-bandwidth is $2\alpha \sqrt{2} \ln 2$.

In these considerations similar assumptions have been made as in the first paper,[1] which are fulfilled in most cases. They are not repeated here.

Calculations

We introduce again the quantities b and k. They have the same physical meaning as in the first paper.[1] The mathematical relations between these quantities and z, α and β are now slightly different, however:

$$b = \frac{\lambda_{I0} - \lambda_{E0}}{\text{half-bandwidth of } I^0_\lambda \text{ curve}} \sqrt{2} = \frac{z}{2\alpha\sqrt{2}\ln 2} \tag{3)*}$$

$$k = \frac{\text{half-bandwidth of } E_\lambda \text{ curve}}{\text{half-bandwidth of } I^0_\lambda \text{ curve}} = \frac{\beta}{\alpha} \tag{4}$$

The measured absorbance E_m and the relative error $\Delta E/E_0$ are given by the same formulae as in the first paper·

$$E_\text{m} = \log \frac{\int I^0_\lambda \, \mathrm{d}\lambda}{\int I^0_\lambda \; 10^{-E\lambda} \, \mathrm{d}\lambda} \tag{5}$$

$$\frac{\Delta E}{E_0} = \frac{E_\text{m} - E_0}{E_0} \tag{6}$$

Substitution from (1) and (2) in (5) gives.

$$E_\text{m} = \log \frac{\int_{-\infty}^{+\infty} I_0 \, e^{-1/2\{(\lambda - z)/\alpha\}^2} \, \mathrm{d}\lambda}{\int_{-\infty}^{+\infty} I_0 \, e^{-1/2\{(\lambda - z)/\alpha\}^2} - 2{\cdot}3 E_0 \, e^{-1/2(\lambda/\beta)^2} \, \mathrm{d}\lambda} \tag{7}$$

---

* *Note* In equation (7) in reference 1 I^0 in the numerator should be replaced by I_0

Table 1 Errors in the absorption measurement

	$k = \beta/\gamma$					
b	10^2	$10^{1\ 5}$	10^1	$10^{0\ 5}$	1	$10^{-0\ 5}$
100	75	>90	>90	>90	>90	>90
50	29 29	>90	>90	>90	>90	>90
20	5 40	42 56 42 65	>90	>90	>90	>90
10	1 38	12 98 13 02	74 79 75 17	>90	>90	>90
5	0 35	3 45 3 47	29 42 30 19	>90	>90	>90
2	0 06	0 60	5 82 6 05	42 58 49 23	>90	>90
1	0 02	0 19	1 85 1 93	16 05 20 96	*	>90
0 5	0 01	0 08	0 84 0 86	7 66 10 04	*	*
0 2	0 01	0 06	0 55 0 56	5 16 6 48	31 71 52 66	*
0	0 01	0 05	0 50 0 51	4 68 5 76	29 74 50 01	*

The values are given in per cent ($-100\ \Delta E/E_0$)
* See Table 2

Results of calculations

Calculations have been performed similar to those in the first paper. Results have been summarized in Tables 1 and 2 If in Table 1 two values are given in one column, the first value gives the error at $E_0 = 0\ 05$, the second at $E_0 = 2{\cdot}0$ In all these cases the error depends practically linearly on the absorbance, the deviation from linearity being always below 1% absolute, generally much less Moreover in many cases one is interested in much smaller absorbance ranges than considered here.[3] In such cases the linearity is better than suggested by the figures given here.

For all cases of practical importance, values for E_m have been compared with those given in Tables I and III of reference 1 The same order of magnitude is found

It seemed useful to compare the results of the calculations with experimental values In practice, measurements made under conditions where non-lenear calibration curves may be expected are most important The Zeiss ELKO-II was known to have good stability, and data provided by the manufacturers showed that the half-bandwidth of the filters was of a suitable magnitude (5–20 nm) It was expected that use of these filters would yield non-linear calibration curves Compounds were selected having absorption-curves fairly resembling Gaussian or parabolic functions in the wavelength-region used Their absorption spectra agreed well with the literature[2] and all solutions were perfectly stable and showed a linear relation between absorption and concentration, as found by measurement with the Hilger UVICHEM H1620 at the tops of the absorption curves and with a bandwidth of about 1 nm These measurements also supplied the E_0 values used.

Table 2 Errors in the absorbance measured for cases marked with an asterisk in Table 1

E_0	$k = 1$ $b = 1$	$k = 1$ $b = 0\ 5$	$k = 10^{-0\ 5}$ $b = 0\ 5$	$k = 10^{-0\ 5}$ $b = 0\ 2$	$k = 10^{-0\ 5}$ $b = 0$
0 05	65 24	41 14	79 08	74 81	60 47
0 1	65 83	41 75	79 75	75 21	61 81
0 2	66 97	42 97	81 03	76 01	64 41
0 5	70 13	46 71	84 34	78 28	71 37
1 0	74 46	52 86	88 28	81 63	79 82
2 0	80 31	63 13	92 46	86 53	88 39

The values are given in per cent ($-100\ \Delta E/E_0$)

Table 3 Errors in the absorption measurement, calculated and measured

Indicator	ELKO II filter			Calculated on EL X-8			Measured with ELKO II			Measured with UVISPEK H700				
*	†	k	b	$-100\,\Delta E/E_0$			$-100\,\Delta E/E_0$			k	b	$-100\,\Delta E/E_0$		
A	e	12·8	1·1	1·4	1·4	1·4	3·0	5·7	—					
A	c	5·4	3·3	41·5	43·2	44·9	39·4	41·1	42·5					
A	b	5·1	4·7	67·7	68·9	70·0	62·0	63·1	64·4					
A	d	4·9	2·0	21·0	22·6	24·4	26·3	30·6	—					
B	a	4·1	3·5	63·1	64·5	65·9	54·6	55·7	56·2					
B	c	3·9	0·3	3·9	4·2	4·5	9·5	14·0	19·5					
B	b	3·7	1·8	28·0	30·2	32·6	36·1	39·4	41·9					
B	d	1·8	0·8	29·5	35·7	42·6	31·5	43·3	54·7					
C	e	9·0	8·6	71·8	72·0	72·3	83·6	82·2	82·1	9·2	8·8	79·3	79·4	79·2
C	c	4·1	1·4	16·2	17·5	18·9	24·0	26·4	28·8	4·1	1·4	28·6	29·1	30·7
C	b	3·9	2·8	49·6	51·5	53·4	55·1	55·8	57·3	4·5	3·2	53·9	53·3	54·8
C	d	3·7	0·2	3·7	4·0	4·3	10·8	16·8	22·4	3·8	0·2	7·8	7·2	9·1
D	e	9·0	8·9	74·0	74·3	74·5	84·0	84·9	84·9	9·2	9·1	82·3	82·2	82·2
D	d	4·8	1·3	11·1	11·8	12·6	18·2	20·6	23·1	4·9	1·3	22·4	23·0	25·0
D	b	4·6	2·7	38·6	40·1	41·8	47·9	49·3	51·2	5·3	3·2	46·8	46·8	48·3
D	c	4·4	0·1	2·6	2·7	2·9	10·2	18·5	26·1	4·5	0·1	2·4	3·9	—
E	e	13·6	0·3	0·3	0·3	0·3	3·6	1·2	—	13·9	0·3	—	—	—
E	c	6·8	3·6	31·7	32·4	33·2	36·2	34·7	36·4	6·9	3·6	37·5	37·2	37·9
E	d	6·2	2·2	16·2	16·8	17·4	24·1	24·6	29·4	6·3	2·2	21·9	22·4	23·9

* A Bromocresol Green pH 7·6 B Chlorophenol Red pH 8·6 C Bromophenol Blue pH 6·8 D Bromocresol Purple pH 9·0 E Bromothymol Blue pH 9·8

† a filter S 53E, $\lambda_{max} = 530$ nm, half-bandwidth = 18 nm b filter S 55E, $\lambda_{max} = 550$ nm, half-bandwidth = 20 nm c filter S 57E, $\lambda_{max} = 571$ nm, half-bandwidth = 19 nm d filter S 59E, $\lambda_{max} = 587$ nm, half-bandwidth = 21 nm e filter I 62, $\lambda_{max} = 620$ nm, half-bandwidth = 5 nm

Because unexpected results were found in a few cases, measurements were also made with a Hilger UVISPEK H700 A theoretical difficulty is that its intensity curve is triangular, but because of the agreement between the results for Gaussian and parabolic functions, it may be expected that calculations with triangular functions will give similar results A practical difficulty is that in its ordinary mode of operation the half-bandwidth of the instrument is too small. Therefore the height of the slit was reduced to 0·1–0 2 mm, thus allowing measurements to be made with values of half-bandwidths comparable to those used with the filter instrument

Measurements were made with acid-base indicators Stock solutions (0·05% in ethanol) were prepared and small amounts of these solutions were diluted with buffers to give the desired values of E_0

Results are given in Table 3 Values of $\Delta E/E_0$ are given only for E_0 values 0 05, 1·0 and 2·0 Values between $E_0 = 0{\cdot}05$ and $E_0 = 1{\cdot}0$ were calculated and measured The calculated values of $\Delta E/E_0$ varied linearly with E_0, the same holds within experimental error for the measured values, if it is taken into account that the values of b, k and E_0 are not known exactly

Conclusions

1 If the calculations with parabolic functions are compared with those made with Gaussian functions, the absolute values of $\Delta E/E_0$ are somewhat different, but the variation of $\Delta E/E_0$ with E_0 is closely similar

2 The value of $\Delta E/E_0$ increases linearly with the concentration in all cases measured This is important for analytical practice, if the following is considered. The use of non-monochromatic light gives rise to non-linear calibration curves Therefore errors are introduced if in the calculation of a calibration curve, a linear relation between concentration and absorbance is assumed From the practical point of view one is interested in the magnitude of the error caused by the non-validity of this assumption The linear relation between $\Delta E/E_0$ and E_0, found here, allows us to calculate this magnitude (see reference 2)

3 The change in $\Delta E/E_0$ often agrees fairly well with the theoretical values, but there are several exceptions if the ELKO-II measurements are considered No explanation can be given (It was for this reason that the UVISPEK measurements were performed) For practical analysis this point seems unimportant, however.

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Résume—On a calcule les erreurs causées par l'emploi de lumiere non-monochromatique dans les mesures d absorption en spectrophotometrie On a admis des fonctions gaussiennes pour la dépendance de l'intensite de la lumiere incidente tombant sur la cuve et de l'absorbance du composé mesure par rapport a la longueur d'onde Les resultats trouvés sont semblables a ceux trouvés avec des fonctions paraboliques On a effectue des experiences pour comparer les resultats des calculs aux valeurs experimentales L'accord est assez bon dans la plupart des cas

Zusammenfassung—Es wurden die Fehler berechnet, die bei Absorptionsmessungen in der Spektrophotometrie durch die Verwendung nicht monochromatischen Lichtes verursacht werden Fur die Wellenlangenabhangigkeit der Intensitat des auf die Zelle einfallenden Lichtes wurden Gaussfunktionen angenommen und die Extinktion der Verbindung gemessen Die Ergebnisse sind denen ahnlich, die man mit parabolischen Funktionen findet Es wurden Versuche gemacht die Ergebnisse der Berechnungen mit experimentellen Werten zu vergleichen Die Ubereinstimmung ist in den meisten Fallen ganz gut.

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THE ERROR IN ABSORPTION MEASUREMENTS CAUSED BY THE USE OF NON-MONOCHROMATIC LIGHT—III

APPLICATION TO LINEAR CALIBRATION CURVES

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Summary—When in spectrophotometry the absorption is measured with non-monochromatic light, a curved calibration curve is often obtained Some errors are introduced if a linear calibration curve is still used The magnitude of these errors has been calculated

In spectrophotometry, calibration curves prepared with non-monochromatic light are often curved Sometimes, however, linear calibration curves are still used, but no information seems available on the consequences of doing so In this paper some of these consequences are discussed It is based on the first papers of this series[1,2] where we investigated the error caused in the absorption measurement itself if non-monochromatic light is used. From the results it followed that in many cases a nearly linear relation exists between the relative error $\Delta E/E_0 = (E_m - E_0)/E_0$ and the absorbance E_0, where E_0 is the absorbance measured with monochromatic light at the absorption maximum of the compound investigated, and E_m is the absorbance measured with non-monochromatic light It has now been found that this relation between the relative error and the absorbance gives some information about the magnitude of the error introduced when linear calibration curves are used in such cases

General aspects of the use of calibration curves

In the use of calibration curves two steps have to be distinguished. the *preparation* of the curve (giving the relation between absorbance and concentration) and the *application* of the curve to the measurement of unknown concentrations. A linear curve is generally represented by the relation $y = \mu x + \gamma$ where $y =$ the absorbance, $x =$ the concentration and μ and γ are estimated from the measurements Absolutely correct values of μ and γ cannot be found, because of the errors made in the measurements. The best estimates of μ and γ, represented by m and c respectively, are generally calculated by the method of least squares

In the present calculation the presence of systematic errors is neglected

Preparation of the curve If the values found in the preparation of the curve are given by curve 2 in Fig 1, the calculated linear curve may depend largely on the choice of the concentrations where the measurements are made. If, however, enough measurements are made and if a random choice over the whole concentration range is carefully considered,

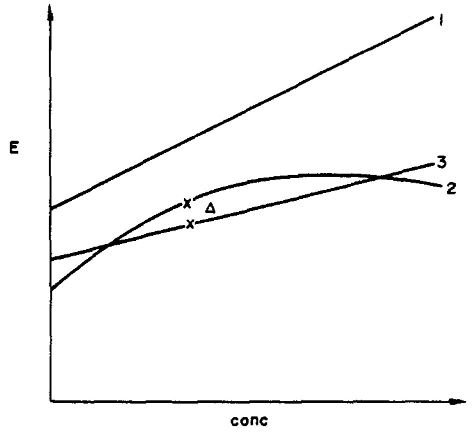

Fig 1 1 Curve obtained by measuring with monochromatic light at the absorption maximum 2 Curve obtained by measuring the non-monochromatic light 3 Calculated straight line from curve 2

it may be assumed that the difference between μ and m and between γ and c (see Fig. 1, curve 3) is very small.

Application of the curve. If the calibration curve is applied in order to convert absorbances into concentrations, it is impossible to eliminate the errors resulting from the assumption that the curve is truly linear. Each measurement made is erroneous except if made at the two points of intersection (Fig. 1). If, however, the calibration curve is used in order to make many measurements over the whole concentration range of the curve, an estimate may be made of random error introduced by doing so. This random error and the conventional random error in the measurement may be combined in the usual way to give the total random error in the application of the curve.

Calculations

Preparation of the curve An example of the calculation is given for the case that the concentrations are 0, 1, 2, 3, 4 and 5 (arbitrary units) and measurements are made against water. The resulting values for the absorbance are given in Table 1, where p is the E_0 of the blank, a gives the increase in E_0 between two calibration points, e is the relative error of the blank and d is the increase of the relative error in each of the calibration steps (e and d generally have negative values). In order to keep the results comparable, in these calculations the same concentration region was considered and the total increases in the absorption and in the relative error over this region were given the values $5a$ and $5d$ respectively in all cases.

With the usual formulae for the least-squares method, we find $m = pd + a + ae + 5d$ and $c = p + pe - 3{\cdot}33ad$. Similar calculations may be made within the same concentration range if the number of equidistant calibration points is changed The results show that m is independent of the number of calibration points However, c gradually changes and if 5, 11 or 26 calibration points are taken we find $c = p + pe - 3{\cdot}13ad$, $c = p + pe - 3{\cdot}75ad$ and $c = p + pe - 4{\cdot}00ad$ respectively. It is apparent that in the limiting case the value will be about $c = p + pe - 4{\cdot}2ad$. The systematic error in c introduced by the non-monochromatic character of the light is therefore about $-0{\cdot}2ad$ if 26 calibration points are used and increases to about $1ad$ if only five calibration points are used

Table 1 Example of the calculation

	Concentration					
	0	1	2	3	4	5
E_0	p	$p + a$	$p + 2a$	$p + 3a$	$p + 4a$	$p + 5a$
Relative error	e	$e + d$	$e + 2d$	$e + 3d$	$e + 4d$	$e + 5d$
Absolute error	pe	$(p + a)(e + d)$	$(p + 2a)(e + 2d)$	$(p + 3a)(e + 3d)$	$(p + 4a)(e + 4d)$	$(p + 5a)(e + 5d)$
$E_m(E_0$ + abs error)	$p(1 + e)$	$(p + a)(1 + e + d)$	$(p + 2a)(1 + e + 2d)$	$(p + 3a)(1 + e + 3d)$	$(p + 4a)(1 + e + 4d)$	$(p + 5a)(1 + e + 5d)$

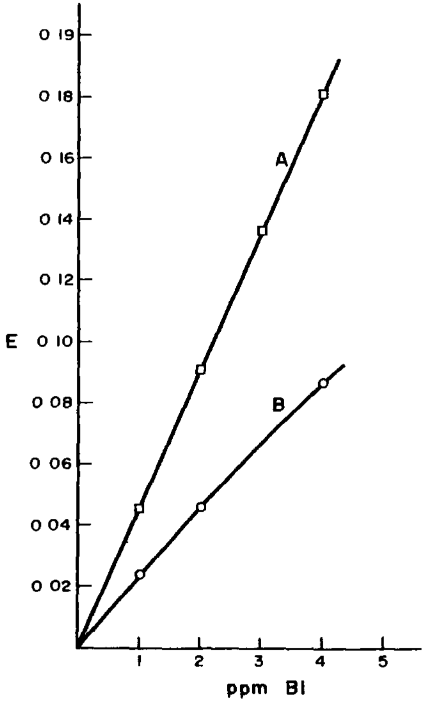

Fig 2 Determination of bismuth by the iodide method (aqueous solution) *A*—at 460 nm (E_0 curve), *B*—with Wratten filter 47

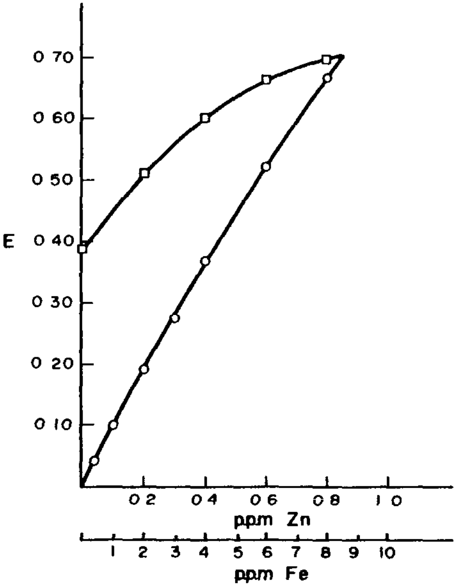

Fig 3 ○, Determination of iron by the thiocyanate method (green filter) □ Determination of zinc with dithizone by the mixed-colour method

Application of the curve. Here two types of error have to be distinguished. One is the conventional error in the measurement, including the sample preparation. This error is random in character and its magnitude can be decreased by the performance of more measurements on the same sample. For us, however, it is interesting to consider the error due to the use of a linear calibration curve Here it does not help us to repeat the measurements of the same sample, because the error is systematic in nature in this case. However, a calibration curve is generally used in order to make a great number of concentration measurements. If this is the case, and if the measurements are situated randomly over the whole concentration range, many different values for this systematic error will occur. These values may be treated as random values The magnitude of the standard deviation now introduced, is approximated by the pooled standard deviation s_p. It is calculated by the formula $s_p^2 = \Sigma\Delta^2/n$ where n is the total number of measurements made during the period that this curve is applied, and Δ is the distance between the "true" curve (2) and the calculated curve (3), see Fig. 1. Calculations performed in a similar way as above show that s_p is about $2{\cdot}0ad$ for large values of n. The same value is obtained if measurements are made against a blank.

Conclusions

1 When non-monochromatic light is used, a non-linear calibration curve often arises The value of $(E_m - E_0)/E_0$ is often directly proportional to E_0. The preceding papers[1,2] give a general impression of the correctness of this proportionality, but it has to be checked for every single case.

2. If conclusion 1 is correct but a linear calibration curve is used, the slope of this curve will be correct, but the intercept will have a systematic error that decreases from about $1{\cdot}0ad$ at $n = 5$ to about $0{\cdot}2ad$ at $n = 26$.

3. In application of the curve, the assumption that the curve is linear leads to a systematic error for each single measurement. This error becomes random if we perform many measurements over the whole concentration range, and its magnitude is about $2{\cdot}0ad$. This value cannot be decreased by replicate determinations

4. The effect on the results of the analysis depends on a and d As an example consider measurement of Chlorophenol Red (absorbance maximum 570 nm) when a filter with a transmission maximum at 587 nm and a half-bandwidth of 21 nm is used.[2] If in the preparation of the calibration curve equidistant measurements are made in the region from $E_0 = 1{\cdot}0$ to $E_0 = 0{\cdot}6$, we find $a = 0{\cdot}1$ and $d = 0{\cdot}012$. If only six measurements are used in this region the systematic error in the intercept of the calibration curve is about $(4{\cdot}2 - 3{\cdot}3) \times 0{\cdot}012 \times 0{\cdot}1 = 0{\cdot}001$ absorbance units (A.U.). If 26 measurements are made and the same absorbance region is used, the systematic error in the intercept decreases to $(4{\cdot}2 - 4{\cdot}0) \times 0{\cdot}012 \times 0{\cdot}1 = 0{\cdot}00024$ A U In the application of the curve the value of s_p is $2 \times 0{\cdot}1 \times 0{\cdot}012 = 0{\cdot}0024$ A U (if the calibration curve is considered correct).

These results have been applied to some examples of practical analysis given in the literature. Calibration curves given by Sandell for the determination of bismuth with iodide,[3] iron with thiocyanate[4] and zinc with dithizone[5] are shown in Figs. 2 and 3. The E^0 values for iron and zinc were estimated by extrapolation of the curve in the lower concentration range. Estimates of d from intermediate points of the calibration curve could be made only very roughly, because of the small size of the curves Therefore a mean value of d was calculated from the value $5d$ for the error at the highest concentration The (rough)

Table 2 Values of *a* and *d* calculated from literature data

	Bi	Fe	Zn
a (in A U)	0.0272	0.164	0.119
d	0.0081	0.038	0.058

estimates calculated from the intermediate points were not in contradiction with this mean value Results of the calculations of *a* and *d* are given in Table 2.

5. The errors calculated in this way may be combined in the conventional way with errors due to measurement and sample treatment. This point is not discussed here.

6. It should be noted that extrapolation of calibration curves in the situations described here is even more dangerous than in other cases.

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Résumé—Quand en spectrophotométrie on mesure l'absorption avec une lumière non-monochromatique, on obtient souvent une courbe d'étalonnage incurvee Quelques erreurs sont introduites si une courbe d'étalonnage linéaire est toutefois utilisee On a calculé la grandeur de ces erreurs

Zusammenfassung—Wenn bei der Spektrophotometrie die Extinktion mit nicht monochromatischem Licht gemessen wird, erhalt man oft eine gekrummte Eichkurve Man macht einige Fehler, wenn man dennoch eine lineare Eichkurve verwendet. Die Große dieser Fehler wurde berechnet

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STEPWISE A.C. AMPEROMETRIC TITRATION OF CADMIUM AND ZINC WITH EGTA

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Summary—The theory of d.c. and a.c. amperometric titrations based on complexometric reactions is presented. It is shown that when $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ and $\log K_{M_IL} < \log K_{M_{II}L}$, M_I and M_{II} can be sequentially determined by d.c. as well as a.c. amperometric titration. If, on the other hand $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ and $\log K_{M_IL} > \log K_{M_{II}L}$, a stepwise titration can be performed only by a.c. amperometry. The effect of oxygen on an a.c. amperometric titration is also discussed. The stepwise a.c. amperometric titration of cadmium and zinc with EGTA at pH 6 in the presence of oxygen and an excess of 0.05 *M* acetate illustrates the theory.

When a solution contains different metal ions, it is often of interest to determine the concentration of a single metal as well as the total metal concentration. A solution containing two metal ions, M_I and M_{II}, can be successively analysed for both by complexometric titration, if the difference between the stability constants is great enough (say, $\Delta \log K > 3$).

Skrifvars and Ringbom[1] have successively titrated two metal ions with the aid of different indicators and complexing agents. The theoretical calculations for stepwise titrations can be performed with conditional constants.[2]

The determination of cadmium and zinc in the same solution has been investigated by several workers. Flaschka and Carley[3] have determined both in the same solution by photometric titration with EGTA in the presence of an excess of Murexide at pH 10. However, no equilibrium calculations were presented. Nakagawa and Tanaka[4] determined zinc in the presence of cadmium by polarography, using a ligand buffer made of a complexing agent and an excess of a polarographically inert metal ion (EGTA–Ba). Theoretical calculations based on equilibrium calculations were presented. The theory of a method for the amperometric titration of cadmium in the presence of zinc, utilizing d.c. polarography, has been discussed.[2] For the titration of 10^{-3} *M* cadmium in the presence of 10^{-2} *M* zinc with EGTA, zinc is masked with 0.1 *M* acetylacetone.

In this study a method is presented by which both metals can be amperometrically titrated with the aid of a.c. polarography.

THEORY

Equilibrium considerations

Equilibrium calculations are useful when considering the feasibility of using alternating current for the stepwise amperometric titration of M_I and M_{II} with a complexing agent L. These calculations are treated briefly below.

When the ratio $K_{M_IL}/K_{M_{II}L}$ exceeds a certain value, M_{II} will not interfere in the titration of M_I. If $K_{M_IL}/K_{M_{II}L}$ and the stability constant for $M_{II}L$ are both high enough,

M_I and M_{II} may be successively titrated with L. For the titration of M_I in the presence of M_{II}, the following expression for the calculation of the minimum conditional constant for M_IL is valid[2] (if $\alpha_{M_I} = 1$, $\alpha_{L(M_{II})} > \alpha_{L(H)}$ and $[M_{II}]K_{M_{II}L} > 1$).

$$\log K_{M_IL} \sim \Delta \log K + pM_{II} \tag{1}$$

where

$$\Delta \log K = \log K_{M_IL} - \log K_{M_{II}L}.$$

If $\alpha_{L(H)} > \alpha_{L(M_{II})}$ interference is caused by protonation of ligand and not by M_{II}, and there is a critical pH value for quantitative titration.

If M_{II} or M_I takes part in interfering side-reactions, the corresponding $\alpha_{M_{II}}$—or α_{M_I}—coefficients must be introduced.

When both M_I and M_{II} participate in interfering side-reactions during the titration of M_I in the presence of M_{II}, the expression for the conditional constant for M_IL can be written

$$\log K_{M_IL'} \sim \Delta \log K + \Delta \log \alpha + pM'_{II} \tag{2}$$

where

$$\Delta \log \alpha = \log \alpha_{M_{II}} - \log \alpha_{M_I}$$

This means that $\Delta \log \alpha$ is positive when $\log \alpha_{M_{II}} > \log \alpha_{M_I}$, which increases the value of $\log K_{M_IL'}$. Thus, it may be advantageous to add a masking agent (HX) in a stepwise titration of M_I and M_{II} with L. It should be noted that a titration of M_{II} with L is possible if $\log K_{M_{II}L} > 7$.

Polarographic considerations

For a stepwise amperometric titration of M_I and M_{II} with L to be possible, the half-wave potentials of M_I and M_{II} must be different, *i.e.*, $E^{1/2}_{M_I} \neq E^{1/2}_{M_{II}}$ *

Direct current amperometric titration. When $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ and $K_{M_IL} > K_{M_{II}L}$ a titration of M_I and M_{II} with L can be performed in two ways

(*a*) The sum of M_I and M_{II} is obtained by titration with the potential set at E_A ($E_A < E^{1/2}_{M_{II}}$), a titration curve of the kind presented in Fig. 1 being obtained.

(*b*) M_I only is determined with the potential set at E_B ($E^{1/2}_{M_I} > E_B > E^{1/2}_{M_{II}}$). The titration curve is also of the kind in Fig. 1.

Thus, two titrations are needed to determine both M_I and M_{II} by d c. amperometric titration with L. Since deaeration after each addition of titrant is necessary, it is a laborious method.

Alternating current amperometric titration. When $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ and $K_{M_IL} > K_{M_{II}L}$, a stepwise titration of M_I and M_{II} with L can be performed with the potential set at $E = E^{1/2}_{M_{II}}$ The titration curve is of the kind shown in Fig. 2. One titration only is needed for the determination of M_I and M_{II}. No deaeration is necessary since the oxygen is irreversibly reduced at a dropping mercury electrode (DME), and thus does not cause any polarographic peak in a.c. polarography.

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* For clarity, $E^{1/2}$ is used throughout instead of the usual $E_{1/2}$

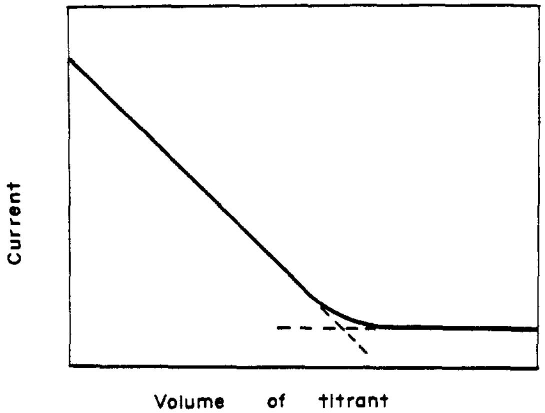

Fig 1 Amperometric titration of an electroactive substance (or the sum of several such substances) with a non-electroactive titrant, the product being non-electroactive at the applied voltage

M_I and M_{II} may be titrated stepwise by both a.c. and d.c. amperometry if $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ and $K_{M_IL} > K_{M_{II}L} > 10^7$. A suitable potential E in d.c. polarography is then $E^{1/2}_{M_I} > E > E^{1/2}_{M_{II}}$ and in a.c. polarography $E = E^{1/2}_{M_I}$.

$[M_{II}]$ should be proportional to i'_d, $[i'_d = i_d(V_0 + V)/V_0]$, where i_d is the diffusion current, V_0 is the initial vol of solution and V the vol of titrant.

Even though an irreversible process may take place at the DME, it does not necessarily follow that the process can be detected by a.c polarography. If the reaction takes place before the reduction (or the oxidation) of the ion to be determined, it may have a considerable effect on the determination of this ion (in this case M_{II}) For example the polarographic reduction of oxygen causes two waves that may interfere with the d.c measurements of other electroactive substances Kolthoff and Miller[5] have found that the half-wave potential for the first wave is practically independent of pH, and is −0·05 V *vs* SCE in most buffer solutions between pH 1 and 10 In biphthalate buffer the half-wave potential is, however, moved from −0·1 to −0·15 V *vs* SCE

Since the reduction of oxygen is irreversible, it can be assumed that the oxygen waves do not interfere with the a c. polarographic analysis. However, the reduction of oxygen

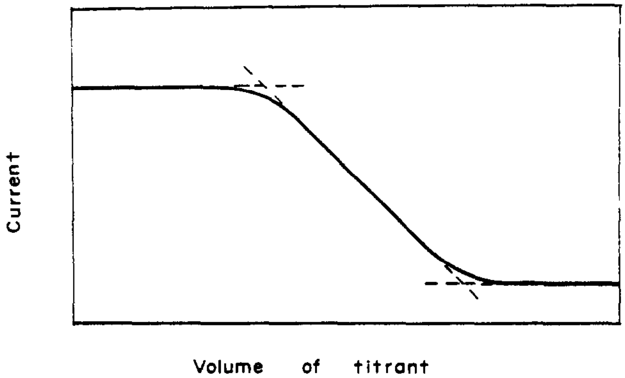

Fig 2 Stepwise amperometric titration of two electroactive substances, M_I and M_{II}, with a non-electroactive titrant, the products being non-electroactive at the applied voltage

causes formation of hydrogen peroxide and hydroxide ions, and if other electroactive substances (metal ions) react with these, the oxygen may give rise to interference, even in a c polarography.

It is well known from d.c. polarography that, in the presence of oxygen, the solution to the electrode is very alkaline in comparison with the total solution This is probably also true for a.c. polarography, where interference due to hydroxide precipitation or hydroxo-complex formation may occur at or close to the electrode

Bond and Canterford[6] have investigated the determination of Cd(II), In(III), Pb(II) and Tl(I) by a.c. polarography and found that oxygen interference is negligible in 5 *M* hydrochloric acid medium, but such a medium cannot be used for complexometric a c amperometric titration of the metals mentioned.

Head[7] has studied the a.c. polarographic determination of zinc in deaerated and oxygenated solutions, and found that the peak heights for zinc are higher for the deaerated solutions. A zinc peak which was not sensitive to oxygen was obtained if the solution was made alkaline or if it was buffered to pH 6·5.

Since it is difficult to measure a correct pH value in the immediate neighbourhood of a mercury drop, theoretical calculations have been performed instead. They indicate the most suitable conditions for the a.c. polarographic determination of zinc, when the formation of hydroxo-complexes is taken into account.

The stability constants for different zinc hydroxo-complexes are $\log \beta_1 = 4{\cdot}4$, $\log \beta_3 = 14{\cdot}4$ and $\log \beta_4 = 15{\cdot}5$ If 99% of the zinc is to be in the form of Zn^{2+} ions, interference due to $ZnOH^+$ begins at pH 7·6. Head[7] found that oxygen does not affect the zinc peak at pH 10. At pH > 10·6 the zinc is in the form of $Zn(OH)_4^{2-}$, which means that OH^--ions do not affect the a.c. polarographic determination of zinc at these pH values The addition of a suitable masking agent (HX), minimizes the formation of the hydroxo-complexes by favouring ZnX_n.

In the presence of, *e.g.*, 0·05 *M* acetate, $ZnOH^+$ begins to form at $pH(7{\cdot}6 + \log \alpha_{ZnAc})$ At pH 6·4, $\alpha_{ZnAc} \sim 10^{0{\cdot}4}$ and the interference of $ZnOH^+$ begins at pH 8. Thus some improvement results from using acetate.

EXPERIMENTAL

Reagents

Cadmium and zinc nitrate solutions
Inert electrolyte Potassium nitrate solution, 0·1 *M*
Buffer solutions Hexamine solutions to give pH 5·0, 5·5 and 6·0
Sodium acetate solution, 1 *M*
EGTA solution, $9{\cdot}5 \times 10^{-3}$ *M*

Polarograph

A Metrohm Polarecord E 261 was used A Metrohm a c Modulator E 393 with an a c voltage of 30 mV_{rms} at 50 Hz, and a Metrohm EA 249 tungsten electrode were used for a c polarography The mercury level was kept at a constant height An SCE with a 1 *M* sodium nitrate agar–agar bridge was used

RESULTS

Alternating current polarography of zinc in the presence of oxygen in different solutions

Figure 3 shows calibration curves for zinc at different pH values, obtained with the use of a c. polarography at $E_{Zn}^{1/2}$. The calibration curve obtained in the presence of 0·05 *M* ace-

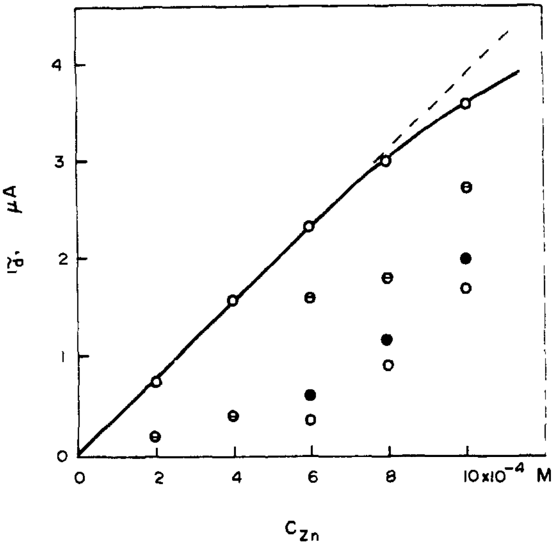

Fig 3 Alternating current polarographic determination of zinc in 0·1 M KNO_3 at $E_{1/2}^{Zn}$ = −1·01 V in the presence of oxygen ○ pH = 5·0–6·0, $[Ac^-]$ = 0·05 M, ⊖ pH = 5·0, ● pH = 5·5, ○ pH = 6·0

tate is linear up to zinc concentrations of 8×10^{-4} M In an acetate-free solution at pH 5–6, zinc cannot be determined in the presence of oxygen because zinc hydroxo-complexes are formed at a dropping mercury electrode Thus the stepwise titration of cadmium and zinc with EGTA should be performed in the presence of 0·05 M acetate

Titration of cadmium and zinc

In the stepwise titration of cadmium and zinc with EGTA the cadmium titration is independent of pH when pH > 6 and $\alpha_{L(Zn)} > \alpha_{L(H)}$, according to equation (2) The titration of zinc, on the other hand, is dependent on pH according to

$$K_{Zn\,L} = \frac{K_{ZnL}}{\alpha_{Zn}\ \alpha_{L(H)}}$$

This step therefore determines the pH for the whole titration. A pH of 6·0 is the optimum value for this titration when the electrode reactions and a suitable buffer substance (hexamine) are taken into account

The conditional constants for CdL at pH 6·0 and $\mu = 0·1$ in the presence of zinc and an excess of 0·05 M acetate, and for ZnL at pH 6·0 and $\mu = 0·1$ in the presence of an excess of 0·05 M acetate, are tabulated below (L = EGTA, $\log K_{CdL} = 15·6$ and $\log K_{ZnL} = 12·8$)[2]

log $K_{Cd\,L}$		
$pC_{Zn} = 3·5$	$pC_{Zn} = 4·0$	log $K_{Zn\,L}$
6·6	7·1	6·0

For the calculation of $\alpha_{M(Ac)}$ according to the equation

$$\alpha_{M(Ac)} = 1 + \sum \frac{[Ac^-]^n}{\alpha^n_{Ac(H)}} \cdot \beta_n \qquad (3)$$

the following constants have been used:

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Cd	1·0	1·9	1·8	1·3
Zn	1·3	2·1		

Since $\alpha_{Ac(H)}$ is $10^{0 \cdot 02} \sim 1$ at pH 6, $\alpha^n_{Ac(H)}$ can be neglected in equation (3).

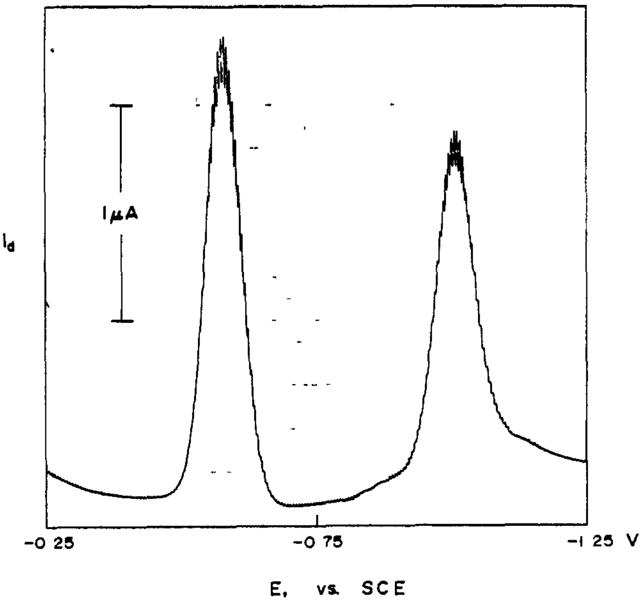

Fig. 4 Alternating current polarogram of an aerated solution that is $3 \cdot 0 \times 10^{-4}$ *M* in both cadmium and zinc at pH 6·0 in the presence of an excess of 0·05 *M* acetate and at 0·1 *M* KNO_3

Figure 4 shows an a.c. polarogram of an aerated solution which is $3 \cdot 0 \times 10^{-4}$ *M* with respect to both cadmium and zinc at pH 6·0. The corresponding d.c. polarogram of a deaerated solution is presented in Fig. 5. The half-wave potentials of cadmium and zinc are −0·58 and −1·01 V respectively. On the basis of the conditional constants calculated above,

Table 1 Results from a.c. amperometric titration of cadmium and zinc with EGTA

Cadmium, *mmole*		Zinc, *mmole*	
Added	Obtained	Added	Obtained
$3 \cdot 00 \times 10^{-2}$	$2 \cdot 99 \times 10^{-2}$ $3 \cdot 04 \times 10^{-2}$ $2 \cdot 95 \times 10^{-2}$	$2 \cdot 68 \times 10^{-2}$	$2 \cdot 71 \times 10^{-2}$ $2 \cdot 66 \times 10^{-2}$ $2 \cdot 69 \times 10^{-2}$
$10 \cdot 00 \times 10^{-2}$	$9 \cdot 83 \times 10^{-2}$ $9 \cdot 88 \times 10^{-2}$ $9 \cdot 79 \times 10^{-2}$	$0 \cdot 893 \times 10^{-2}$	$0 \cdot 950 \times 10^{-2}$ $0 \cdot 950 \times 10^{-2}$ $0 \cdot 980 \times 10^{-2}$

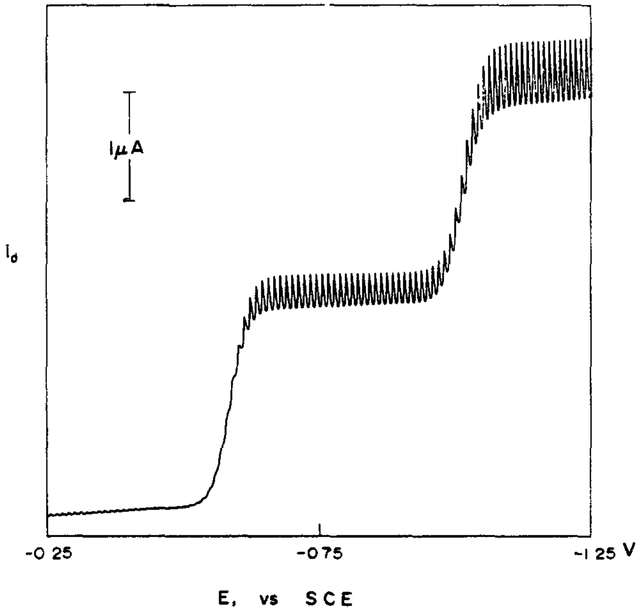

Fig 5 Direct current polarogram of a dearated solution that is 3 0 × 10^{-4} *M* in both cadmium and zinc at pH 6 0 in the presence of an excess of 0 05 *M* acetate and at 0 1 *M* KNO_3

it can be deduced that a stepwise a.c amperometric titration of cadmium and zinc with EGTA can be performed at pH 6·0.

A typical titration curve is similar to that in Fig 2, and some typical results are gathered in Table 1 Good results are achieved when the cadmium and zinc concentrations are of the same order of magnitude but high zinc values (by about 6%) and low cadmium values (2%) are obtained when the ratio Cd/Zn is 10 However, the results achieved are relatively good

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Résumé—On presente la theorie des titrages ampérometriques en courant continu et courant alternatif bases sur des reactions complexométriques On montre que si $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ et $\log K_{M_IL} < \log K_{M_{II}L}$, M_I et M_{II} peuvent être determinés sequentiellement par titrage amperometrique en courant continu aussi bien qu'en courant alternatif Si, d'autre part, $E^{1/2}_{M_I} > E^{1/2}_{M_{II}}$ et $\log K_{M_IL} > \log K_{M_{II}L}$, un titrage par paliers ne peut être effectue que par ampérométrie en courant alternatif On discute aussi de l'influence de l'oxygène sur un titrage ampérométrique en courant alternatif Le titrage amperometrique en courant alternatif par paliers du cadmium et du zinc a l'EGTA a pH 6 en presence d'oxygene et d'un excès d'acétate 0 05 *M* illustre la theorie

Zusammenfassung—Für amperometrische Titrationen mit Gleichund Wechselstrom, die auf komplexometrischen Reaktionen beruhen, wird die Theorie vorgestellt. Es wird gezeigt, daß unter den Bedingungen $E^{1/2}_{\mathrm{M_I}} > E^{1/2}_{\mathrm{M_{II}}}$ und $\log K_{\mathrm{M_IL}} < \log K_{\mathrm{M_{II}L}}$ $\mathrm{M_I}$ und $\mathrm{M_{II}}$ durch amperometrische Titration mit Gleich- und Wechselstrom nacheinander bestimmt werden können. Ist dagegen $E^{1/2}_{\mathrm{M_I}} > E^{1/2}_{\mathrm{M_{II}}}$ und $\log K_{\mathrm{M_IL}} > \log K_{\mathrm{M_{II}L}}$, dann kann eine stufenweise Titration nur mittels Wechselstrom-Amperometrie durchgeführt werden. Auch der Einfluß von Sauerstoff auf die amperometrische Titration mit Wechselstrom wird diskutiert. Die stufenweise amperometrische Wechselstrom-Titration von Cadmium und Zink mit EGTA bei pH 6 in Gegenwart von Sauerstoff und einem Überschuß von 0.05 *M* Acetat illustriert die Theorie.

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SHORT COMMUNICATION

RAPID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(IV) WITH THIOTHENOYLTRIFLUOROACETONE

(*Received* 23 *May* 1973 *Accepted* 26 *June* 1973)

Thiothenoyltrifluoroacetone (STTA) has been used in this laboratory for the extraction of transition elements[1] The studies have been extended to the extraction of vanadium(IV) It can be extracted at pH 5 0 with 0 001 *M* thiothenoyltrifluoroacetone in carbon tetrachloride–butanol mixture (1 1) The greenish-yellow complex can be measured spectrophotometrically at 450 nm The proposed method is simple, rapid, selective and affords clean-cut separation and quantitative determination of vanadium(IV) at microgram levels

EXPERIMENTAL

Reagents

Thiothenoyltrifluoroacetone [1 1,1-*trifluoro*-4-2-(*thienyl*)-4-*mercaptobut*-3-*en*-2-*one*(*STTA*)] Synthesized from 2-thenoyltrifluoroacetone by the usual procedure[2] An approximately 0 001 *M* STTA solution in carbon tetrachloride was used The reagent is preferably preserved in a refrigerator, but is stable for 6 months at room temperature provided the temperature does not exceed 0^c during the synthesis

Vanadyl sulphate solution The monohydrate (1 70 g) was dissolved in 100 ml of distilled water containing 1% of sulphuric acid The solution was standardized complexometrically with EDTA[3] with Eriochrome Black T as indicator The stock solution was diluted 10-fold (vanadium concentration 91 µg/ml)

General procedure

A 1-ml aliquot of the diluted vanadyl sulphate solution (91 µg of V) was diluted and its pH adjusted to 5 0 with 0 01 *M* sulphuric acid and 0 01 *M* ammonia solution, in a total volume of 25 ml It was then shaken for about 10 min with 5 ml of 0 001 *M* thiothenoyltrifluoroacetone in carbon tetrachloride and 5 ml of butanol The layers were allowed to separate The greenish-yellow complex of vanadium(IV) was measured spectrophotometrically at 450 nm against a reagent blank The concentration of vanadium(IV) was computed from a calibration graph

RESULTS AND DISCUSSION

Spectral properties

The absorption spectrum of the complex measured against a reagent blank, has a maximum at 450 nm (Fig 1) The reagent has an absorption maximum at about 425 nm, and the difference in absorbance between the complex and the excess of reagent used is maximal at 450 nm The molar absorptivity of the complex at 450 nm is $3\ 5 \times 10^3$ l mole^{-1} cm^{-1} The sensitivity of the method as defined by Sandell is 0 0014 µg/cm^2 Beer's law is obeyed up to a concentration of about 1 1 µg/ml in the extract at 450 nm The absorbance of the complex remains constant for up to 80 hr

Effect of pH

The extraction was studied over the pH range from 0 5 to 8 00 (Fig 2) The optimum pH is 4 4–5 3, and 5 0 was selected as being about in the middle of the range

Effect of reagent concentration

All other factors being kept constant the concentration and volume of the reagent were varied, and an equal volume of butanol was used It was observed that the extraction of 91 µg of vanadium was complete with 5 ml of 0 001 *M* STTA in the presence of 5 ml of butanol The extraction was incomplete at lower concentrations of reagent Varying the volume of 0 001 *M* reagent used showed that the extraction is quantitative with 5 ml of reagent in the presence of equal volume of butanol Hence for quantitative extraction it is sufficient to use 5 ml of 0 001 *M* STTA in the presence of 5 ml of butanol for about 90 µg of vanadium The amounts of 0 001 *M* STTA

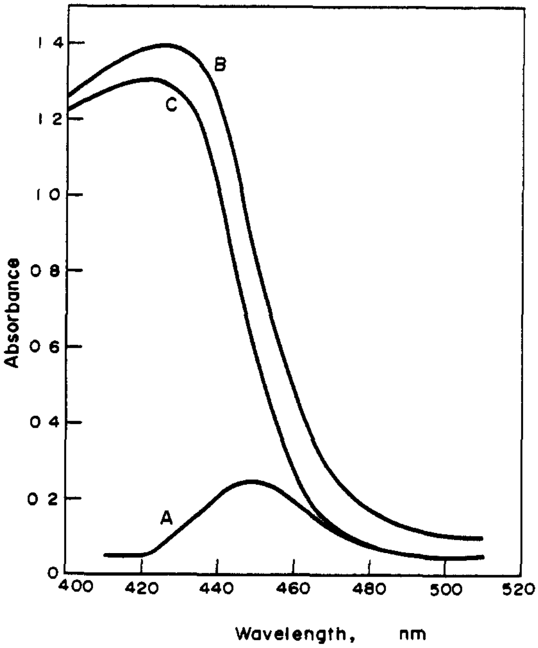

Fig 1 Absorption spectra A = V (IV)-STTA complex against reagent, B = V (IV)-STTA complex against CCl_4, C = Reagent against CCl_4, $V = 7\,138 \times 10^{-5}$ *M*, STTA = 0 001 m in CCl_4 + butanol (1 1)

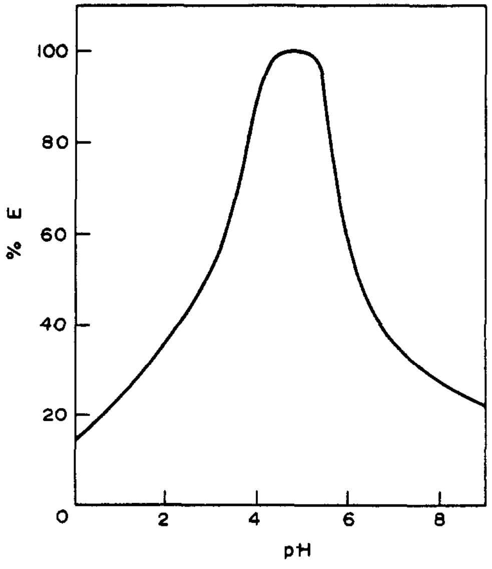

Fig 2 Extraction of V (IV) as a function of pH V (IV) = $7\,138 \times 10^{-5}$ *M* 0 001 *M* STTA + butanol (1 1)

and butanol were varied the total volume being kept at 10 ml Extraction was maximal when the volume ratio was 1 1

Period of equilibration

The period of equilibration was varied from 2 to 20 min, a wrist-action flask-shaker being used. Extraction was quantitative after 8 min of equilibration It is therefore recommended to shake the mixture for at least 10 min

Effect of salting-out agents

Lithium sodium, potassium ammonium and magnesium sulphates were tested as salting-out agents in the concentration range 1–4 *M* None enhanced the extraction

Effect of diverse ions

Several ions were examined for their effect on the extraction of vanadium(IV) The tolerance limit was taken as the amount of foreign ion required to cause ±2% error in the vanadium(IV) recovery (Table 1) It was observed that a large number of ions were tolerated in weight ratios (to vanadium) of 120 1 and 60 1 Other ions were tolerated at much lower ratios (1 1) The ions showing strongest interference were cadmium, mercury(II), manganese(II) and EDTA Several sequestering agents were tolerated in larger proportions Hence they were used to reduce the interferences of some ions *e g* gold and aluminium with oxalic acid, or iron(III), cerium(IV) and zirconium (IV) with citric acid, by formation of anionic complexes which are not extracted along with vanadium (IV) Also tributyl phosphate[4 5] was used to extract silver and lead selectively, diethylammonium diethyldithiocarbamate[1] for cobalt(II), α-furildioxime[1] for nickel and acetylacetone[1] for copper At the acidity used for extraction of these ions vanadium(IV) remained unextracted in the aqueous phase, and could subsequently be extracted and determined with 0 001 *M* STTA in carbon tetrachloride

Table 1 Effect of diverse ions on determination of 91 μg of V

Foreign ions	Added as	Tolerance limit, *mg*	Foreign ions	Added as	Tolerance limit, *mg*
Tl^{+}	$TlNO_3$	5 0	Ge^{4+}	$GeCl_4$	12 0
Ag^{+}	$AgNO_3$	0 1^{a}	Rb^{+}	$RbCl$	10 0
Pb^{2+}	$Pb(NO_3)_2\ 2H_2O$	0 1^{a}	Cs^{+}	$CsCl$	10 0
Cu^{2+}	$CuSO_4\ 5H_2O$	0 25^{d}	ReO_4^{-}	$KReO_4$	2 0
Sb^{3+}	$SbCl_3\ 3H_2O$	1 0^{e}	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}\ 4H_20$	2 0
As^{3+}	$AsCl_3$	10 0^{e}	WO_4^{2-}	$Na_2WO_4\ 2H_2O$	5 0
Au^{3+}	$HAuCl_4\ H_2O$	0 5	SeO_3^{2-}	Na_2SeO_3	10 0
Pt^{4+}	$H_2PtCl_6\ H_2O$	0 1	TeO_3^{2-}	Na_2TeO_3	5 0
Ti^{4+}	$TiCl_4\ 4H_2O$	0 3	NO_2^{-}	$NaNO_2$	5 0
Fe^{3+}	$FeSO_4\ 7H_2O$	0 5^{f}	F^{-}	NaF	10 0
Cr^{3+}	$Cr(NO_3)_3$	0 5	I^{-}	KI	10 0
Co^{2+}	$Co(NO_3)_2\ 6H_2O$	0 1^{b}	Br^{-}	$NaBr$	10 0
Ni^{2+}	$NiSO_4\ 2H_2O$	0 1^{c}	CN^{-}	KCN	10 0
Nb^{5+}	Nb_2O_5	0 5	SCN^{-}	$KSCN$	10 0
Ta^{5+}	Ta_2O_5	0 5	$S_2O_3^{2-}$	$Na_2S_2O_3\ 5H_2O$	10 0
UO_2^{2+}	$UO_2(NO_3)_2\ 6H_2O$	0 5	SO_3^{2-}	$Na_2SO_32H_2O$	10 0
Th^{4+}	$Th(NO_3)_4\ 4H_2O$	10 0	PO_4^{3-}	Na_2HPO_4	10 0
Ce^{4+}	$Ce(SO_4)_2\ 4H_2O$	1 0^{f}	$C_2O_4^{2-}$	$H_2C_2O_4\ 2H_2O$	20 0
Be^{2+}	$BeSO_4\ 4H_2O$	0 2	CH_3COO^{-}	CH_3COOH	20 0
Zr^{4+}	$Zr(NO_3)_4$	1 0^{f}	Ascorb^{-}	Ascorbic acid	20 0
Rh^{3+}	$RhCl_3\ 2H_2O$	1 0	Malonate^{2-}	Malonic acid	20 0
Ru^{3+}	$RuCl_3$	0 2	Cit^{3-}	Citric acid	20 0
Ba^{2+}	$Ba(NO_3)_2\ 2H_2O$	10 0	Tart^{3-}	Tartaric acid	20 0
Sr^{2+}	$Sr(NO_3)_2\ 2H_2O$	10 0	TU^{-}	Thiourea	20 0

Selective extraction with (*a*) tributyl phosphate, (*b*) diethylammonium diethyldithiocarbamate, (*c*) α-furildioxime (*d*) acetylacetone Interference eliminated by masking with (*e*) oxalic (*f*) citric acid

Thus the proposed method possesses several advantages The method is rapid, simple and reasonably selective It is possible to quantitatively extract and determine vanadium (IV) at trace concentrations Extraction and determination is complete within 30 min As little as 4 6 μg of vanadium can be determined and the results are reproducible The average recovery of vanadium (IV) is 99 9 ± 0 1% relative standard deviation ±1 1%

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Summary—Thiothenoyltrifluoroacetone in carbon tetrachloride–butanol (1 1) is used for extraction and spectrophotometric determination of vanadium (IV) at pH 4 5–5 The greenish–yellow complex is measured spectrophotometrically at 450 nm The system conforms to Beer's law over the range 2–11 μg/ml of extract The colour of the complex is stable for at least 80 hr Vanadium (IV) was quantitatively extracted and determined in the presence of 120 1 w/w ratios of various ions The method was made selective by using common sequestering agents or prior extraction with tributyl phosphate, diethylammonium diethyldithiocarbamate, α-furildioxime or acetylacetone The method is rapid, simple, selective and sensitive

Résumé—On utilise la thiothenoyltrifluoracétone en tétrachlorure de carbone–butanol (1 1) pour l'extraction et le dosage spectrophotometrique du vanadium (IV) a pH 4 5–5 On mesure spectrophotométriquement le complexe jaune-verdâtre a 450 nm Le système obeit a la loi de Beer dans le domaine 2–11 μg/ml d'extrait La coloration du complexe est stable pendant au moins 80 hr Le vanadium (IV) a été extrait et déterminé quantitativement en presence de divers ions dans les rapports 1 120 p/p On a rendu la méthode sélective en utilisant des agents sequestrants communs ou une extraction prealable avec le phosphate de tributyle, le diethyldithiocarbamate de diéthylammonium, l'α-furyldioxime ou l'acétylacetone La méthode est rapide, simple, sélective et sensible

Zusammenfassung—Thiothenoyltrifluoraceton in Tetrachlorkohlenstoff–Butanol (1 1) wird zur Extraktion und spektrophotometrischen Bestimmung von Vanadium(IV) bei pH 4,5–5 verwendet Der grunlichgelbe Komplex wird bei 450 nm spektrophotometrisch gemessen Das System gehorcht im Bereich 2–11 μg/ml Extrakt dem Beerschen Gesetz Die Farbe des Komplexes ist wenigstens 80 h lang stabil Vanadium(IV) wurde in Gegenwart verschiedener Ionen im Gewichtsverhaltnis 120 1 qualitativ extrahiert und bestimmt Das Verfahren wurde durch Verwendung gangiger Abfangreagentien oder durch vorausgehende Extraktion mit Tributylphosphat, Diathylammoniumdiathyldithiocarbamat, α-Furildioxim oder Acetylaceton selektiv gemacht Es geht schnell und ist einfach, selektiv und empfindlich

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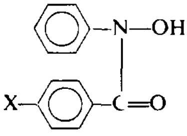
ANALYTICAL DATA

THERMODYNAMIC IONIZATION CONSTANTS OF PARA-SUBSTITUTED *N*-PHENYLBENZOHYDROXAMIC ACIDS

(*Received* 30 *April* 1973. *Accepted* 15 *August* 1973)

The thermodynamic ionization constants, pK_a, of para-substituted *N*-phenylbenzohydroxamic acids represented by the general formula



(X = OCH_3, CH_3, F, Cl, Br or NO_2) have been determined by the pH-titration method. Owing to the insufficient solubility of hydroxamic acids in water and 10% dioxan water medium the titrations were performed in mixed solvent media *viz* 20, 30, 40, 45 and 50% v/v dioxan–water mixtures. The hydroxamic acids were prepared by the modified method of Priyadarshini and Tandon.[1] The method of measurement was described earlier.[2] The magnitude of the errors in pK_a is of the same order as reported for the ortho-acids.[2] The results are given in Table 1. An empirical linear relationship between pK_a and mole fraction *n*, of dioxan is given in Table 2.

Table 1. Thermodynamic pK_a values of *p*-substituted *N*-phenylbenzohydroxamic acids at 35° in dioxan–water

	Dioxan %, *v/v*				
	20	30	40	45	50
X	*n* = 0.050	*n* = 0.083	*n* = 0.123	*n* = 0.147	*n* = 0.174
OCH_3	9.49	9.90	10.42	10.76	11.13
*CH_3	9.27	9.75	10.33	10.67	10.98
*H	9.13	9.63	10.20	—	10.96
F	Insoluble	9.61	10.16	10.49	10.84
Cl	Insoluble	Insoluble	10.02	10.35	10.68
Br	Insoluble	Insoluble	Insoluble	10.34	10.65
NO_2	Insoluble	9.02	9.52	9.82	10.15

* Reported earlier.[3]
n = mole fraction of dioxan.

This linearity is similar to that for the ortho-substituted acids.

The effect of para-substituents on the pK_a of hydroxamic acids is similar to that for the benzoic acids, *viz*

$$OCH_3 > CH_3 > H > Cl > Br > NO_2$$

Table 2. Empirical relationship between pK_a and *n* at 35°. pK_a = *mn* + *c*

X	*m*	*c*
OCH_3	13.00	8.84
*CH_3	13.90	8.55
*H	14.51	8.45
F	14.00	8.46
Cl	13.00	8.44
NO_2	12.25	8.00

* Reported earlier.[3]
Values for the bromo-compound could not be determined because the compound was soluble in 50 and 45% dioxan–water only.

Acknowledgements—The authors are thankful to (*a*) the authorities of Ravishankar University for granting a scholarship to one of them (KRG), (*b*) the Principal, Government College of Science, Raipur for providing facilities, and (*c*) to the Government of M P for granting study leave to one of them (KRG) Grateful acknowledgement is made to the Chemical Society, London and Van't Hoff Fund, Amsterdam, for partial financial assistance

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Summary—Thermodynamic ionization constants of para-substituted *N*-phenylbenzohydroxamic acids have been determined in dioxan-water mixtures at 35° The plot of mole fraction of dioxan *vs* pK_a is linear at this temperature, whereas that of pK_a *vs* $100/D$ is linear over a narrow range of dielectric constants (D) but at higher mole fraction of dioxan is influenced by non-electrostatic factors

Résumé—On a determiné les constantes d'ionisation thermodynamiques d'acides N-phénylbenzohydroxamiques para-substitués en mélanges dioxane-eau a 35° Le tracé de la fraction molaire de dioxane par rapport au pK_a est linéaire à cette température, tandis que celui du pK_a par rapport à 100/D est linéaire dans un étroit domaine de constantes dielectriques (D), mais à une fraction molaire plus élevée du dioxane il est influencé par des facteurs non-electrostatiques.

Zusammenfassung—Die thermodynamischen Ionisationskonstaten parasubstituierter *N*-Phenylbenzhydroxamsauren wurden in Dioxan-Wasser-Gemischen bei 35° ermittelt Die Auftragung von pK_a gegen den Molenbruch von Dioxan ist bei dieser Temperatur linear, die von pK_a gegen $100/D$ ist in einem engen Bereich von Dielektrizitatskonstanten (D) linear, bei einem hoheren Molenbruch von Dioxan wird sie jedoch durch nichtelektrostatische Faktoren beeinflußt

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PROTONATION CONSTANTS OF *N,N'*-ETHYLENE-BIS-[2-(*o*-HYDROXYPHENYL)]GLYCINE

(*Received* 7 *June* 1973 *Accepted* 16 *August* 1973)

The protonation constants of *N,N'*-ethylene-bis [2-(*o*-hydroxyphenyl)]glycine (EHPG = H_4X) hitherto reported have been determined potentiometrically[1] and spectrophotometrically[2] Investigations of the iron compounds of EHPG being carried out in this laboratory[3 4] require very reliable values of the hydrolytic constants of the EHPG Preliminary investigations indicated that the constants were somewhat at variance with those given

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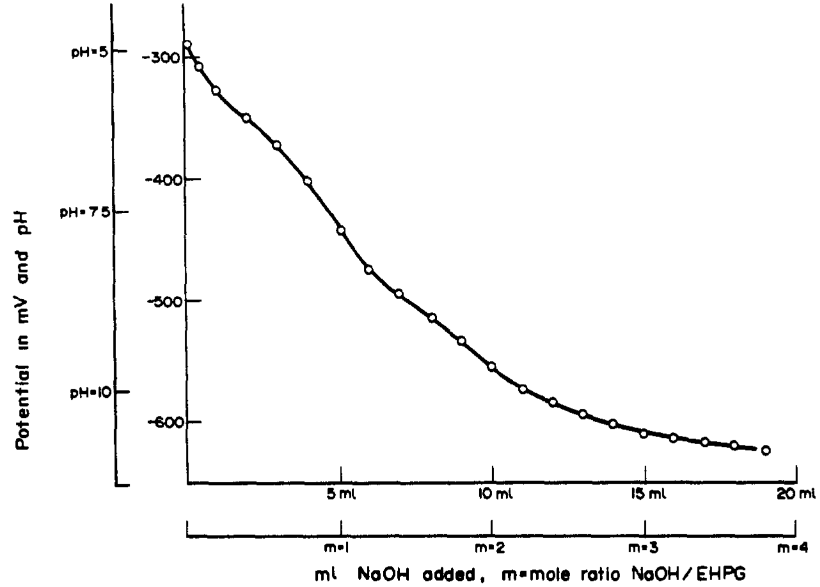

Fig. 1. Titration of $2 \times 10^{-3}M$ EHPG (total acid content $7.905 \times 10^{-3}M$) with 0.0100M NaOH $\mu = 0.1$ ($NaNO_3$) at 25.0°C. The curve is calculated from the values reported in Table 1 (U_1 data). The points represent the experimental data.

The results are reported in Table 1. The first and second protonation constants are nearly equal, thus the species H_2X^{2-}, HX^{3-} and X^{4-} exist simultaneously, and under these circumstances faulty values for the constants are liable to be found. The present calculation method, comparing two completely different least-squares functions, is assumed to exclude incorrect results. The nearly equal magnitude of these two constants is reasonable since the two phenol groups involved are at sites remote from each other. Previously, the first constant was reported as higher ($\log k = 11.85$). In the spectrophotometric determinations in 0.1M potassium nitrate media, at 297 nm, an error may have been caused by the absorption maximum (*vs* distilled water) observed in this region (295 nm) for solutions containing potassium nitrate only (the absorptivity of which is also somewhat pH-dependent). This and the similar magnitude of the first two protonation constants might explain the different values obtained previously.

Table 1. Protonation constants of EHPG (H_4X) at (25.0°C and $\mu = 0.1$ ($NaNO_3$))

	Minimizing U_1		Minimizing U_2		Previous work	
Reaction	log *k*	Std devn	log *k*	Std devn	(*a*) log *k*	(*b*) log *k*
$H^+ + X^{4-} = HX^{3-}$	10.80	0.05	10.75	0.05	11.68	11.85
$H^+ + HX^{3-} = H_2X^{2-}$	10.58	0.04	10.56	0.03	10.24	10.56
$H^+ + H_2X^{2-} = H_3X^-$	8.75	0.05	8.71	0.02	8.64	8.78
$H^+ + H_3X^- = H_4X$	6.29	0.05	6.24	0.01	6.32	6.39

(*a*) potentiometry[1]
(*b*) spectrophotometry[2]

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Summary—Protonation constants of *N,N'*-ethylene-bis[2-(*o*-hydroxyphenyl)]glycine have been determined potentiometrically, with least-squares treatment of the results The constants (0 1*M* $NaNO_3$) are $\log k_1 = 10\ 80$, $\log k_2 = 10\ 58$, $\log k_3 = 8\ 75$, $\log k_4 = 6\ 29$

Résumé—On a déterminé les constantes de protonation de la N N'-ethylene-bis[2-(*o*-hydroxyphényl)]glycine potentiométriquement, avec traitement des résultats par la methode des moindres carres Les constantes ($NaNO_3$ O, 1 *M*) sont $\log k_1 = 10.80$, $\log k_2 = 10.58$, $\log k_3 = 8\ 75$ $\log k_4 = 6{,}29$

Zusammenfassung—Die Protonierunskonstanten von *N,N'*-Athylen-bis[2-(*o*-hydroxyphenyl)] glycin wurden potentiometrisch bestimmt und die Ergebnisse nach der Methode der kleinsten Quadrate ausgewertet Die Konstanten in 0 1 *M* $NaNO_3$ sind $\log k_1 = 10\ 80$ $\log k_2 = 10\ 58$ $\log k_3 = 8{,}75$, $\log k_4 = 6{,}29$

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PROTON MAGNETIC RESONANCE STUDIES OF 8-HYDROXYQUINOLINE DERIVATIVES

(*Received* 20 *July* 1973 *Accepted* 13 *September* 1973)

Although several PMR studies[1–9] of 8-hydroxyquinoline and its derivatives have been reported, these have generally been concerned with a small number of similar compounds examined at a frequency of 60 MHz In the present work, we report new information obtained at 220 MHz for a wide range of derivatives, including a number of 8-hydroxyquinolines that have not been studied previously The use of the 220 MHz frequency allows easier interpretation of spectra

EXPERIMENTAL

Derivatives of 8-hydroxyquinoline

8-Hydroxyquinoline and its 2-methyl, 5-chloro, 5-nitro, 5,7-dichloro and 5,7-dibromo derivatives were obtained commercially and purified by standard procedures The following derivatives were synthesized by methods in the literature 2-methyl-5,7-dibromo,[10] 2-phenyl,[11] 2-(2'-thienyl),[12] 2-(2'-pyridyl),[13] 4-methyl,[14] 5-phenyl,[15] 5-chloromethyl,[16] 5-methyl,[17] 7-phenyl,[15] 7-chloro,[18] 7-t-butyl,[19] and 7-methyl [20] The 2,7-dimethyl derivative was available in the laboratory

PMR spectra

All spectra were obtained from approximately 0 1 *M* solutions in deuterochloroform at a frequency of 220 MHz, by using a Varian HR-220 spectrometer with tetramethylsilane as an internal reference The operating temperature of the spectrometer was 18 ± 1° Many of the spectra showed first-order splitting and assignments were made on the basis of previous work[21] and comparison of coupling constants Results are summarized in Table 1

DISCUSSION

The aromatic protons of 8-hydroxyquinoline exhibit two almost independent spin systems those in the pyridine ring showing AMX structure and those in the phenolic ring ABC Substitution on the ring nucleus significantly simplifies the spectrum, permitting easier assignments The coupling constants lie in a fairly narrow range and agree with literature data [5–7]

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Table 1 PMR data for 8-hydroxyquinoline and derivatives

Derivative	Chemical shift *ppm*							
	H_2	H_3	H_4	H_5	H_6	H_7	H_{subs}	H_{range}
8-hydroxyquinoline	8.79	7.35	8.15			7.19		7.52–7.25 (H_5, H_6)
2-methyl			7.94			7.14	2.63	7.39–7.17 (H_3, H_5, H_6)
2,7-dimethyl	—		7.96			—	2.68 (2-CH_3) 2.45 (7-CH_3)	7.29–7.15 (H_3, H_5, H_6)
2-phenyl	—	7.89	8.20			7.20	8.15 (H_2, H_6)	7.59–7.24 (H_5, H_6, Ph)
2-(2′-thienyl)	—	7.76	7.97				7.69 (H_3)	7.56–7.10 (H_5, H_6, H_7, Th)
2-(2′-pyridyl)	—		8.26			7.21	8.73 (H_6) 8.60 (H_4) 8.56 (H_3) 7.85 (H_5)	7.52–7.26 (H_3, H_5, H_6)
2-methyl-5,7-dibromo	—	7.40	8.27	—	7.80	—	2.75	
4-methyl	8.63	7.44	—				2.70	7.20–7.10 (H_5, H_6, H_7)
5-methyl	8.74	7.41	8.23	—	7.22	7.03	2.52	
5-phenyl	8.78		8.26	—	7.44	7.23		7.54–7.35 (H_3, Ph)
5-chloro	8.81	7.53	8.49	—	7.50	7.10	—	
5-chloromethyl	8.81	7.52	8.55	—	7.45	7.11	5.02	
5-nitro	9.35	7.75	8.90	—	8.60	7.20	—	
5,7-dichloro	8.87	7.59	8.52	—	7.61	—	—	
5,7-dibromo	8.83	7.60	8.47	—	7.92	—	—	
7-methyl	8.74	~7.3	8.09	7.24	7.34	—	2.46	
7-phenyl	8.79		8.14			—	7.81 (H_2, H_6)	7.85–7.23 (H_3, H_5, H_6, Ph)
7-t-butyl	8.73	7.35	8.09	7.21	7.55	—	1.53	
7-chloro	8.81	~7.4	8.15	7.29	7.49	—	—	

Coupling constants $J_{2,3} = 4.0$, $J_{2,4} = 1.5$, $J_{3,4} = 8.5$, $J_{5,6} = 8.7$, $J_{5,7} = 1.5$, $J_{6,7} = 7.5$ Hz

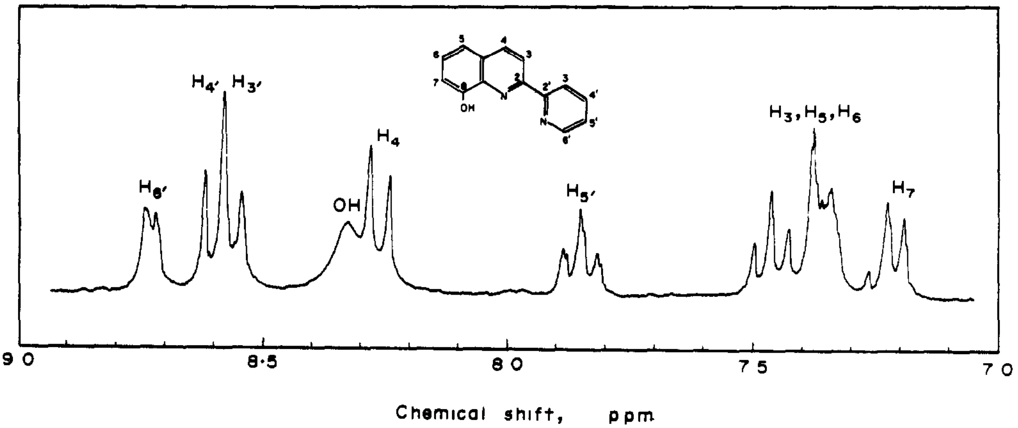

Fig 1

The chemical shifts of the H_2 protons are in the range 8 63–9 35 ppm, although all except the value for the 5-nitro derivative are below 8·87 ppm. Apart from the 5-nitro substituent, the chemical shifts of H_2 are not appreciably influenced by substituents in the phenolic ring. The proton is shielded the most by the 4-methyl substituent and deshielded the most by the 5-nitro group The H_3 protons have chemical shifts in the range 7 3–7 89 ppm the two highest values corresponding to the 2-phenyl and 2-(2'-thienyl) derivatives The deshielding of the proton *ortho* to an aromatic ring is consistent with results for 2-phenylquinoline [5] The chemical shifts of the H_4 protons lie in the range 7 94–8 90 ppm and, as expected, are affected by 5-substituents somewhat more than are the H_2 and H_3 protons Methyl substituents in the 2-position shield the H_4 proton the most whereas greatest deshielding is exhibited by electron-withdrawing groups in the 5-position The H_5, H_6 and H_7 protons have shifts in the 7 0–7 6 ppm region (except for the H_6 proton adjacent to the 5-nitro substituent, which is at 8 60 ppm), and of these the H_7 protons adjacent to the phenolic OH have shifts which are almost all within 0 1 ppm of the chemical shift of the corresponding proton in the parent molecule The chemical shifts of the various alkyl substituents are as expected, *e g*, the 7-methyl protons of the 2,7-dimethyl derivative, adjacent to the phenolic OH are shielded the most whereas the deshielding influence of the quinoline nitrogen and bromine atoms affect the 2-methyl substituent of the 2-methyl-5,7-dibromo derivative to the greatest extent The OH absorption is present in the spectra of all the derivatives as a broad peak

The spectra of the more complex molecules, *e g*, 2-(2'-pyridyl), 2-(2'-thienyl) and 2-phenyl-8-hydroxyquinoline illustrate the increased information that can be obtained by using a frequency of 220 MHz The facile interpretation of the spectrum of the 2-(2'-pyridyl) derivative (Fig 1) affords an interesting example The doublet of doublets at 8 73 ppm is assigned to the pyridyl proton adjacent to the nitrogen atom (H_6) by comparison with the spectra of pyridine and its 2-substituted derivatives [22] This proton is split by H_5 and H_4 $J_{5\,6}$ = 5 0 Hz and $J_{4\,6}$ = 1 5 Hz respectively, further coupling is indistinguishable An apparent triplet at 8 58 ppm integrating for two protons can be assigned to a partial superposition of the peaks due to H_3 and H_4 of the pyridyl group The proton with a shift slightly downfield at 8 60 ppm is assigned to H_4 in view of the 8 7-Hz coupling constant $J_{4\,6}$ = 1 5 Hz respectively, further coupling is indistinguishable An apparent triplet at 8 58 ppm integrating H_5, has its shift at 7 85 ppm and the 8-hydroxyquinoline H_4 doublet its at 8 26 ppm A complex area of peaks at 7 26–7 52 ppm, integrating for three protons, can be ascribed to H_3, H_5 and H_6 Proton H_7 can be distinguished clearly at 7 21 ppm

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Summary—The PMR spectra of 8-hydroxyquinoline and eighteen derivatives have been obtained at 220 MHz For several of the compounds, PMR spectra have not been reported previously The use of 220-MHz frequency considerably facilitates the interpretation of spectra from such complex derivatives as 2-(2′-pyridyl) and 2-(2′-thienyl)-8-hydroxyquinoline

Résumé—On a obtenu les spectres RMP de la 8-hydroxyquinoléine et de dix huit dérivés à 220 MHz Pour plusieurs des composés les spectres RMP n'ont pas eté rapportés anterieurement. L'usage de la force de champ 220 MHz facilite considerablement l'interprétation de spectres de derives complexes tels que les 2-(2′-pyridyl) et 2-(2′-thiényl) 8-hydroxyquinoleine

Zusammenfassung—Die ^{1}H-NMR-Spektren von 8-Hydroxychinolin und achtzehn Derivaten wurden bei 220 MHz aufgenommen Von mehreren dieser Verbindungen waren bisher keine Protonenresonanzspektren bekannt Die Verwendung der Feldstarke zu 220 MHz erleichtert die Interpretation der Spektren so komplizierter Derivate wie 2-(2′-Pyridyl)- und 2-(2′-Thienyl)-8-hydroxychinolin erheblich

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A TEMPERATURE-CONTROLLED GRAPHITE TUBE FURNACE FOR THE DETERMINATION OF TRACE METALS IN SOLID BIOLOGICAL TISSUE

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Summary—A temperature-controlled graphite furnace for atomic-absorption analysis has been built and tested. The temperature of the graphite tube was monitored with an infrared-sensitive detector. Samples were introduced directly or *via* a separately heated graphite cup. Micro-samples of solid biological tissue were analysed directly for Zn, Mn and Co and the sensitivities for 1% absorption were 0·05, 2 and 10 pg respectively. The salt content of the tissue limits the sample sizes, owing to non-specific absorption. The ashing conditions were investigated and found to be especially critical for Zn.

During the last few years there has been an increased interest in flameless methods for atomic-absorption analysis because of the increased sensitivity which can be obtained with this technique. A number of different cells have been described in the literature and several makers of atomic-absorption equipment now offer flameless cells as accessories. L'vov[1] described a furnace consisting of an electrically heated graphite tube in a closed cuvette chamber. The sample was introduced by means of a carbon electrode in the middle of the tube. The electrode was heated by an electrical spark. This construction has been developed further by L'vov and co-workers and their work has been summarized.[2] Massmann[3] used an open electrically heated graphite tube for atomic absorption and a slotted tube for atomic fluorescence. The tubes were flushed with an inert gas. The sample was introduced into the tube with a syringe before heating. West and Williams[4] described an arrangement in which a carbon rod, suspended between tungsten clamps, was heated electrically. The rod was mounted in a closed quartz cell and the sample was applied directly on the rod. A lightbeam passes just above the rod and when the heat is switched on vaporization starts and absorption by the atomic vapour may thus be recorded. Similar constructions using other materials and other means for producing atomic vapours have also been developed. A recent review[5] covers the work on flameless methods. Modified models of the cells used by Massmann and by West are available commercially. Headridge and Smith[6] described an induction-heated oven with a larger vapour chamber for the determination of the easily vaporized elements in steel samples.

It should be possible to modify Massmann's and West's apparatus so that solid samples can be analysed directly. L'vov has already used his cell for solids. A cell similar to that described by L'vov was therefore built. Preliminary tests showed that close control of atomization is essential, especially for the easily vaporized metals Zn, Cd, and Pb. An improved model incorporating separate heating of the cuvette and the sample cup will be described in this paper.

A number of papers have described the analysis of biological samples. Blood, serum and urine have been analysed by Matoušek and Stevens[7] (Mg, Fe, Cu, Pb, Zn), by Welz and Wiedeking[8] (Cu, Fe, Li, Pb), by Norval and Butler[9] (Pb), Hwang, Ullucci, Smith and Malenfant[10] (Pb), and by Glenn *et al.* [11] (Cu). A more thorough investigation, in which interferences in clinical applications were studied, has been made by Amos *et al.*[12] Davidson and Secrest[13] analysed blood plasma and urine for chromium, using both dry and wet combustion. Biopsies were analysed for copper, after dissolution in nitric acid, by Stevens.[14] All these workers used liquid samples which were diluted or ashed before analysis by the flameless method. Analysis for trace metals in biological samples has also been carried out by helium glow spectrophotometry. An electric glow discharge surrounding a heated filament in a helium atmosphere excites atomic emission. Vurek[15] reports detection limits for Ca, Cd, Cu, Fe, Hg, K, Mg, Na, Pb and Zn in the range 10^{-11}–10^{-12} g. The sensitivity approaches that of the flameless absorption methods but the sample handling is more difficult, especially for solids. The sample sizes are restricted to the amount which can be applied to the filament without loss. Vurek applied nanolitre liquid samples. Barnett and Kahn[16] determined copper directly in solid biological samples with a heated graphite tube atomizer.

EXPERIMENTAL

Apparatus

Cell design. A carbon cuvette, 10 cm long, was made from spectro-grade carbon (Ringsdorff RWO). A 4-mm hole was drilled through the carbon rod. The electrical connection consisted of heavy brass blocks, 1 in Fig. 1. Samples were put into a cup of a prefabricated spectrographic electrode (Ringsdorff RWO). The sample cups could easily be interchanged by placing them in a metal holder which could be tightly fitted into the oven by a bayonet socket. The sample cup was spring-loaded so that direct contact was made with the graphite cuvette.

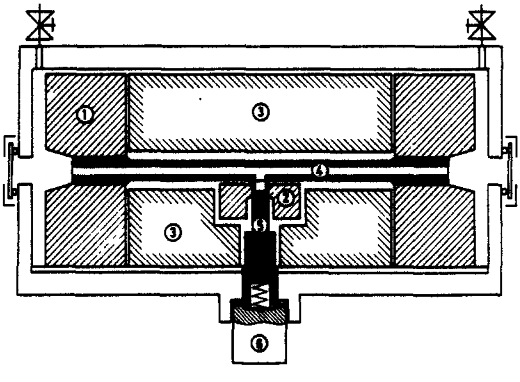

Fig. 1. Schematic view of graphite furnace.
1—brass contact, 2—graphite contacts fitted into steel holders, 3—heat shields of carbon, 4—graphite cuvette, 5—sample electrode, 6—electrode holder.

It was heated by a separate, electrically insulated, circuit connected to the cup by two spring-loaded contacts, 2 in Fig. 1. The contacts consisted of carbon, fitted into steel holders. An eccentric was used to control the contact movements. Heat shields, 3 in Fig. 1, of carbon were used to reduce radiation heat losses. The cuvette and sample cup were enclosed by a water-cooled gas-tight chamber with O-ring-sealed quartz windows. Electrical insulation was achieved with mica sheets and connections to the power supplies were made through 10-mm copper "banana"-jacks. An inert gas could be introduced *via* a Hamilton valve. Another Hamilton valve was used as outlet to a vacuum pump, a pressure meter or to the atmosphere.

A quartz window was mounted orthogonally to the plane shown in Fig. 1. A hole was drilled through the heat shield so that radiation from the cuvette could be monitored. A photodiode (HP 4220) was mounted in a screw contact which could be attached to the window holder. A red filter permitted only radiation of wavelength longer than 700 nm to reach the photodiode. A lens, $f = 10$ mm, could also be mounted in the holder to collect more radiant energy. The lens was only used for temperature control below 900°. The infrared-radiation was used as input to a temperature controller. The control was synchronized with the mains frequency so that one power cycle could be passed through the cuvette as the smallest energy unit. A power triac was used to switch the current and the switching was always performed when the a.c. passed zero. The maximum output of the power supply was 550 A at 27 V, or 15 kW. The voltage could be decreased so that thermal overshoot at a given operating temperature was largely prevented. The sample cup was heated by an unregulated floating power supply providing 300 A at 5 V, or 1·5 kW. This voltage could be decreased with a variable transformer. A switch network allowed low heating for solvent evaporation and medium heat for ashing. The temperature-control circuit is described in a separate paper.[17]

By rotating the cuvette, the furnace could be used in the Massmann mode. The samples could be loaded directly into the cuvette by an Oxford sampler.

Optical arrangement. A hollow-cathode lamp was mounted on an optical bench, followed by a quartz condenser and a mechanical chopper which interrupted the light-beam at a frequency of 100 Hz. The light-beam then passed through the graphite furnace and into a monochromator (Heath Co., 700 E). A Hamamatsu R 456 photomultiplier was used together with an amplifier containing a parametric operational amplifier (Analog Devices model 303), a phase-sensitive amplifier synchronized with the chopping frequency and a filter. A Heath logarithmic recorder was used so that the readings were linear in absorbance.

Procedure

Solid samples were weighed in aluminium boats and transferred to the carbon sample cups with glass micro-tweezers. The handling was carried out under a stereo-microscope. Normal sample size was between 1 and 30 μg. Liquid samples, *e.g.*, standard solutions, were transferred to the sample cups with an Oxford micro-sampler with disposable plastic tips. These plastic tips gave better results than micro-syringes since metal ions adhered to the needle and glass walls of the latter. The solvent was evaporated either in a separate oven or in the graphite furnace in the low-power mode. Samples up to 100 μl could be handled conveniently, depending on the size of the cup. Normally 10-μl or 25-μl samples were used.

After drying, which in the graphite furnace required about 1 min, the samples were ashed for usually 3 min at a temperature below that at which noticeable vaporization of the metal starts. Argon, or in some cases air, was flushed through the oven during these two steps. After that the oxygen was flushed out of the graphite furnace with argon or nitrogen and the pressure was adjusted to the desired value, usually 1–2 atm, before the gas flow was stopped. The heating cycle was started so that the cuvette attained the desired operating temperature; 2–3 sec after this temperature was reached the heating of the sample cup was started. The metal vaporizes into a cuvette at a constant temperature. The metal vapour diffuses through the graphite walls and through the open ends. The absorption increases during 1–2 sec, reaches a maximum and decreases owing to diffusion losses. The heaters were switched off after about 10 sec. After a cooling time of about 1 min the furnace is ready for the next sample. A sample can thus be analysed every 6th min.

The graphite cuvette could be used for 400–500 analyses at the temperatures used for metals such as zinc and lead. The graphite flakes off and the thickness of the walls decreases during the life-time of the cuvette. As a result of this the calibration curve will change slowly but the temperature remains constant as it is controlled optically.

Reagents

A synthetic stock salt solution for the preparation of standards for body fluids was made according to Dawson and Walker.[18] It contained NaCl 5·08 g/l., KCl 2·86 g/l., $CaCO_3$ 0·312 g/l., $MgCl_2 . 6H_2O$ 0·418 g/l., 98% H_2SO_4 0·67 ml/l., conc. HCl 8·7 ml/l., $NH_4H_2PO_4$ 3·09 g/l. For standards this solution was diluted 50 times.

RESULTS AND DISCUSSION

Evaporating conditions

The vaporization conditions were determined for each metal by introducing standard liquid samples into the sample cup, drying and ashing at different voltages of the sample-cup heater. A voltage sufficient to vaporize the metal into the heated graphite cuvette was then applied and the absorbance was measured. The procedure was repeated and the absorbance was plotted *vs.* the ashing temperature, see Fig. 2. The temperatures were determined by using a thermocouple or an optical pyrometer. The maximum permissible ashing temperatures were found to be 420° for Zn, 1180° for Mn and 900° for Co. The melting points are zinc 417°, manganese 1244°, cobalt 1495° and cobalt chloride 724°.

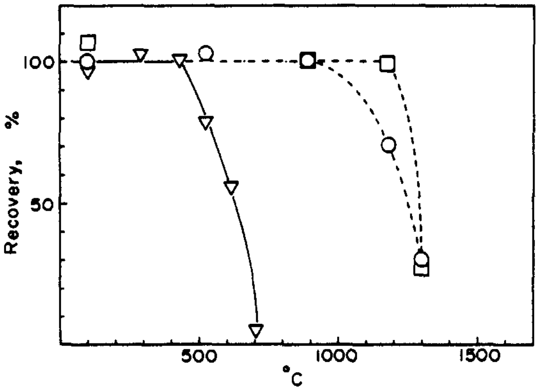

Fig. 2. Ashing temperatures for Zn (▽), Co (○) and Mn (□) in an inorganic salt solution. 40 ng of Zn (307·6 nm), 1·5 ng of Co (240·7 nm) and 0·5 ng of Mn (279·5 nm) were determined in 50-fold diluted matrix solution.

It thus seems likely that the chloride in the matrix provided by the standard text solution decreases the vaporization temperature of cobalt. The decrease in recovery of cobalt starts more slowly than it does for the other metals, which might indicate a mixture of cobaltous compounds. Gorsuch[19] has shown that dry-ashing of zinc in the presence of chloride results in large losses, but that these can be reduced by the presence of sodium. The matrix used contains large amounts of sodium chloride, which reduces zinc losses. The operating temperature for actual samples should be below that at the knee of the curve as the vaporization temperature might be slightly dependent on the dominating anion in the sample. For actual biological samples there might be a loss of low-melting zinc compounds even at temperatures considerably below 420°. A separate investigation with different equipment is necessary in order to study this source of error. In the present set-up, smoke and salt make measurements during ashing impossible. Investigations of the conditions necessary for complete ashing were made with a hydrogen lamp instead of the hollow-cathode lamp. Smoke and salt produced a non-specific absorption whereas the specific metal resonance absorption could be neglected when this lamp was used.

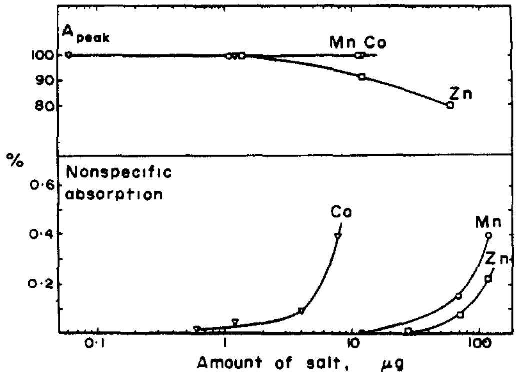

Fig. 3. Salt effect on the absorption of Mn, Co and Zn. The upper curves show the depression effect on resonance absorption in presence of the salt. The lower curves show the non-specific absorption and scattering by the salt.

It was found that the temperature needed for complete ashing was higher for Zn than the temperature at which vaporization losses occurred. It was therefore necessary to apply a correction for the non-specific absorption and this correction was obtained from a separate run on a similar sample, with a hydrogen lamp. Complete ashing was possible for Mn, Ni, Cr, and Co without losses of metal.

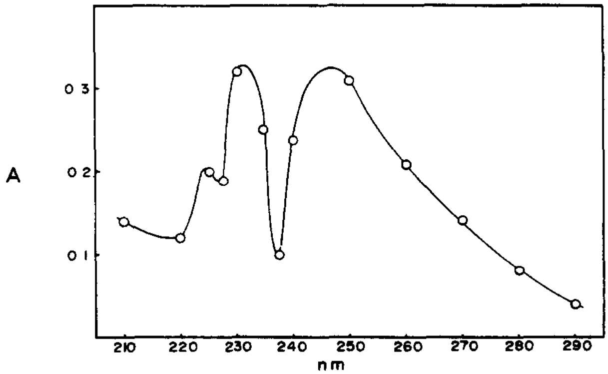

Fig. 4. Absorption of 4 μg of synthetic salt as a function of wavelength, obtained with a continuous light source.

Samples to be analysed for zinc were ashed at a temperature at which the losses were negligible (400°). The ashing was thus incomplete but most of the organic material was removed. A temperature sufficient for complete vaporization was set (1250°) and the analysis was performed as described under "Experimental". Two absorption peaks were obtained on the recorder. The first was caused by residual organic material, as shown by a similar run with a hydrogen lamp. The second peak, which for small residues is separated from the first, represents the sample resonance absorption. Matoušek and Stevens[7] noted a similar time separation between organic material and metals. Segar and Gonzales[20] tried selective evaporation as a means of separating metals and separating them from major salts in sea-water. The method was unsuccessful for Zn, Cd, Pb, and Ag but showed some success for Cu, Fe, Mn, Co, Ni, and V. In sea-water the method was successful only for Fe.

Salt effects

The influence of various amounts of the synthetic salt solution described above was investigated with the hollow-cathode lamps, using the lines at 240·7 nm for Co, 403·1 for Mn and 307·6 for Zn. The lower part of Fig. 3 shows how the lines were attenuated because of the non-specific absorption and scattering when the amount of synthetic salt was increased.

Figure 3 also shows another effect of the presence of larger amounts of salt, namely a decrease in the selective absorption. The zinc was vaporized at a slower rate than Co and Mn. Salt decreases the rate of heat transport in such a way that the ratio of atomization time to mean lifetime of zinc in the cuvette increases. This affects the peak height.[2]

The wavelength-dependence of the non-specific absorption was also studied by means of the hydrogen lamp. This absorption was found to be highest at 230 and 245 nm as shown in Fig. 4, but is so large that it cannot be neglected in any part of the range investi-

Table 1. Recovery tests for Co and Zn in tissue samples

Element (wavelength, *nm*)	Type of sample	Standard addition, *ng*	Found, *ng*	Recovery, %
Co (240·7)	Myocardium	—	0·0	
	Myocardium	6·5	6·9	106
	Myocardium	8·5	8·2	96
Zn (307·6)	Pancreatic tissue	—	0·0	
	Pancreatic tissue	22·0	24·0	109
	Pancreatic tissue	42·0	43·0	102

Table 2. Sensitivities and detection limits in organic matrices for elements determined

Element (wavelength, *nm*)	Sensitivity,* *g*	Det. limit† in a 200-μg tissue sample, *ng/g*
Co (240·7)	9×10^{-12}	45·0
Mn (279·5)	7×10^{-13}	3·5
Mn (403·1)	8×10^{-12}	40·0
Zn (213·9)	7×10^{-14}	0·35
Zn (307·6)	6×10^{-10}	3000

* Extrapolated values from calibration curves.

† Det. limit corresponds to about 1% absorption and is calculated from sensitivity data.

Table 3. Effect of dry ashing of tissues at the ashing temperature used for Zn (420°)

	Type of tissue	Total weight, μg	After ashing, μg	Residue, %
Ashing in the cuvette	Myxine-liver	377	76·5	20·3
	Myxine-liver	354	65·0	18·4
Ashing in a muffle furnace	Myxine-liver	271	58·8	21·7
	Myxine-liver	206	52·1	25·3
	Myxine-islets	98	15·0	15·3
	Myxine-islets	165	35·1	21·3
			Mean	20·4%

Table 4. Zinc content in some solid tissues from hamsters

Type of sample	Number of determinations	Range, *mg*/100 *g* wet weight	Values obtained with flame AAS,[21] *mg*/100 *g* wet weight
Pancreatic islets	4	7·1–10·4	6–13
Pancreatic tissue	4	1·1–1·5	1·1–2·4
Myocardium	8	1·0–2·1	—

gated. This absorption is likely to result from scattering by condensed particles as well as from molecular absorption.

The upper limit of the amount of salt which can be present in an analysis will depend on the salt composition and it will probably also depend on the dimensions and construction of the cuvette. The lowest concentration of an element that can be determined in a tissue can be calculated from this maximum sample weight and the detection limit for the element. The maximum weight of tissue which could be analysed before interference from the salt was found to be 200 μg dry weight, for Zn at 213·9 nm.

Table 5. Metal contents in hagfish (*mg*/100 *g* wet weight, mean values)

Type of sample	Zn	Mn	Co
Liver	3·5	0·15	0·06
Skeletal musculature	2·9	0·10	—
Pancreatic islets	1·7	0·42	0·10

Recovery and sensitivity

Standard additions were made with the appropriate metal and the synthetic salt solution to samples of heart and pancreatic tissues. The results are shown in Table 1. The cobalt and zinc contents of the tissues used were below the detection limit. A comparison of analytical curves made from standard additions and directly from standard salt solutions showed the results were identical.

Standard solutions were analysed and the amount of metal which produces 1% absorption, *i.e.*, the sensitivity, was calculated and the result is shown in Table 2. The sensitivities found are about the same as those reported by L'vov and better than those reported for commercial instruments.

The relative standard deviation was about 5% when standard solutions were used. The evaluation was made from the peak height on the recorder.

The losses of weight when the samples were ashed in platinum boats in the cuvette and in an oven with an air atmosphere at 420° for 15 min were compared. Table 3 shows that direct ashing in the graphite furnace destroys the same amount of material as ashing in air.

Some typical results are given in Tables 4 and 5. To make these results comparable with published data the values given are referred to wet weight of tissue, it being assumed that the dry weight of the sample was 25% of the wet weight. The values in Table 4 can be compared with those obtained with flame AAS by Havu.[21] There is good agreement between the results obtained by the flame AAS and the flameless AAS.

For Myxine, however, there are no references for Zn, Mn or Co, but it has been shown that Mn can take part in the liberation of insulin. Our investigation indicates good agreement with the values reported by Havu (Table 4) and there was a four times higher concentration of manganese in islets than in normal tissues.

Samples weighing a few micrograms may show an inherent variation in composition compared with larger samples which may level out some inhomogeneities. Such effects will be studied separately as well as the effects of various dissection procedures.

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Zusammenfassung—Ein Graphitofen mit geregelter Temperatur zur Atomabsorptionsanalyse wurde gebaut und getestet. Die Temperatur des Graphitrohrs wurde mit einem infrarotempfindlichen Detektor überwacht. Die Proben wurden direkt oder über einen getrennt geheizten Graphittiegel eingeführt. Mikroproben von festem biologischem Gewebe wurden direkt auf Zn, Mn und Co analysiert; die Empfindlichkeiten für 1% Absorption betrugen 0, 05, 2 bzw. 10 pg. Der Salzgehalt des Gewebes begrenzt wegen nichtspezifischer Absorption die Probengröße. Die Veraschungsbedingungen wurden untersucht und bei Zn für besonders kritisch befunden.

Résumé—On a construit et essayé un four en graphite à température contrôlée pour l'analyse par absorption atomique. La température du tube en graphite est contrôlée par un détecteur sensible à l'infrarouge. Les échantillons sont introduits directement ou par l'intermédiaire d'une capsule en graphite chauffée séparément. Des micro-échantillons de tissus biologiques solides ont été analysés directement pour Zn, Mn et Co, et les sensibilités pour 1% d'absorption ont été respectivement de 0,05, 2 et 10 pg. La teneur en sel du tissu limite les grosseurs des échantillons à cause de l'absorption non spécifique. On a étudié les conditions d'incinération et les a trouvées particulièrement critiques pour Zn.

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REACTION RATES BETWEEN WATER AND THE KARL FISCHER REAGENT

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Summary—Reaction rates between water and the Karl Fischer reagent have been determined by potentiometric measurement for various compositions of the Karl Fischer reagent. The study has been made with an iodine complex concentration of 0·3–1·2 mM and sulphur dioxide complex at 0·01–0·5M. The concentration of excess of pyridine had no measurable effect on the rate of the main reaction. The reaction was found to be first-order with respect to iodine complex, to sulphur dioxide complex, and to water. The rate constant was $(1{\cdot}2 \pm 0{\cdot}2) \times 10^3$ l^2. mole^{-2}. sec^{-1}. In an ordinary titration it is therefore essential to keep the sulphur dioxide concentration high for the reaction to go to completion within a reasonable time. The extent of side-reactions was found to be independent of the iodine concentration at low concentrations. The side-reactions increased somewhat with increasing sulphur dioxide and pyridine concentrations and decreased to about 60% when the temperature was lowered from 24° to 7°.

Since its introduction in 1935 many variations in the composition of the Karl Fischer reagent have been described in the literature. Stoichiometrically, 1 mole of iodine, 1 mole of sulphur dioxide and 3 moles of pyridine are necessary for each mole of water. The pyridine enters the reaction as complexing agent for the other constituents.

$$C_5H_5N.I_2 + C_5H_5N.SO_2 + CH_3OH + H_2O \rightarrow 2\,C_5H_5NH^+.I^- + C_5H_5NH^+.SO_4CH_3^-. \qquad (1)$$

Smith, Bryant and Mitchell[1] recommend a three-fold excess of sulphur dioxide and pyridine. A hydroxylic solvent like methanol is also necessary in order to obtain a complete reaction. Kolthoff and Elving[2] state that the most widely used reagent is prepared as a methanolic solution containing the other components in the ratio $I_2{:}3\,SO_2{:}10\,C_5H_5N$. There seems to be no systematic investigation which relates the composition to the function of the reagent.

It is known that parasitic side-reactions[1] take place in the reagent and that these cause difficulties in the storage of standardized solutions. A number of preventive measures have been tried, *e.g.*, cold storage, splitting into two solutions, use of methylcellosolve or formamide, *etc.* instead of methanol. The effect of the side-reactions is not limited to a decrease of the titre, as there are also side-reactions at the end-point when nearly all the iodine has been consumed. Clearly these latter cause more difficulties as they give rise to drift of the end-point whereas the former can easily be controlled by standardization. The nature of the side-reactions taking place in the vicinity of the end-point is not known, but it has been observed[3, 4] that the rate is nearly independent of the iodine concentration within the range 0–1mM iodine complex.

The rate of the electrode response in the indicating system will of course be critical in the determination of the homogeneous reactions taking place in the reagent. A study of the electrode response has been made and is reported in a separate paper[5] together with a coulometric procedure for the trace determination of water. It was shown that the response was rapid when the concentration of the iodine complex was at least 0·1m*M* in excess at the end-point. A potentiometric procedure was described and it has been used in the present investigation.

EXPERIMENTAL

The cell has been described earlier[5] as well as the source of the chemicals. The sample compartment was filled with 4·0 ml except where stated otherwise. The reference and auxiliary chambers were filled with Karl Fischer reagent to the same level. Some of the added sulphur dioxide will be stoichiometrically consumed by the iodine added. In order to obtain an accurate measure of the excess of sulphur dioxide, it was determined iodimetrically in water solution. An excess of iodine was added and back-titrated with thiosulphate.

An LKB 16300 Coulometric Analyser was used in a constant current mode, *i.e.*, a constant current was passed through a generating electrode-pair. The anode was located in the sample compartment and the cathode in the auxiliary compartment. The concentration of the iodine complex thus increased linearly with time. The indicating electrode system of the cell, described earlier,[5] was used to follow the reactions in the solution. It was connected to a digital voltmeter, and the potential readings were noted as a function of time.

The response of the reagent towards stepwise changes in the water content was studied by addition of 5–10μl of methanol–water mixture with a Hamilton syringe. The response of the indicating electrode system was monitored on the voltmeter as described above. The generating current was of course switched off during that time.

RESULTS

The main reaction

The relation between the electrode potential of the indicating electrode system and the concentration of the iodine complex ($C_5H_5N.I_2$), was determined from a titration curve obtained by generation of small amounts of iodine. Such a titration curve is shown in the inset in Fig. 1 and the abscissa gives the number of μmoles of complex in 4·0 ml of Karl Fischer reagent. A separate curve was made for each reagent composition and it was

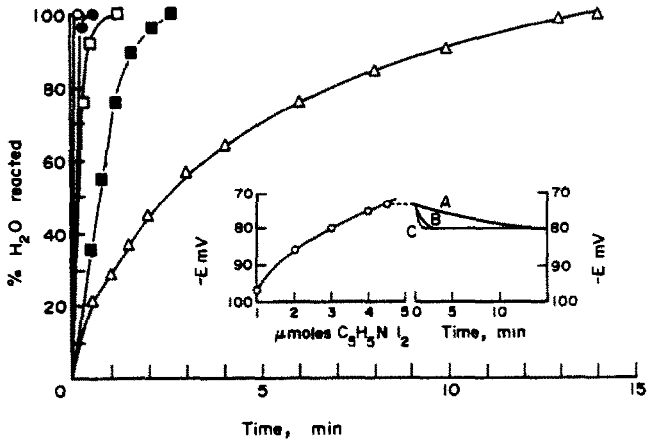

Fig. 1. The influence of various concentrations of sulphur dioxide on the rate of reaction at an initial iodine complex concentration of 1·0m*M*. 1·4 μmoles of water were added so that the final iodine complex concentration was 0·65m*M*. [SO_2]:(△) 0·01*M*, (■) 0·03*M*, (□) 0·06*M*, (●) 0·17*M*, (○) 0·50*M*. The left inset curve shows the redox potential of the indicating electrode system as a function of μmole of iodine complex generated. The right inset curve shows the redox potential as a function of time when 1·4 μmoles of water were added to the sample compartment. Curve (A) 0·01*M* SO_2, (B) 0·03*M* SO_2, (C) 0·17*M* SO_2.

repeated each day in order to cancel changes in the reference electrode potential. These titration curves were used to calculate the amount of water reacted at a certain time. The right-hand part of the inset in Fig. 1 shows the response of the indicating electrode when 1·4 μmoles of water were added rapidly to the solution in the cell.

The response time of the indicating electrode system was checked by rapidly generating a small amount of iodine and noting the electrode response. The combined mixing and electrode response time was found to be 2–5 sec in the interval 0·3–1·5m*M* iodine complex and was independent of the concentration of the other components in the solution. This time delay and its variation are superimposed on all results presented in the following.

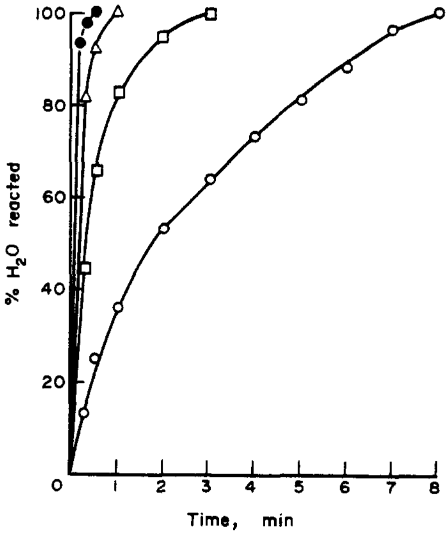

Fig. 2. The influence of various concentrations of sulphur dioxide on the rate of reaction at an initial iodine complex concentration of 0·35m*M*. 0·35 μmole of water was added. [SO_2]: (○) 0·03*M*, (□) 0·06*M*, (△) 0·17*M*, (●) 0·50*M*.

The influence of the pyridine–sulphur dioxide complex concentration on the reaction rate was studied in a methanol solution 1·0m*M* in iodine complex, 0·2*M* in pyridinium iodide and 1*M* in pyridine. The concentrations of sulphur dioxide were determined by analysis so that the amount of pyridinium methyl sulphate formed could be taken into account. Figure 1 shows the result and it is seen that the reaction becomes very slow for low concentrations of sulphur dioxide. Figure 2 shows a similar experiment in which a lower concentration of iodine complex was used and it is seen that the reaction rate has decreased further. Figure 3 shows the variation of reaction rate with the iodine complex concentration, with a magnified time scale. During the reaction this concentration will decrease by 0·088m*M* in the runs shown in Figs. 2 and 3 and 0·35m*M* in Fig. 1. Figure 3 also shows the effect of a decrease in the temperature from 24° to 7° and it is seen that the temperature-dependence of the main reaction is rather low.

The total pyridine concentration was varied in the range 0·7–3*M* in order to study its influence on the rate of the main reaction. The rate seemed to be independent of the pyridine concentration. In all cases there was an excess of pyridine of at least 0·1*M* over the amount required stoichoimetrically.

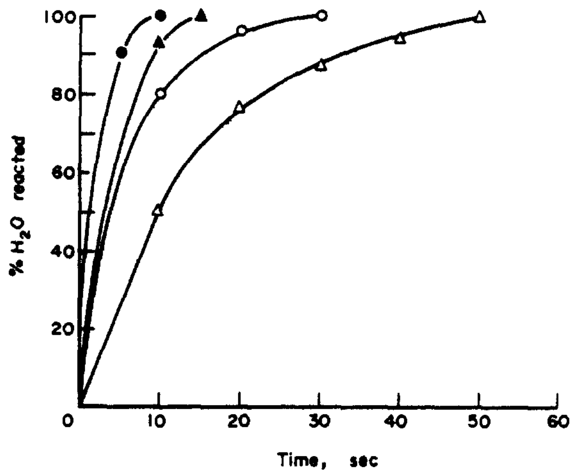

Fig. 3. The rate of reaction at a constant concentration of 0·50*M* sulphur dioxide as a function of the iodine complex concentration and the temperature. 0·35 μmole of water was added. (●) 1·0m*M* $C_5H_5N.I_2$ at 24°, (▲) 1·0m*M* $C_5H_5N.I_2$ at 7°, (○) 0·35m*M* $C_5H_5N.I_2$ at 24°, (△) 0·35m*M* $C_5H_5N.I_2$ at 7°.

Kinetics of the reaction

From the results presented in Figs. 1–3, the rate of reaction can be calculated for various combinations of reactant concentration and various assumptions of reaction order. The rate was determined graphically as the time derivative. A plot of pseudo second-order rate equation, where the sulphur dioxide complex was present in 0·06*M* excess, gave good linearity, proving that the reaction is first-order with respect to the iodine complex and also with respect to water. Table 1 shows the rate expression for a number of values of the concentrations. It was found that the experiments could be satisfied by the following equation:

Table 1. Reaction rate and rate constant for various combinations of reactants

Time, *sec*	$(C_5H_5N.I_2)$, *mM*	$(C_5H_5N.SO_2)$, *M*	(H_2O), *M*	$\frac{d[C_5H_5N.I_2]}{dt}$ *mole.l⁻¹.sec⁻¹*	*k*, $10^3.l^1.mole^{-2}.sec^{-1}$
45	0·81	0·03$_0$	0·00016	$3{\cdot}8 \times 10^{-6}$	1·0
95	0·68$_5$	0·03$_0$	0·0003$_5$	$0{\cdot}9 \times 10^{-6}$	1·3
10	0·28	0·57	0·000018	$3{\cdot}0 \times 10^{-6}$	1·2
15	0·27$_8$	0·17	0·000016	$1{\cdot}0_5 \times 10^{-6}$	1·4
30	0·26$_9$	0·17	0·000007	$0{\cdot}4_1 \times 10^{-6}$	1·3
15	0·30$_1$	0·06$_0$	0·000049	$1{\cdot}2_5 \times 10^{-6}$	1·4
60	0·27$_7$	0·06$_0$	0·000015	$0{\cdot}3_5 \times 10^{-6}$	1·4
120	0·26$_6$	0·06$_0$	0·000004	$0{\cdot}9_0 \times 10^{-7}$	1·4
				Mean value:	1·3

$$-\frac{d[C_5H_5N.I_2]}{dt} = k.[C_5H_5N.I_2].[C_5H_5N.SO_2].[H_2O]. \qquad (2)$$

The rate constant, *k*, includes any possible contribution from the pyridine and methanol, which were always present in a large excess. The rate constant calculated from equation

(2) shows good constancy. Tests of other kinetic models could not be made to fit at all. As the concentrations vary over a large range such a test becomes quite sensitive.

The rate constant found, $k = (1{\cdot}2 \pm 0{\cdot}2) \times 10^3 . l^2 . mole^{-2} . sec^{-1}$ can be used to calculate the reaction rates in cases where it is difficult to make accurate measurements and to differentiate between slow electrode response and slow reaction. If 1·8 μg of water are titrated coulometrically in 4·0 ml of the solution used by the author in an earlier paper[5] (0·5 *M* sulphur dioxide complex, 0·1*M* iodine complex, 1*M* pyridine) 82 sec will be required for 99·9% reaction and 54 sec for 99·0% reaction. It was assumed that the iodine complex concentration was kept around 0·15m*M*.

Side-reactions

The extent of the side-reactions at the end-point was measured by connecting the titration cell to the coulometric analyser in the normal operating mode as described earlier.[5] A decrease in the concentration of the iodine complex from the preset value resulted in generation of more iodine and the amount was measured by the integrator of the instrument as a function of time. The cell was filled with 4·0 ml of reagent and the amount of iodine generated was noted. Then another experiment was made with 2·5 ml of reagent of the same composition. It was found that the rate of iodine consumption was approximately proportional to the reagent volume. This proves that the cell was gas-tight and that the observed effects were due to homogeneous reactions in the reagent.

Table 2 shows the drift expressed as μg of water/min for different concentrations of pyridine and sulphur dioxide complex at two temperatures. There was a significant decrease in the drift with temperature. The drift was only slightly influenced by the amount of pyridine and even less by the amount of sulphur dioxide complex. The concentration-dependence of the drift is so low that it should be safe to conclude that these components are not directly involved in the kinetics of the side-reaction.

Table 2. Drift expressed as μg of H_2O per min in 4 ml of reagent as a function of the concentration of sulphur dioxide, pyridine and the temperature

Temp., °*C*	$[C_5H_5N]$ *M*	Drift, *μg/min* 0·03*M* SO_2	0·17*M* SO_2	0·5*M* SO_2
24	0·5	0·18	0·21	—
	0·7	—	—	0·22
	1·0	—	—	0·23
	1·5	0·23	0·29	0·34
	3	—	—	0·38
7	0·5	0·15	0·15	—
	0·7	—	—	0·13
	1·0	—	—	0·15
	1·5	0·17	0·18	0·22
	3	—	—	0·32

The effect of the iodine complex concentration on the drift was investigated by comparing the drift in a reagent when the generating system was in operation all the time and when it was switched off for some period. When the generation was stopped, all the iodine was successively consumed and after some additional time during which no iodine complex was present, the generating electrodes were switched on again. Then there was an immediate generation of iodine until the original concentration was reached again. It was found that the drift was independent of whether the iodine complex was present or not.

This experiment was repeated for a few compositions with various amounts of sulphur dioxide and pyridine and the result was the same. It was observed earlier[3,4] that the drift is constant and independent of the iodine complex concentration. The drift values given by those authors are of the same size as those given above when the volume and composition of the reagent are taken into account. For low iodine complex concentrations the extent of side-reactions seemed to be independent of even the presence of the iodine complex. The drift value was found to be higher than the decrease in titre of a fresh unspent Karl Fischer reagent with the same composition. The rates of side-reactions in an unused reagent are known to be dependent on the source of the pyridine and to decrease with the age of the prepared solution. It was also observed that the drift rate at the coulometric end-point was dependent on the make of the pyridine.

The finding that the drift in the spent reagent was independent of the iodine complex would seem to contradict the mechanisms for the side-reactions given as possible explanations by Smith *et al.*,[1] equations (3) and (4).

$$I_2 + SO_2 + 3C_5H_5N + 2CH_3OH \rightarrow C_5H_5N(CH_3)SO_4CH_3 + 2C_5H_5NHI \quad (3)$$

$$I_2 + 2SO_2 + 4C_5H_5N + 3CH_3OH \rightarrow C_5H_5NHSO_4CH_3 + 2C_5H_5NHI + C_5H_5N(CH_3)SO_4CH_3. \quad (4)$$

DISCUSSION

Close to the end-point of a titration the concentration of both water and iodine complex must be very low. In order to get as high a reaction rate as possible the concentration of the third constituent influencing the rate should be kept as high as possible. Even when the sulphur dioxide concentration is as high as 0·5*M*, which is higher than that normally used in the published procedures, the reaction still takes rather a long time, namely 54 sec to 99% and 82 sec to 99·9% completion in the example given above. In this example the titration was made to a defined concentration of iodine complex, 0·1–0·15m*M*. Attempts to titrate to a point corresponding to "zero" concentration of iodine complex will therefore fail, as the reaction slows down before "zero" concentration.

For determination of small concentrations of water large samples are normally required and this will dilute the reagent so that the actual sulphur dioxide concentration becomes very low at the end-point. Of course, dilution with pure methanol in the titration vessel should be avoided and for standardization purposes pure water added with a microsyringe should be considered as a better alternative than a larger amount of water–methanol solution. Back-titration with water–methanol has been extensively used as it is assumed to give a better end-point. As shown in this paper the reaction may appear to stop at a false end-point if the reagent is diluted so that the sulphur dioxide concentration becomes low. This procedure may thus result in a systematic titration error and the water content of the sample may appear to be a function of the waiting time.

Taking all these aspects into account it should be possible to formulate an optimum reagent composition for application in coulometric titrations: 1·0*M* pyridine was chosen, as the rate of the drift increased with the pyridine concentration. A properly made Karl Fischer reagent should contain as small an excess of pyridine as possible as the rates of the side-reactions then become lower. There must be sufficient pyridine for complexing the other components and for neutralization of acids in the sample. A concentration of

1·0M pyridine was selected with these aspects taken into account, giving an excess of 0·2M. The iodine concentration was selected to be 0·1M as this, after reaction with water, produced a sufficiently high concentration of pyridinium iodide for 100% current efficiency at the generating electrode.[5] A larger amount would have consumed more sulphur dioxide. Sulphur dioxide was added in an amount corresponding to 0·6M which, after reaction with water, gives an effective excess of sulphur dioxide complex of 0·5M. This was sufficient for the present application as the dilution with sample amounted to at most 20%. A survey of the literature, see, *e.g.*, British Standards,[6] and ASTM,[7] shows that most determinations are carried out with an actual concentration of sulphur dioxide complex around 0·1M. This results in a reaction five times slower than with the mixture recommended here.

For manual titration with a burette, a procedure in which unnecessary dilutions are avoided will result in great improvement. In this case a thorough study of the titre stability should be performed before recommending a new composition.

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Zusammenfassung—Reaktionsgeschwindigkeiten zwischen Wasser und dem Karl Fischer-Reagens wurden durch potentiometrische Messungen bei verschiedenen Zusammensetzungen des Karl Fischer-Reagens bestimmt. Die Untersuchung wurde mit Konzentrationen des Jodkomplexes von 0,3–1,2 mM und des Schwefeldioxidkomplexes von 0,01–0,5 M durchgeführt. Die Konzentration des uberschüssigen Pyridins hatte keinen meßbaren Einfluß auf die Geschwindigkeit der Hauptreaktion. Es wurde gefunden, daß die Reaktion in Bezug auf Jodkomplex, Schwefeldioxidkomplex und Wasser erster Ordnung ist. Die Geschwindigkeitskonstante betrug $(1{,}2 \pm 0{,}2) \times 10^3\ l^2 \cdot mol^{-2} \cdot sec^{-1}$. Es ist daher bei einer gowöhnlichen Titration wesentlich, daß man die Schwefeldioxidkonzentration hoch hält, damit die Reaktion in angemessener Zeit abgeschlossen ist. Bei niedrigen Konzentrationen ist das Ausmaß der Nebenreaktionen unabhängig von der Jodkonzentration. Die Nebenreaktionen nahmen mit steigender Schwefeldioxid- und Pyridinkonzentration etwas zu und fielen auf etwa 60% wenn die Temperatur von 24° auf 7° gesenkt wurde.

Résumé—On a déterminé les vitesses de réaction entre l'eau et le réactif de Karl Fischer par mesure potentiométrique pour diverses compositions du réactif de Karl Fischer. L'étude a été faite avec une concentration en complexe d'iode de 0,3–1,2 mM et en complexe d'anhydride sulfureux de 0.01–0.5 M. La concentration de l'excès de pyridine n'a pas d'influence mesurable sur la vitesse de la réaction principale. On a trouvé que la réaction est du premier ordre par rapport au complexe d'iode, au complexe d'anhydride sulfureux, et à l'eau. La constante de vitesse est $(1{,}2 \pm 0{,}2) \times 10^3\ l^2 \cdot mole^{-2} \cdot sec^{-1}$. Dans un titrage ordinaire, il est par conséquent essentiel de maintenir élevée la concentration en anhydride sulfureux pour que la réaction soit complète dans un temps raisonnable. On a trouvé que le taux des réactions secondaires est indépendant de la concentration en iode aux faibles concentrations. Les réactions secondaires augmentent quelque peu avec l'augmentation des concentrations en anhydride sulfureux et pyridine et décroissent à environ 60% quand la température est abaissée de 24° à 7°.

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COMPLEXING PROPERTIES OF 2-(2'-HYDROXYPHENYL)-8-HYDROXYQUINOLINE

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Summary—The reactions of the new ligand, 2-(2'-hydroxyphenyl)-8-hydroxyquinoline with selected metal ions have been studied. With Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), 1:1 complexes are formed in solution which are considerably more stable than the corresponding complexes of 8-hydroxyquinoline. With Al(III), stable 1:1 and 2:1 complexes are formed. With the aid of molecular models, the enhanced stability is attributed to the formation of a strain-free 5,6 bicyclic chelate-ring system.

The metal complexes of 2-substituted 8-hydroxyquinoline ligands have been the subject of several studies. It is well known that 2-alkyl and 2-aryl substitution results in metal chelates of lower stability than those of 8-hydroxyquinoline, presumably because of steric interactions which inhibit chelate formation.[1-3] Of interest are 8-hydroxyquinoline ligands with 2-substituents containing a potential donor atom. It has been shown that for rigid ligands such as 4,5-disubstituted acridines, which can be regarded as 2-substituted 8-hydroxyquinolines, both the 2-substituent steric effect and chelate ring-strain may operate, with the result that terdentate co-ordination, if it occurs at all, may not necessarily lead to more stable chelates than those of 8-hydroxyquinoline.[4] In studies with derivatives containing more flexible 2-substituents such as 2'-thienyl,[5] aminomethyl,[6] hydroxymethyl,[6] and carboxaldehyde oxime,[6] it was found that only the 2-aminomethyl derivative behaves clearly as a terdentate ligand and gives metal chelates substantially more stable than those of 8-hydroxyquinoline. With other ligands, low donor basicity and/or strain in closing the second chelate ring cause the formation of either terdentate complexes with little enhancement in stability, or bidentate complexes in which the 2-substituent behaves as a blocking group.

We wish to report here on the complexing behaviour of a new terdentate ligand, 2-(2'-hydroxyphenyl)-8-hydroxyquinoline (HPQ). This ligand forms terdentate complexes of greatly enhanced stability and the principle upon which this behaviour is based could be of importance in the design of useful analytical reagents.

EXPERIMENTAL

Reagents

All chemicals used were either of analysed grade or of a purity suitable for the purpose intended. Reagent-grade 1,4-dioxan was purified as described elsewhere.[5] Stock metal-ion solutions (~0·01 *M*) were prepared from the perchlorates and standardized by accepted EDTA procedures.

2-(2'-Hydroxyphenyl)-8-hydroxyquinoline. HPQ was prepared as follows. To a fresh solution of 2-lithium-lithium phenoxide (0·082 mole), prepared as described by Gilman and Arntzen,[7] an anhydrous ether solution (100 ml) of 8-methoxyquinoline (0·075 mole)[8] was added dropwise with stirring over a 30-min period The orange

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reaction mixture was stirred for an additional 2 hr and then poured over ice. The aqueous layer was removed and neutralized to yield a mixture of a solid and an oil. Complete recovery of the product was ensured by extraction of the ether layer with 200-ml aliquots of 2 *M* sodium hydroxide until no further precipitation occurred on neutralization of the basic solution. Recrystallization from aqueous ethanol yielded a flaky yellow solid (a dihydro compound), m.p. 91–95°. Two grams of this compound were refluxed in 50 ml of nitrobenzene for 1 hr. Extraction of this solution with 200 ml of 2 *M* hydrochloric acid gave a yellow solid on neutralization. Recrystallization from aqueous ethanol produced bright yellow crystals of 2-(2′-hydroxyphenyl)-8-methoxyquinoline, m.p 160–161°; yield 20% (4 g), based on 8-methoxyquinoline. Four grams (0·016 mole) of this compound were refluxed for 24 hr in 48% hydrobromic acid. After cooling to 0°, the precipitated hydrobromide salt was filtered off and dissolved in water. This solution was made basic and filtered to remove any insoluble matter, and the filtrate neutralized. The orange precipitate obtained was recrystallized from aqueous ethanol to give HPQ, m.p. 116–117°; yield 16% based on 8-methoxyquinoline. Calculated for $C_{15}H_{11}O_2N$: C, 75·9%; H, 5·06%; N, 6·05%. Found: C, 75·9%, H, 4·8%; N, 5·9%. The infrared spectrum (hexachloro-1,3-butadiene mull) showed two broad —OH absorption bands at ~3200 (as in 8-hydroxyquinoline) and at ~2500 cm^{-1}. The band-shift to 2500 cm^{-1} indicates strong hydrogen-bonding of the 2′-OH group, probably intramolecularly to the ring nitrogen atom. Strong hydrogen bonding is also indicated by the large downfield shift (to 15·6 ppm) of the 2′-OH group in the 100-MHz PMR spectrum; the 8-OH resonance is at 10·6 ppm. Integration accounted for the correct number of protons. The involvement of the 2′-OH group in hydrogen bonding was confirmed by the PMR spectrum of 2-(2′-hydroxyphenyl)-8-methoxyquinoline in which a single —OH resonance at 16 ppm is observed. The absence of the H_2 resonance (a quartet) in the spectrum of HPQ showed that substitution of the hydroxyphenyl group had occurred in the 2-position of the quinoline nucleus. The mass spectrum gave a parent-ion peak (m/e = 237) corresponding to the calculated molecular weight. HPQ absorbs strongly in the ultraviolet region: for H_3L^+ (pH 1), $\epsilon = 4{\cdot}1 \times 10^4$ l. $mole^{-1}$ cm^{-1} at $\lambda_{max} = 290$ nm; for H_2L (pH 7), $\epsilon = 4{\cdot}2 \times 10^4$ at $\lambda_{max} = 277$ nm; for HL^- (pH 12), $\epsilon = 3{\cdot}0 \times 10^4$ at $\lambda_{max} = 291$ nm. In the range pH 13–15, the spectra indicated a further dissociation to L^{-2}.

Test-tube reactions of HPQ

The reactivity of HPQ was determined in test-tubes with drop quantities of 24 different metal-ion solutions (~0·02 *M*) and an excess of the reagent (alcoholic solution). The pH was fixed at 1·0, 2·6, 5·0, 7·5 and 10·0 with a small quantity of appropriate buffer solutions. The aqueous phase was extracted with a few ml of chloroform. The appearance of a precipitate or a colour in either the aqueous or organic phase was noted.

Appropriate metal-ion and reagent blank tests were made. As expected, HPQ is not selective, particularly at pH 10. Of special note was a positive test recorded for Al(III).

Acid dissociation constants

The p*K*(NH) and p*K*(8-OH) values were obtained potentiometrically in 50% v/v aqueous dioxan at ionic strength 0·1 (adjusted with sodium perchlorate) and 25°, using a weighed quantity of ~0·7 mmole of HPQ. The titration procedure, the value of the correction factor and of pK_w, and the method of calculation were essentially as described previously.[9,10] Corrections were made for sodium-ion error and volume contraction of aqueous dioxan solutions. In equations for $[H_3L^+]$ and $[H_2L]$, the terms $([HL^-] + [L^{2-}])$ and $[L^{2-}]$, respectively, were ignored. Because of its high value, p*K*(2′-OH) was determined spectrophotometrically. Absorbance measurements were made at two chosen pH values and the following equation was solved for *K*(2′-OH):

$$K(2'\text{-OH}) = \{\epsilon_{HL^-} . C_L([H^+]_2 - [H^+]_1) + A_1[H^+]_1 - A_2[H^+]_2\}/(A_2 - A_1),$$

where C_L = analytical concentration of HPQ. The value of ϵ_{HL^-} was obtained at pH 12, where $[H_2L]$ and $[L^{2-}]$ are negligible. A series of *K*(2′-OH) values was obtained at 302 and 291 nm, using several pairs of calculated pH values in the pH range 13·5–14. The p*K* values for HPQ are: p*K*(NH) = 2·74 ± 0·02, p*K*(8-OH) = 10·28 ± 0·02, p*K*(2′-OH) = 14·3 ± 0·3.

Metal–chelate formation constants

These were determined potentiometrically in the usual manner,[4,10] using 5·00 ml of standard metal-ion solution (~0·01 *M*) and HPQ:metal-ion ratios of 1:1, 2:1 and 3:1 [5:1 for Al(III)]. The hydrolysis curve of each metal ion was obtained by titration in the absence of ligand. For the 2+ ions, analysis of the titration curves and Job plots suggested that only 1:1 complexes are formed. Thus, it was possible to calculate a formation constant for each point in that part of the titration curve over which chelation occurs, using $K_1 = \bar{n}/(1 - \bar{n})[L^{2-}]$. The final value of the formation constant was taken as the mean value in the $\bar{n}$ range 0·2–0·8. The general equations of Hearon and Gilbert[4] were used for the calculation of $[L^{2-}]$ and $\bar{n}$. For Al(III), a 2:1 complex is formed; below $\bar{n}$ = 0·8, a drift in pH occurred (see Discussion), causing a distortion in the formation curve, and reliable values of K_1 could not be obtained; nevertheless, Bjerrum's $\bar{n}/2$ method was used to get approximate values of K_1 and K_2. Formation constants for the metal-ions studied are given in Table 1.

Table 1. Formation constants of HPQ with selected metal ions, 50% v/v aqueous dioxan, ionic strength = 0·1, 25°

	log K_1	log K_2
Al(III)	19·8 ± 0·5 (11·98)	14·9 ± 0·1
Co(II)	15·42 ± 0·02 (9·65)[6]	—
Ni(II)	16·00 ± 0·03 (10·50)[6]	—
Cu(II)	23·60 ± 0·06 (13·29)[6]	—
Zn(II)	15·82 ± 0·04 (9·45)[6]	—
Cd(II)	12·57 ± 0·03 (8·22) .	—

The numbers in brackets are log K_1 values for the corresponding 8-hydroxyquinolinates, for which the Al(III) and Cd(II) values were determined in the present work. The precision measure for the HPQ formation constants is the average deviation from the mean value given by several titrations.

DISCUSSION

The synthesis of HPQ has been previously reported by Towle[11] who was interested in the potential antiseptic properties of the compound. Towle's procedure, which does not employ an oxidizing agent (*e.g.*, nitrobenzene), gave a yield of 1%. The use of nitrobenzene as reported above increased the yield 16-fold. A mild oxidant is required for the oxidation of the 1,2-dihydro compound which results from hydrolysis of the intermediate of the organolithium reaction. Evidence for the dihydro compound was obtained from the infrared and mass spectra of the hydrolysis product. In Towle's report, a complete characterization of HPQ was not made. The characterization reported herein provides conclusive evidence for the synthesis.

The low pK(NH) value (2·74) of HPQ relative to that for 8-hydroxyquinoline (4·16)[6] could be attributed to steric hindrance to solvation of the protonated nitrogen, owing to the 2-substituent,[5,9] and to hydrogen-bonding between the 2'-OH proton and the ring nitrogen atom. The infrared and PMR evidence for such bonding is supported by Courtauld molecular models. This interaction would also account for the decreased pK(8-OH) value (10·28) compared to that for 8-hydroxyquinoline (11·20),[6] since bonding of the 8-OH proton to the nitrogen atom would be inhibited and an increase in acidity expected. The precision (±0·3) of the pK(2'-OH) value is poor for several reasons, primary among which are a slow decomposition of HPQ in strongly basic solutions, non-constancy of ionic strength because of the high concentrations of alkali required, and incomplete dissociation of sodium hydroxide in the medium.[12]

The titration curves for the HPQ complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were of a simple form, yielding a single buffer zone in the range pH 5–7·5 [for Cu(II), 2·5–3] corresponding to the release of two protons per metal ion. Job plots, which were ideal in shape, showed the stoichiometry of the complexes to be 1:1, *i.e.*, of the type ML with both —OH protons liberated on chelation. These plots were obtained at 290 nm and at pH 8 (*i.e.*, beyond the pH range for the formation of ML). Under the conditions used, no potentiometric or spectrophotometric evidence was obtained to suggest the formation of complexes of the type ML_2^{2-}. In the titrations, precipitation of the Cu(II), Zn(II) and Cd(II) chelates occurred, but sufficient results were obtained before the precipitation to allow computation of the formation constants. Although the pH range for reaction between HPQ and Cd(II) was 7–8, the precision of the formation constant calculated from results for titrations of different molar ratios was good, suggesting that hydrolysis was not a serious problem. Also, hydrolysis of water co-ordinated to the terdentate complexes was not observed in the range pH 8–10, as has been found with 1:1 (cationic) complexes of other terdentate ligands.[4] We conclude that for the HPQ complexes, it must occur at a higher pH range as a result of the formation of both neutral and more stable chelates. Our attempts to prepare solid metal chelates in high purity for analysis failed, due primarily to precipitation of the ligand, but the results obtained corresponded much more closely to 1:1 than 2:1 complexes.

The reaction of HPQ with Al(III) is more complex. For each reactant molar-ratio (*i.e.*, 1:1, 2:1 and 5:1), a buffer zone was observed in the range pH 3·5–5·0, corresponding to two protons per Al(III) ion. This pH range decreased with increasing molar ratios, suggesting that the proton release is due to chelation rather than hydrolysis. Since the titration for a 1:1 molar ratio also yielded two protons per Al(III), the reaction must correspond to the formation of a 1:1 terdentate complex. For the ratios 2:1 and 5:1, a second buffer zone also corresponding to two protons per Al(III) ion was observed at pH 6–8. The pH range of this zone decreased with increasing molar ratio, indicating the formation of AlL_2^-. Beyond pH 8, the titration curves for the 2:1 and 5:1 molar ratios could be quantitatively interpreted in terms of the amount of free ligand calculated to be present on the basis of a 2:1 stoichiometry for the complex. For the 1:1 molar ratio, two regions of proton release were observed above pH 5 (at ~pH 7 and 9), each corresponding to a one-proton release. During the titration, an orange–yellow precipitate appeared at about pH 7 and redissolved above pH 9. These results suggest the formation of AlLOH and $AlL(OH)_2^-$.

The formation constants for the Al(III)–HPQ complexes were interpolated from the $\bar{n}$ curve which, apart from a small distortion in the $\bar{n}$ range 0·2–0·8, was classical in form, with plateaux at $\bar{n} = 1{\cdot}0$ and 2·0. The distortion can be traced to a downward drift in pH readings, beginning at ~pH 3·7, when the titration solution is allowed to stand. The drift is not due to either the formation of a solid phase or to simple Al(III) hydrolysis, even though partial hydrolysis of Al(III) has occurred by pH 3·7. The reactions which are involved in the hydrolysis of Al(III) have been studied extensively. There is agreement that polymeric hydroxo species predominate over mononuclear species, and that a characteristic of these species is their slowness in reaching equilibrium. Turner[13] has shown that the reaction between 8-hydroxyquinoline and such polymeric Al(III) species is slow. A similarly slow reaction with HPQ would account for the drift in pH-meter readings. This condition means that the reaction between HPQ and Al(III) (in polynuclear form) is mechanistically complex and that during titration, it was not at equilibrium in the pH range corresponding to the first buffer zone. Thus, the value for log K_1 must be regarded as questionable.

The 1:1 complexes of HPQ are much more stable than the corresponding 1:1 complexes of both 8-hydroxyquinoline (Table 1) and the 2-alkyl and aryl substituted derivatives,[5] providing strong evidence that HPQ functions as a terdentate ligand. The complexes are also considerably more stable than the reported 8-hydroxyquinoline derivatives with 2-substituents bearing potential donor atoms. For example, the Cu(II) complex is 14·5 log units more stable than the 1:1 4,5-dihydroxyacridine complex,[4] even though the total donor atom basicity of HPQ is only 2 p*K* units greater. Because of the chelate-ring strain, 4,5-dihydroxyacridine behaves as a bidentate ligand in which the unco-ordinated —OH group acts as a sterically hindering group.[4] Molecular models (Courtauld) show a high-strain barrier to the formation of a bicyclic chelate-ring system in which each ring contains five members. The strain is eliminated, however, if the 2-substituent is flexible and contains a donor atom situated such that a 5,6 bicyclic system is formed. This is the case with HPQ; the models show an essentially strainless fit for terdentate co-ordination. In turn, terdentate co-ordination results in the elimination of the 2-substituent steric effect, a more favourable entropy factor (*e.g.*, in terms of particle numbers), and a more favourable enthalpy term (*e.g.*, an M–OR bond *vs.* an $M-OH_2$ bond).

It is of special interest to compare the complexing behaviour of HPQ with that of 2-hydroxymethyl-8-hydroxyquinoline (HMQ). Stevenson and Freiser[6] were unable to conclude from stability data whether HMQ behaves as a terdentate ligand in solution. Construction of models suggests, however, that formation of a terdentate complex (*i.e.*, 5,5 bicyclic system) involves ring strain which would reduce the stability from a maximal value; replacement of the $—CH_2OH$ substituent by a $—CH_2CH_2OH$ group would yield a more effective ligand. An additional factor with HMQ involves the very weakly acidic nature of the side-chain —OH group. Once complexed to a metal ion, a very stable –O–M bond should result; however, the pH range required for this particular interaction may be so high that hydrolysis would result. It is possible that the pH range over which Stevenson and Freiser computed $\bar{n}$ data was such that the —OH group either remained uncomplexed or was involved in a weak interaction as $\mathrm{M}\text{---}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\text{—}\mathrm{R}$. These two possibilities may not apply to the Cu(II) complex, which is apparently so stable that its formation is complete at low pH. The Cu(II)–HPQ complex is also extremely stable and was noted to behave similarly in the present study.

HPQ and 2-aminomethyl-8-hydroxyquinoline (AMQ)[6] are the only two reported 2-substituted derivatives which clearly form terdentate complexes. In the case of HPQ, the orientation of the donor atoms yields an unstrained 5,6 bicyclic ring system. For AMQ, the models suggest that some strain exists in the 5,5 ring system, but apparently it is not sufficient to reduce the formation constants to the level of those for 8-hydroxyquinoline. The formation constants for the complexes of 2-aminoethyl-8-hydroxyquinoline would be most interesting in this regard, but we have not been able to synthesize this ligand.

The present work suggests that the most stable complexes derived from terdentate ligands based on 2-substituted 8-hydroxyquinoline will result from the formation of a strain-free 5,6 bicyclic chelate-ring system (in conjunction with the selection of a suitable donor atom). Such ligands would be useful, for example, as sequestering agents or spectrophotometric reagents, or even as titrants after sulphonation to enhance aqueous solubility.

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Zusammenfassung—Die Reaktionen des neuen Liganden 2-(2′-Hydroxyphenyl)-8-hydroxychinolin mit ausgewählten Metallionen wurden untersucht. Mit Co(II), Ni(II), Cu(II), Zn(II) und Cd(II) werden in Lösung 1:1-Komplexe gebildet, die wesentlich stabiler sind als die entsprechenden Komplexe mit 8-Hydroxychinolin. Mit Al(III) bilden sich stabile 1:1- und 2:1-Komplexe. Mit Hilfe von Betrachtungen an Molekülmodellen wird die erhöhte Stabilität der Bildung eines spannungsfreien 5,6-bicyclischen Chelatringsystems zugeschreiben.

Résumé—On a étudié des réactions du nouveau coordinat, 2-(2′-hydroxyphényl) 8-hydroxyquinoléine avec des ions métalliques choisis. Avec Co(II), Ni(II), Cu(II), Zn(II) et Cd(II), il se forme en solution des complexes 1:1 qui sont considérablement plus stables que les complexes correspondants de la 8-hydroxyquinoléine. Avec Al(III), il se forme des complexes stables 1:1 et 2:1. Avec l'aide de modèles moléculaires, la stabilité accrue est attribuée à la formation d'un système noyau chélaté bicyclique 5,6 exempt de tension.

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GRAPHICAL ANALYSIS OF THE FORMATION FUNCTION—II

THE PSEUDO CROSS-OVER POINT

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Summary—In a further attempt to enhance the possibility of interpreting the formation function, a number of special shapes of the formation function are discussed, which give rise to a pseudo cross-over point. It is shown that under certain conditions a pseudo cross-over point can be found in the following cases: (1) two series of homonuclear complexes, (2) a mixture of a series of homonuclear and polymeric complexes, (3) a series of mononuclear complexes and two polynuclear complexes with nearly the same composition, (4) a system which gives a real cross-over point, and one or more polynuclear complexes, (5) a system of two polynuclear complexes. The conditions are mainly discussed in terms of the composition of the complexes. Calculated curves illustrate the different possibilities.

In a previous paper[1] it was reported that a system composed of mononuclear and homonuclear or polymeric complexes gives rise to a family of formation functions showing a real cross-over point: all curves intersect at one single point. Taking into account the experimental uncertainty, however, the experimentally obtained formation curves will intersect each other within a small range. Nevertheless for a number of systems it can be proved that the theoretical formation curves will intersect each other not in a single point but within a small range. This can be called a pseudo or apparent[2] cross-over point.

In the case of acid–base systems some authors make the same distinction. Byé[3] and Souchay[4] assert that in acid–base equilibria a real isohydric point is found in a system where two species dominate. The cross-over point is called here the isohydric point, since it appears at a fixed pH value. According to these authors a pseudo isohydric point will be found when at least three species are present in solution. Other authors, such as Carpéni[5–7] and McBryde[8] make no distinction between those two forms of cross-over points.

In this paper a number of systems are discussed which give under certain conditions a pseudo cross-over point. In this discussion the cases for which the probability of fulfilling all conditions is extremely low are excluded. The discussion is essentially restricted to the composition of the complexes.

MATHEMATICAL TREATMENT

For a series of complexes B_qA_p the degree of formation Z is given by

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^{q-1} a^p}{1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p} \tag{1}$$

where b is the concentration of free metal ion, a the concentration of free ligand, β_{qp} the overall concentration stability constant of the complex B_qA_p, defined as

$$\beta_{qp} = \frac{[B_qA_p]}{b^q . a^p}. \tag{2}$$

In these equations B stands for the metal ion and A for the ligand. In a previous paper[1] it was proved that the sign of $(\partial Z/\partial B)_a$ was determined by the function ψ_A which in its general form is given by equation (3)

$$\psi_A = \sum_q \sum_p (q-1)(p-Zq)\beta_{qp}b^{q-2}a^p. \tag{3}$$

The conditions for a pseudo cross-over point can be given by: (a) $(\partial Z/\partial B)_a = 0$ for a value of a' in the range $pa - \Delta pa \leqslant pa' \leqslant pa + \Delta pa$, Δpa having an arbitrary value of about 0·01; (b) $(\partial Z/\partial B)_{a'}$ has a sign different from $(\partial Z/\partial B)_{a''}$ for $pa' \leqslant pa - \Delta pa$ and $pa'' \geqslant pa + \Delta pa$; (c) the conditions under (a) and (b) must be fulfilled for a relatively large range of total metal ion and ligand concentration.

The following systems can be discussed.

1. Two series of homonuclear complexes $B_{Q'}A_p$ and $B_{Q''}A_p$ in a region where b is negligibly small in comparison with B. The functions ψ_1 and ψ_2 are defined as:

$$\psi_1 = \frac{\sum p\beta_{Q'p}a^p}{Q'\sum \beta_{Q'p}a^p}, \tag{4}$$

$$\psi_2 = \frac{\sum p\beta_{Q''p}a^p}{Q''\sum \beta_{Q''p}a^p}. \tag{5}$$

If the minimum value for p in the first homonuclear series is $p_{1\,\min}$ and the maximum value is $p_{1\,\max}$, then ψ_1 will go from $p_{1\,\min}/Q'$ to $p_{1\,\max}/Q'$. In the same way ψ_2 will vary from $p_{2\,\min}/Q''$ to $p_{2\,\max}/Q''$. These limits are called $\psi_{i\,\min}$ and $\psi_{i\,\max}$. Substitution of ψ_1 and ψ_2 in equation (1), taking into account that $b \ll$ B gives:

$$Z \sim \frac{\psi_1 Q'b^{Q'}\sum \beta_{Q'p}a^p + \psi_2 Q''b^{Q''}\sum \beta_{Q''p}a^p}{Q'b^{Q'}\sum \beta_{Q'p}a^p + Q''b^{Q''}\sum \beta_{Q''p}a^p}. \tag{6}$$

This can be transformed into:

$$Q'b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p \sim -Q''b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p. \tag{7}$$

Substitution of ψ_1 and ψ_2 in ψ_A gives

$$\begin{aligned}\psi_A = {} & Q'(Q'-1)b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p, \\ & + Q''(Q''-1)b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p.\end{aligned} \tag{8}$$

Substitution of (7) in (8) gives

$$\psi_A = (Q' - Q'')Q'b^{(Q'-2)}(\psi_1 - Z)\sum \beta_{Q'p}a^p, \tag{9}$$

or

$$\psi_A \doteq (Q'' - Q')Q''b^{(Q''-2)}(\psi_2 - Z)\sum \beta_{Q''p}a^p. \tag{10}$$

It can be derived from equation (6) that if $\psi_1 = \psi_2$ then $\psi_1 = \psi_2 = Z$; if $\psi_1 < \psi_2$ then $\psi_1 < Z < \psi_2$ and if $\psi_1 > \psi_2$ then $\psi_1 > Z > \psi_2$.

The following two cases can be discussed:

(*a*) $\psi_{1\,\mathrm{min}} < \psi_{2\,\mathrm{min}}$ and $\psi_{1\,\mathrm{max}} > \psi_{2\,\mathrm{max}}$.

ψ_1 and ψ_2 will have an odd number of intersection points. Suppose there is one intersection point. At that point $\psi_1 = \psi_2 = Z$ and $\psi_A = 0$. Below that point $\psi_1 < Z < \psi_2$ and from (9), $\psi_A > 0$ if $Q' < Q''$ and $\psi_A < 0$ if $Q' > Q''$. Beyond that point, $\psi_1 > Z > \psi_2$ and ψ_A will take the sign of $Q' - Q''$.

(*b*) $\psi_{1\,\mathrm{min}} < \psi_{2\,\mathrm{min}}$ and $\psi_{1\,\mathrm{max}} < \psi_{2\,\mathrm{max}}$.

ψ_1 and ψ_2 will have an even number of intersection points or none at all. Suppose there are two intersection points. The sign of ψ_A is given below as a function of ψ_1 and ψ_2.

	$\psi_A(Q' > Q'')$	$\psi_A(Q' < Q'')$
$\psi_1 < \psi_2$	< 0	> 0
$\psi_1 = \psi_2$	$= 0$	$= 0$
$\psi_1 > \psi_2$	> 0	< 0
$\psi_1 = \psi_2$	$= 0$	$= 0$
$\psi_1 < \psi_2$	< 0	> 0.

In Figs. 1 and 2 these two possibilities are illustrated. The curves are calculated with the computer program ALTH described before.[1] In Fig. 1 the formation curves for a mixture of complexes with composition B_2A, B_2A_4 and B_4A_5, B_4A_7 are shown. ψ_1 varies from 0·5 to 2 and ψ_2 from 1·25 to 1·75. One cross-over point is found. In Fig. 2 a mixture of a series B_2A, B_2A_2 and a series B_4A_3, B_4A_8 is considered. Here ψ_1 varies from 0·5 to 1 and ψ_2 from 0·75 to 2. Two cross-over points are found.

2. A series of homonuclear complexes $B_{Q'}A_p$ and a polymeric series $(B_{q''}A_{p''})_n$ when *b* is negligibly small in comparison with B gives a pseudo cross-over point.

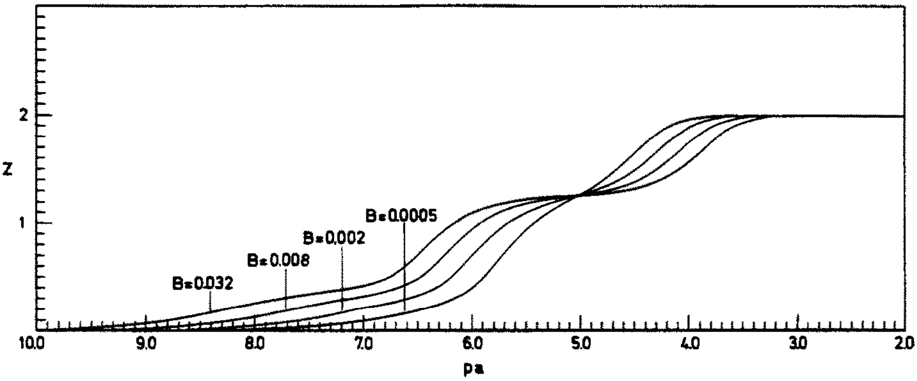

Fig. 1. Theoretical curves for two series of homonuclear complexes: B_4A_5, B_4A_7 and B_2A, B_2A_4.
$\log\beta_{45} = 40{\cdot}0$, $\log\beta_{47} = 45{\cdot}0$
$\log\beta_{21} = 9{\cdot}5$, $\log\beta_{24} = 25{\cdot}0$.

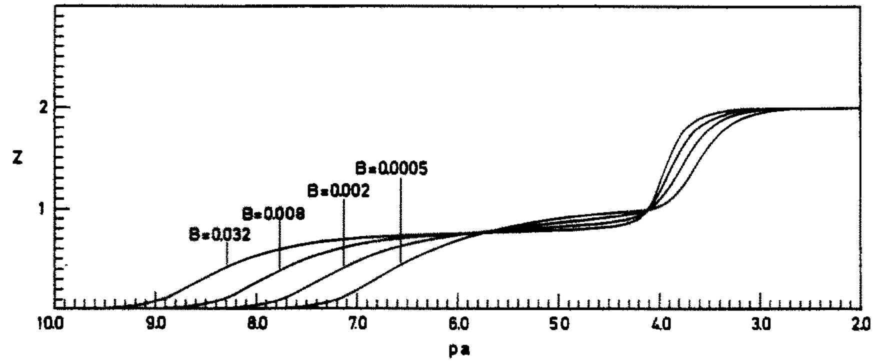

Fig. 2. Theoretical curves for two series of homonuclear complexes: B_2A, B_2A_2 and B_4A_3, B_4A_8.
$\log \beta_{21} = 9{\cdot}0$, $\log \beta_{22} = 16{\cdot}0$
$\log \beta_{43} = 30{\cdot}0$, $\log \beta_{48} = 50{\cdot}0$.

Let ψ_1 and ψ_2 be defined as:

$$\psi_1 = \frac{\sum p\beta_{Q'p}a^p}{Q'\sum \beta_{Q'p}a^p}, \tag{11}$$

$$\psi_2 = \frac{p''}{q''}. \tag{12}$$

ψ_A can be expressed as:

$$\psi_A = (Q' - 1)b^{(Q'-2)} \sum_p (p - Q'Z)\beta_{Q'p}a^p + \sum_n (nq'' - 1)(np'' - nZq'')\beta_n b^{(nq''-2)}a^{np''}, \tag{13}$$

where β_n is the stability constant of the complex $B_{nq''}A_{np''}$. Substitution of ψ_1 and ψ_2 in ψ_A gives:

$$\psi_A = Q'(Q - 1)(\psi_1 - Z)b^{(Q'-2)} \sum_p \beta_{Q'p}a^p + q''(\psi_2 - Z)\sum_n n(nq'' - 1)\beta_n b^{(nq''-2)}a^{np''}. \tag{14}$$

Substitution of ψ_1 and ψ_2 in Z gives, after some transformations:

$$(\psi_1 - Z)Q'b^{Q'} \sum \beta_{Q'p}a^p = -(\psi_2 - Z)q'' \sum_n nb^{nq''}\beta_n a^{np''}. \tag{15}$$

Substitution of the left-hand term of equation (15) into equation (14) gives:

$$\psi_A = (\psi_2 - Z)q'' \{q'' \sum n^2\beta_n b^{(nq''-2)}a^{np''} - Q' \sum n\beta_n a^{np''}b^{(nq''-2)}\}. \tag{16}$$

The sign of ψ_A is determined by both the expression $(\psi_2 - Z)$ and the expression between curly brackets. However it is very improbable that the sign of the latter will change in the neighbourhood of the cross-over point, thus the sign of ψ_A is determined by $(\psi_2 - Z)$. For $\psi_2 = Z$, ψ_A will vanish. It can be seen from equation (16) that the sign of ψ_A will change at that point: a pseudo cross-over point will be found.

An example of such a cross-over point is given in Fig. 3. A series of homonuclear complexes B_2A, B_2A_4 and a polymeric series $(B_3A_3)_n$ gives a pseudo cross-over point at $Z \sim 1$.

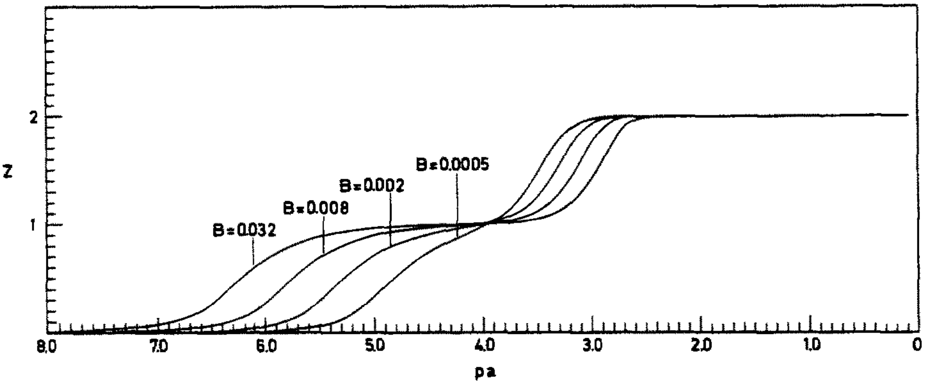

Fig. 3. Theoretical curves for a series of homonuclear complexes and a polymeric series: B_2A, B_2A_4 and B_3A_3, B_6A_6.

$\log\beta_{21} = 7{\cdot}5$, $\log\beta_{24} = 20{\cdot}0$

$\log\beta_{33} = 21{\cdot}0$, $\log\beta_{66} = 46{\cdot}0$.

3. Mononuclear complexes with two polynuclear complexes with nearly the same composition give a pseudo cross-over point. Let ψ_1 and ψ_2 be defined as

$$\psi_1 = \frac{p'}{q'}, \tag{17a}$$

$$\psi_2 = \frac{p''}{q''}. \tag{17b}$$

If $\psi_2 > \psi_1$ and $Z = \psi_1$ then

$$\psi_A = q''(q'' - 1)(\psi_2 - \psi_1)\beta_{q''p''}b^{(q''-2)}a^{p''} > 0, \tag{18}$$

For $Z = \psi_2 = p''/q''$

$$\psi_A = q'(q' - 1)(\psi_1 - \psi_2)\beta_{q'p'}b^{(q'-2)}a^{p'} < 0. \tag{19}$$

If mononuclear complexes BA ... BA_N with $N > \psi_{2_{\max}}$ are present, all formation functions intersect each other between ψ_1 and ψ_2. If ψ_1 and ψ_2 do not differ too much, this system gives a real cross-over point. In Fig. 4 an example of a mixture of BA, BA_2 and $B_{10}A_{10}$, $B_{10}A_{11}$ is shown. As can be seen, all formation curves intersect between $Z = 1$ and $Z = 1{\cdot}1$.

4. A system consisting of a series of complexes which gives a real cross-over point, and one or more complexes the contribution of which to the formation function may be neglected in the region of that point, can give a pseudo cross-over point. This case is obvious and needs no further proof.

In order to illustrate this case theoretical curves were calculated. The initial set of complexes was BA_2 and B_4A_6. As mentioned before, a real cross-over point at $Z = 1{\cdot}5$ is found. To this system a complex B_2A_2 was added, with increasing stability constant: a pseudo cross-over point at $Z = 1{\cdot}5$ is found. For still higher values of β_{22} the contribution of B_4A_6 is small and the pseudo cross-over point is found at $Z = 1$. For intermediate values of β_{22} both complexes contribute to the formation function and the intersection

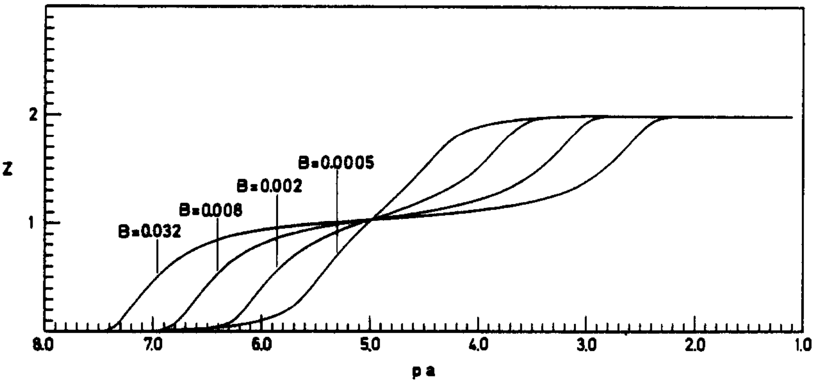

Fig. 4. Theoretical curves for a mixture of mononuclear complexes and two polynuclear complexes with nearly the same composition: BA, BA_2 and $B_{10}A_{10}$, $B_{10}A_{11}$.
$\log\beta_{11} = 5{\cdot}0$, $\log\beta_{12} = 10{\cdot}0$
$\log\beta_{10,10} = 85{\cdot}0$, $\log\beta_{10,11} = 90{\cdot}0$.

points will fall between 1 and 1·5. This is shown in Fig. 5. It certainly cannot be considered as a pseudo cross-over point, but it illustrates that a family of formation curves which at first sight cross each other at random is theoretically well possible. Therefore it should be emphasized that only if there is sufficient evidence, may formation curves with an abnormal shape be rejected on account of too great experimental errors.

5. A system consisting of two polynuclear complexes $B_{q'}A_{p'}$ and $B_{q''}A_{p''}$ can give a cross-over point.

Substitution of equation (1) into ψ_A gives

$$\psi_A = \frac{\begin{array}{l}[p'(q'-1)\beta_{q'p'}b^{(q'-2)}a^{(p'-2)} + p''(q''-1)\beta_{q''p''}b^{(q''-2)}a^{p''} \\ \qquad + (p'q''-p''q')(q'-q'')\beta_{q'p'}\beta_{q''p''}b^{(q'+q''-3)}a^{(p'+p'')}]\end{array}}{(1 + q'\beta_{q'p'}b^{(q'-1)}a^{p'} + q''\beta_{q''p''}b^{(q''-1)}a^{p''})}. \tag{20}$$

A necessary condition that the formation curves intersect each other is that the third term of the numerator is negative. Thus if $p'/q' < p''/q''$ then $q' > q''$: the complex with the

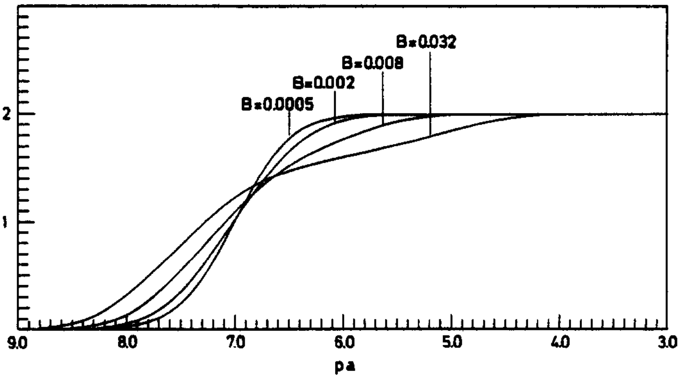

Fig. 5. Theoretical curves for three complexes BA_2, B_2A_2, B_4A_6.
$\log\beta_{12} = 14{\cdot}0$; $\log\beta_{22} = 17{\cdot}0$; $\log\beta_{46} = 50{\cdot}0$

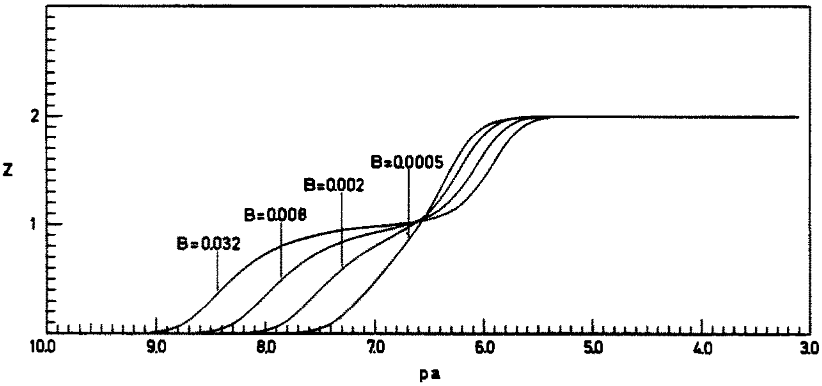

Fig. 6. Theoretical curves for two polynuclear complexes: B_4A_4, B_2A_4. $\log \beta_{24} = 30{\cdot}0$; $\log \beta_{44} = 38{\cdot}0$.

lowest p/q ratio must contain the most metal ions. It can easily be shown that two complexes belonging to a "core + links" series $B(A_tB)_n$ do not fulfil this condition and the formation curves will not intersect each other. Two complexes with the same amount of ligand molecules will always fulfil this condition. However, the observance of a pseudo cross-over point in this case will be critically dependent on the values of the stability constants and therefore it is not very probable that it will be found in a system consisting of two polynuclear complexes in a region where b is not negligible in comparison with B. Otherwise it is a special case of 1. In Fig. 6 an example of such a pseudo cross-over point is shown for the two complexes B_4A_4 and B_2A_4.

CONCLUSION

In this paper five systems of complexes are discussed, giving under certain conditions a family of formation curves with a pseudo cross-over point that can hardly be distinguished from a real cross-over point. The conditions are, with the exception of case 5, to a first approximation independent of the values of the stability constants.

When treating experimental data showing a cross-over point, methods should be used to distinguish a pseudo from a real cross-over point. This can be achieved by enlarging the concentration ranges and changing the ratio of total ligand to total metal ion concentration. This is mostly limited in scope, however. At higher concentrations precipitation may occur and at lower concentrations the accuracy of the measurements may be questioned. Also the change of the ratio of total ion to total ligand concentration is in some cases limited as has been shown by Cabani.[9] Another method is, when possible, to calculate the mean value for p and q, using methods described by Sillén.[10]

At any rate, to avoid premature conclusions about the composition of the complexes, care should be taken when treating experimental data showing formation curves with a cross-over point and all possible compositions should be thoroughly discussed.

Acknowledgement—The authors wish to thank Prof. Z. Eeckhaut for helpful discussions.

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Zusammenfassung—In einem neuen Anlauf, die Interpretations-möglichkeiten der Bildungsfunktion zu verbessern, werden eine Anzahl besonderer Formen der Bildungsfunktion diskutiert, die zu einem Pseudo-Kreuzungspunkt führen. Es wurde gezeigt, daß unter bestimmten Bedigungen in folgenden Fällen ein Pseudo-Kreuzungspunkt gefunden werden kann: (1) zwei Reihen homonuklearer Komplexe; (2) ein Gemisch einer Reihe homonuklearer und polymerer Komplexe; (3) eine Reihe einkerniger und zwei mehrkernige Komplexe mit nahezu der gleichen Zusammensetzung; (4) ein System, das einen reellen Kreuzungspunkt und einen oder mehrere polynukleare Komplexe gibt; (5) ein System von zwei mehrkernigen Komplexen. Die Bedingungen werden hauptsächlich in Bezug auf die Zusammensetzung der Komplexe diskutiert. Berechnete Kurven verdeutlichen die verschiedenen Möglichkeiten.

Résumé—Dans un nouvel essai pour accroître la possibilité d'interprétation de la fonction de formation, on discute d'un certain nombre de formes spéciales de la fonction de formation, qui donnent naissance à un point de pseudo-chevauchement. On a montré que dans certaines conditions un point de pseudo-chevauchement peut être trouvé dans les cas suivants: (1) deux séries de complexes homonucléaires, (2) un mélange d'une série de complexes homonucléaires et polymères, (3) une série de complexes mononucléaires et deux complexes polynucléaires ave sensiblement la même composition, (4) un système qui donne un point de chevauchement réel, et un ou davantage de complexes polynucléaires, (5) un système de deux complexes polynucléaires. Les conditions sont principalement discutées en fonction de la composition des complexes. Des courbes calculées illustrent les différentes possibilités.

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INVERSE VOLTAMMETRY OF ANTIMONY WITH TRIPHENYLMETHANE DYES

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Summary—A method is suggested for the determination of traces of antimony by inverse voltammetry of the solid phases formed with triphenylmethane dyes (Crystal Violet, Methyl Violet and Malachite Green) as the precipitants. The authors have studied the effect of concentration, adsorption and oxidation of the triphenylmethane dyes, potential and time of pre-electrolysis, and concentration of antimony(III) and some other elements on the polarogram shape and stripping current. A method for determining antimony traces in chromic salts is described as an example.

Triphenylmethane dyes (TPMD) are widely used in solvent extraction. Usually, the ion-pairs formed by the interaction between dye cations and inorganic anions are quite soluble in organic liquids. In aqueous media polyionic aggregates are formed which precipitate under certain conditions. As a rule, the oxidation state of the element is important, *e.g.*, antimony(V) interacts with TPMD, but antimony(III) at similar concentrations does not form a precipitate. This feature makes it possible to utilize TPMD in the technique of inverse voltammetry of solid phases,[1] for concentrating and determining elements which exhibit different oxidation states. Since in inverse voltammetry preconcentration occurs on an electrode, its course must depend on at least the following factors: (1) dye adsorption on the electrode–solution interface, (2) orientation of the dye relative to the electrode surface, (3) electrode passivation by the precipitate formed.

In the present work an attempt has been made to investigate the role of these factors in the preconcentration of traces of antimony on a graphite electrode, in the form of ionic associates with Crystal Violet (I), Methyl Violet (II) and Malachite Green (III), and the possibility of determining traces of antimony by this means.

EXPERIMENTAL

Reagents

Doubly distilled water and high-purity reagents were used. Solutions were always freshly prepared.

Apparatus

Polarograph ОП-02ЦЛА was used. Polarograms of dye oxidation and reduction at different rates of electrode potential scan were obtained with the aid of a potentiostat II-5827 with potentiometer KCII-4 as a recording device. Graphite electrodes were soaked with epoxy resin, with polyethylene–polyamine, or paraffin plus polyethylene.[1,2] A saturated calomel electrode served as the auxiliary and reference electrode.

Procedure

The experimental technique has already been described.[1,2] The adsorption of the dye is followed from the cathodic and anodic polarograms recorded with constant scanning rate from +1·0 to −1·0 V.

RESULTS AND DISCUSSION

Neither oxidation nor reduction currents are observed when the dye concentration in the solution is low ($C < 1 \times 10^{-5}M$) and the electrode has not been preliminarily kept at a certain potential. The anodic polarogram recorded after cathodic polarization of the electrode for a certain period of time shows anodic current peaks (Fig. 1, peaks 1 and 2) near +0·8 and +0·9 V in 0·1*M* sulphuric acid. If hydrochloric acid is used as a background electrolyte, the second peak is masked, probably by the chloride–ion oxidation current. Preliminary polarization of the electrode at potentials more positive than +0·7 V in acid medium is accompanied by the appearance of two cathodic peaks, one at a potential of +0·5 V, which corresponds to the data given elsewhere,[3] and the other at −0·35 V (Fig. 1, peaks 3 and 4); peak 3 increases with shift of the preliminary electrolysis potential in a positive direction. The peaks are apparently due to oxidation (1 and 2) or reduction (3) of the substance on the electrode surface, indicated[3] by the linear dependence of the current maximum on the electrode potential scanning rate.

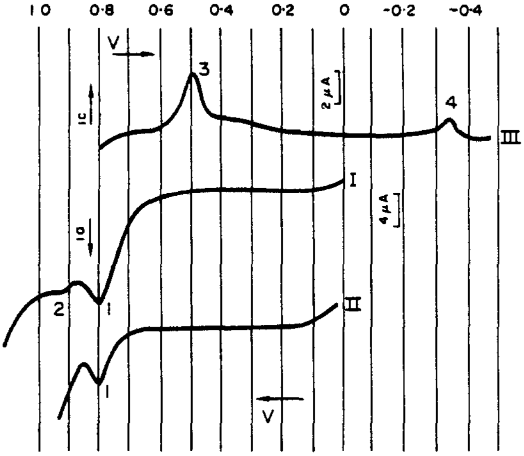

Fig. 1. Polarograms for Crystal Violet.
Solution: 0·1*M* H_2SO_4 + 1 × $10^{-6}M$ CV (I); 1·5*M* HCl + 1 × $10^{-6}M$ CV (II,III)
Electrolysis duration (*t*) 3 min at potential of 0·0 V (I, II); +0·8 V (III); scan-rate = 0·125 V/sec.

Peak 3 is explained by reduction of the dye oxidation products accumulated during the preliminary electrolysis. The data presented by Galus and Adams[4] confirm this supposition together with the fact that this peak does not appear if the preconcentration electrolysis is done at potentials too low for the dye to be oxidized.

Peaks 1 and 2 appear to be due to adsorption processes since the reverse electrode processes do not take place. No reduction currents are observed on the cathodic polarograms. Thus it may be thought that the heights of peaks 1 and 2 and the quantities of electricity in the respective potential ranges would give information about the dye adsorption. As the dye cations carry an electrical charge, the dye adsorption and orientation must obviously depend on the sign and magnitude of the electrode surface charge.

Figure 2 shows the dependence of the peak oxidation current (peak 1) for Crystal Violet upon the electrode potential during the preliminary electrolysis. Similar results were found for all the dyes investigated. The zero-charge potential for graphite in solutions which do not contain a specific adsorbate lies in the interval from 0 to −0·2 V *vs.* SCE.[5,6] In the

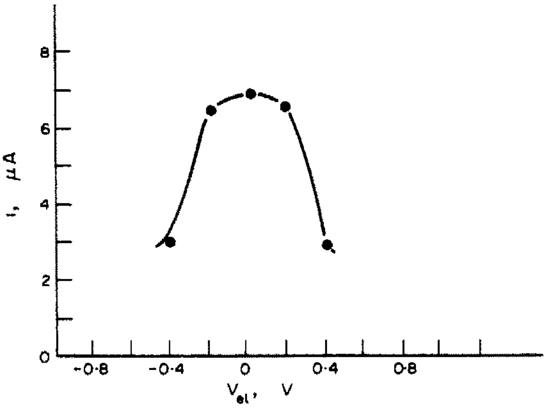

Fig. 2. The dependence of the maximum current of Crystal Violet oxidation (Peak 1, Fig 1) on the preconcentration potential.
1·5M HCl + 1 × $10^{-6}M$ CV; t = 3 min; scan-rate = 0·125 V/sec.

presence of specifically adsorbing cations the zero-charge potential shifts in a positive direction by 0·1–0·2 V, depending on the cation and its concentration.[7] Taking into consideration the properties described and the data given in Fig. 2, it may be concluded that the maximum dye adsorption is observed in the potential range near the electrode zero-charge potential the dye cations are oriented to the electrode surface by the portion with the maximum electron density. Meantime unoccupied electropositive portions appear to serve as locations for association of the dye with anionic antimony complexes.

The preconcentration of antimony at the electrode–solution interface may be presented schematically similarly to that described earlier.[1,2,8]

$$[SbCl_6]^{3-} \rightarrow [SbCl_6]^{-} + 2e \qquad (1)$$

$$[SbCl_6]^{-} + TPMD^{+} \rightarrow [SbCl_6]TPMD \downarrow \qquad (2)$$

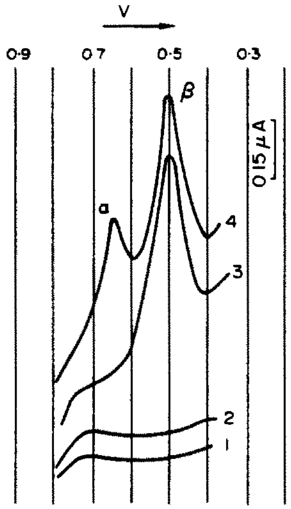

Fig. 3 Cathodic polarograms obtained after electrolysis.
(1) 1·5M HCl + 8 × $10^{-8}M$ $SbCl_3$; (2) 5 × $10^{-6}M$ CV + 8 × $10^{-8}M$ $SbCl_3$; (3) 5 × $10^{-6}M$ CV + 1·5M HCl; (4) 5 × $10^{-6}M$ CV + 1·5M HCl + 8 × $10^{-8}M$ $SbCl_3$.
t = 10 min; potential = +0·8 V; scan-rate = 0·125 V/sec.

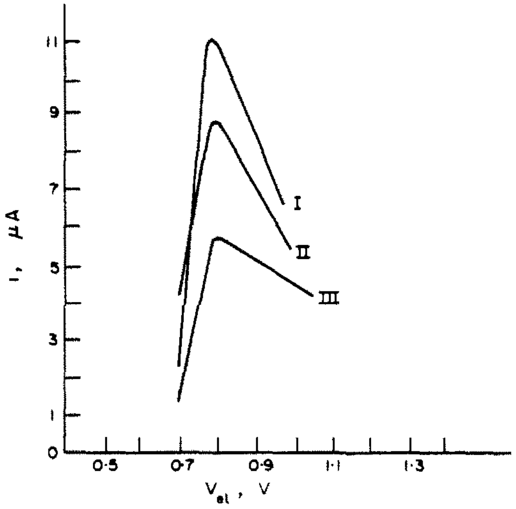

Fig. 4. The dependence of the maximum current of electro-dissolution of the antimony compound with various dyes on the preconcentration electrolysis potential.

(I) $4 \times 10^{-6}M$ $SbCl_3$ + $1{\cdot}5M$ HCl + $2 \times 10^{-4}M$ CV; (II) $4 \times 10^{-6}M$ $SbCl_3$ + $1{\cdot}5M$ HCl + $22 \times 10^{-5}M$ MV; (III) $4 \times 10^{-6}M$ $SbCl_3$ + $1{\cdot}5M$ HCl + $2 \times 10^{-5}M$ MG.

t = 1 min; scan-rate = 0·125 V/sec.

The reaction is apparently possible only in the presence of at least three components in solution: antimony(III) ions, chloride ions and TPMD. The data in Fig. 3 confirm the validity of the statement. The cathodic polarogram shows an antimony reduction current only when all the necessary components are available in the solution. The peak current for stripping a compound formed from reactions (1) and (2) depends on the electrode potential during the preconcentration stage (V_{el}) on the pH, on the concentrations of antimony, TPMD and chloride, and on the duration of the electrolysis.

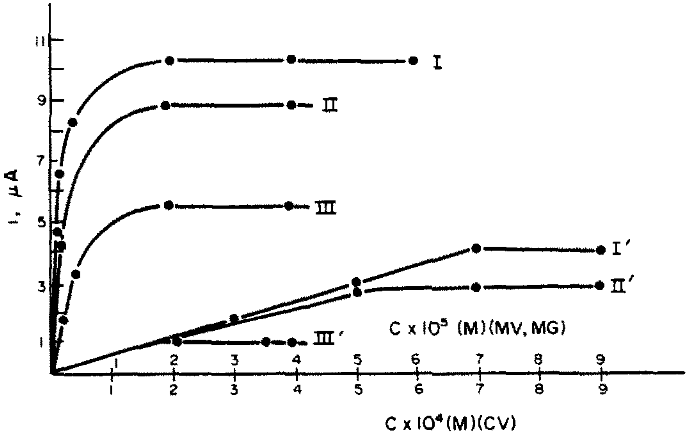

Fig. 5. The dependence of the electro-dissolution maximum current of antimony compounds with various dyes and the cathodic currents of the dye oxidation products (peak 3, Fig. 1) on the concentration of the latter.

Solutions: $1{\cdot}5M$ HCl + $4 \times 10^{-6}M$ $SbCl_3$ + xM CV (I); MV (II); MG (III); I'–III'—the same without $SbCl_3$.

Scan-rate = 0·125 V/sec; t_{el} = 1 min; potential = 0·8 V.

The first of these effects is illustrated in Fig. 4. The maximum preconcentration takes place at +0·8 V. At potentials below this, antimony(III) is not oxidized, and at higher potentials there is interference from oxidation of the electrolyte. At this electrode potential, besides the dye cations, their oxidation products may also take part in the preconcentration of antimony because of simultaneous oxidation of the antimony and the dyes under these conditions. It is important to choose the optimum dye concentration: on the one hand, it must be sufficient to ensure an adequate sensitivity of the determination but, on the other hand, an increase in the dye concentration will result in a greater accumulation of the oxidation products on the electrode surface and thus a larger current for the reduction of these products (Fig. 5, curves I′, II′, III′) which in turn interferes with the antimony peak. Figure 5 shows that the dye concentration must be chosen between 0 and $2 \times 10^{-4}M$ for I and 0 and $2 \times 10^{-5}M$ for II and III. Further increasing the dye concentration without improving the preconcentration conditions for antimony just leads to increased interference (peak *b*, Fig. 3). A 100-fold excess of the dye in relation to Sb(III) is the optimum. Making the solution 1·2–1·5*M* in hydrochloric acid provides the optimum acidity and chloride concentration.

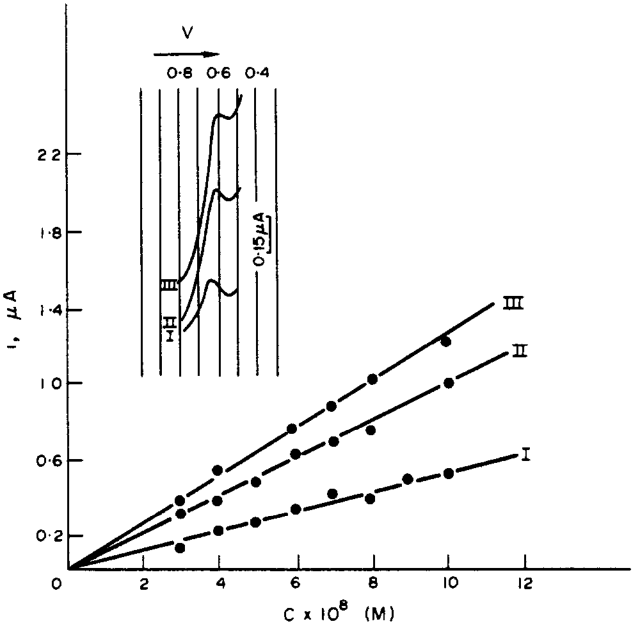

Fig. 6. The dependence of the electro-dissolution current of the chloroantimonates of Crystal Violet (I), Methyl Violet (II) and Malachite Green (III) on antimony(III) concentration, in 1·5*M* HCl that is $5 \times 10^{-6}M$ in TPMD.
Polarograms correspond to 4×10^{-8} *M* $SbCl_3$;
$t = 10$ min (*a*); 5 min (*b*); scan-rate = 0·125 V/sec; potential = +0·8 V.

Figure 6 shows the dependence of the peak height on antimony concentration for the three dyes studied. At high concentrations of antimony(III) or after prolonged electrolysis, electrode passivation is observed and compound formation practically ceases (Fig. 7). A linear calibration graph may be obtained with $Ct < 4 \times 10^{-5}$ mole·min·l.$^{-1}$. The antimony reduction current is then directly proportional to electrolysis time and antimony concentration.

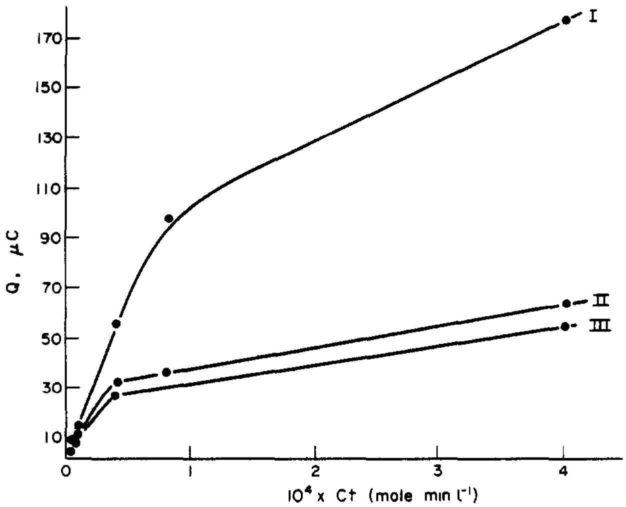

Fig. 7. The dependence on Ct of the electricity equivalent to the amount of chloroantimonates of Crystal Violet (I), Methyl Violet (II) and Malachite Green (III) deposited from solutions 1·5M in HCl, xM in $SbCl_3$ and $2 \times 10^{-4}M$ in CV, or $2 \times 10^{-5}M$ in MV or MG. Potential = 0·8 V; scan-rate = 0·125 V/sec; t_{el} = 1 min.

It may be seen from comparison of the data in Figs. 6 and 7 that the determination of traces of antimony with Malachite Green as precipitant has an advantage because the current corresponding to a given antimony concentration is higher than with the other dyes studied. This may be due to the better stability of the Malachite Green molecule.[9]

For the analysis of solutions containing relatively large amounts of antimony, ($C \sim 10^{-5}M$) higher dye concentrations may be used, and in this case a larger peak is produced if Crystal Violet is used. Moreover, electrode passivation starts later in this case, enabling the method to be used over a wider concentration range.

Table 1. The influence of some ions on the reduction current of the antimony(V) compound with Malachite Green (MG). Solution: 1·5M HCl + $4 \times 10^{-7}M$ $SbCl_3$ + $2 \times 10^{-5}M$ MG; t = 5 min; scan-rate = 0·125 V/sec; potential = +0·8 V

Ion introduced	Concentration, M	Maximum reduction current, μA
—	—	1·14
Cd^{2+}	5×10^{-3}	1·16
Zn^{2+}	6×10^{-8}	1·14
	5×10^{-3}	1·13
Fe^{3+}	5×10^{-4}	1·15
	5×10^{-3}	1·11
Cu^{2+}	5×10^{-4}	1·12
	5×10^{-3}	1·10
Bi^{3+}	6×10^{-4}	1·13
	1×10^{-3}	1·14
I^-	5×10^{-6}	1·14
	5×10^{-5}	1·13
Cr^{3+}	no influence	
Sn^{2+}	5×10^{-5}	1·14
	5×10^{-4}	1·15

The relative standard deviation for the determination of antimony is 6%, the limit of detection (by the 3σ criterion) being $3 \times 10^{-8}M$ Sb(III).

The results in Table 1 illustrate the effect of certain other ions on the determination of antimony with Malachite Green. It is apparent that the method is much more selective than those described earlier.[8,10] As an example, the determination of traces of antimony in chromium(III) salts is given.

Procedure

Dissolve 1 g of the chromium(III) salt in 15 ml of 1·5*M* hydrochloric acid, add 0·5 ml of a $4 \times 10^{-4}M$ solution of Malachite Green, dilute the solution to 20 ml, transfer it to the electrolysis cell and carry out preconcentration of antimony on a graphite electrode at +0·8 V potential (*vs.* SCE) for 5–10 min. Wait 15 sec after stopping stirring, and record the polarogram with a constant potential-scanning rate. The dissolution current peak for antimony is observed in the range from +0·7 to +0·6 V. The antimony content in the test sample is calculated from the peak height with the aid of the calibration graph or by the standard addition method.

CONCLUSION

It may be concluded that electrode polarization at a sufficiently high potential in a solution containing TPMD, chloride and antimony(III) ions is followed by formation of sparingly soluble compounds of Sb(V) with TMPD on the electrode surface. These compounds can be stripped when the potential is scanned in a negative direction. The cathodic peak current is proportional to the concentration of antimony(III) in the test solution.

It is necessary to choose the optimum TPMD concentration because of possible distortion of Sb(V) cathodic polarograms as a result of adsorption and oxidation–reduction of the TPMD.

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Zusammenfassung—Ein Verfahren zur Bestimmung von Antimonspuren durch inverse Voltammetrie der mit Triphenylmethanfarbstoffen (Kristallviolett, Methylviolett und Malachitgrün) als Fällungsmittel gebildeten Festkörper wird vorgeschlagen. Die Autoren untersuchten den Einfluß von Konzentration, Adsorption und Oxidation der Triphenylmethanfarbstoffe, Spannung und Dauer der Vorelektrolyse sowie der Konzentration von Antimon(III) und einigen anderen Elementen auf die Form des Polarogramms und auf den WiederauflösungsStrom. Als Beispiel wird ein Verfahren zur Bestimmung von Antimonspuren in Chrom(III)-Salzen beschrieben.

Résumé—On suggère une méthode pour le dosage de traces d'antimoine par voltammétrie inverse des phases solides formées avec les colorants du triphénylméthane (Cristal Violet, Violet de Méthyle et Vert Malachite) comme agents de précipitation. Les auteurs ont étudié l'influence de la concentration, de l'adsorption et de l'oxydation des colorants du triphénylméthane, du potentiel et du temps de pré-électrolyse, et de la concentration de l'antimoine (III) et de quelques autres éléments sur l'allure du polarogramme et le courant de dissolution. On décrit une méthode pour le dosage de traces d'antimoine dans les sels chromiques comme exemple.

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SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL AND SURFACTANTS

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Summary—A simple and highly selective spectrophotometric method for the determination of cobalt based upon the rapid reaction with PAN in the presence of surfactants and minute amounts of ammonium persulphate at pH 5·0 is described. The cobalt(III) chelate is made water-soluble by a neutral surfactant, Triton X-100, combined with sodium dodecylbenzene sulphonate (DBS). Iron(III), bismuth, tin(IV) and aluminium are masked with oxalate or citrate. Iron(II) must be absent. The other metal-PAN chelates, except that of nickel, are readily decomposed by EDTA. Up to 150 μg of nickel does not interfere. When larger amounts up to 625 μg are present, the absorbance can be corrected by measurements at two wavelengths. In a strongly acid medium (below pH 0·5) the nickel and other metal chelates are completely and instantaneously decomposed, while the cobalt(III) chelate remains unchanged. When, in place of EDTA, several ml of 6*M* hydrochloric acid are added after the colour development, nickel in quantities up to 1250 μg can be tolerated. A several hundredfold excess of zinc and manganese does not interfere. At 620 nm Beer's law is obeyed over the cobalt concentration range 0·4–3·2 μg/ml. The precision (95% confidence) is $\pm 1{\cdot}0$ μg for 100 μg of cobalt. The molar absorptivity is $1{\cdot}90 \times 10^4$ l. mole^{-1}.cm^{-1}.

The analytical application of 2-pyridylazo compounds has been extensively studied. It is generally accepted that 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)-resorcinol (PAR) are very versatile reagents for the determination of numerous trace metals.[1]

The immediate advantage of PAR over PAN is the water-solubility of both it and its chelates. Hence the applications of PAN as a spectrophotometric reagent are generally associated with extraction of the metal chelates into an organic solvent. Except in the determination of palladium most PAR complexes have absorption maxima lying between 490 and 550 nm.[2] With PAN a wider range of wavelength can be used, which gives a greater possibility of choosing a measurement wavelength at which the interference of foreign ions is minimized. This increases the selectivity of PAN and makes possible certain simultaneous determinations.[3] Accordingly, if the PAN chelates could be dissolved in water, a highly selective and simple spectrophotometric method could be established, which would be superior to PAR methods, especially in selectivity.

In a few studies with PAN, solvent extraction has been avoided by using mixed solvent systems[4] or by adding a dispersing agent such as gum arabic.[5] Recently it has been found that several kinds of metal chelates, such as germanium phenylfluoronate,[6] metal oxinates[7] and metal diethyldithiocarbamates,[8,9] can be made soluble in water by addition of surfactants. This appears to be a good means for dissolving the PAN chelates in water.

In the present study on a variety of PAN chelates it was found that for spectrophotometric determination with PAN, cobalt was the most suitable element because of its rapid reaction with PAN and the formation of a stable chelate. The cobalt chelate can successfully be rendered soluble when both a neutral and an anionic surfactant are used. The method established is simple, rapid and highly selective.

EXPERIMENTAL

Reagents

Standard solutions of nickel and cobalt were prepared from high purity metal sponge. Other metal-ion solutions were prepared from high purity reagents dissolved in an appropriate acid solution and then diluted to the desired concentration. The final acidity of the solutions was about 0·01*N*. Other reagents used were of analytical grade. A 0·1% PAN solution in methanol was used. Buffer solution of pH 5·0 was prepared from 0·5*M* acetic acid and 0·5*M* sodium acetate. The surfactant solution consisted of 20 g of Triton X-100, 2·5 g of sodium dodecylbenzenesulphonate (DBS) and 77·5 g of water.

Procedure

An aliquot of standard metal solution was placed in a 50-ml volumetric flask and 5 ml of 0·1*M* ammonium oxalate and 2 ml of the surfactant solution were added. Next, 2 ml of 0·1% PAN solution, 5 ml of pH 5 buffer (with additions of suitable amounts of sodium hydroxide solution if required) and 0·05 g of ammonium persulphate were added successively. The flask was shaken gently so that bubbles were not formed. The solution was allowed to stand for 3 min, and finally 5 ml of 0·05*M* EDTA were added. The mixture was then made up to volume with distilled water and mixed well by shaking vigorously. The colour intensity was determined against a blank as the reference solution, at a wavelength of 620 nm. Except for the surfactants, the order in which the reagents are mixed has a marked effect on the colour reaction of metals with PAN.

RESULTS AND DISCUSSION

As has already been shown, EDTA can be used to decompose all PAN chelates except those of cobalt, iron and nickel, thus improving the selectivity of PAN very considerably.[3] Hence it was important to examine the influence of iron and nickel on the determination of cobalt with PAN.

When PAN is added to a slightly acidic or neutral solution of cobalt(II), the cobalt(II) chelate is first formed, but is readily oxidized by dissolved oxygen to form the green cobalt(III) chelate,[1] which is formed quantitatively and fairly rapidly in the pH range 2·4–6·5. A period of 10 min is required for full colour development, but by the addition of several tiny crystals of ammonium persulphate constant intensity is reached in 3 min at room temperature. Absorption spectra of cobalt(III), nickel and iron(II) and (III) chelates formed at pH 5 are presented in Fig. 1. It is apparent that both iron(II) and (III) seriously influence the determination of cobalt. In the present study, 620 nm was chosen for determining the

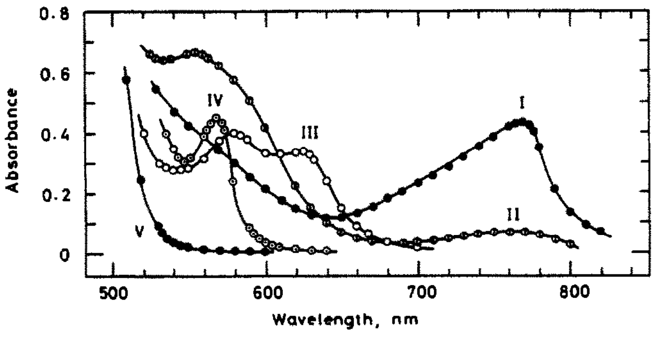

Fig. 1. Absorption spectra of PAN chelates for cobalt(III), nickel and iron(II, III) formed at pH 5.
I, Fe(II) 26 μg; II, Fe(III) 26 μg; III, Co(III) 54 μg; IV, Ni 23 μg; V, blank

absorbance of cobalt(III) chelate, because the absorbance at 620 nm due to the nickel chelate seems negligible if the nickel concentration is low.

As has been reported, the iron(II) chelate is unstable,[1] the solution becoming turbid after standing for 20 min. Furthermore, no suitable masking reagents were found for iron(II). On the other hand the influence of iron(III) can be eliminated by the addition of ammonium oxalate or citrate before colour development. Hence any iron in the sample must be made tervalent.

The nickel chelate is formed over a wide pH range (3–10) but the rate of colour development depends largely on the pH. In acetate buffer it requires about 60 min for full colour development, but only 10 min in ammonia buffer. The slow reaction in acetate medium (Fig. 2) makes it possible to reduce the influence of nickel, by masking the unreacted nickel with EDTA. The pH of the solution is adjusted to 5 with acetate buffer, because iron(III) is effectively masked with either oxalate or citrate at this pH, and the buffer solution has maximum buffer index at this pH.

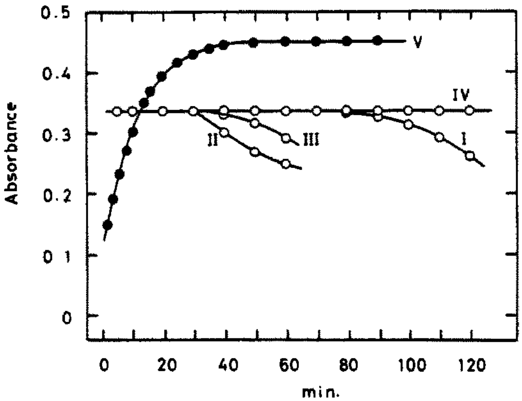

Fig. 2. Rate of colour development and stability of PAN chelates for Co (54 μg) and Ni (28 μg) at pH 5.
Absorbance is measured at 620 nm for Co (I–IV) and at 568 nm for Ni (V). I DBS, oxalate and EDTA are absent; II oxalate is added before colour development. DBS is absent; III DBS and oxalate are absent. EDTA is added after colour development; IV DBS, oxalate and EDTA are present; V DBS and oxalate are added before colour development.

Figure 2 shows the rate of colour development and stability of the cobalt(III) chelate. When DBS is omitted, the cobalt(III) chelate solution is less stable, and the solution tends to become turbid after 70 min (curve I), or even sooner when oxalate or EDTA is present (curves II and III). Curve IV shows that the combination of the two surfactants is required to stabilize the solution. The effect might be regarded as ion-pairing between DBS and the chelate, as the chelate is of the type $(CoL_2)^+$. The rate of colour development of the cobalt(III) chelate is not affected by the presence of either oxalate or citrate.

Table 1 shows that up to 2 mg of iron(III) can be tolerated in the presence of oxalate or citrate. However, if calcium is present in large amounts, calcium oxalate is precipitated, thus restricting the use of oxalate as a masking reagent. Accordingly, citrate is preferred in such cases. Up to 5 mg, and probably more, of iron(III) is masked when fluoride is used in conjunction with oxalate.

As shown in Table 2, quantities up to 150 μg of nickel are tolerated without appreciable

Table 1. Influence of iron(III) on the determination of cobalt

Cobalt, μg	Iron(III), μg	Absorbance at 620 nm	Masking reagents
54	0	0·339	
54	1010	0·340	5 ml of 0·1*M*
54	1510	0·339	ammonium oxalate
54	2010	0·346	
54	2520	0·352	
27	0	0·169	
27	1010	0·169	5 ml of 0·1*M*
27	1510	0·170	ammonium citrate
27	2010	0·173	
27	2520	0·176	
27	0	0·170	
27	2520	0·170	5 ml of 0·1*M*
27	3520	0·170	ammonium oxalate
27	4530	0·170	and 0·1 g of
27	5040	0·172	KF crystals

Table 2. Influence of nickel on the determination of 27 μg of cobalt

Nickel, μg	Absorbance at 620 nm
0	0·170
50	0·170
100	0·172
150	0·173
200	0·182
250	0·196

error. When larger amounts are present, there are two means of eliminating their interference. One involves correction of the absorbance by measurement at two suitable wavelengths, *e.g.*, 620 and 606 nm. If the ratios of the cobalt absorbances at each wavelength, $A_{620}^{\mathrm{Co}}/A_{606}^{\mathrm{Co}}$, and the nickel absorbances at the same wavelengths, $A_{606}^{\mathrm{Ni}}/A_{620}^{\mathrm{Ni}}$, are constant then

$$(A_{620} - A_{620}^{\mathrm{Ni}})/(A_{606} - bA_{620}^{\mathrm{Ni}}) = a, \tag{1}$$

where A_{620} and A_{606} are the total absorbances at the wavelengths indicated, and a and b are the cobalt and nickel ratios respectively. The experimental value of a was found with fairly good accuracy to be 1·050 ± 0·005. On the other hand the value of b was not reproducible because the wavelengths are far from that of a peak for the nickel chelate (568 nm). However, a value of 1·87 for b, gives satisfactory correction, as shown in Table 3. It is evident that nickel in quantities up to 625 μg does not interfere in the determination of 27 μg of cobalt.

The other way to reduce the influence of nickel depends on the difference in the behaviour of the two PAN chelates towards acid. The cobalt(III) chelate is very stable and remains unchanged even in strongly acidic solution, whereas that of nickel is rapidly decomposed below pH 0·5. This behaviour is put to good use in determining cobalt in the presence of nickel and most other metals forming chelates with PAN which are com-

Table 3. Influence of foreign ions on the determination of cobalt

Elements	Added, μg	Absorbance at 620 nm	Remarks
Co	27	0·170	
Ni	250	0·167	Correction method
	625	0·168	
	1250	0·130	
	2500	0·107	
	625	0·171	Decomposition with acid
	1250	0·170	
	1900	0·158	
Ca	500	0·170	
	1000	0·168	Filtered
Fe(III)	2010	0·173	Oxalate or citrate added
	2520	0·176	
	5030	0·172	Oxalate and KF (0·1 g) added
Bi	2700	0·171	
Sn(II)	1500	0·172	Prior oxidation to Sn(IV), and oxalate added
	2700	0·171	
Al	5700	0·172	
Cr(III)	1830	0·171	
V(V)	1500	0·170	
Cu	1010	0·170	
Pb	2500	0·170	
	4100	—	White precipitate
Zn	3750	0·170	
	5190	0·170	
Mn	3580	0·172	
	9470	0·170	

pletely dissociated in a strongly acid medium. The addition of several ml of 6*M* hydrochloric or nitric acid instead of 5 ml of 0·05*M* EDTA is more than adequate for the purpose. In the recommended procedure pH 5 was chosen for the colour development, but the more acid the solution is during the colour development, the slower the rate of the formation of the nickel chelate. Even below pH 3, the cobalt(III) chelate is formed quantitatively but the rate is gradually reduced so that the lower limit of pH for quantitative and rapid formation is 2·4. The rates of formation of nickel, cobalt and iron chelates are summarized in Figs. 3 and 4. When 2 ml of 6*M* hydrochloric acid are added to the coloured solution developed at pH 2·4 in a citrate buffer solution, the pH is lowered to 0·5. Under these conditions the nickel chelate is completely and instantaneously decomposed, and quantities up to 1·25 mg of nickel can be tolerated. These results are also summarized in Table 3. The larger the amounts of nickel that are present, the more incomplete is the reaction of cobalt with PAN, because the 2 ml of PAN solution is insufficient for the quantitative formation of the chelate. Formation of the cobalt chelate at pH 2·4 shows the disadvantage of being unable to prevent completely the formation of the iron(III) chelate by means of citrate or oxalate (Fig. 4). Although the iron–PAN chelate is decomposed by acid, the PAN released cannot be utilized by the cobalt (curve III, Fig. 3), and iron(III) in large amounts

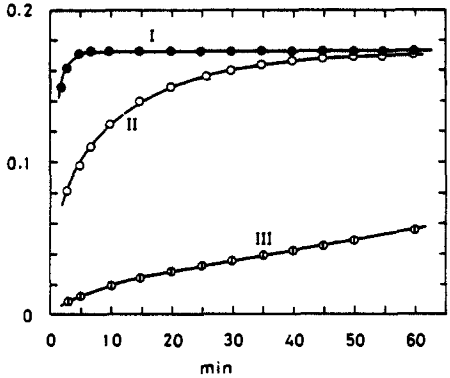

Fig. 3. Influence of pH on the rate of colour development for Co(III)–PAN chelate. Sodium citrate and hydrochloric acid were used to adjust pH. Co: 27 μg. I, pH 2·4; II, pH 1·7; III, pH 1·1.

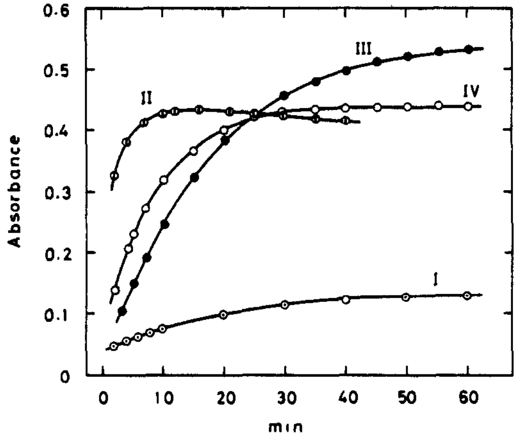

Fig. 4. The rate of colour development for nickel and iron(II, III) chelates in acid solutions. Buffer solutions (HCl–citrate) were added before colour development. Absorbance is measured at 552 nm for Fe(III), at 770 nm for Fe(II) and at 568 nm for Ni. I, Fe(III) 26 μg pH 2·5; II, Fe(II) 26 μg pH 2·5; III, Ni 50 μg, pH 2·4; IV, Ni 25 μg, pH 3·2.

consumes so much PAN that lower values for cobalt are obtained. Hence the recommended procedure is preferred for samples containing larger amounts of iron, and the acid decomposition method for samples containing larger amounts of nickel.

The absorbance of the cobalt(III) chelate measured at 620 nm follows Beer's law for solutions containing 0–160 μg of cobalt in 50 ml of solution. On the basis of the calibration curve, the 95% confidence limit was calculated by the least-squares method for the median of nine samples, the absorbance of which was 0·530: 100 μg of cobalt can be determined with a precision of ± 1·0 μg. The molar absorptivity was found to be $1{\cdot}9 \times 10^4$ l. mole^{-1}. cm^{-1} at 620 nm.

The influence of other ions is summarized in Table 3. It is apparent that the influence of nickel is very pronounced, and copper was found to behave similarly. When larger amounts of nickel and copper are present than those indicated in Table 3, the amount of

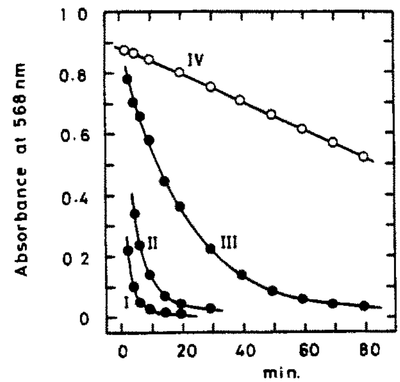

Fig. 5. Decomposition of nickel chelate (Ni 56 μg) with 1,10-phenanthroline (5 ml of 0·1% soln.) and EDTA (5 ml of 0·05*M* soln.) at room temperature or 1,10-phenanthroline; I pH 3·2; II pH 3·6; III pH 4·0 EDTA; IV pH 3·2.

PAN and EDTA must be increased. For the complete and rapid decomposition of the copper chelate, 1,10-phenanthroline is more effective than EDTA. The nickel chelate is also decomposed by 1,10-phenanthroline in 10 min at pH < 3 at room temperature. Although EDTA can decompose the nickel chelate at pH below 4, the reaction is very slow and heating to above 50° is necessary for rapid decomposition. In this respect EDTA is inferior to 1,10-phenanthroline. The behaviour of the nickel chelate towards both 1,10-phenanthroline and EDTA in an acid medium is shown in Fig. 5. At pH 5, used in the recommended procedure, the reaction of 1,10-phenanthroline with the nickel chelate is slow, since about 2 hr are required for complete decomposition. Therefore it is difficult to measure the absorbances at the two wavelengths precisely. On the other hand, although the decomposition by 1,10-phenanthroline is complete in 10 min below pH 3, the alternative use of the strong acid method is preferred because the chelates are instantaneously decomposed. Therefore, no further studies were made of the use of 1,10-phenanthroline. Among the elements not examined in the present study palladium would have a serious influence on the determination.[1] Since it is generally accepted that palladium reacts with PAN even in the presence of EDTA whereas cobalt and nickel are completely masked, correction of the absorbance would be possible.

Although the suitability of various surfactants as solubilizing agents has not been shown in detail, Triton X-100 was found to have the best properties in general, for the various PAN chelates. It has the advantage of dissolving more of the chelates and PAN itself. Cationic surfactants, such as cetyltrimethylammonium chloride, have the property of promoting the second acid dissociation of PAN whereby the blank solution turns red even at pH 7. Hence Triton X-100 was the preferred surfactant for the present purpose, used in conjunction with DBS.

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Zusammenfassung—Eine einfache und sehr selektive spektrophotometrische Methode zur Bestimmung von Kobalt wird beschrieben. Sie beruht auf der raschen Reaktion mit PAN bei pH 5,0 in Gegenwart oberflächenaktiver Stoffe und ganz geringer Mengen Ammoniumpersulfat. Das Kobalt(III)-Chelat wird durch ein neutrales Netzmittel. Triton X-100, in Verbindung mit Natriumdodecylbenzolsulfonat-(DBS) wasserlöslich gemacht. Eisen(III), Wismut, Zinn(IV) und Aluminium werden mit Oxalat oder Citrat maskiert. Eisen(II) muß abwesend sein. Die anderen Metall-PAN-Chelate außer dem von Nickel werden durch EDTA leicht zerlegt. Bis 150 µg Nickel stören nicht. Sind größere Mengen, bis 625 µg, anwesend, dann kann die Extinktion durch Messungen bei zwei Wellenlängen korrigiert werden. In einem stark sauren Medium (unter pH 0.5) werden die Chelate von Nickel und den anderen Metallen augenblicklich und vollständig zerlegt, während das Kobalt(III)-Chelat unverändert bleibt. Werden statt EDTA einige ml 6*M* Salzsäure nach der Farbentwicklung zugesetzt, kann Nickel in Mengen bis zu 1250 µg zugelassen werden. Ein mehrhundertfacher Überschuß von Zink und Mangan stört nicht. Bei 620 nm gilt das Beersche Gesetz im Konzentrationsbereich 0,4–3,2 µg Kobalt pro ml. Die Genauigkeit (Vertrauensgrenze 95%) beträgt ± 1,0 µg auf 100 µg Kobalt. Der molare Extinktionskoeffizient beträgt $1{,}90 \times 10^4$ l $mol^{-1}cm^{-1}$.

Résumé—On décrit une méthode spectrophotométrique simple et hautement sélective pour le dosage du cobalt, basée sur la réaction rapide avec le PAN en la présence d'agents tensioactifs et de faibles quantités de persulfate d'ammonium à pH 5,0. Le chélate de cobalt (III) est rendu soluble dans l'eau par un surfactant neutre, le Triton X-100, combiné avec du dodécylbenzènesulfonate de sodium (DBS). Les fer (III), bismuth, étain (IV) et aluminium sont dissimulés par l'oxalate ou le citrate. Le fer (II) doit être absent. Les autres chélates métal-PAN, à l'exception de celui du nickel, sont aisément décomposés par l'EDTA. Une quantité de nickel jusqu'à 150 µg ne gêne pas. Quand des quantités supérieures allant jusqu'à 625 µg sont présentes, l'absorbance peut être corrigée par mesures à deux longueurs d'onde. Dans un milieu fortement acide (en-dessous de pH 0.5), les chélates du nickel et des autres métaux sont décomposés complètement et instantanément. tandis que le chélante du cobalt (III) reste inchangé. Quand, au lieu d'EDTA, on ajoute plusieurs ml d'acide chlorhydrique 6*M* après développement de la coloration, le nickel en quantités allant jusqu'à 1250 µg peut être toléré. Le zinc et le manganèse plusieurs centaines de fois en excès n gênent pas. A 620 nm, la loi de Beer est suivie dans le domaine de concentration en cobalt 0.4–3.2 µg/ml. La précision (confiance 95%) est ± 1,0 µg pour 100 µg de cobalt. Le coefficient d'absorption molaire est 1.90×10^4 l. $mole^{-1}$ cm^{-1}.

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SHORT COMMUNICATIONS

THERMOMETRIC TITRATION OF ACIDS IN PYRIDINE

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Titration of simple monobasic acids in pyridine with an uncharged base, has been shown[1,2] to involve the following equilibria:

$$HX(H^+X^-) \overset{K_{HX}}{\rightleftharpoons} H^+ + X^-, \tag{1}$$

$$B + H^+ \overset{K_B}{\rightleftharpoons} BH^+, \tag{2}$$

$$BH^+ + X^- \overset{K'}{\rightleftharpoons} BH^+X^-(BHX). \tag{3}$$

Although the evidence from potentiometric titrations[1] is not convincing, in our conductometric titration[2] of nitric acid *vs.* 1,3-diphenylguanidine (DPG) consideration of the equilibria above has yielded satisfactory agreement between the observed and calculated plots. The conductance of the solution decreased linearly up to the end-point and then rose gradually (also in a linear fashion) and the detection of the end-point was relatively easy. It was of interest to investigate the thermometric titration of such acids in pyridine. The acids considered for the study were: perchloric, hydriodic, nitric, hydrobromic, acetic, benzoic, *o*-nitrobenzoic and picric acids and 2,4- and 2,5-dinitrophenol.

With the exception of *o*-nitrobenzoic acid for which no pK_a estimate is available the pK_a values of all these acids and phenols are known.[3,4] An approximate estimate of pK_a is available for picric acid.[1] It was expected that a correlation between these values and the trends observed in the thermometric titrations would be exhibited. It was further expected that the results would be of value in providing some estimate of the heats of reaction (neutralization) in favourable cases.

EXPERIMENTAL

Reagents

The picric, benzoic and *o*-nitrobenzoic acids were of reagent quality; the slightly damp picric acid sample was squeezed between folds of filter paper and then air-dried at room temperature. Reagent-quality acetic acid was dried by the usual method. Preparation and purification of all other chemicals have been reported earlier.[3]

Procedure

The titrant was delivered at a constant rate into a calorimeter, while the change in temperature of the solution was detected by a thermistor (Sargent Model S-81620) and recorded. In each run, 40 ml of titrand were placed in a vacuum-jacketed (glass) calorimeter. A constant-drive syringe pump (Sage Instrument Model 249:2) burette was used; a length of Teflon tubing was attached to the end of the syringe for delivering the titrant into the calorimeter. Before starting a run, the solution of acid in the calorimeter and the titrant, *i.e.*, the solution of DPG contained in the syringe burette, were allowed to attain temperature equilibrium in an air-conditioned room maintained at 21 ± 2°. The contents of the calorimeter were kept agitated with a Teflon-coated magnetic stirrer for about a minute before a titration was actually started, and stirring was continued until well beyond the theoretical end-point.

A Wheatstone bridge (Sargent Model S-81601) was used, with the thermistor as one arm. The bridge imbalance was amplified through a Keithley Model 150 AR microvolt ammeter and then recorded on a Sargent strip-chart recorder. An *R*-*C* hook-up with a 250-mF capacitor and a 100:1 voltage divider consisting of a 1-MΩ resistor and a 10-kΩ resistor, was attached across the recorder terminals to minimize the noise.

A chart speed of 1 in./min and a rate of titrant delivery of 0·843 ml/min were used in all runs.

Determination of water-equivalent of the calorimeter assembly. The water-equivalent of the calorimeter system was ascertained by determining the temperature change caused by the addition of a known amount of ice-cold water to a given quantity of water contained in the calorimeter assembly. An average value of 16·0 cal/deg was obtained from three separate determinations.

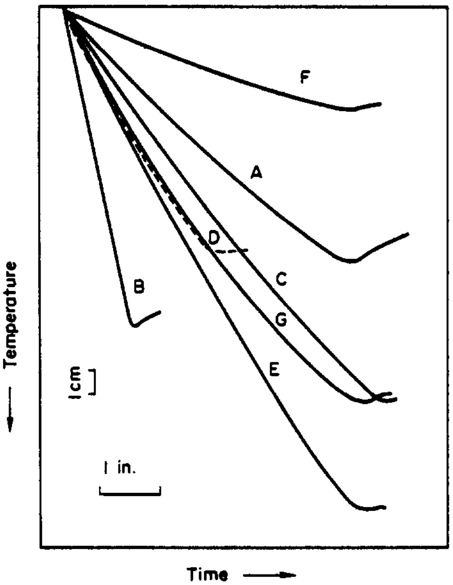

Fig. 1. Time-temperature plots. *A*—$HClO_4$ (0·1000*M*); *B*—HI (0·0247*M*); *C*—HNO_3 (0·1105*M*); *D*—HBr (0·0479*M*); *E*—2,4-dinitrophenol (0·1013*M*); *F*—picric acid (0·1013*M*); *G*—*o*-nitrobenzoic acid (0·1013*M*).
Full-scale recorder sensitivity: plots *A*, *C*, *D*, *E*, *G*, 3mV; plot *B*, 1 mV; plot *F*, 10 mV.

Temperature calibration of the chart paper. The temperature change as recorded in mm of chart paper was calibrated by running several titrations of aqueous solutions of sodium hydroxide against hydrochloric acid under identical experimental conditions. The total heat liberated per mole of reactant in each of these titrations was obtained on the basis of the average number of chart divisions (mm) representing the temperature change at the titration end-point, the volume of solution at the end-point and the water-equivalent of the calorimeter

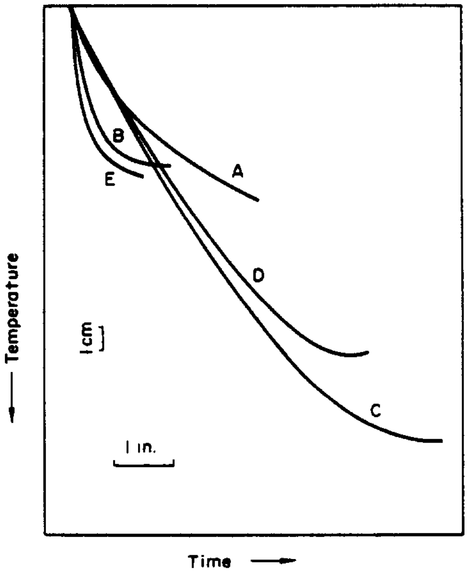

Fig. 2. Time–temperature plots. *A*—acetic acid (0·0112*M*); *B*—benzoic acid (0·0116*M*); *C*—benzoic acid (0·1164*M*); *D*—2,5-dinitrophenol (0·0990*M*); *E*—2,5-dinitrophenol (0·0099*M*).
Full-scale recorder sensitivity: plots *A*, *B*, *E*, 1 mV; plots *C*, *D*, 3 mV.

determined as above. The average of the heats (6·57 ± 0·30 × 10^6 mm·cal/deg) was then equated with the heat of neutralization of sodium hydroxide, 13·5 kcal/mole. Thus, at a sensitivity of 1 mV full-scale deflection, 1 mm of chart paper on the temperature axis would correspond to 2·06 ± 0·09 × 10^{-3} deg. This value was used in ascertaining the temperature change associated with a particular titration in pyridine.

RESULTS AND DISCUSSION

Typical titration curves for perchloric, hydriodic, nitric, hydrobromic, picric and *o*-nitrobenzoic acids and 2,4-dinitrophenol are given in Fig. 1. The plots are linear with little or no curvature and are marked by fairly sharp breaks in the vicinity of the theoretical end-points. Comparison of the results summarized in Table 1, indicates that at higher concentrations the correspondence of the thermometric end-points with those calculated on the basis of a 1:1 reaction between the acid and DPG is good. The lack of agreement at lower concentrations of the acids may be due to a number of factors. The amount of heat evolved at lower concentrations is small, and dilution effects may become serious. This suggests that higher titrant concentrations might improve the situation, but when a higher concentration of the titrant is used, the small time-interval required in delivering the titrant introduces additional problems.

Table 1. Results of thermometric titrations of acids in pyridine

HX*	C_{HX}, *M*†	C_{DPG}, *M*	Number of chart divisions,§ *mm*	Volume of DPG, *ml* Obsd.	Volume of DPG, *ml* Calcd.	Heat of reaction,¶ *kcal/mole*
$HClO_4$	0·1000	1·023	107·5 (3)	3·890	3·890	5·74
(3·26)	0·0100	0·486	17·5 (1)	0·762	0·823	—
HI	0·0247	1·057	135·0 (1)	0·940	0·940	9·35
(3·39)	0·0025	0·486	48·5 (0·3)	0·227	0·210	—
HNO_3	0·1105	1·023	166·5 (3)	4·290	4·000	8·12
(4·06)	0·0111	1·023	208·0 (0·3)	0·480	0·400	—
	0·0055	0·486	86·5 (0·3)	0·472	0·455	—
HBr	0·0479	1·043	103·5 (3)	1·910	1·830	11·27
(4·36)	0·0104	1·043	67·5 (1)	0·446	0·397	—
	0·0014	0·486	32·5 (0·3)	0·160	0·115	—
Picric	0·1013	1·043	44·0 (10)	3·840	3·870	7·74
acid	0·0101	1·043	198·0 (0·3)	0·420	0·387	—
(3·5)	0·0010	0·486	16·0 (0·3)	0·084	0·082	—
o-Nitro-	0·1013	1·043	167·0 (3)	3·850	3·880	8·85
benzoic	0·0101	1·039	93·0 (1)	0·432	0·388	—
acid	0·0010	0·486	9·0 (1)	0·118$_5$	0·082$_5$	—
2,4-Dinitro-	0·1013	1·039	210·5 (3)	3·880	3·910	11·19
phenol	0·0101	1·039	83·5 (1)	0·440	0·391	—
(4·38)	0·0010	0·486	10·0 (0·3)	0·084	0·083	—
Acetic	0·0112	1·057			0·425	—
acid						
(10 1)						
Benzoic	0·1164	1·039			4·500	—
acid	0·0116	1·039			0·446	—
(9·8)	0·0011	0·486			0·091	—
2·5-Dinitro-	0·0990	1·039			3·820	—
phenol	0·0099	1·039			0·380	—
(5·76)	0·0010	0·486			0·080	—

* Numbers in brackets indicate the pK_a values of the acids.

† 40·0 ml of solution used.

§ Represents the distance travelled by the pen, on the temperature axis, to reach the end-point at the full-scale sensitivity (mV) given in parentheses.

¶ The specific heats and the densities of the solutions were taken to be the same as those of pyridine (specific heat = 0·431 cal/deg, density = 0·9781 g/ml at the experimental temperature), and heats of mixing and dilution were not taken into account. Each mm of chart paper was equated to 2·06 × 10^{-3} deg, at 1·0 mV sensitivity, for calculating the heats, assuming a 1:1 reaction between the acid and the base.

The plots for acetic and benzoic acid, and 2,5-dinitrophenol show considerable curvature (Fig. 2), and the curve-shape is not improved at increased acid concentration. Consequently, location of the end-point for these acids is not feasible. In view of the large difference in pK_a values (acetic acid:[4] 10·1; benzoic acid:[4] 9·8; 2,5-dinitrophenol:[3] 5·8) it seems possible that the titrations in these cases are far less complete than for the first group of acids discussed above (Fig. 1). Incidentally, the earlier report[1] on potentiometric titration of the acids appears to be vague and incongruous. We have not noticed any homoconjugation for any of the acids, and we are inclined to believe that they all conform to the simple titration scheme suggested in equations (1)–(3). It is interesting to note in this connection that although acetic acid proved too weak for end-point estimation, thermometric titration using DPG as the base[5] yielded a distinct end-point for benzoic acid in acetonitrile which is an aprotic but protophobic solvent of moderate dielectric constant.

The molar heats of reaction (in kcal) as calculated in the present work from titration data at the highest acid concentration used are given in Table 1. Excluding the case of *o*-nitrobenzoic acid for which no pK_a estimate is available, and of hydriodic acid which might involve a large experimental error due to the low concentration (0·0247 M) used, the heats seem to follow the same sequence as the pK_a values of the acids. No explanation of the trend can be offered at this stage.

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Summary—Thermometric titration of $HClO_4$, HI, HNO_3, HBr, picric acid, *o*-nitrobenzoic acid, 2,4- and 2,5-dinitrophenol, acetic acid and benzoic acid have been attempted in pyridine as solvent, using 1,3-diphenylguanidine as the base. Except in the case of 2,5-dinitrophenol, acetic acid and benzoic acid, the results are, in general, reasonably satisfactory. The approximate molar heats of neutralization have been calculated.

Zusammenfassung—Die thermometrische Titration von $HClO_4$, HJ, HNO_3, HBr, Pikrinsäure, *o*-Nitrobenzoesäure, 2,4- und 2,5-Dinitrophenol, Essigsäure und Benzoesäure wurde in Pyridin als Lösungsmittel mit 1,3-Diphenylguanidin als Base versucht. Außer bei 2,5-Dinitrophenol, Essigsäure und Benzoesäure sind die Ergebnisse im allgemeinen recht zufriedenstellend. Die ungefähren molaren Neutralisationswärmen wurden berechnet.

Résumé—On a essayé le titrage thermométrique de $HClO_4$, HI, HNO_3, HBr, acide picrique, acide *o*-nitrobenzoïque, 2,4- et 2,5-dinitrophénols, acide acétique et acide benzoïque en pyridine comme solvant, utilisant la 1,3-diphénylguanidine comme base. En exceptant les cas du 2,5-dinitrophénol, de l'acide acétique et de l'acide benzoïque, les résultats sont, en général, raisonnablement satisfaisants. On a calculé les chaleurs molaires de neutralisation approximatives.

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EXTRACTION OF PRUSSIAN BLUE INTO CHLOROFORM IN THE PRESENCE OF AJATIN

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The Prussian Blue method remains the best for the determination of small amounts of ferrocyanide.[1,2] Roberts and Wilson[2] optimized the conditions for rapid development of stable colloidal solutions of Prussian Blue by adding a mixture of ferrous and ferric sulphates to an acidic solution of ferrocyanide ion. In adapting their method to the analysis of beet molasses, we found the optimum concentrations are in the range 0·0025–0·1*M* ferrous iron, 0·001–0·01*M* ferric iron, and 0·005–0·25*M* (or more) sulphuric acid, these values being related to the final volume. Under these conditions, the absorbance reaches its maximum value after about 15 min and remains unchanged during the next two hours. After a day the Prussian Blue coagulates, but if the solution is shaken for a few seconds the precipitate is redispersed and the original absorbance value is restored.

The procedure of Roberts and Wilson allows determination of down to 2·5 μg of ferrocyanide ion in a final volume of 25 ml. For the samples containing very low amounts of ferrocyanide, they suggested a concentration step to bring the total amount of ferrocyanide above this level. This is done by collecting the Prussian Blue on a kieselguhr pad, redissolving it in a small volume of potassium hydroxide solution and forming it again under controlled and reproducible conditions and in a small volume.

The present paper deals with the extraction of Prussian Blue into chloroform in the presence of ajatin (dimethyl-laurylbenzylammonium bromide), which seems to be a promising alternative for concentration purposes.

EXPERIMENTAL

Reagents

All reagents were of analytical-reagent grade except the 10% w/v ajatin solution (Slovakofarma, Hlohovec, CSSR). Doubly distilled water was used. The chloroform was purified by washing with dilute sulphuric acid, then dilute sodium hydroxide solution and distilling twice.

Standard ferrocyanide stock solution. Potassium ferrocyanide trihydrate (0·249 g) was dissolved in water containing 2 ml of 0·05*M* potassium hydroxide and made up to 250 ml. The solution was stored in the dark. Standard dilute ferrocyanide (10 μg/ml) solution was prepared on the day of use by fiftyfold dilution of the stock solution with 0·005*M* potassium hydroxide.

Solution of iron sulphates. To 50 g of ferrous ammonium sulphate hexahydrate and 5·25 g of ferric ammonium sulphate dodecahydrate 15 ml of *ca.* 18*M* sulphuric acid were added, and after dissolution of the salts in water, the solution was made up to 250 ml and filtered into a polyethylene bottle.

Procedure

For the calibration curve, to a series of 25-ml standard flasks add dilute ferrocyanide solution to cover the range 0–100 μg, followed by 0·5 ml of 10% ajatin solution to each. Fill to the marks with water, transfer the contents to 50-ml separatory funnels each containing 10 ml of chloroform, add 1 ml of "iron sulphates" solution, let stand for 15 min, then shake them for 1 min. Measure the absorbances of the chloroform extracts at 700 nm against pure chloroform in 2-cm cells. Treat samples in the same way.

Effect of the concentration of ajatin. A mixture of 10 ml of water, 3 ml of dilute ferrocyanide solution, 1 ml of iron sulphates solution and a varied amount (< 1 ml) of ajatin solution was diluted to 15 ml with water and let stand in 50-ml separatory funnel for 15 min. The Prussian Blue formed was extracted into 10 ml of chloroform by shaking for 1 min. The extract was filtered through paper and its absorbance A measured against chloroform as reference. The distribution coefficient D was calculated from

$$D = \frac{A_{\text{observed}} \times 1{\cdot}5}{A_{\text{maximal}} - A_{\text{observed}}}.$$

Effect of the concentration of sulphuric acid. A mixture of water, a chosen amount of sulphuric acid of known concentration, 0·5 ml of 10% ajatin solution, 1 ml of iron sulphates solution and 3 ml of standard ferrocyanide solution was diluted to 25 ml in a standard flask, transferred into a 50-ml separatory funnel, and after 15–20 min, extracted with 10 ml of chloroform, and the absorbance of the extract measured.

Selectivity of the extraction. A weighed amount of the salt to be investigated was placed in a 25-ml graduated flask and dissolved in about 15 ml of water, then 1 ml of 0·36*M* sulphuric acid and 5 ml of standard ferrocyanide solution were added and the flask was filled to the mark with water. The solution was transferred into a 50-ml separatory funnel containing 10 ml of chloroform, 0·5 ml of 10% ajatin solution and 1 ml of iron sulphates solution were added and after 30 min the Prussian Blue was extracted and its absorbance measured and compared with that obtained with the same amount of ferrocyanide in the absence of the salt being investigated.

RESULTS AND DISCUSSION

The extraction of Prussian Blue from 0·043*M* sulphuric acid is maximal when the concentration of ajatin in the aqueous phase exceeds about 0·003*M*. At higher ajatin concentrations, the aqueous phase tends to foam when shaken and therefore concentrations above *ca.* 0·006*M* are not suitable. Moreover, at these higher concentrations the extracts exhibit a white turbidity, so they are not suitable for spectrophotometry. When the concentration of ajatin is below 0·003*M*, the degree of extraction decreases, and the unextracted Prussian Blue forms a precipitate at the phase boundary. A similar effect was observed when the concentration of sulphuric acid increased above 0·1*M*, as shown in Fig. 1. Aqueous solutions of Prussian Blue behave markedly differently from the chloroform extracts: the aqueous solutions are only moderately stable and the Prussian Blue coagulates overnight, but the solutions in chloroform are stable for at least one month. Further, when aqueous solutions of Prussian Blue are filtered through paper (Schleicher & Schuell No. 589[3]) about 90% of the Prussian Blue is retained by the filter, but there is virtually no loss from chloroform solutions.

These observations raise the question of the nature of the extraction process. Some information on this can be obtained from Fig. 2, where it can be seen that at higher concentrations ajatin combines with Prussian Blue in a 1:1 molar ratio, and at low concentrations in about 2:1 ratio. Since no attempt has been made to determine the molecular weight of the species extracted, the mechanism of the extraction remains unclear, but the extraction obviously cannot be explained by the formation of ion-pairs since Prussian Blue is not an ionic species; on the other hand, formation of mixed ferrocyanides (such as those known for alkali metals) is improbable with such a large cation as ajatin.[3] Only negligible differences were found between the visible absorbance spectra of Prussian Blue are filtered through paper (Schliecher and Schuell No. 589[3]) about 90% of the Prussian Blue is retained

Although the mechanism is unknown, the extraction of Prussian Blue would be of value for analytical purposes provided it is sufficiently selective. The results of a preliminary investigation of this aspect are listed in Table 1. The extraction is essentially unaffected by thousandfold molar ratios (with respect to ferrocyanide) of sodium chloride, potassium fluoride, potassium dihydrogen phosphate, and boric, acetic, lactic, tartaric, citric and succinic acids, hundredfold ratio of potassium iodate, and tenfold ratios of potassium iodide, potassium nitrate, sodium thiosulphate and oxalic acid, but potassium bromide, potassium thiocyanate, sodium dihydrogen hypophosphite or salicylic acid can be tolerated only in molar amounts similar to that of ferrocyanide. The suppression of the interferences has to be based on understanding their mode of action. By increasing the acidity of

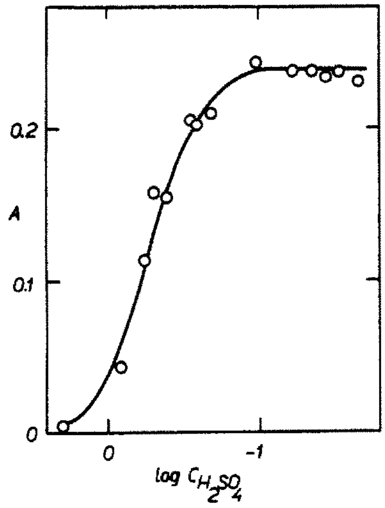

Fig. 1. Effect of the acidity on the extraction of Prussian Blue from $5{\cdot}2 \times 10^{-3}M$ ajatin medium.

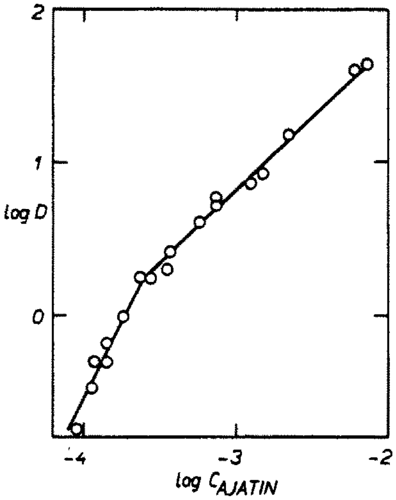

Fig. 2. Effect of the concentration of ajatin on the extraction of Prussian Blue from 3·84 × $10^{-2}M$ H_2SO_4 medium.

the aqueous phase from 0·02*M* to 0·0935*M* sulphuric acid, weak acids can be converted into their undissociated forms and then cannot bind the ajatin cation, and decrease its effective concentration. Otherwise, at lower acidity, part of the Prussian Blue remained unextracted, just as though there were not enough ajatin. Another source of interference is the presence of reduction or oxidation agents which can change the proportion of ferrous to ferric iron being added. For example, oxalic acid reduces ferric iron and slows down the rate of formation of the Prussian Blue. Such interferences may obviously be avoided by adjustment of the redox potential of the aqueous phase before the addition of the solution of iron sulphates. Other compounds such as thiocyanate or salicylic acid interfere by complexing iron. Their effect might be avoided by increasing the amount of iron sul-

Table 1. Selectivity of the extraction of Prussian Blue from 0·0935*M* H_2SO_4

	Recovery of ferrocyanide, %			
Compound added	1000*	100*	10*	1*
NaCl	100·5	97		
KBr	24·4		44	110
KI	1		102	
KF	95·5			
KSCN	31		87	97
KNO_3	22		106	
KIO_3	168		92·5	
H_3BO_3	112			
$Na_2S_2O_3$	1		92	
KH_2PO_4	96			
NaH_2PO_2			49	100
Acetic acid	104			
Succinic acid	101			
Lactic acid	108			
Citric acid	98			
Tartaric acid	94·5			
Oxalic acid			109	100
Salicylic acid			52	100

* Numbers indicate the molar ratio of the compound to the ferrocyanide.

phates added. A special case is represented by nitrate, which interferes by precipitating ajatin. Increasing the amount of ajatin might eliminate this unwanted effect. Another way to achieve higher selectivity might be to use another solvent.

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Summary—Extraction of Prussian Blue into chloroform in the presence of ajatin (dimethyl-laurylbenzylammonium bromide) is proposed for the concentration and determination of ferrocyanide ion. Optimum concentrations of sulphuric acid and of ajatin have been established and the selectivity of the extraction has been investigated. Ways of eliminating some interferences are discussed.

Zusammenfassung—Es wird die Extraktion von Berlinerblau in Chloroform in Gegenwart von Ajatin (Dimethyllaurylbenzylammoniumbromid) beschrieben und für die Anreicherung und Bestimmung des Ferrocyanions vorgeschlagen. Es wurden die optimalen Konzentrationen von Schwefelsäure und von Ajatin ermittelt und die Selektivität der Extraktion untersucht. Die Wege zur Eliminierung einiger Störungen werden diskutiert.

Résumé—L'extraction du bleu de Prusse en chloroforme en présence d'Ajatin (bromide de dimethyllaurylbenzylammonium) est décrite et proposée pour la concentration et détermination du ion de ferrocyanide. Les meilleures concentrations de l'acide sulfurique et d'Ajatine furent établies et la selectivité de l'extraction fut examinée. La façon d'élimination de quelques difficultés est discutée.

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SEPARATION OF CARRIER-FREE ^{48}Sc TRACER AND ITS DETERMINATION BY ISOTOPIC DILUTION

(*Received* 29 *August* 1973. *Accepted* 30 *October* 1973)

A survey of earlier work on the analytical chemistry of scandium reveals that the separation, purification and estimation of the element is one of the most difficult problems in inorganic chemistry. Conventional procedures[1–4] such as solvent extraction, ion-exchange, chromatography *etc.*, are generally applied for its separation. Attempts have been made by several workers [5–8] to separate carrier-free scandium tracer from irradiated titanium by chemical methods which are often time-consuming and difficult. The present work describes a simple method of separating carrier-free ^{48}Sc (half-life 1·83 days) from an irradiated metal titanium target.

EXPERIMENTAL

Chemical reagents used were of analytical grade. Spectroscopically pure titanium metal, in small pieces, was encased in polyethylene bags and irradiated with a 14-MeV neutron source at a flux of 2×10^9 n.cm^{-2}sec^{-1} for 20 hr. ^{48}Sc tracer with 44-hr half-life was formed according to the reaction $^{48}\text{Ti}_{22}$ (n,p) $^{48}\text{Sc}_{21}$.

The irradiated metal was left for 12 hr to eliminate any short-lived radioactive species, and then was dissolved in hydrofluoric acid in a polyethylene beaker. The solution was almost neutralized with ammonia and the pH phates added. A special case is represented by nitrate, which interferes by precipitating ajatin. Increasing the amount of ajatin might eliminate this unwanted effect. Another way to achieve higher selectivity might be to use another solvent.

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The irradiated metal was left for 12 hr to eliminate any short-lived radioactive species, and then was dissolved in hydrofluoric acid in a polyethylene beaker. The solution was almost neutralized with ammonia and the pH adjusted to ~4 by addition of 20 ml of a mixture of 0·1*M* acetic acid and 0·1*M* ammonium acetate (1:1), then 10 ml of 0·1*M* calcium chloride were added. The tracer was completely co-precipitated with the calcium fluoride formed. The calcium fluoride was reprecipitated, filtered off, transferred to a beaker and fumed with perchloric acid to remove any hydrofluoric acid. It was then dissolved in 25 ml of conc. hydrochloric acid. To the acid solution about 0·5 ml of 30% hydrogen peroxide was added and the scandium tracer was extracted with an approximately equal volume of tributyl phosphate.[2] The tracer was finally stripped into aqueous medium, in the carrier-free state, by shaking the organic phase with 75 ml of water Any residual tributyl phosphate was removed by shaking the aqueous phase with 25 ml of diethyl ether. The amount of scandium activity in the aqueous phase was determined by isotopic dilution.

Calcium fluoride was used as the non-isotopic diluent for determining the scandium. To the aqueous solution containing the tracer (polyethylene beaker) a few drops of dilute ammonia solution were added and the pH was adjusted to 2–3 with acetic acid. Then 10 ml of 0·1*M* calcium chloride were added and the scandium was co-precipitated with calcium fluoride by addition of dilute hydrofluoric acid in presence of alcohol. The solution and precipitate were stirred on a hot water-bath with alcohol–water mixture for about 15 min. The precipitate was separated by centrifugation. Various fractions of the precipitate were transferred to previously dried and weighed counting trays and dried and weighed. The activity in each tray was measured with an end-window G.M. counter.

To verify the half-life, the activity measurements were repeated at intervals for 100 hr. The decay curve was linear and gave a half-life of 44 hr.

DISCUSSION

Calcium fluoride was found to be a good non-isotopic diluent for scandium. It has little tendency to complex-formation under the experimental conditions and is highly insoluble in acetic acid. The tracer was uniformly distributed in the solid phase. The uptake of scandium by calcium fluoride was shown to be complete by using carrier-free ^{48}Sc to determine calcium. A known amount of the ^{48}Sc activity was added to a solution containing a known quantity of calcium which was then precipitated as fluoride in acetic acid medium as described. The activity of a known weight of precipitate was measured and used to determine the precipitate weight. The results had a maximum error of 2·5% which is reasonable for the technique.

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Summary—An easy method for speedy and quantitative separation of carrier-free scandium tracer formed by the ^{48}Ti$_{22}$(n,p)^{48}Sc$_{21}$ nuclear reaction has been developed. Separation of ^{48}Sc (1·83 days) from the target titanium metal was carried out by co-precipitating the tracer with calcium fluoride precipitated at pH ~ 4 from the solution of irradiated titanium in hydrofluoric acid. The freshly formed fluoride precipitate was dissolved in conc. hydrochloric acid, and the tracer extracted with tributyl phosphate and then stripped into aqueous medium. The carrier-free tracer was estimated by isotopic dilution, with calcium fluoride as non-isotopic diluent.

Zusammenfassung—Eine leichte Methode zur raschen und quantitativen Abtrennung von trägerfreiem Scandiumtracer wurde entwickelt, der durch die Kernreaktion ^{48}Ti$_{22}$ (n,p) ^{48}Sc$_{21}$ gebildet wurde. Die Abtrennung von ^{48}Sc(1,83 Tage) vom Target aus metallischem Titan erfolgte durch Mitfällung des Tracers mit Calciumfluorid, das bei pH ~4 aus der Lösung des bestrahlten Titans in Flußsäure gefällt wurde. Der frisch gebildete Fluoridniederschlag wurde in konzentrierter Salzsäure gelöst, der Tracer mit Tributylphosphat extrahiert und dann in wäßriges Medium zurückextrahiert. Der trägerfreie Tracer wurde durch Isotopenverdünnung mit Calciumfluorid als nichtisotopem Verdünnungsmittel bestimmt.

Résumé—On a élaboré une méthode simple pour la séparation rapide et quantitative du traceur scandium exempt de support formé par la réaction nucléaire $^{48}\mathrm{Ti}_{22}$ (n,p) $^{48}\mathrm{Sc}_{21}$. La séparation de $^{48}\mathrm{Sc}$ (1,83 jour) de la cible de titane métallique a été menée par coprécipitation du traceur avec le fluorure de calcium précipité à pH ~ 4 de la solution de titane irradié dans l'acide fluorhydrique. Le précipité de fluorure fraîchement formé a été dissous en acide chlorhydrique concentré, et le traceur extrait au phosphate de tributyle puis réextrait en milieu aqueux. Le traceur exempt de support a été dosé par dilution isotopique, avec du fluorure de calcium comme diluant non-isotopique.

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DIREKTTHERMOMETRISCHE BESTIMMUNG VON THORIUM UND LANTHAN IN GLÄSERN

(*Eingegangen am* 10. *September* 1973. *Angenommen am* 29. *Oktober* 1973)

Einige optische Spezialgläser sind nichtsilicatischer Natur und enthalten Thorium(IV)- und Lanthan(III)-oxid als Hauptbestandteile. Die Salpetersäurelöslichkeit solcher Gläser bietet günstige Bedingungen für die quantitativ-direktthermometrische Thorium- und Lanthanbestimmung. Bekanntlich läßt sich Thorium(IV) mit Jodat aus salpetersaurer Lösung in Form schwerlöslichen Thorium(IV)-jodats fällen:

$$\mathrm{Th}^{4+} + 4\,\mathrm{JO_3}^{-} \rightarrow \mathrm{Th(JO_3)_4}\downarrow. \tag{1}$$

Die dabei auftretende Enthalpieänderung ist exotherm und wird für eine Thorium(IV)nitratlösung, die 0,3M an Salpetersäure ist, direktthermometrisch zu $\Delta H_{298} = -43{,}9$ kJ/Mol ermittelt.[1] Der Reaktionsablauf wird in Gegenwart von La^{3+} und anderen Seltenen Erdmetallionen nicht gestört.

Die Fällungsreaktionen des Thorium(IV) und Lanthan(III) mit Oxalat verlaufen in 0,3M Salpetersäure gleichfalls exotherm:

$$\mathrm{Th}^{4+} + 2\,\mathrm{C_2O_4}^{2-} \rightarrow \mathrm{Th(C_2O_4)_2}\downarrow\,; \Delta H_{298} = -52{,}3\ \mathrm{kJ/Mol}, \tag{2}$$

$$2\,\mathrm{La}^{3+} + 3\,\mathrm{C_2O_4}^{2-} \rightarrow \mathrm{La_2(C_2O_4)_3}\downarrow\,; \Delta H_{298} = -40{,}6\ \mathrm{kJ/Mol}. \tag{3}$$

Die quantitative Bestimmung der beiden Glaskomponenten wird in aliquoten Anteilen der salpetersauren Aufschluß-Stammlösung vorgenommen. Der Thoriumgehalt der untersuchten Glasprobe ergibt sich unmittelbar durch direktthermometrische Indikation der Thorium(IV)-jodat-Fällung, während der Lanthangehalt aus der direktthermometrischen Summenbestimmung beider Kationen als Oxalate erhalten wird.

EXPERIMENTELLER TEIL

Apparatur und Meßbedingungen

Thermometrisches Analysengerät "Directhermom".[2] Eichgeradenverfahren, Meßbereich: "2x" ($\Delta T = 0{,}5°$); Gehalt: 100–400 mg $\mathrm{ThO_2}$ bzw. $\mathrm{La_2O_3}$. Reagenzimmersionspipette, 20 ml.

Reagenzien und Lösungen

Salpetersäure, 65%ig z.A.

Reagenz I: 100 g Kaliumjodat, z.A. werden in einer Mischung von 250 ml destilliertem Wasser und 250 ml konzentrierter Salpetersäure in der Wärme aufgelöst. Nach dem Abkühlen der salpetersauren Kaliumjodatlösung auf Raumtemperatur wird von eventuell Auskristallisiertem abfiltriert.

Reagenz II: 100 g Oxalsäuredihydrat werden zu 1 Liter destilliertem Wasser gelöst.

Thoriumnitrat-Stammlösung. Es wird eine wäßrige Thoriumnitrat-Stammlösung bereitet, die in 1 ml 4 mg $\mathrm{ThO_2}$ enthält. Als Eichsubstanz wird Thorium(IV)nitrat-hexahydrat, z.A. verwendet, dessen effektiver Thoriumgehalt durch komplexometrische Titration gegen Brenzcatechinviolett vorher ermittelt wird.[3]

Lanthannitrat-Stammlösung. Es wird eine wäßrige Lanthannitrat-Stammlösung angesetzt, die in 1 ml 4 mg $\mathrm{La_2O_3}$ enthält. Als Eichsubstanz dient Lanthan(III)nitrat-hexahydrat; der tatsächliche Lanthangehalt ist vorher durch komplexometrische Titration gegen Xylenolorange zu bestimmen.[3]

Eichlösungen. In 250-ml Meßkolben werden jeweils 5 ml Salpetersäure, 65%ig z.A. vorgelegt, 25, 50, 75, 100 und 125 ml Thoriumnitrat- bzw. Lanthannitrat-Stammlösung abpipettiert, und mit destilliertem Wasser wird bis zu den Eichmarken aufgefüllt.

Résumé—On a élaboré une méthode simple pour la séparation rapide et quantitative du traceur scandium exempt de support formé par la réaction nucléaire $^{48}Ti_{22}$ (n,p) $^{48}Sc_{21}$. La séparation de ^{48}Sc (1,83 jour) de la cible de titane métallique a été menée par coprécipitation du traceur avec le fluorure de calcium précipité à pH ~ 4 de la solution de titane irradié dans l'acide fluorhydrique. Le précipité de fluorure fraîchement formé a été dissous en acide chlorhydrique concentré, et le traceur extrait au phosphate de tributyle puis réextrait en milieu aqueux. Le traceur exempt de support a été dosé par dilution isotopique, avec du fluorure de calcium comme diluant non-isotopique.

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DIREKTTHERMOMETRISCHE BESTIMMUNG VON THORIUM UND LANTHAN IN GLÄSERN

(*Eingegangen am* 10. *September* 1973. *Angenommen am* 29. *Oktober* 1973)

Einige optische Spezialgläser sind nichtsilicatischer Natur und enthalten Thorium(IV)- und Lanthan(III)-oxid als Hauptbestandteile. Die Salpetersäurelöslichkeit solcher Gläser bietet günstige Bedingungen für die quantitativ-direktthermometrische Thorium- und Lanthanbestimmung. Bekanntlich läßt sich Thorium(IV) mit Jodat aus salpetersaurer Lösung in Form schwerlöslichen Thorium(IV)-jodats fällen:

$$Th^{4+} + 4\,JO_3^{-} \rightarrow Th(JO_3)_4 \downarrow . \qquad (1)$$

Die dabei auftretende Enthalpieänderung ist exotherm und wird für eine Thorium(IV)nitratlösung, die 0,3M an Salpetersäure ist, direktthermometrisch zu $\Delta H_{298} = -43{,}9$ kJ/Mol ermittelt.[1] Der Reaktionsablauf wird in Gegenwart von La^{3+} und anderen Seltenen Erdmetallionen nicht gestört.

Die Fällungsreaktionen des Thorium(IV) und Lanthan(III) mit Oxalat verlaufen in 0,3M Salpetersäure gleichfalls exotherm:

$$Th^{4+} + 2\,C_2O_4^{2-} \rightarrow Th(C_2O_4)_2 \downarrow ; \Delta H_{298} = -52{,}3 \text{ kJ/Mol}, \qquad (2)$$

$$2\,La^{3+} + 3\,C_2O_4^{2-} \rightarrow La_2(C_2O_4)_3 \downarrow ; \Delta H_{298} = -40{,}6 \text{ kJ/Mol}. \qquad (3)$$

Die quantitative Bestimmung der beiden Glaskomponenten wird in aliquoten Anteilen der salpetersauren Aufschluß-Stammlösung vorgenommen. Der Thoriumgehalt der untersuchten Glasprobe ergibt sich unmittelbar durch direktthermometrische Indikation der Thorium(IV)-jodat-Fällung, während der Lanthangehalt aus der direktthermometrischen Summenbestimmung beider Kationen als Oxalate erhalten wird.

EXPERIMENTELLER TEIL

Apparatur und Meßbedingungen

Thermometrisches Analysengerät "Directhermom".[2] Eichgeradenverfahren, Meßbereich: "2x" ($\Delta T = 0{,}5°$); Gehalt: 100–400 mg ThO_2 bzw. La_2O_3. Reagenzimmersionspipette, 20 ml.

Reagenzien und Lösungen

Salpetersäure, 65%ig z.A.

Reagenz I: 100 g Kaliumjodat, z.A. werden in einer Mischung von 250 ml destilliertem Wasser und 250 ml konzentrierter Salpetersäure in der Wärme aufgelöst. Nach dem Abkühlen der salpetersauren Kaliumjodatlösung auf Raumtemperatur wird von eventuell Auskristallisiertem abfiltriert.

Reagenz II: 100 g Oxalsäuredihydrat werden zu 1 Liter destilliertem Wasser gelöst.

Thoriumnitrat-Stammlösung. Es wird eine wäßrige Thoriumnitrat-Stammlösung bereitet, die in 1 ml 4 mg ThO_2 enthält. Als Eichsubstanz wird Thorium(IV)nitrat-hexahydrat, z.A. verwendet, dessen effektiver Thoriumgehalt durch komplexometrische Titration gegen Brenzcatechinviolett vorher ermittelt wird.[3]

Lanthannitrat-Stammlösung. Es wird eine wäßrige Lanthannitrat-Stammlösung angesetzt, die in 1 ml 4 mg La_2O_3 enthält. Als Eichsubstanz dient Lanthan(III)nitrat-hexahydrat; der tatsächliche Lanthangehalt ist vorher durch komplexometrische Titration gegen Xylenolorange zu bestimmen.[3]

Eichlösungen. In 250-ml Meßkolben werden jeweils 5 ml Salpetersäure, 65%ig z.A. vorgelegt, 25, 50, 75, 100 und 125 ml Thoriumnitrat- bzw. Lanthannitrat-Stammlösung abpipettiert, und mit destilliertem Wasser wird bis zu den Eichmarken aufgefüllt.

Glasaufschluß und Analysenlösung

Die Einwaagengrößen der zu untersuchenden Gläser werden so bemessen, daß ihre Gehalte an Thorium bzw. Lanthan dem Bereich zwischen 150 und 350 mg ThO_2 bzw. La_2O_3 entsprechen.

Die Einwaage der feinzerriebenen Glasprobe wird in einem 250-ml Becherglas mit 40 ml konzentrierter Salpetersäure bis zur Trockene eingedampft. Der Rückstand wird in 12,5 ml Salpetersäure, 65%ig z.A. aufgenommen. Die Aufschlußlösung wird in einem 250-ml Meßkolben mit destilliertem Wasser bis zur Eichmarke ergänzt. Für die Bestimmungen werden von dieser Aufschluß-Stammlösung jeweils 100 ml in 250-ml Meßkolben pipettiert, und mit destilliertem Wasser wird bis zu den Eichmarken aufgefüllt.

Ausführen der Messungen

Die Eich-, Analysenlösungen und das Reagenz werden auf die Ausgangstemperatur von 25 ± 0,1 eingestellt. Die Prüflösung wird in die Meßzelle des Analysengerätes gegeben. Die 20-ml Immersionspipette wird mit dem Reagenz I bzw. II gefüllt. Die Meßzelle wird verschlossen und das Magnetrührwerk in Betrieb gesetzt. Der Temperaturausgleich zwischen Prüflösung, Reagenz in der Immersionspipette und Meßzellenumgebung findet innerhalb 5 Minuten statt. Die Meßbrücke wird eingeschaltet. Nach Kontrolle auf vollständigen Temperaturausgleich wird die Meßbrücke auf Nullstellung des Anzeigegerätes abgeglichen, das Reagens aus der Immersionspipette in die Prüflösung eingespritzt und der sich einstellende Meßwert registriert.

VERSUCHSERGEBNISSE UND VERFAHRENSBEWERTUNG

Die Abhängigkeit der Temperaturänderung des Reaktionsgemisches vom analytischen Gehalt folgt der linearen Funktion

$$y = a + bx \tag{4}$$

Die Konstanten a und b der Eichfunktion (4) werden aus den Eichdaten für x (mg ThO_2 bzw. La_2O_3) und y ($\Delta T = {}^\circ C$) mittels vereinfachter Regressionsrechnung erhalten.[4]

Der Thoriumgehalt der Probe ergibt sich dann zu

$$\text{Masse-\% } ThO_2 = \frac{\dfrac{y_A\{Th(JO_3)_4\} - a}{b\{Th(JO_3)_4\}} \cdot 100}{\text{mg Glaseinwaage}}, \tag{5}$$

der Lanthangehalt errechnet sich nach

$$\text{Masse-\% } La_2O_3 = \frac{\dfrac{M_I - M_{II}}{b\{La_2(C_2O_4)_3\}} \cdot 100}{\text{mg Glaseinwaage}}. \tag{6}$$

In Gleichung (6) bezeichnen:

$$M_I = y_B\{La_2(C_2O_4)_3\} + y_B\{Th(C_2O_4)_2\}, \tag{7}$$

$$M_{II} = y_A\{Th(JO_3)_4\} \cdot \frac{\Delta H_{298}\{Th(C_2O_4)_2\}}{\Delta H_{298}\{Th(JO_3)_4\}}, \tag{8}$$

(y_A, y_B: Meßwerte der Analysenprobe; Reaktionstypen in Klammern { }). Die an mehreren Gläsern erzielten Ergebnisse wurden übereinstimmend zu den aus konventionellen Analysen stammenden Daten gefunden.

Die Verfahrensbewertung ergibt für die Standardabweichung in der Mitte des Meßbereiches[5] $s = 3{,}1$ mg ThO_2 (20 Bestimmungen) und $s = 1{,}7$ mg La_2O_3 (20 Bestimmungen). Für die Doppelbestimmung beider Glaskomponenten werden etwa 1,5 Stunden benötigt.

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LITERATUR

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Zusammenfassung—Es wird ein für die Betriebskontrolle geeignetes Schnellverfahren zur quantitativen Thorium- und Lanthanbestimmung in nichtsilicatischen Gläsern beschrieben. Die Analyse erfolgt aus salpetersaurer Glasaufschlußlösung. Der Thoriumgehalt ergibt sich durch direktthermometrische Indikation der exotherm verlaufenden Thoriumjodat-Fällungsreaktion, während der Lanthangehalt aus der Summenbestimmung beider Kationen als Oxalate erhalten wird. Anwendung findet das "direktthermometrische Eichgeradenverfahren". Die Standardabweichung in der Mitte des Meßbereiches wird zu $s = 3{,}1$ mg ThO_2 und 1,7 mg La_2O_3 ermittelt. Die Analysenzeit beträgt *ca.* 1,5 Stunden.

Summary—A rapid method is described for the determination of thorium and lanthanum in non-silicate glasses. It is suitable for routine use in a works laboratory. The samples are dissolved in nitric acid. The thorium content is calculated from the measured heat of precipitation of thorium iodate, and the lanthanum content by difference from the heat of precipitation of both thorium and lanthanum oxalates together. The apparatus is calibrated by using standard solutions of the two metal ions. The standard deviations for the middle of the range (around 250 mg of the oxides) were 3·1 mg for ThO_2 and 1·7 mg for La_2O_3. An analysis takes about 1·5 hr.

Résumé—On décrit une méthode rapide pour le dosage du thorium et du lanthane dans des verres sans silicate. Elle convient pour l'usage de routine dans un laboratoire de fabrication. Les échantillons sont dissous dans l'acide nitrique. La teneur en thorium est calculée à partir de la mesure de la chaleur de précipitation de l'iodate de thorium, et la teneur en lanthane par différence à partir de la chaleur de précipitation des deux oxalates de thorium et de lanthane ensemble. L'appareil est étalonné en utilisant des solutions étalons des deux ions métalliques. Les écarts types pour le milieu du domaine (aux environs de 250 mg des oxydes) sont de 3,1 mg pour ThO_2 et 1,7 mg pour La_2O_3. Une analyse nécessite environ 1,5 h.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH 1,10-PHENANTHROLINE IN THE PRESENCE OF LARGE AMOUNTS OF IRON(III)

(*Received* 5 *September* 1973. *Accepted* 8 *October* 1973)

The determination of iron(II) in the presence of large amounts of iron(III) has practical importance in the investigation of the corrosion of iron and in the treatment of waste-waters from mining and the steel industries.

For determining Fe(II) the 1,10-phenanthroline (phen) method has been widely used. However, when the concentration of Fe(III) is more than a few 10's of ppm, selective or specific determination of Fe(II) is impossible, since high results are obtained owing to the formation of Fe(III)–phen complexes and/or an Fe(III)–hydroxide precipitate. To avoid this difficulty, it has been proposed that the bathophenanthroline method and an extraction procedure should be used,[1–4] with or without a masking agent (phosphate,[3] pyrophosphate[4]) for the Fe(III).

Verbeek[5] proposed a modification of the phenanthroline method, in which fluoride was used as masking agent for Fe(III), but this modification has not been widely accepted perhaps for fear of interference by the fluoride[6] in formation of $Fe(phen)_3^{2+}$. In fact, the development of colour is sometimes impaired by the excess of fluoride if it is added to the solution previously. In view of this situation, it seemed worth examining the effect of fluoride in the formation of $Fe(phen)_3^{2+}$ and finding the proper conditions for use of fluoride as the masking agent.

It was found in the present investigation that the fluoride interferes by accelerating the aerial oxidation of Fe(II). Fortunately, this effect can be inhibited almost completely by keeping the solution at a low pH. Thus, we were able to use fluoride for masking by choosing proper working conditions.

Zusammenfassung—Es wird ein für die Betriebskontrolle geeignetes Schnellverfahren zur quantitativen Thorium- und Lanthanbestimmung in nichtsilicatischen Gläsern beschrieben. Die Analyse erfolgt aus salpetersaurer Glasaufschlußlösung. Der Thoriumgehalt ergibt sich durch direktthermometrische Indikation der exotherm verlaufenden Thoriumjodat-Fällungsreaktion, während der Lanthangehalt aus der Summenbestimmung beider Kationen als Oxalate erhalten wird. Anwendung findet das "direktthermometrische Eichgeradenverfahren". Die Standardabweichung in der Mitte des Meßbereiches wird zu s = 3,1 mg ThO_2 und 1,7 mg La_2O_3 ermittelt. Die Analysenzeit beträgt *ca.* 1,5 Stunden.

Summary—A rapid method is described for the determination of thorium and lanthanum in non-silicate glasses. It is suitable for routine use in a works laboratory. The samples are dissolved in nitric acid. The thorium content is calculated from the measured heat of precipitation of thorium iodate, and the lanthanum content by difference from the heat of precipitation of both thorium and lanthanum oxalates together. The apparatus is calibrated by using standard solutions of the two metal ions. The standard deviations for the middle of the range (around 250 mg of the oxides) were 3·1 mg for ThO_2 and 1·7 mg for La_2O_3. An analysis takes about 1·5 hr.

Résumé—On décrit une méthode rapide pour le dosage du thorium et du lanthane dans des verres sans silicate. Elle convient pour l'usage de routine dans un laboratoire de fabrication. Les échantillons sont dissous dans l'acide nitrique. La teneur en thorium est calculée à partir de la mesure de la chaleur de précipitation de l'iodate de thorium, et la teneur en lanthane par différence à partir de la chaleur de précipitation des deux oxalates de thorium et de lanthane ensemble. L'appareil est étalonné en utilisant des solutions étalons des deux ions métalliques. Les écarts types pour le milieu du domaine (aux environs de 250 mg des oxydes) sont de 3,1 mg pour ThO_2 et 1,7 mg pour La_2O_3. Une analyse nécessite environ 1,5 h.

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It was found in the present investigation that the fluoride interferes by accelerating the aerial oxidation of Fe(II). Fortunately, this effect can be inhibited almost completely by keeping the solution at a low pH. Thus, we were able to use fluoride for masking by choosing proper working conditions.

EXPERIMENTAL

Reagents

Analytical-grade chemicals were used in the preparation of reagent solutions.

Sulphuric acid (1 + 4).

Ammonium fluoride solution, 2M Dissolve 18·5 g of ammonium fluoride in water and dilute to 250 ml.

1,10-*Phenanthroline monohydrochloride monohydrate solution*, 1%.

Hexamethylenetetramine buffer solution, 3M. Dissolve 105 g of hexamethylenetetramine in water and dilute to 250 ml.

Standard iron(II) solution. 100 ppm. Dissolve 0·7022 g of Mohr's salt [$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$] in 500 ml of water previously acidified with 2 ml of concentrated sulphuric acid, and dilute with water to 1 litre.

Recommended procedure

Pipette 15 ml of sample solution containing Fe(II) (up to 7 ppm) and Fe(III) (up to 2500 ppm) into a polyethylene beaker. Add 1 ml of sulphuric acid (1 + 4), 2 ml of ammonium fluoride solution, 2 ml of 1,10-phenanthroline solution, and 3 ml of hexamethylenetetramine buffer in that order, swirling the solution after addition of each reagent. Transfer the solution to a 25-ml graduated flask and dilute to the mark. Mix thoroughly and measure the absorbance at 510 nm.

DISCUSSION

Optimum conditions

It was intended to mask about 1000 ppm of Fe(III) with fluoride. The working conditions were determined so that fluoride did not interfere with the reaction between Fe(II) and 1,10-phenanthroline but masked Fe(III) completely.

Amount of sulphuric acid. To a solution containing Fe(II), sulphuric acid and ammonium fluoride were added in that order, and the colour was measured after the additions of phenanthroline and buffer. Figure 1 shows the effect of the amount of acid on the colour intensity. It is seen that, in the presence of fluoride, the absorbance is constant if the volume of acid added is at least 1 ml. The pH-values indicated in Fig. 1 were measured just after addition of the fluoride

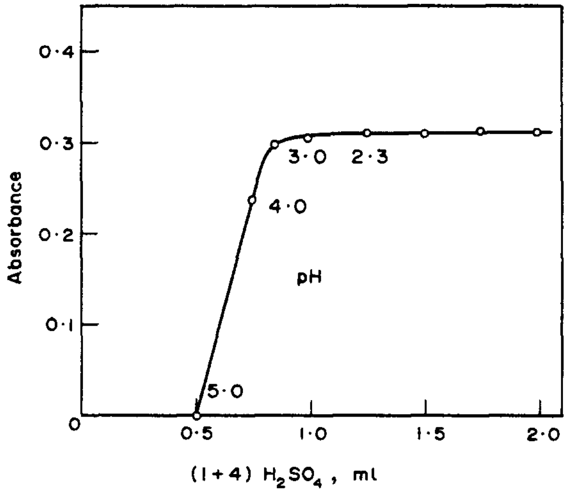

Fig. 1. Effect of sulphuric acid on the absorbance.
Volume 25 ml. 40 µg Fe^{2+}

Amount of fluoride. Ammonium fluoride was chosen because of its large solubility. Figure 2 shows the effect of the amount of fluoride on determination of Fe(II) in a mixture of Fe(II) (40 µg) and Fe(III) (20 mg). The masking was done at pH 2·5. The positive error caused by Fe(III) is eliminated by the addition of more than 2 ml of the fluoride solution. A large excess of the fluoride has no effect. This means that Fe(phen)$_3^{2+}$ is quite stable towards fluoride substitution. It should be noted that the use of hydrofluoric acid in place of fluoride salts gives low results. Presumably hydrofluoric acid accelerates even at low pH the aerial oxidation of Fe(II).

Amount of phenanthroline. Figure 3 shows that in the presence of 20 mg of Fe(III) at least 1 ml of 1% phenanthroline solution is required for maximum colour development for Fe(II) even though the Fe(III) is masked by fluoride. This is several times the quantity required in the absence of Fe(III). It may be that much of the phenanthroline is consumed by the formation of colourless mixed complexes of Fe(III) with fluoride and phenanthroline. It cannot be due to competition[6] between fluoride and phenanthroline for Fe(II), since log K for FeF^+ is only 1·5 and log K for $Fe(phen)^{2+}$ is 5·9.[7,8]

Choice of buffer. Hexamethylenetetramine was used as buffer. Ammonium acetate can also be used. Sodium acetate cannot be used because of the formation of a white precipitate, presumably Na_3FeF_6.

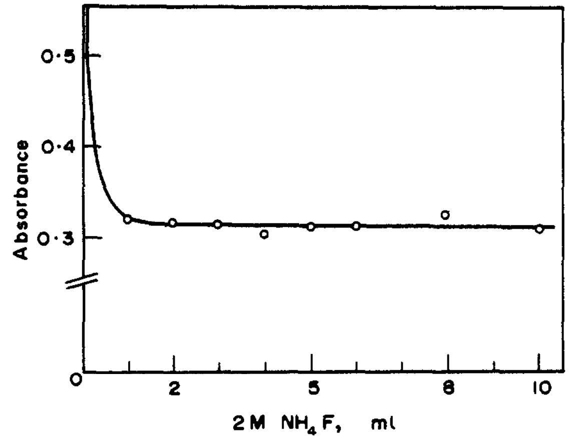

Fig. 2. Effect of ammonium fluoride on the determination of Fe^{2+} in the presence of Fe^{3+}. Masking pH < 2·5, volume 25 ml, 40 μg Fe^{2+}, 20 mg Fe^{3+}.

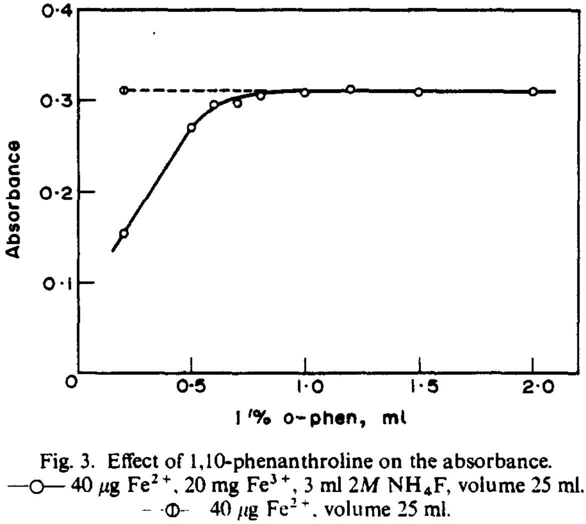

Fig. 3. Effect of 1,10-phenanthroline on the absorbance.
—○— 40 μg Fe^{2+}, 20 mg Fe^{3+}, 3 ml 2M NH_4F, volume 25 ml.
- -⦶- - 40 μg Fe^{2+}, volume 25 ml.

Stability of colour. When phenanthroline and buffer are added to a mixed solution of Fe(II) and Fe(III), without masking with fluoride, the colour intensity increases with time[1] owing to photoreduction of the Fe(III)-phen complex.[9,10] In the present procedure with fluoride, the colour is stable for more than an hour under diffused sunlight, even at 1000 ppm concentration of Fe(III). Thus, the reduction of Fe(III) is effectively inhibited by the addition of fluoride. However, the colour intensity increases with time even in the presence of fluoride when an old phenanthroline solution is used. Hence, the phenanthroline solution should be renewed every 4 weeks.

Amount of Fe(III). It was found that up to 2500 ppm of Fe(III) had no effect on the determination of Fe(II). Larger quantities of acid and fluoride should be added if the Fe(III) concentration is higher than 2500 ppm. The calibration curve is not affected by the presence of Fe(III) if the proper conditions are used.

Function of fluoride

The extent of interference of fluoride in the colour development was found to increase with the time t elapsing before the addition of phenanthroline and buffer. A detailed study was made of this phenomenon on Fe(II) solutions at different pH-values with and without fluoride addition. Figure 4 shows how the logarithm of the absorbance A changes with t, A_0 being the absorbance for $t = 0$. It is seen in all cases that log A/A_0 decreases linearly with time. The decrease in A is considered to be caused by decrease of the amount of Fe(II) by aerial oxidation which is known to be a first-order reaction with respect to Fe(II).[11-14] The oxidation is apparently accelerated by the presence of fluoride but is completely inhibited even in the presence of fluoride, if the pH is lowered below 2·5. In the proposed procedure, enough acid is added for pH to be 2·5 after the addition of the fluoride solution.

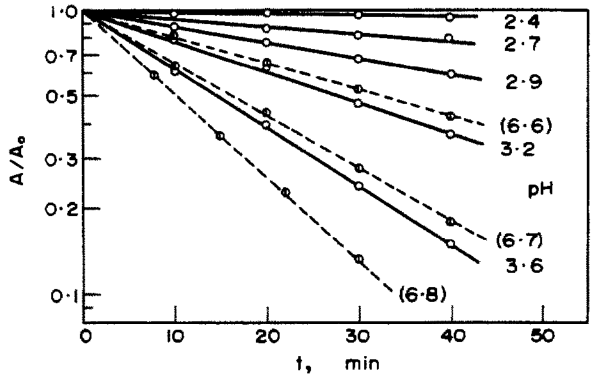

Fig 4. Effect of the time elapsing before the addition of 1,10-phenanthroline and buffer on the absorbance.

Temp. 25°, $[Fe^{2+}]_0$ = 5 ppm, P_{O_2} = 1 atm (O_2 gas was bubbled through the solution).

—○— 0·1M NaF.

--◐-- No NaF was added.

Order of addition of reagents

In Verbeek's procedure[5] the fluoride is added after the phenanthroline, the reverse of the order used by us. His procedure is successful to a certain extent since the phenanthroline stabilizes Fe(II) against oxidation and the simultaneously formed Fe(III)-phen complex is easily decomposed by fluoride. However, if the determination is carried out in daylight, a high value is obtained because the Fe(III)-phen complex undergoes photoreduction to the Fe(II)-phen complex before the addition of fluoride. The effect of the time of exposure to direct sunlight is shown in Table 1. Hence, considerable care must be taken when Verbeek's procedure is applied to the determination of Fe(II). Our procedure has the advantage that exposure to sunlight during the addition of reagents does not affect the determination. The proposed order of addition of reagents is more reasonable than that of Verbeek's procedure.

Table 1. Effect of the time of exposure to sunlight before the addition of fluoride, on the absorbance obtained by Verbeek's procedure. (Volume 25 ml, 40 μg Fe^{2+}, 20 mg Fe^{3+})

Time, *min*	0	5	10	15
Absorbance	0·311	0·350	0·420	0·740

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Summary—A study was made to establish proper conditions for the selective determination of Fe(II) by the 1,10-phenanthroline method in the presence of large amounts of Fe(III). It was shown that Fe(III) is effectively masked by fluoride. The pH of the solution to be masked should be below 2·5 in order to prevent acceleration by the fluoride of aerial oxidation of Fe(II).

Zusammenfassung—Geeignete Bedingungen zur selektiven Bestimmung von Fe(II) mit dem 1,10-Phenanthrolin-Verfahren in Gegenwart großer Mengen Fe(III) wurden ermittelt. Es wurde gezeigt, daß Eisen(III) durch Fluorid wirksam maskiert wird. Der pH-Wert der Lösung, in der maskiert werden soll, sollte unter 2,5 liegen, damit nicht die Luftoxidation von Fe(II) durch Fluorid beschleunigt wird.

Résumé—On a effectué une étude pour établir les conditions convenables pour le dosage sélectif de Fe(II) par la méthode à la 1,10-phénanthroline en la présence de grandes quantités de Fe(III). On a montré que Fe(III) est efficacement dissimulé par le fluorure. Le pH de la solution à dissimuler doit être au-dessous de 2,5 afin d'éviter l'accélération par le fluorure de l'oxydation de Fe(II) par l'air.

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RAPID AND PRECISE DETERMINATION OF TOTAL SULPHUR IN SODA–LIME–SILICA GLASSES

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Fincham and Richardson[1,2] have shown that sulphur will exist in silicate and aluminate melts entirely as sulphide if the partial pressure of oxygen is less than 10^{-5} atm and as sulphate at oxygen partial pressures above 10^{-3} atm. There is no reason to suppose that glass will behave differently and, since the glasses under consideration are made under oxidizing conditions, it can be assumed that the sulphur is present as sulphate. Sulphur dioxide is released from the melt by reaction of the sulphate with the silica of the glass but in the absence of a flux this is a lengthy process requiring extremely high temperatures.[3]

A few workers have used an iron/tin flux for the determination of sulphur in glass[4,5] whilst others have used this or vanadium pentoxide for siliceous[6,7] or refractory materials.[8] Takahashi[9] has investigated boric acid and red lead as fluxes for glass. Some of the authors avoided the troublesome conversion of sulphur dioxide into trioxide by operating with inert atmospheres; all have absorbed the sulphur oxides in aqueous solutions. The reliabilities of the methods have been assessed by testing pure compounds or comparing the results with those obtained gravimetrically.

The method discussed here is superficially similar to those mentioned above, *i.e.*, thermal decomposition of the sample with the addition of a flux and measurement of the sulphur oxides. The possible sources of error

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The method discussed here is superficially similar to those mentioned above, *i.e.*, thermal decomposition of the sample with the addition of a flux and measurement of the sulphur oxides. The possible sources of error in the method are (*a*) incomplete destruction of the sample, (*b*) the oxidation of sulphur dioxide to trioxide, (*c*) incomplete absorption of these gases, (*d*) reliability of the standard glasses. In earlier work[10] we showed that (*b*) and (*c*) could be successfully compensated for by using sulphur dioxide as the standard (by injecting the gas into the furnace tube in such a way that it reproduced the variable rate of production and molar ratio of sulphur oxides from the sample). Our initial work showed that the precision obtainable by using the "Sulmhograph" sulphur analyser was an order of magnitude better than that expected of gravimetric analysis. This indicated that the latter could not be used for standardizing glasses with the reliability required to test either (*a*) or the accuracy of the whole method. To overcome these problems it was felt necessary, at the risk of repeating the work of others, to survey the whole field of possible fluxes in order to find at least two useful ones so that a collaborative assessment could be made with equivalent levels of precision.

EXPERIMENTAL

Apparatus

Wösthoff Sulmhograph 12, sulphur analyser.
Wösthoff electrostatic precipitator.
Carbolite furnace, type CFM4/1450/VT.
Alumina furnace tubes (500 mm × 20 mm i.d.).
Unglazed porcelain boats (50 × 10 × 10 mm).
Wösthoff gas pump, type M22aX.
Wösthoff gas dosing devices, types DS10 and DS2.
Mixing vessels, borosilicate glass (various sizes).

The instrumental layout was as described previously[10] with the addition of a halide absorber. Chloride in the glass is volatilized as hydrogen chloride; the alumina furnace tube and heat shield removed some 83% of the chloride and the absorber a further 15%. The absorber was placed between the electrostatic precipitator and the conductivity cell. The use of the standardization equipment has also been described.[10]

Reagents

Vanadium pentoxide. Heat ammonium metavanadate (analytical-reagent grade) for several hours at 550°.[11] The finely ground material has a very low sulphur blank.

Halide absorber.[12] Fuse together 25·4 g of potassium pyrosulphate and 31·2 g of silver sulphate, cool and crush to 10–30 mesh (about 0·5–1·75 mm).

Procedure

Accurately weigh about 100 mg of glass (30 mesh) and 50 mg of vanadium pentoxide and mix thoroughly. Transfer to a porcelain boat and pyrolyse at 1450° in oxygen with a fast gas flow to minimize adsorption (for our instrument, 652 ml/min). Record the sulphur dioxide absorption and measure its height, slope and curvature. Calibrate the instrument with sulphur dioxide by suitable choice of the variables in the standardization equipment to match these parameters.

DISCUSSION

During analysis the removal of the sulphur dioxide from the glass is aided by high temperature to ensure reaction, low viscosity to allow bubble formation, and maintenance of the glass in a thin layer to facilitate rapid diffusion. The fluxes studied were intended to assist at least one of these functions.

A semi-quantitative investigation was carried out on a wide range of fluxes consisting of acidic, basic and amphoteric oxides, metals and inert supports. As would be expected some fell into more than one category. Seven were chosen for more detailed study; in all analyses a thin layer of melt was ensured by limiting the weight of glass to 100 mg.

(1) Silica, 1 g, furnace temperature 1400°. The silica was thought to act mainly as an inert support, as the product was a sintered mass.

(2) Vanadium pentoxide, 50 mg, 1450 . The exact function was a little uncertain but it probably acted to some degree in breaking down the sulphate[8] in addition to reducing the viscosity.[13]

(3) Sodium carbonate, 100 mg, 1450°. The main function was to reduce the viscosity.

(4) Iron powder, 250 mg, 1400°. The glass and iron were heated under nitrogen for two minutes before the combustion in oxygen, to give a smooth melt and to reduce the sulphate to sulphide.[1,2] About 10% of the sulphur was released during this stage, the rest was burnt off in the oxygen.

(5) Copper foil, 600 mg, 1400°. The function and procedure were similar to those for iron and although very effective, the copper proved to be too reactive for the porcelain boats, as well as giving poor precision.

(6) Tin rod, 2 g, 1400° The tin was used as a means of attaining a very high temperature. Glass was piled on to a pellet of tin, which had a long combustion time[14] (about 20 sec) and reached a temperature well above 2000 .

(7) Lead oxide (red lead). Although very reactive there was considerable carry-over of lead oxides, which caused a continually diminishing signal by absorbing sulphur dioxide.

The fluxes were used to analyse two soda–lime–silica glasses (Table 1). As most of the fluxes act in different ways the results were therefore derived from different analytical methods, each requiring its own characteristic calibration. There is remarkable agreement, particularly between those using vanadium pentoxide, iron and copper, suggesting that there was complete reaction. At that time halide interference (hydrogen chloride carry-over into the cell, causing increased conductivity) was not considered to be a problem and the absorber was not included. Later work revealed the error.

An interlaboratory test was carried out on the vanadium pentoxide and iron methods (with halide absorber) and a vacuum-fusion/mass spectrometric method, for five different production glasses. The mass spectrometric method is specific for sulphur dioxide and systematic errors arise only from inefficient evolution or calibration; no systematic bias was found for any of the three methods. The results (Table 2) show the agreement to be good.

It had been noted earlier that some sulphur dioxide is lost from the iron melt during the preliminary reduction under nitrogen. The sulphur is therefore evolved in two stages which are impossible to match exactly during calibration. For this reason, together with ease of manufacture, low blank and more easily controlled reaction rate (hence better calibration), vanadium pentoxide is the preferred flux.

The completeness of reaction was confirmed by analysing sodium sulphate. The reaction proved to be extremely rapid, making calibration difficult (*cf.* ref. 10, organic compounds) giving a slightly high result ($\bar{x}$ = 22·7% S, s = 0·18; theoretical = 22·5%). As it was expected that the technique would be used also for barium- and lead-containing glasses, barium sulphate ($\bar{x}$ = 13·7% S, s = 0·04; theoretical = 13·7%) and lead sulphate ($\bar{x}$ = 10·3% S, s = 0·15; theoretical = 10·6%) were tested. The results indicate that barium glasses should present little trouble but that slight losses will occur with lead glasses.

Table 1. Comparison of fluxes (all results expressed as % SO_3)

Flux	Glass 1, $\bar{x}$	s	Glass 2, $\bar{x}$	s
Silica	0·229	0·005	0·300	0·003
Vanadium pentoxide	0·225	0·007	0·340	0·002
Sodium carbonate	0·194	0·003	0·290	0·002
Iron	0·211	0·004	0·328	0·007
Copper	0·217	0·011	0·325	0·016
Tin	0·197	0·014	0·305	0·005

Table 2. Collaborative results (all results expressed as % SO_3)

Glass	Iron flux, $\bar{x}$	s	V_2O_5 flux, $\bar{x}$	s	Mass spec., $\bar{x}$
1	0·205	0·004	0·213	0·007	0·207
2	0·328	0·007	0·338	0·002	0·319
3	0·267	0·004	0·257	0·007	0·229
4	0·321	0·003	0·357	0·004	0·301
5	0·244	0·004	0·220	0·002	0·248

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Summary—A method is described for the determination of total sulphur in small amounts of soda-lime-silica glasses (100 mg or less). The crushed glass is mixed with vanadium pentoxide and decomposed at 1450° under oxygen. The sulphur is quantitatively removed from the glass and determined by a conductometric technique. The method is standardized by accurately injecting sulphur dioxide into the furnace tube. The analysis time is about 10 min and the overall precision (2*s*) is of the order of 5%.

Zusammenfassung—Eine Methode zur Bestimmung des Gesamtschwefels in kleinen Mengen von Soda-Kalk-Kieselsäure-Gläsern (100 mg oder weniger) wird beschrieben. Das gemahlene Glas wird mit Vanadiumpentoxid gemischt und bei 1450 unter Sauerstoff zersetzt. Der Schwefel wird dem Glas quantitativ entzogen und mit einem konduktometrischen Verfahren bestimmt. Die Methode wird durch genaue Injektion von Schwefeldioxid in das Ofenrohr standardisiert. Die Analysendauer beträgt etwa 10 min und die Brutto-Genauigkeit (2*s*) liegt in der Gegend von 5%.

Résumé—On décrit une méthode pour le dosage du soufre total dans de petites quantités de verres de silice-chaux sodée (100 mg ou moins). Le verre broyé est mélangé avec du pentoxyde de vanadium et décomposé à 1450° sous oxygène. Le sulfure est séparé quantitativement du verre et déterminé par une technique conductimétrique. La méthode est étalonnée en injectant avec précision de l'anhydride sulfureux dans le tube dur four. Le temps d'analyse est d'environ 10 mn et la précision globale (2 *s*) est de l'ordre de 5%.

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ANNOTATION

LIMITS OF THE MOLAR-RATIO METHOD

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The molar-ratio method introduced by Yoe and Jones[1] for investigation of complexation equilibria is still favoured by some authors owing to its simple experimental background. A recent study of the method and a list of previous papers in the area has been published by Momoki *et al.*[2] Many textbooks of analytical chemistry discuss the method, but usually inadequately. The conditions for proper application of the molar-ratio method are similar to those for the obeying of the Lambert-Beer law. For these reasons it is useful to point out some particular features of the molar-ratio method.

The method can produce quite wrong results if (*a*) metal and ligand do not react in *one* constant ratio, (*b*) a certain *limit of effective stability* is not reached, and (*c*) other complexing species (from buffers and masking reagents) are not present in *excess* and *constant* concentration.

Constant ratio of metal and ligand in the reaction is checked by plotting the molar-ratio curves for several *sufficiently different* wavelengths ($\Delta\lambda \geqslant 30$ nm). The break in the curve should occur at the same ratio of total metal and total ligand concentrations.

The limit of effective stability can be most conveniently estimated by writing the concentration–effective stability constant relationship in a normalized form

$$Ry = (x - my)^m(1 - ny)^n, \tag{1}$$

where

$$R = c_L K^{1-m-n}, \tag{2}$$

and $x = c_M/c_L$, $y = c/c_L$. K designates the effective stability constant, c is the actual concentration of the complex with a metal to ligand ratio m/n and c_M and c_L are the total concentrations of the metal and ligand, respectively. The intensity of the measured signal (effective absorbance, fluorescence intensity, number of pulses, *etc.*) should be proportional to the actual concentration of the complex (i = const. c). The total ligand concentration is kept constant.

If the complexation is complete ($R = 0$ and $K = \infty$) the function $y = f(x)$ gives two straight lines. The first passes through the points $x = y = 0$ and $x = m/n$, $y = 1/n$. The second goes through the latter point and is parallel to the x-axis. Obviously the point $x = m/n$, $y = 1/n$ is the intersection of both straight lines, where the value of x estimates the ratio m/n, and therefore determination of this is the goal of the method.

For real complexes $y = f(x)$ is a complicated curve (with points of inflection in the range $0 < x < m/n$ if $m > 1$) that approaches the theoretical straight lines at points $x = y = 0$ and $x \gg 1$, $y = 1/n$ as the complexation becomes complete. Since the determination of $x = m/n$ is required we must define a limiting deviation from m/n that makes that determination still reliable. Taking into account the usual complexes with ratios m/n 1/1, 1/2, 1/3, 1/4, 2/2 and 2/3 it is convenient to introduce for that deviation $\Delta_{\text{lim}} = 0{\cdot}05$.

Further we must introduce a limiting deviation from the shape of the quantitative curve. The quantitative curve has its tangent at the point $x = y = 0$, $\tan\alpha = 1/m$. For minimum experimental value of the tangent we may take $\tan\alpha_{\text{exp}} = 0{\cdot}99/m$ so that we have the equation of the straight line

$$y = 0{\cdot}99x/m. \tag{3}$$

The second straight line (which should be parallel to the x-axis) can be constructed from measurements obtained for $x = 2$ and $x = 3$. The reason for using these particular values is that if $x > 10$ there is often a change in the complex composition so that a complex with a different ratio m/n or a mixture of several complexes with various ratios m/n are formed (the latter occurs in complexation with dithizone,[3] 8-hydroxyquinoline[4] and acetylacetone). The equation of the straight line through the points $x = 2$, y_2 and $x = 3$, y_3 is given by

$$y = (y_3 - y_2)(x - 2) + y_2. \tag{4}$$

The intersection of these two straight lines is usually at a lower value of x than the theoretical m/n for quantitative complexation (the experimental curve more or less indicates the formation of complexes with a higher number of ligands than n, see Fig. 1) so that after the introduction of the deviation $\Delta_{\lim}$ we have for the limit of intersection

$$x = m/n - 0{\cdot}05. \tag{5}$$

Combining equations (3)–(5) we obtain

$$y_3 = \frac{0{\cdot}99(1/n - 0{\cdot}05/m) - y_2}{m/n - 0{\cdot}05 - 2} + y_2. \tag{6}$$

If we write equation (1) for points $x = 2$, y_2 and $x = 3$, y_3 we obtain two equations which after the elimination of R give

$$\left(\frac{3 - my_3}{2 - my_2}\right)^m = \frac{y_3}{y_2}\left(\frac{1 - ny_2}{1 - ny_3}\right)^n. \tag{7}$$

From equations (6) and (7) we can easily calculate the value of y_2 for various values of m and n. The values of R we calculate from (1) written for $x = 2$ and y_2. These values (they are the highest acceptable limit) indicate the conditions where the error in the determination of m/n does not exceed 0·05. They are collected in Table 1.

Table 1. Limiting values of $-\log R$ for some common complexes

m	n	y_2*	$-\log R$*	y_2†	$-\log R$†
1	1	0·9735	1·554	0·9603	1·367
1	2	0·4740	2·059	0·4590	1·646
1	3	0·3066	2·546	0·2905	1·904
1	4	0·2228	2·950	0·2059	2·074
2	2	0·4923	3·298	0·4886	2·950
2	3	0·3205	3·480	0·3135	2·895

* $x = m/n - 0{\cdot}03$.
† $x = m/n - 0{\cdot}05$.

To satisfy the values of R from Table 1 we should make a proper selection of total concentrations and the cell path-length. The curves $y = f(x)$ corresponding to the limiting values of $-\log R$ are presented in Fig. 1 and compared with other curves.

The good methods for quantitative determination of metals based on complexation require that the function $i = F(c_M)$ (for the meaning of i see above) should be relatively independent of the total ligand concentration. The formation of a single complex between a metal and a ligand is described by equation (1). Assuming that a decrease from c_L to $c_L/2$ gives a 1% decrease in the amount of complex formed, we have from (1)

$$2^n Ry = (x - 0{\cdot}99my)^m(1 - 1{\cdot}98ny)^n. \tag{8}$$

The elimination of R by combination of (1) and (8) results in

$$x = my(t - 0{\cdot}99)/(t - 1), \tag{9}$$

where

$$t = [2(1 - ny)/(1 - 1{\cdot}98ny)]^{n/m}. \tag{10}$$

Employing (9) and (10), we can calculate the relationship between y and x for any particular complex and by inserting the values obtained into equation (1) we get the value of R. That calculation has been performed and is expressed graphically as the dependence between $-\log R$ and x in Fig. 2.

In spectrophotometry the usual total ligand concentration is 10^{-4} M. That means that for complexes with metal/ligand molar ratio 1/1, 1/2, 1/3, 1/4, 2/2 and 2/3 the minimum values of log K are 4·37, 9·65, 13·90, 18·07, 14·95 and 18·90 respectively, if the determination of the value of m/n is to be true ($\Delta_{\lim} = 0{\cdot}05$). The calculation is based on the values of R given in Table 1. Assuming $x = 0{\cdot}10$ (tenfold excess of ligand) a good method for determination of metals (based on Fig. 2) requires for the same total ligand concentration and sequence of com-

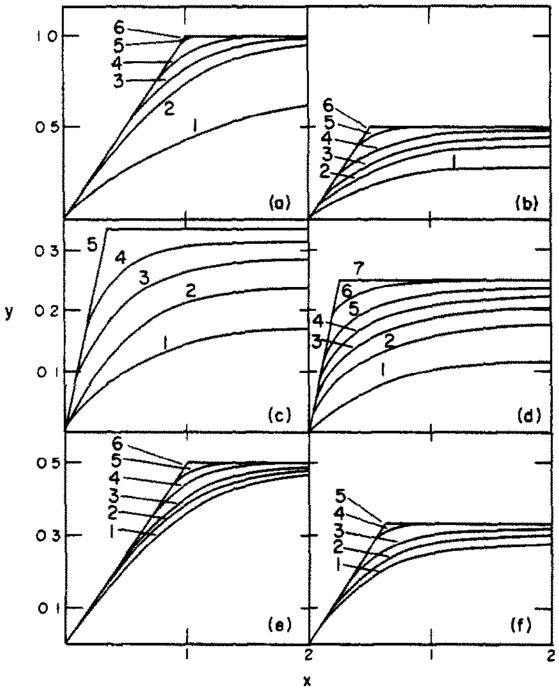

Fig. 1. The function $y = f(x)$ for complexes of various ratio m/n (and $-\log R$).
(*a*) $m/n = 1/1$: 1 ($-\log R = 0{\cdot}00$), 2 (1·00), 3 (1·37), 4 (2·00), 5 (3·00), 6 (∞); (*b*) 1/2: 1 (0·00), 2 (1·00), 3 (1·65), 4 (2·00), 5 (3·00), 6 (∞); (*c*) 1/3: 1 (0·00), 2 (1·00), 3 (1·90), 4 (3·00), 5 (∞); (*d*) 1/4: 1 (0·00), 2 (1·00), 3 (2·07), 4 (3·00), 5 (4·00), 6 (5·00), 7 (∞); (*e*) 2/2: 1 (2·00), 2 (2·45), 3 (2·95), 4 (4·00), 5 (5·00), 6 (∞); (*f*) 2/3: 1 (2·00), 2 (2·90), 3 (4·00), 4 (5·00), 5 (∞).

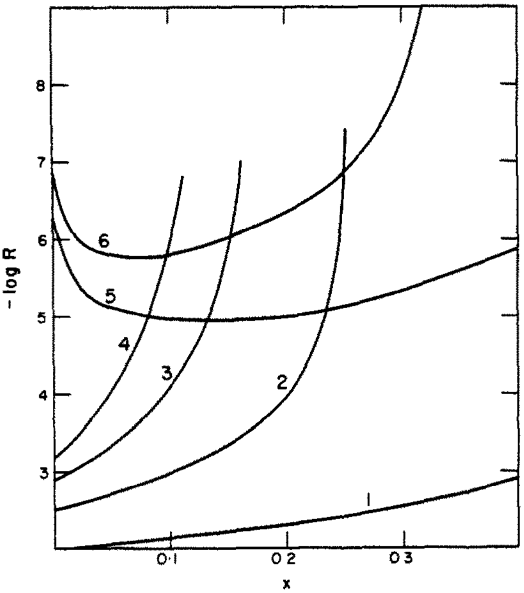

Fig. 2. The function $-\log R = f(x)$ for complexes of various ratio m/n.
1 (1/1), 2 (1/2), 3 (1/3), 4 (1/4), 5 (2/2), 6 (2/3).
The degree of complex formation is ≥ 99% ($my/x \geqslant 0{\cdot}99$).

plexes the following minimum values of log K: 6·14, 10·97, 16·06, 21·93, 16·98 and 21·80 respectively. It is obvious that not many spectrophotometric methods meet these requirements.

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Summary—The limiting factors (one constant molar-ratio of metal to ligand, constant excess of masking reagent and buffer, and high enough effective stability) of the molar ratio method are discussed. The lowest values of the effective stability constant for the true metal/ligand ratio to be determined for the complex and for a metal determination to be relatively independent of ligand concentration are calculated.

Zusammenfassung—Die Grenzen der Methode des molaren Verhältnisses werden diskutiert: nur ein Komplex, konstantes molares Verhältnis Metall:Ligand, konstanter Überschuß von Maskierungsreagens und Puffer, hinreichend hohe effektive Stabilität. Die Mindestwerte der effektiven Stabilitätskonstanten wurden berechnet, die für den Komplex das wahre Metall:LigandVerhältnis zu ermitteln gestatten und eine Metallbestimmung von der Ligandkonzentration relativ unabhängig machen.

Résumé—On discute des facteurs limitatifs (un complexe seulement, rapport molaire constant du métal au coordinat, excès constant d'agent dissimulant et de tampon, et stabilité réelle suffisamment élevée) de la méthode des rapports molaires. On calcule les valeurs les plus faibles de la constante de stabilité réelle pour que le vrai rapport métal/coordinat soit déterminé pour le complexe et pour que le dosage d'un métal soit relativement indépendant de la concentration du coordinat.

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RECENT PROBLEMS AND LIMITATIONS IN THE ANALYTICAL CHARACTERIZATION OF HIGH-PURITY MATERIAL*

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Summary—The trend toward increasingly pure metals and semiconductor materials makes increasing demands upon their analytical characterization. The limits of direct methods of analysis (optical spectroscopy, mass spectroscopy, and activation analysis) can already be observed. In many cases, therefore, the contaminating elements have to be enriched before their determination, or they have to be separated from the matrix. These additional procedures increase the systematic possibilities of error (blank value, effects of adsorption, volatilization, *etc.*). General methods are described for their extensive elimination, especially during the decomposition and enrichment procedures. When these procedures are closely coupled with suitable detector systems, numerous elements (Be, B, C, N, O, Si, P, S, Se, Te, As, Sb and others) can still be determined very accurately in ng and pg amounts in the most diversified matrices.

All the naturally-occurring chemical elements are in practice to be found in all materials, inorganic or organic, though of course in very different amounts. The abundances of the elements depend primarily on the history of the creation of our solar system. The elements have, however, been markedly separated and enriched on the earth. The original distribution of the elements—that of our solar system—is found, in the world accessible to us, only in living things (Fig. 1). However, our raw materials come for the most part from the earth's crust, of which some eight elements account for more than 98·6% (Table 1, first column). From these simple considerations we can deduce that the analytical determination of traces of these very common elements is likely to meet with greater difficulties than is that of the considerably less common elements such as Hg, Tl, Au, Re and so on (Table 1, last column).

That every sample contains all the elements—even if in very small amounts—arouses scientific curiosity as to the true properties of the elements. Even today it is the properties of considerably impure forms which are being studied and described. Thus, *e.g.*, the plasticity of Ti, Zr and W increases with increasing purity. Beryllium is also described in most textbooks as a hard, particularly brittle metal at normal temperatures, but the same metal purified by zone-melting is, in contrast, in certain crystallographic planes, a very ductile material.

Just as surprising is the variation of the electrical, optical and magnetic properties of many elements with purity. This dependence of properties on the presence of impurities is however much more complex than one might at first assume: as an example, the chemical impurities in crystalline materials do not have an independent existence; they interact with the "physical" impurities—the lattice defects such as holes, displacements, dislocations and so on (Fig. 2).[1]

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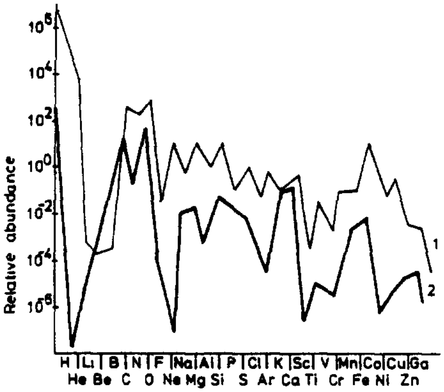

Fig. 1. The abundance of the elements in the cosmos (1) and in living organisms (2) (after C. T. Horovitz; Scientific Report, University of Tübingen, BRD, 1972)

What then do we understand by an "ultrapure" metal? In basic research on an ultrapure metal is understood as one having properties which do not change significantly upon further purification.

In the particular case of the interdependence of foreign atoms and crystal lattice defects, it has been possible for metallurgical physicists to deduce from the number of dislocations occurring in a given volume, and the number of foreign atoms involved, that the properties of the parent material will no longer be dependent on the concentration of the impurity when it falls below 10^{-8} to 10^{-10}%. In other words, a metal may be considered to be pure in the sense of this limiting purity, when the concentration of foreign atoms falls below 1 part per milliard (ppM). Present-day technology simply does not allow this degree of

Table 1. Order of abundance of the elements in the continental crust (after R. S. Taylor, *Geochim. Cosmochim. Acta*, 1964, **28**, 1273)

%		10^{-2} %		10^{-3} %		10^{-4} %		10^{-5} %	
O	46·4	Ti	57	Rb	9	Th	9	Tb	9·1
Si	28·15	H	14	Ni	7	Pr	8·2	I	5
Al	8·23	Mn	10	Zn	7	Sm	6·0	Tl	4·5
Fe	5·63	P	10	Ce	6	Gd	5·4	Cd	2
Ca	4·15	F	6·3	Y	3·3	Ge	5·4	Sb	2
Na	2·36	Ba	4·3	La	3	Dy	3.	Hg	1·8
Mg	2·33	Sr	3·7	Nd	2·8	Hf	3	Bi	1·7
K	2·09	S	2·6	Co	2·5	Yb	3	In	1·0
	99·34	C	2·0	Sc	2·2	Be	2·8	Ag	0·7
		Zr	1·6	Li	2	Er	2·8	Se	0·5
		Cl	1·3	N	2	U	2·7	Re	0·05
		Cr	1·0	Nb	2	Sn	2	Au	0·04
			113·8	Ga	1·5	Ta	2		28·3
				Pb	1·2	As	1·8		
				B	1·0	Mo	1·5		
					52·5	Eu	1·2		
						Ho	1·2		
						Cs	1·0		
						W	1		
							63·0		

purity to be obtained. The levels of impurities, including gases, in the purest metals available at present are still in the ppM region.

Further purification means that the analyst must extend the limits of detection of his methods by at least an order of magnitude beyond the desired degree of purity of the particular matrix, to help optimize the refining procedure. In order to simplify the concept of this task, we suppose that the impurities are uniformly distributed in the sample, although we are aware that this state is only approximately attained even in the case of a single crystal.

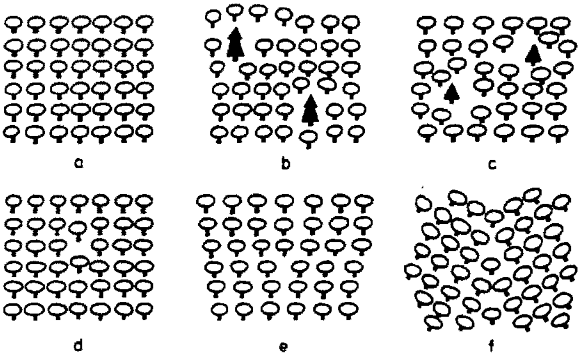

Fig. 2. Order and disorder in a crystal lattice.
(*a*) perfect order; (*b*) deformation by foreign atoms; (*c*) deformation by interstitial foreign atoms; (*d*) vacancy; (*e*) dislocation; (*f*) twinning plane.

Nowadays we can grow quite large single crystals of a few selected materials. However, as the purity of a material increases, not only its scientific but also its monetary value increases exponentially with the size, and it is a sound assumption that quite insufficient amounts of high-purity materials are likely to be available for analytical investigation. Therefore the trend of trace techniques is in the direction of smaller sample amounts, and of course of lower limits of detection, aiming at the limiting concentrations already mentioned.

This simple question of the complete listing of the impurities in an ultrapure sample has already necessitated the development of a completely new field of analysis to cope with the determination of absolute amounts of elements in the pg range (Fig. 3).

A further aspect of increasing interest, particularly in the case of polycrystalline materials, is the micro-distribution of the impurities, for example along grain boundaries in the crystal. This problem calls for the use of such techniques as laser emission spectroscopy, electron- and ion-microprobe techniques, to determine absolute amounts of elements at the pg level and below. But impurities accumulated on the surface of a sample lead to very misleading analytical results, with the discrepancy between the observed and the real values increasing as the surface-to-volume ratio of the sample increases. Metals exposed to air rapidly adsorb gas molecules on their surface. A monomolecular layer on a 1-mm cube corresponds to about 10^{14} atoms, so one can calculate that this represents about one adsorbed atom for 10^6 metal atoms in the cube, or about 1 ppm of impurity. It is clear that such an amount must be taken into account as a blank value when making a bulk analysis, and further, that concentrations below this level simply cannot be determined. Here the analyst must modify his techniques or develop new ones so as to be able to detect

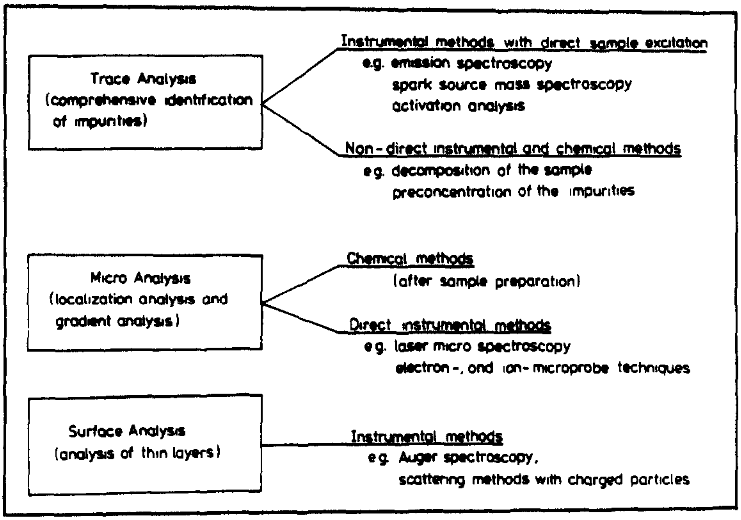

Fig. 3. Methods for the analytical characterization of purest materials.

these small amounts. Auger spectroscopy and secondary-ion mass spectroscopy offer attractive possibilities in such cases.

All trace analysts should be in agreement that direct instrumental methods (Fig. 4B) in which the sample is directly excited to produce a signal proportional to the concentration of the element sought, must be preferable to multistep procedures such as the classical separation schemes (Fig. 4A).[2] The advantages lie in the smaller systematic errors and expenditure of time, particularly in the case of large numbers of similar samples. For the determination of extreme traces we can already fall back on non-destructive activation analysis, emission spectrography, or spark-source mass spectroscopy. But one may often find that the resolution of the method is inadequate, or that the standards required for calibration of these direct methods are not available. For such reasons we are often obliged, in extreme trace analysis, to fall back on procedures with branching structure or perhaps with the more preferable chain structure (Fig. 4C), whereby the errors of the individual steps accumulate in an alarming way according to the law of propagation of errors.

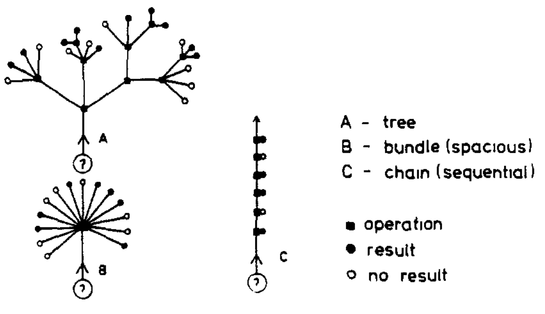

Fig. 4. Structure of analytical procedures (after Kaiser[2]).

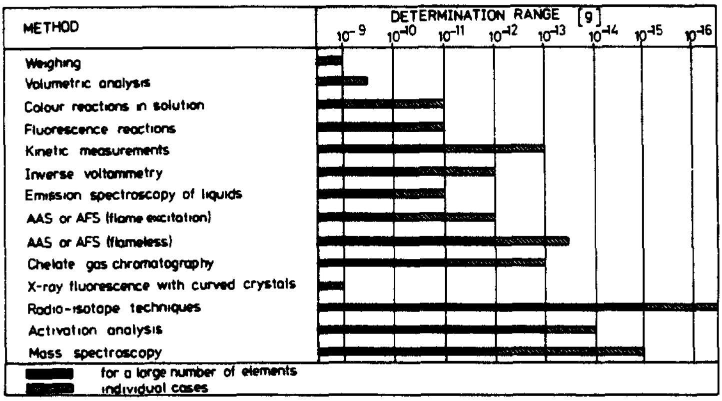

Fig. 5. Survey of application ranges of the most important determination methods for individual elements under optimal conditions.

The core of the problem lies not only in the preparation of the sample, but also in the separate steps for decomposition, separation, and enrichment of the traces.[3] Sensitivity is perhaps the least of our worries at the moment, as we have available a whole range of detectors, both chemical and physical, which offer very good sensitivities for many elements—even in the pg range—after they have been separated, though the variation from element to element and method to method is quite considerable (Fig. 5).[4]

Far from being satisfactorily solved, however, is the problem of getting the ng or pg amounts of the trace to be determined out of the sample and to the appropriate detector while introducing the absolute minimum of systematic error. For this reason we are primarily concerned with optimizing the combination of decomposition, separation, and determination steps so as to reduce the accumulated errors to a minimum (Fig. 6). The difficulty of eliminating these sources of systematic errors becomes even more serious in

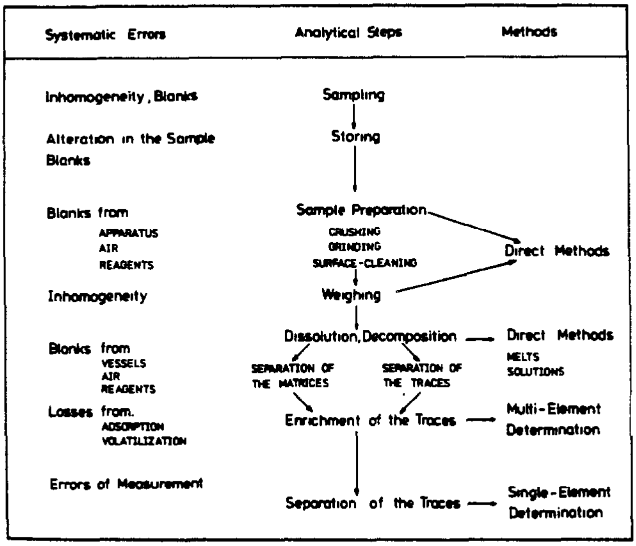

Fig. 6. Scheme for trace analytical procedure.

the ppM range, and eventually it becomes the main problem. In this case it must be mentioned that one can be very successful, if the experiences and methods of ultramicro analysis[5] are used. There is also another reason to introduce micro techniques. The majority of direct instrumental methods used in extreme trace analysis are comparative methods. which are sensitive to changes in the matrix. Further, it is unusual to find standard samples which have very low concentrations of a particular element, and at the same time a similar composition to the unknown sample. Therefore determination procedures which are applicable after separation are much easier to calibrate. One only needs to prepare from a pure material a dilute solution (10^{-4} to 10^{-5} M) of the appropriate element, and add this to the sample or the reference solution, *e.g.*, from an ultramicroburette, which can be handled with good reproducibility.[5] Most solution techniques—emission spectroscopy with liquid samples, atomic-absorption spectroscopy, inverse voltammetry *etc.*—can be calibrated in this manner for many elements down to the pg range, and sometimes with statistical errors less than 5%. Multi-stage procedures involving preconcentration of very small amounts of traces may sometimes, because of this ease of calibration, be preferable to a single-stage direct method.

The best way of eliminating systematic errors would be to carry out all stages of the multi-stage procedure in a single closed system with the minimum of surface area, and made of an inert material. We might describe this in terms of the earlier analogy, as cultivating a branch-like or chain-like procedure with as short and as few branches as possible, and protected in a glasshouse from external influences. Of course in practice, and depending on the matrix and the elements to be determined, this may be far from easy.

This principle may be successfully exploited when the element to be determined can be liberated straight away in the decomposition stage as a gaseous compound and remain so in the subsequent separation and trapping stages before the determination. Examples are the determinations of carbon as CO_2, or sulphur as SO_2 or as H_2S, depending on whether the sample is combusted in oxygen or pyrolysed in hydrogen. This principle can be applied to any of the other elements which readily form gaseous compounds, such as boron, silicon, phosphorus, selenium, arsenic and antimony.

We can always start with the very attractive assumption that gaseous reagents such as oxygen and hydrogen can be prepared in a very high state of purity, and remain so on

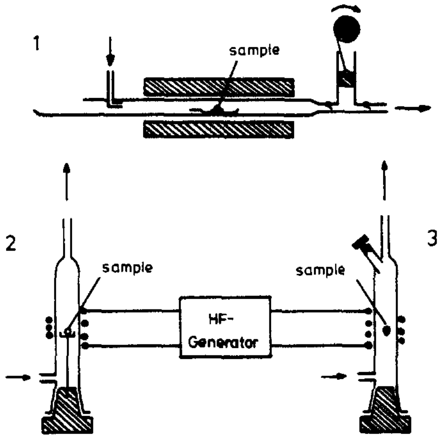

Fig. 7. Sample heated (1) in a tube furnace; or by high-frequency excitation with (2) and without (3) crucible.

storage over long periods. The interaction between sample during decomposition and the containing vessel, and therefore also the blank value, can be kept very small, since the size of the sample can be optimized in relation to the surface area of the reaction vessel and the contact time minimized. The first condition can be met by constructing a very small sample-holder out of a particularly suitable material, and the second by heating the sample only for as long as is necessary to ensure complete conversion, for example by high-frequency or microwave induction heating of only the sample and its holder [Fig. 7(2)], and not the complete apparatus [Fig. 7(1)]. The ideal conditions of no contact between sample and container can be attained by means of levitation-melting in which the sample is both suspended and heated in a magnetic field of suitable high frequency and power until completion of the decomposition reaction [Fig. 7(3)]. Adsorption of the gaseous products on the walls of the vessel can be largely eliminated by baking out the entire vessel, particularly when the vessel can be flushed with a suitable carrier gas. Interfering components may be separated on a time basis by gas chromatography, and if need be may themselves also be determined.

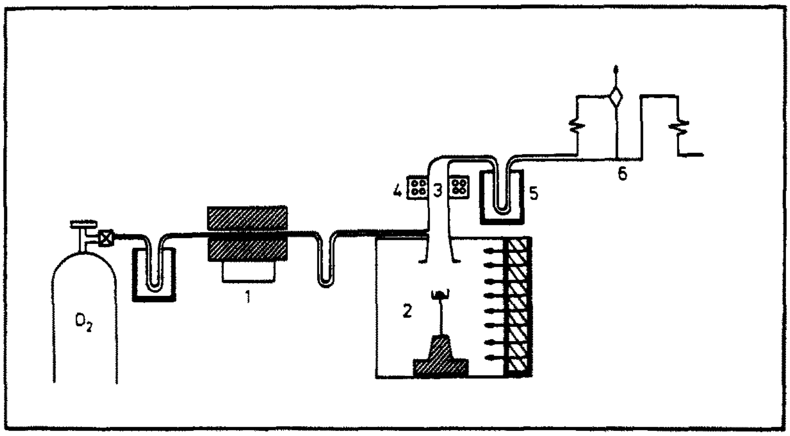

Fig. 8. Scheme for the relative conductometric determination of C and S in the ng-range in high purity metals.
(1) O_2-Purification; (2) clean bench; (3) decomposition vessel; (4) HF generator; (5) separation column; (6) measurement cell for relative conductometry.

This attractive principle may be illustrated by the following real example. It is now possible for us to determine less than 5 ng of carbon and sulphur simultaneously in a variety of metallic matrices and thus to improve on the existing procedures by at least two orders of magnitude (Fig. 8).[6] The etched sample is weighed in a dust-free atmosphere and then transferred through a dust-free, air-lock [Fig. 8(2)] to the reaction chamber [Fig. 8(3)], and decomposed by induction heating in very pure oxygen. The reaction products CO_2 and SO_2 pass together with the oxygen as carrier gas through a special separating column [Fig. 8(5)] with very different retention times for the two components (about 5 min difference) and are absorbed in a dilute solution of sodium hydroxide [Fig. 8(6)]. They are detected (first the CO_2 and then the SO_2) by measuring the small change in conductance of the solution as compared to a reference cell. This relative conductimetric measurement has been optimized so that less than 1 ng of carbon or of sulphur gives a detectable signal. The limitations of the system lie not in the detector system, however, but in the spread of the blank values which are mainly due to traces brought in by the sample and the oxygen. Nevertheless we are in the position to determine 5×10^{-9} g of carbon or sulphur in 100 mg of metal with a relative standard deviation of around 10%. This corresponds to a limit of detection of about 5 ppM.

However, the problem of calibration of this relative method raises a number of questions.

(1) Exactly what change in conductance does a given amount of CO_2 or SO_2 produce?
(2) How much CO_2 or SO_2 is lost by adsorption between combustion and measurement?
(3) To what extent and in what way do the combustion characteristics of the matrix material affect the formation of CO_2 and SO_2?
(4) Do the metal oxides produced act as getters for these gases?

The first two questions can be answered by the simple process of adding known amounts of synthetic gas mixtures to the combustion cell and to the absorption cell by micro techniques, but such a calibration procedure still does not automatically allow one to state the carbon or sulphur content of a metal sample with confidence. For this, the last two questions also have to be answered. Again it must be pointed out that we rarely have standards for trace elements in this concentration range, and this conventional approach to calibration is invalid. However, it proved possible in the case of iron as matrix, to obtain results in agreement with those from the gas standard-addition method, by adding instead mg amounts of standard steel samples.

The same technique of addition of small amounts of standard steels enabled the combustion characteristics of other metals to be investigated, and the important parameters of rate and duration of heating to be established. For the standardization of the sulphur determination, however, we had to fall back on a second, independent, and absolute method, to check the combustion procedure. This may be done, in the case of metals with melting points below 1200° (*e.g.*, Cu, Ag, Au), by heating the metal in a stream of hydrogen at 1200° and determining the resultant hydrogen sulphide argentometrically with bipotentiometric end-point detection (Fig. 9). This titration method was developed earlier for sulphur determination in organic elemental ultramicro analysis.[7]

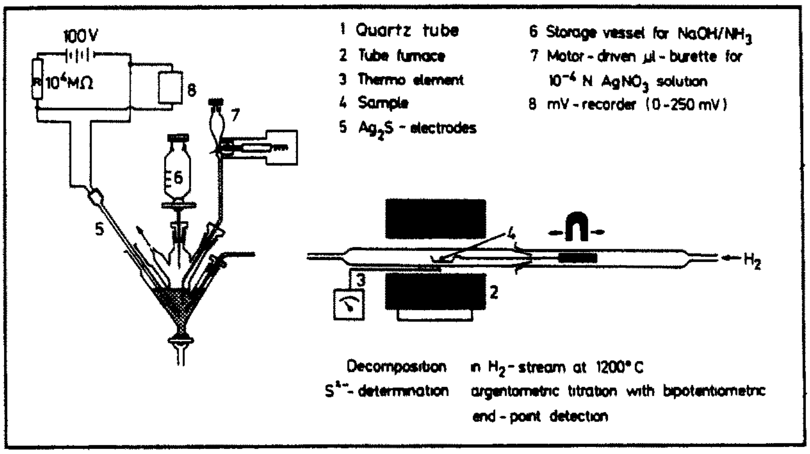

Fig. 9. Apparatus for a titrimetric determination of ng-amounts of sulphur in metals after decomposition in hydrogen.

This example serves to show that under some circumstances one is obliged in the development of a new method to fall back on other independent methods. Another example also illustrates this approach. In the determination of very small amounts of nitrogen in refractory metals such as niobium the existing methods based on fusion-extraction suffer from limits of detection in the ppm range, and need to be improved by at least two orders of magnitude. In this case as in the previous one, the difficulty lies not in the detector but in the blank due to adsorbed nitrogen on the surface of the sample and the decomposition vessel, and we had to develop a new decomposition procedure in which the sample is melted while freely suspended in a high frequency field, as already described. Because there is no contact with the sample holder (Fig. 10) the blank can be kept very small, and moreover stepwise heating makes it possible to bake out nitrogen adsorbed on the surface of the sample before the fusion stage at a higher temperature, when the nitrogen within the sample is released and then determined. The actual determination of the nitrogen released is carried out mass spectrometrically.[8]

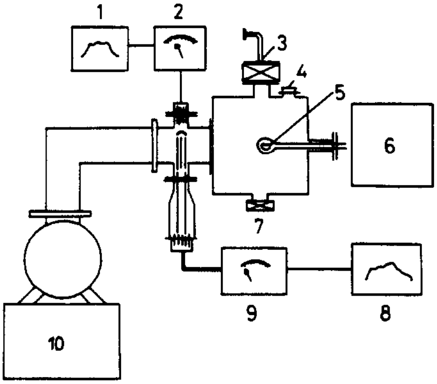

Fig. 10. Apparatus for the determination of gas contents below 1 ppm in metals after levitation-melting.[8]

(1) Recorder; (2) total-pressure indicator; (3) sample inlet *via* air-lock; (4) window; (5) water-cooled boat in which the sample is melted by induction heating (levitation) without evolution of gas from the crucible; (6) HF oscillator; (7) control valve for reactive and for inert carrier gas; (8) partial-pressure recorder; (9) partial-pressure indicator; (10) turbomolecular pump.

The improvement in the detectability realized by this new method is particularly apparent when one compares the coefficients of variation of both procedures as a function of the amount of nitrogen being determined (Fig. 11).

This relative method, based on purely physical techniques, had of course to be calibrated, and as usual there were no reliable standards. Another research group tackled this problem from a purely chemical standpoint. It is somewhat ironic that the answer should lie in the old classical absolute method developed over 100 years ago by Kjeldahl. The various improvements introduced during a century of use of Kjeldahl method—in which all the stages were still carried out quite separately—had made possible a reproducibility of 1–2 μg of nitrogen, which was not good enough for the purpose. The reasons for the error are the high N-blanks from the reagents and the air in the laboratory, coupled with the rather large volume of solution for the final determination after separation of the ammonia by steam-distillation. The amount that can be determined can be reduced by two orders of magnitude by using a special micro decomposition stage in a Teflon bomb,

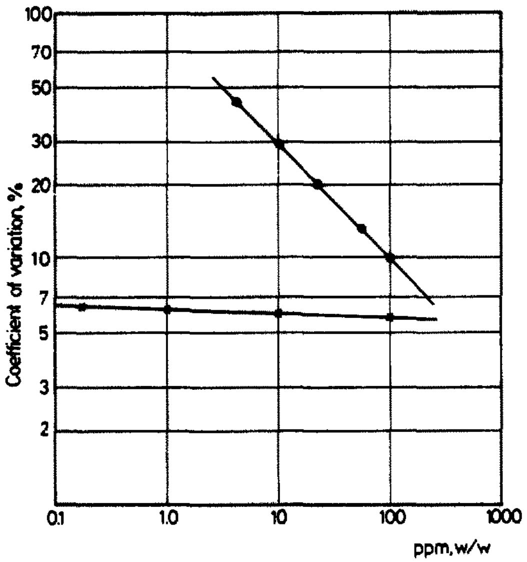

Fig. 11. Comparison of the coefficients of variation for the determination of nitrogen in niobium. ● By conventional fusion extraction; X by levitation melting.

liberating the ammonia by treatment with specially purified sodium hydroxide, distilling it in a circulating distillation apparatus and titrating with biamperometric end-point detection (Fig. 12). The standard deviation of this micro procedure is about 5 ng.[9]

Combined decomposition–separation procedures are also useful even in applications where the reaction products can be retained in the gas phase only at relatively high temperatures. This principle, originally introduced by Bunsen, attracted an awakened interest in the 1950's under the name "volatilization analysis" (Fig. 13).[3] Nanogram amounts of volatile elements or compounds can be separated in a stream of carrier gas from relatively non-volatile matrices at temperatures up to a practical limit of 1400°, and condensed in a capillary or on a cold-finger. In this way, *e.g.*, zinc, cadmium, lead or thallium may be separated from, *e.g.*, aluminium, iron or manganese. Similarly selenium and arsenic can be separated as their oxides at temperatures up to 800° from, *e.g.*, copper or silver. The principle may be extended by the application of induction heating, whereby the whole process may be carried out in a closed system. The second renaissance of these techniques has been in flameless atomic-absorption spectroscopy today, but both variations are only applicable when the volatile elements do not form non-volatile compounds such as spinels, carbides, nitrides or phosphates with the material of the excitation source, the matrix, or with other components present in the matrix. Such sources of systematic errors, which seriously restrict the usefulness of such methods, are all too often overlooked.

How do these combined decomposition–separation–determination procedures compare when a liquid or a solid reagent has to be used in the reaction to produce the volatile compound? Apart from the increasing difficulty of obtaining the reagents in the necessary state of purity, the principle of the closed system can rarely be adhered to. Either the decomposi-

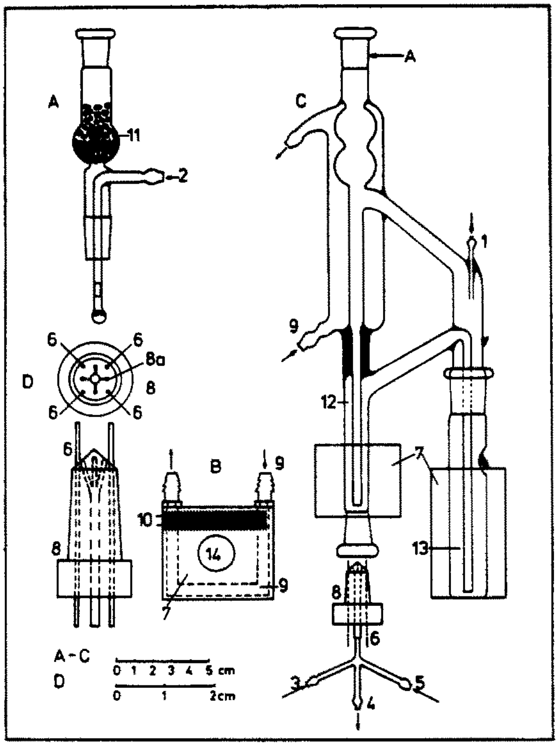

Fig. 12. Circulating distillation apparatus for the determination of ng-amounts of nitrogen according to the Kjeldahl principle.

(1) Sodium hydroxide solution; (2) wash and absorption solution; (3) buffer solution; (4) outlet tube; (5) gas stirring; (6) platinum generator and indicator electrode pairs; (7) aluminium block with electrical heating elements; (8) PTFE stopper with holes 8a; (9) cooling water; (10) heating element; (11) sulphuric acid adsorbed on pumice stone; (12) determination cell; (13) sample compartment; (14) cavity for determination cell.

tion and separation or the separation and determination stages may be combined. Whenever such a combination is feasible, it makes some improvement possible. Combination of the decomposition and separation steps can be illustrated by the determination of < 1 ppm of silicon in pure metals. If the matrix forms no volatile fluoride the sample can be dissolved in a micro-distillation apparatus made of PTFE (Fig. 14) with a mixture of hydrofluoric, nitric and perchloric acids. The volatile fluoride of silicon can be collected by carrier-gas techniques. After its isolation the silicon can be determined by various sensitive methods in the ng range.[10]

The combination of the separation and determination steps can be illustrated by the following example. None of the usual methods for the determination of boron, such as spectrophotometry or flame atomic-absorption came anywhere near coping with the problem in extreme trace analysis. The one method is too prone to systematic errors, and the other is not sensitive enough. Flameless atomic-absorption spectroscopy also runs into serious difficulties as the cell materials used—graphite, tantalum or rhenium—react with boron at the high temperatures involved, to form non-volatile compounds. An alternative is to convert the boron in a close system (Fig. 15) by chemical reaction into a volatile compound, *e.g.*, BF_3, which can then be passed into an argon plasma where its emission is

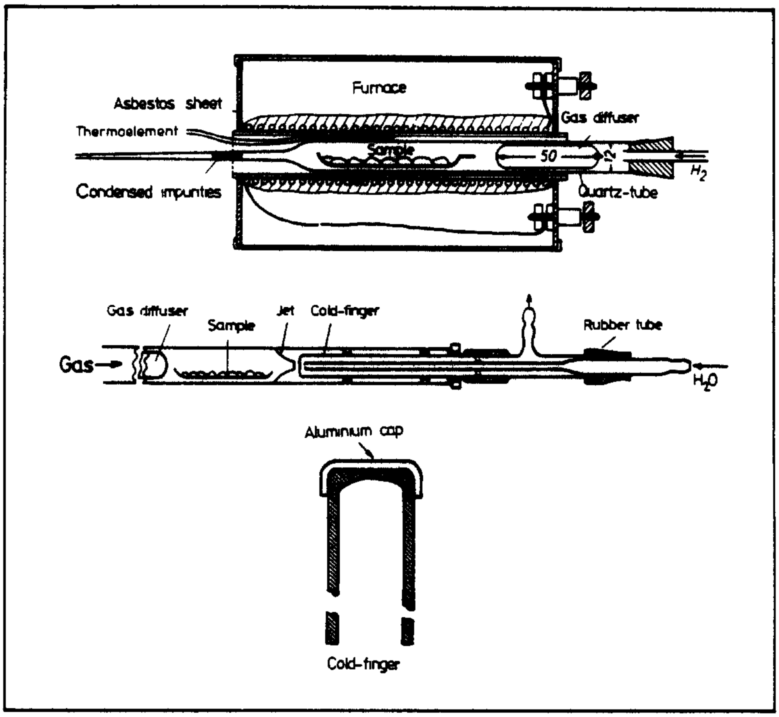

Fig. 13. Device for the separation of volatile impurities from a non-volatile matrix by evaporation into a capillary or onto a cooling finger.

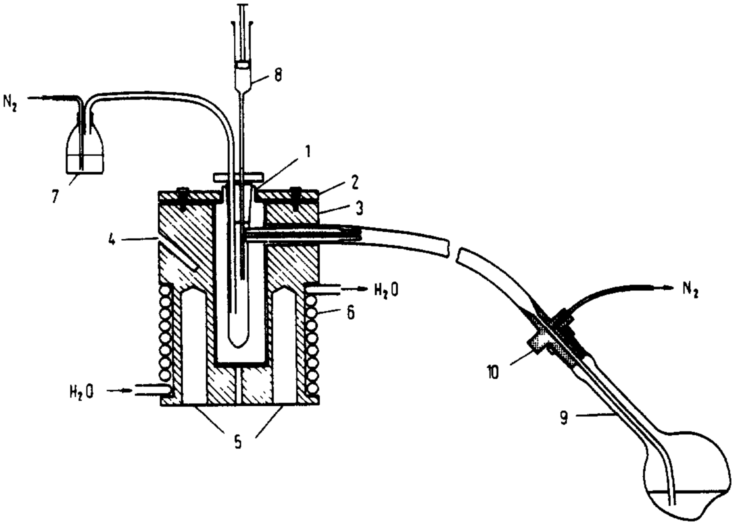

Fig. 14. PTFE apparatus for sample decomposition with hydrofluoric acid and separation of silicon and boron in the ng-range by fluoride distillation.

(1) Decomposition vessel (PTFE); (2) aluminium heating block; (3) aluminium pressure plate screwed to 2; (4) cavity for thermo-element; (5) cavity for heating-elements; (6) cooling water spiral; (7) bubble counter; (8) PTFE syringe for decomposition acid; (9) PTFE connecting tube and stopper; (10) polypropylene standard flask.

excited. So far it is possible to detect less than 1 ng of the isolated boron in this way.[11] The principle may of course be extended to all those elements which can form volatile halogen compounds or hydrides.

But what of those procedures in which all three steps have to be carried out separately —unfortunately by far the commonest state of affairs? To the systematic errors of the individual steps are now added those arising from transfer of the elements from one system to the next. Positive errors are generally attributable to impurities present in the laboratory air, in the reagents and in the material of the containing vessels, and negative ones to adsorption and volatilization.

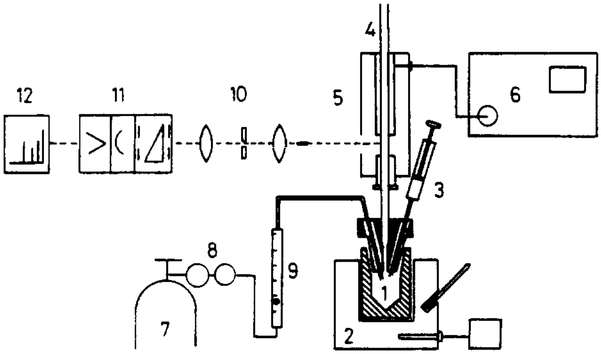

Fig. 15 Microwave excitation for the emission spectrophotometric determination of elements in the ng- and pg-range after their volatilization into an argon plasma.
(1) Decomposition vessel; (2) heating block with temperature controller and thermometer; (3) syringe; (4) quartz tube; (5) resonant cavity; (6) microwave generator (200 W); (7) carrier gas (argon); (8) fine control valve; (9) flowmeter; (10) optical system; (11) monochromator, detector, amplifier; (12) recorder.

One of the most demanding and also important problems is that of meeting the necessary conditions of cleanliness at the workbench and in the laboratory. In addition to the abundant elements already discussed, the air in densely populated areas contains numerous other less common elements from industrial and domestic emission and automobile exhaust fumes, in sometimes quite appreciable concentrations. These and yet more elements may turn up in surprising concentrations in laboratory air, and—depending on the past history of the work done—just about all the elements may be found in laboratory dust.

The development in the last few years of high-capacity ultrafilters in connection with laminar flow techniques has now reached such a level that whole rooms may be maintained nearly free from dust particles and suspended matter.[3,12] The necessary precautions are very demanding, but are an important if not essential step towards improving the limits of detection of conventional "open" multi-step procedures by one or two orders of magnitude, especially in the case of the determination of very low Si, Al, Ca, Cu, Fe and Pb contents. For this purpose "dust-free" laboratories have been built, typical floor plans of which are shown in Fig. 16. The purification and storage of the reagents now needed in increasing variety is a science in itself. The purest commercially available reagents satisfy our criteria in only a very few cases. There are only a handful of reagents such as water, hydrochloric, hydrofluoric and nitric acids which can be prepared in an extremely high state of purity

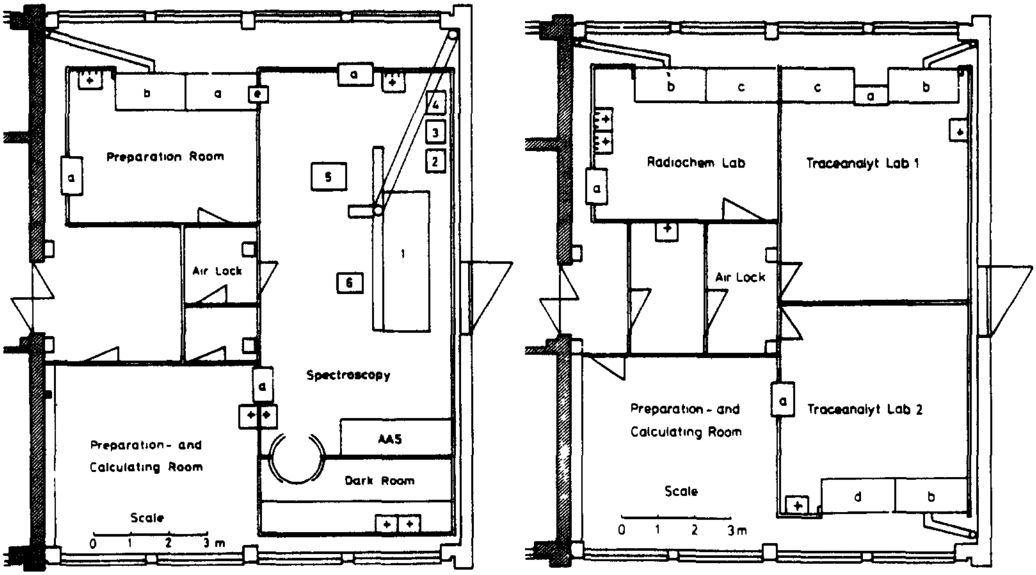

Fig. 16. Floor plans of "dust free" analytical laboratories of the Max-Planck-Institute for Metal Research in Schwäbisch Gmünd, BRD.
(*a*) Air filter system; (*b*) clean bench, polypropylene exhaustive system; (*c*) clean bench, stainless steel; (*d*) clean bench, polypropylene.

with reasonable ease (Table 2). The impurities in these reagents lie at present in the lower ppM range.[12,13] Other reagents which may from time to time be required can only be purified with great expenditure of time and effort for each special case.[3]

Of the three separate steps already discussed for solution techniques, it is the first—the decomposition or dissolution of the sample—which is beset by the most serious systematic

Table 2. Degree of purity attainable for water and the most important decomposition acids (ppM = parts per milliard)[13]

Element	H_2O, *ppM*	HNO_3, *ppM*	HCl, *ppM*	H_2SO_4, *ppM*
Pb	0·008	0·02	0·07	0·6
Tl	0·01	—	0·01	0·1
Ba	0·01	0·01	0·04	0·3
Te	0·004	0·01	0·01	0·1
Sn	0·02	0·01	0·05	0·2
Cd	0·005	0·01	0·02	0·3
Ag	0·002	0·1	0·03	0·3
Sr	0·002	0·01	0·01	0·3
Zn	0·04	0·04	0·2	0·5
Cu	0·01	0·04	0·1	0·2
Ni	0·02	0·05	0·2	0·2
Fe	0·05	0·3	3	7
Cr	0·02	0·05	0·3	0·2
Ca	0·08	0·2	0·06	2
K	0·09	0·2	0·5	4
Mg	0·09	0·1	0·6	2
Na	0·06	1	1	9
Σ	0·5	2·3	6·2	27

Table 3. Survey of the most important separation procedures in ultratrace analysis of the elements

Precipitation:	co-precipitation
	electrolytic deposition
Evaporation:	distillation
	sublimation
	gas-evolution
Distribution between two phases:	
Liquid–liquid	(shaking)
Liquid–solid	(adsorption)
	(ion-exchange)
	(zone melting)
Gas–solid	(GSC)
Gas–liquid	(GLC)

errors.[3] For this reason much attention has been paid to this particular problem, and most inorganic and organic matrices, with the exception of some noble metals, can now be brought into solution without gain or impurities from reagents or the environment even in the pg range, as has been checked by numerous radiochemical experiments.[14,15]

For the second step—the separation of the impurity elements from the matrix—many physical and chemical separation methods can be used, which are very similar to those used by the producers of ultrapure materials (Table 3). It is often just a case of choosing from the variety of existing procedures or suitably modifying one of them so as to arrive at the minimum systematic error. Radioisotopes of the elements in question should, if available, always be used to check the recoveries of such procedures.

Two examples of such multi-step procedures may be quoted, first, the determination of traces of Cu, Pb, Zn, Fe, Ni and Co in ultrapure niobium.[4] The principle can be applied in any system in which the impurities can be electrolytically deposited on a mercury cathode, leaving the matrix element completely in solution. The sample is dissolved in ultrapure hydrofluoric acid in a Teflon bomb under pressure (Fig. 17). Then the solution must be transferred in a dust-free atmosphere into the electrolysis cell, which is also constructed of Teflon (Fig. 18A). Ultrasonic stirring of the solution assists the deposition of the trace elements at controlled potential, under other conditions which have been optimized by using tracer techniques. Ultrapure graphite is used as the anode. Radiochemical yields of nearly 100% have been recorded for as little as a few ng of impurity.

In a second step, the mercury is transferred into an apparatus in which it can be distilled off under vacuum, leaving the non-volatile impurities on the bottom of a small graphite cup (Fig. 18B). The elements are then determined by flameless atomic-absorption spectroscopy, using this graphite cup for excitation. The limit of determination of this method lies around 10^{-8} to 10^{-11} g for the different elements. But of course, if need be, other even more sensitive methods could be used for the final determination, such as activation analysis, chelate GLC, or mass spectrometry.

The second example serves to show in more detail that in some circumstances only some unconventional combinations of steps lead to the desired extremely low limits of detection, and that even with otherwise rather favourable general conditions, there are many sources of systematic error which have to be investigated in the course of working out the complete method.

The problem is the determination of very low beryllium levels in ultrapure copper. The actual method of determination of the separated beryllium is, as is so often the case, the

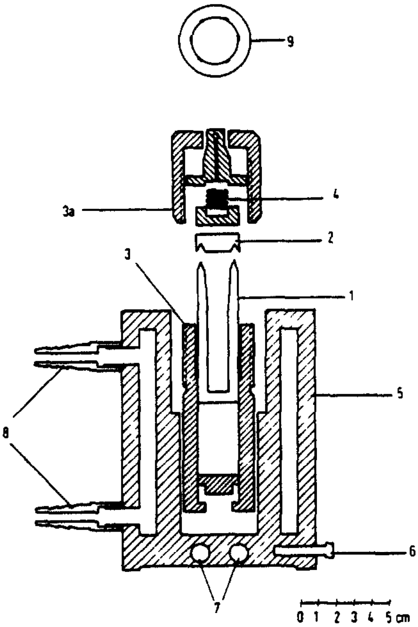

Fig. 17. Device for sample-decomposition in a PTFE vessel under pressure.
(1) PTFE vessel; (2) PTFE cover; (3) cylinder of stainless steel; (4) pressure spring; (5) heating block; (6) thermocontroller; (7) heating element (200 W); (8) PTFE tubes for water cooling; (9) grooves of the blow-off valve.

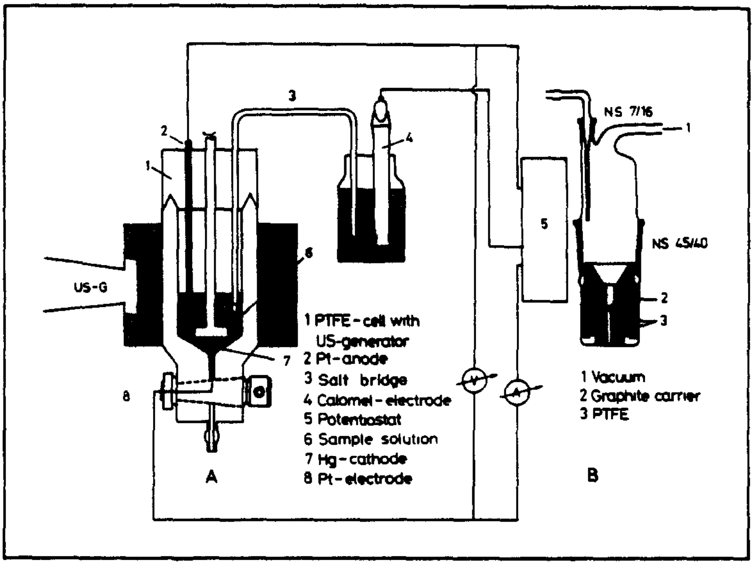

Fig. 18. (A) Electrolytic cell of PTFE for deposition of traces of elements in mercury; (B) device for transferring the elements enriched in mercury onto a target for spectrographic determination.

least of our worries. It can be determined by chelate GLC or by flameless atomic-absorption spectroscopy in absolute amounts as low as 10^{-13} g if necessary.[16] As it is generally present in only very low concentrations in laboratory reagents and air, the question of the blank is also not very serious. Finally, we have in ^{7}Be a very convenient radioisotope (half-life 53 days, γ-emission energy 0·4 MeV) for the study of the method and optimization of the working conditions. The systematic errors obtained after optimization of the different steps of the procedure are listed in Table 4.

Table 4. Systematic errors from sample decomposition to GLC-determination of beryllium

Procedure steps	Losses (%)
Decomposition with excited oxygen	<1
Decomposition with HNO_3 under pressure	$\leqslant 2$
Elimination of the interferences	<1
Formation of the Be–TFA complex	0·5 1
Removal of the excess of TFA	$\leqslant 2$
Stripping of alkali from the benzene	~ 1
Transfer of benzene phase into the vessel	$\leqslant 2$
Concentration step	$\leqslant 2$
Injection onto the column	~ 1

The difficulties begin with the handling of amounts of the order of 10^{-9} to 10^{-11} g of beryllium for addition to the sample: $10^{-6}M$ solutions change their concentration after only a short time in glass or polythene vessels to such an extent that reproducible spiking is not possible. The solution has to be prepared fresh each day and stored in preconditioned quartz vessels. Amounts less than 1 ng have to be delivered from a carefully conditioned ultramicroburette. In the dissolution of the copper sample—as before in a Teflon bomb with an excess of nitric acid—at most 2% of 10^{-10} g of beryllium spike is lost, about half an order of magnitude better than with an open system.

In the subsequent electrolytic separation of the copper—the matrix is deposited this time—on to a mercury cathode, serious losses of beryllium are caused by adsorption onto the glass walls of the cell. These can be reduced to 1% of their value by using a Teflon cell.

Further enrichment of the beryllium can be achieved by forming the beryllium trifluoracetylacetonate complex and extracting this into benzene.

The use of a conventional glass or polypropylene separation funnel with a Teflon tap leads to considerable losses. In addition, the complex forms about 20 times more slowly at these levels than when μg amounts are being handled. Therefore the solution must be shaken vigorously for 20 min. Quite surprising too, is the observation that the beryllium trifluoracetylacetonate complex in the benzene phase can also be adsorbed onto glass, but scarecely at all onto quartz. So only quartz vessels should be used for the centrifugal separation of the phases. The benzene phase is then transferred into a small evaporation vessel, also of quartz, in which the solution can be concentrated to a definite low volume without loss, but only if the temperature does not exceed 50^{c} (Fig. 19). From this small, known volume, μl aliquots are taken and injected onto the GLC column.

It has proved possible, by following the complete procedure exactly, to transfer about 10^{-10} g of beryllium through the entire series of steps to the determination, with more than

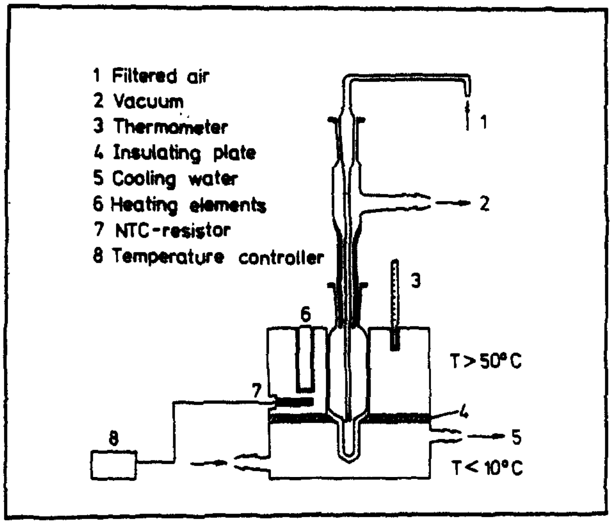

Fig. 19. Device for the reduction of the volume of an organic solvent to a fixed amount in the μl-range after liquid–liquid extraction.

90% efficiency. If glass vessels are used in place of the quartz of Teflon ones, the systematic errors rise by more than an order of magnitude.

This example is typical of many in the field of analysis of ultrapure materials. Even in the ng range in solution chemistry, many new types of interferences begin to disturb our trusted accumulated experience in analytical chemistry, and in the pg range one begins as a matter of principle to mistrust the conventional analytical approach and to disbelieve the results obtained by it.

From all this it can easily be appreciated why it is important in such multi-step procedures, which must be developed for each individual problem, that the impurities to be determined should be separated from the sample and transferred to the detecting system in as few steps as possible, in vessels of as inert a material as possible, with the minimum of surface area, and with the addition of the minimum amount of the purest available reagents: added to that, the detector should have very high sensitivity and be specific for the element concerned, and all of this without either loss or gain of the element in question.

The question of which method of determination offers the best sensitivity and accuracy for a given element is not easily answered: it must be considered in relation to the whole procedure and indeed the whole analytical problem. It is not just that the sensitivities of a given detector change very much from one element to the next, but also that the determination step must be chosen to match the preceding decomposition and separation steps.

Microanalytical techniques offer more often than not the possible solutions to the problems of transferring preconcentrated trace elements in very small volumes or, as in flameless atomic-absorption or emission spectroscopy, onto very small areas for excitation.

The careful working up of such a procedure takes 1–2 man-years. Also there is no question that such combined methods are in most cases too time-consuming for their application in routine analysis. Nevertheless this expense and effort are necessary for the introduction and further improvement of less time-consuming direct instrumental methods with success in extreme trace analysis. To pursue each aspect, chemical and instrumental, independently, can only lead to an unsatisfactory partial solution for the analytical characterization of ultrapure materials. We need them both in a suitably balanced equilibrium.

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Zusammenfassung—Der Trend zu immer reineren Metallen und Halbleiter-Materialien stellt ständig wachsende Anforderungen an deren analytische Charakterisierung. Die Grenzen der direkten Analysenverfahren (optische Spektroskopie, Massenspektroskopie und Aktivierungsanalyse) zeichnen sich bereits ab. In vielen Fällen müssen deshalb die verunreinigenden Elemente vor ihrer Bestimmung angereichert oder von der Matrix abgetrennt werden. Diese zusätzlichen Verfahrensschritte erhöhen die systematischen Fehlermöglichkeiten (Blindwerte, Adsorptionseffekte, Verflüchtigungen usw.). Es werden generelle Wege zu ihrer weitestgehenden Ausschaltung vor allem bei den Aufschluß- und Anreicherungsverfahren aufgezeigt. Bei möglichst enger Kopplung dieser Verfahrensschritte mit geeigneten Detektorsystemen lassen sich zahlreiche Elemente (Be, B, C, N, O, Si, P, S, Se, Te, As, Sb und andere) noch in ng- und pg-Mengen in den verschiedensten Matrices bestimmen. Ausgewählte Beispiele aus dem eigenen Arbeitsbereich sollen veranschaulichen, daß dieses noch junge Gebiet der extremen Spurenanalyse der Metalle besonders erfolgreich bearbeitet werden kann, wenn die Probleme von chemisch und physikalisch orientierten Analytikern gemeinsam angegangen werden.

Résumé—La tendance vers des métaux et des matériaux semi-conducteurs de plus en plus purs provoque des demandes croissantes sur leur caractérisation analytique. Les limites des méthodes directes d'analyse (spectroscopie optique, spectroscopie de masse et analyse par activation) peuvent déjà être observées. Dans de nombreux cas, par conséquent, les éléments de contamination doivent être enrichis avant leur dosage, ou doivent être séparés de la matrice. Ces techniques supplémentaires accroissent les possibilités systématiques d'erreur (valeur du témoin, effets d'adsorption, volatilisation, etc.). On décrit des méthodes générales pour leur élimination poussée, spécialement pendant les techniques de décomposition et d'enrichissement. Quand ces techniques sont étroitement couplées avec des systèmes détecteurs convenables, de nombreux éléments (Be, B, C, N, O, Si, P, S, Se, Te, As, Sb et autres) peuvent encore être dosés très exactement en quantités de l'ordre du ng et du pg dans les matrices les plus diverses.

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DETERMINATION OF BISMUTH BY FORCED-FLOW LIQUID CHROMATOGRAPHY

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Summary—Bismuth(III) is retained on a cation-exchange column from dilute acid and is then separated from most other metal ions by elution with 0·5*M* hydrobromic acid. The elution curve can be measured spectrophotometrically and automatically recorded. This separation method is rapid and is selective for bismuth.

Although bismuth can be separated from most other metal ions by anion-exchange chromatography in dilute chloride media, the chloride complex is so stable that bismuth is somewhat difficult to elute from the column. Recently, a forced-flow chromatographic method involving elution with a mixture of hydrochloric and perchloric acids was suggested.[1] Hydrobromic acid has been used to separate mercury(II), bismuth(III), and cadmium(II) from each other and from other metals, on a cation-exchange column.[2] Bismuth was determined by evaporating the hydrobromic acid and titrating with EDTA.

Several spectrophotometric methods for bismuth make use of the high molar absorptivity of the bromide complex. Nielsch and Boltz[3] added enough hydrobromic acid to make the sample solution 1·75*M* in HBr and measured the absorbance of the bismuth complex at 375 nm. Stolyarova[4] proposed a spectrophotometric method for bismuth in which the sample was dissolved in 1*M* potassium bromide plus hydrochloric acid.

In the present work bismuth is sorbed onto a cation-exchange column and eluted with 0·5*M* hydrobromic acid, by forced-flow chromatography. The absorbance of the bismuth bromide complex is detected spectrophotometrically in a flow-through cell and the elution curve is automatically recorded. The amount of bismuth is determined with the aid of a calibration curve simply by measuring the peak height. This method is selective, very fast, and is sensitive to concentrations of bismuth as low as 12 ppM (parts per milliard).

EXPERIMENTAL

Apparatus

The liquid chromatography used was the same as that described previously with the exception of minor modifications.[5] The "hats" were made from polypropylene instead of Teflon. An on–off valve was placed just before the eluent-selection valve. This was used to turn off the flow of eluent through the column. Previously, this was done by turning the selector valve to midway between two openings, which works but is not recommended.

Column

Preliminary work on this project was done with a Chromatronix column LC-6M-13. This column is 6·3 mm × 13 cm but was shortened for this project to 6 cm. After about a month of use on this project, the non-Teflon plastic parts on the column decomposed. The column was replaced with a Kel-F rod, 1/4 × 6 in. with a 2·6-mm hole drilled the length of the rod. Each end was threaded on the outside for 1/4 in. with 28 threads per inch. This allowed the column to be connected to the tubing preceding and following the column by means of Chromatronix tube end-fittings and couplings. The resin was held in the column by placing a small wad of

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glass-wool in the outlet end of the column. The glass-wool stayed in place because the diameter of the tubing following the column was smaller than the inner diameter of the column. This worked at all pressures used, including pressures as high as 400 psig. The inner dimensions of the column were 2·6 mm × 13 cm.

Reagents

The hydrobromic acid used in this study was Baker Analyzed Reagent, which is contaminated with a little bromine. To decrease the intensity of the solvent blank, the bromine was removed by passing the acid through a column of Amberlite XAD-7 resin. When the concentration of hydrobromic acid is greater than about 4–5*M*, the bromine is retained by the XAD-7. In this case, the hydrobromic acid was passed through the column as the concentrated reagent just as supplied. The bromine is rapidly eluted from the column with water.

Resins

The resins used in this study were Dowex 50W-X8 and Amberlyst 15. The Dowex 50W-X8 was supplied as 200–400 mesh. The Amberlyst 15 resin was ground and sieved, and the fines were decanted. The grain-size used was 250–325 mesh.

Sample preparation

Solutions for interference study. All solutions used for the interference study except those of antimony and tin were prepared by dissolving about 10 mmole of the chloride or nitrate of the desired metal in 100 ml of either 1*M* or 0·1*M* nitric acid. Aliquots of these solutions were mixed with an aliquot of a similarly prepared bismuth solution and diluted to volume.

A 0·001*M* antimony(III) solution was prepared by dissolving 1·2175 g of antimony metal in 20–30 ml of concentrated sulphuric acid. It was evaporated to dryness on a hot-plate set at low heat and with a heat-lamp shining on it from above. This takes about two days. The residue was dissolved in 100 ml of 2*M* hydrochloric acid with stirring, (glass rod). One ml of this solution was mixed with 10 ml of 1*M* hydrochloric acid and then diluted with water to 100 ml. Aliquots of this solution were then mixed with bismuth solution.

A 0·001*M* antimony(V) solution was prepared by dissolving 1·2175 g of antimony metal in 10–20 ml of *aqua regia*, and evaporated to dryness on a hot-plate; the residue was dissolved in 25 ml of 6*M* hydrochloric acid, and then diluted to 100 ml. One ml of this solution was diluted to 100 ml with water.

A tin(IV) solution was prepared by dissolving tin in *aqua regia*, evaporating to dryness, dissolved in 100 ml of 2*M* hydrochloric acid, and diluting with water.

NBS 53b. About 150 mg of the alloy were dissolved in 5 ml of concentrated hydrobromic acid and six drops of concentrated nitric acid from a Pasteur pipette. The solution was then evaporated to dryness under a heat-lamp. The residue was dissolved in 20 ml of 2*M* hydrobromic acid and diluted to 100 ml with water. During this procedure, a precipitate sometimes formed. When a precipitate did form, it was allowed to settle and solution to be injected into the column was obtained by decanting some of the clear solution. Since antimony(III) was present it was necessary to wait 3 min longer before changing eluents from 0·5*M* to 0·05*M* hydrobromic acid.

Standard bismuth solution. Prepared by dissolving 0·1 g of bismuth metal in 10 ml of 6*M* nitric acid and diluting to 200 ml with water. Five ml of this solution were then diluted to 500 ml with 1*M* nitric acid, followed by further dilution by factors of 0·1, 0·15, 0·2 and 0·25 to yield solutions from which a calibration curve could be made. After each injection of an unknown, an injection was made of the standard that had a peak height closest to that of the unknown.

Procedure

The sample containing bismuth was dissolved in nitric, sulphuric, hydrochloric or hydrobromic acid and diluted so that the final acid concentration was 0·25–3·0*M*, 0·15–8·0*M*, 0·1–0·7*M* or 0·07–0·2*M* respectively. The pressure on the chromatograph was adjusted to yield a flow-rate of 3·2 ml/min when the injection valve was set in "inject" position with 0·05*M* hydrobromic flowing through the column. The valve was returned to the "load" position so that the sample could be loaded and injected. At 1·5 min the eluent was changed to 0·5*M* hydrobromic acid. During the first 1·5 min any anionic species present in the sample were eluted. At 2·5 min, all the bismuth was eluted and so the eluent was switched back to 0·05*M* hydrobromic acid. At 3·5 min the column was sufficiently equilibrated with the 0·05*M* acid for the next sample to be injected. The injection port could be returned to "load" position any time after 2·5 min.

The height (or area) of the bismuth peak, measured at 254 nm, is proportional to the amount of bismuth in the sample. The amount of bismuth is found from a calibration curve of peak height *vs.* bismuth in standards. However, if this procedure is used for actual samples some metal ions are left on the column, occupying exchange-sites and shortening the effective column length somewhat. To counteract this effect, which changes the peak height, it was found necessary to alternate injections of samples with a standard having a bismuth concentration between 50% and 200% of that of the sample. The amount of bismuth in the sample is then calculated by proportion from the measured peak heights of the standard and the sample. When the peak height of the standard had increased by 10–20% from that on the calibration curve the metal ions were stripped from the column with 4*M* hydrochloric acid.

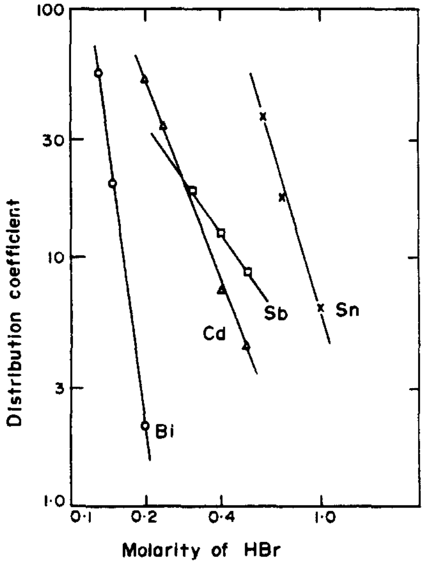

Fig. 1. Distribution coefficients for bismuth(III), cadmium(II), antimony(III), and tin(IV) on Dowex 50W-X8.

RESULTS AND DISCUSSION

Since bismuth(III), cadmium(II), antimony(III) and tin(IV) are eluted under similar conditions from a cation-exchange column, a study was made of the distribution coefficients as a function of hydrobromic acid concentration. The results in Figs. 1 and 2 indicate that better separations would be expected with Dowex 50 resin. However, an actual column study showed that bismuth is eluted much more rapidly from an Amberlyst 15 (A-15) column under conditions where the other metal ions would still be retained. Therefore, A-15 resin was used in all subsequent column experiments with 0·5*M* hydrobromic acid to elute bismuth.

Data have been reported for molar absorptivities of bismuth and other metal bromide complexes,[6,7] but no data have been given for wavelengths shorter than 300 nm. For that reason the ultraviolet spectrum of bismuth in 0·5*M* hydrobromic acid was obtained. The sample was prepared by dissolving bismuth chloride in concentrated hydrobromic acid and evaporating to dryness twice under a heat-lamp. The residue was then dissolved in 0·5*M* hydrobromic acid and the spectrum of the solution obtained (Fig. 3).

The wavelength of maximum absorbance is at 256 nm with a molar absorptivity of $3{\cdot}70 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. The absorptivity at 254 nm, the wavelength at which the detector operates, is essentially the same.

It was found that with 0·05*M* hydrobromic acid in the column during sample injection, bismuth and most other metal ions are retained but mercury(II) is eluted. The bismuth is then eluted with 0·5*M* hydrobromic acid and the peak height is measured. Figure 4 shows the acceptable concentration range of various acids that may be in the sample solution without affecting the bismuth peak height.

Calibration curves relating peak height to concentration are shown in Fig. 5. By the use of three different sample loops it is possible to use the method for a wide range of concentrations. The lower limit obtained with the 969-μl sample loop was 12 ppM, which gave a signal about three times the noise level. Since the signal depends on the absolute amount

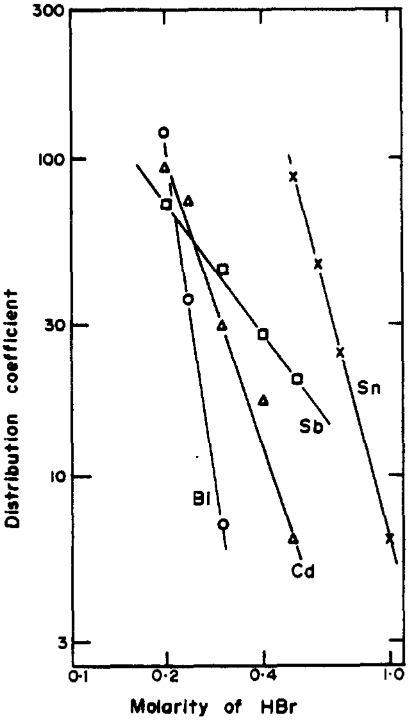

Fig. 2. Distribution coefficients for bismuth(III), cadmium(II), antimony(III), and tin(IV) on Amberlyst 15.

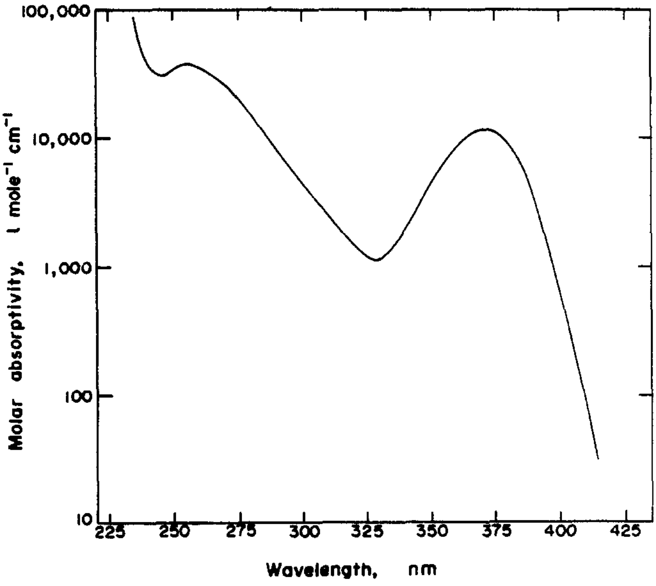

Fig. 3. Ultraviolet spectrum of bismuth(III) in 0·5*M* HBr.

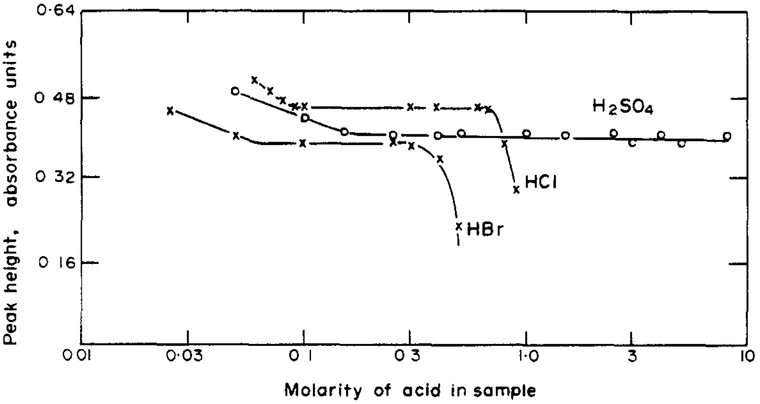

Fig. 4. Peak height of bismuth *vs.* concentration of acid in sample. Amount of bismuth injected each time: HCl, 0·247 μg; HBr, 0·211 μg; H_2SO_4, 0·216 μg; sample loop, 214 μl; flow-rate of 0·05*M* HBr, 3·2 ml/min.

of bismuth in the sample loop rather than the concentration, using larger sample loops should make possible the determination of even lower concentrations.

At low concentrations there is a slight curvature in the calibration curve but otherwise the curve is linear. A calibration curve for the area under the peak as a function of concentration can also be prepared. At concentrations less than 0·1 ppm the blank and the unknown had areas which were large in comparison to their difference. For this reason the use of area for determining concentration of bismuth is not recommended.

For the interference studies, a separate calibration curve relating both area and height to concentration was prepared from 0·3 to 1 ppm bismuth. For both area and height, the curve was linear and passed through the origin on extrapolation.

A typical separation is shown in Fig. 6. In this case the sample was injected while 0·05*M* sulphuric acid was passing through the column. Under these conditions all four metal ions

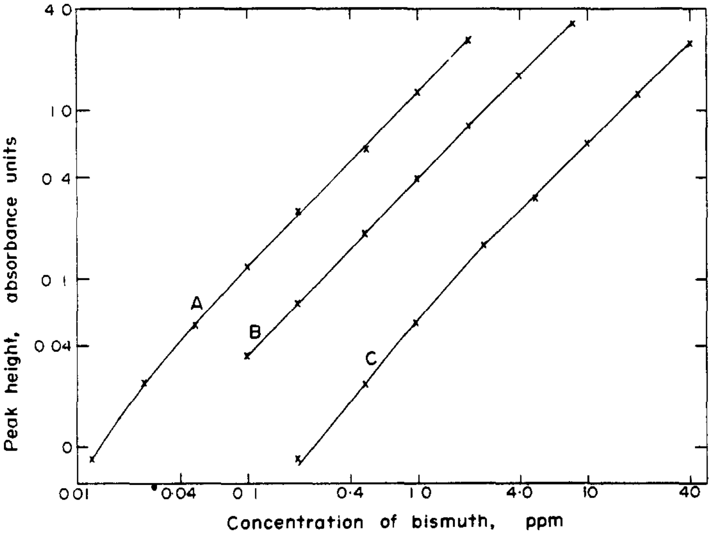

Fig. 5. Calibration curves for bismuth, with different size sample loops. Sample loop sizes: *A*, 969 μl; *B*, 214 μl; *C*, 38·1 μl.

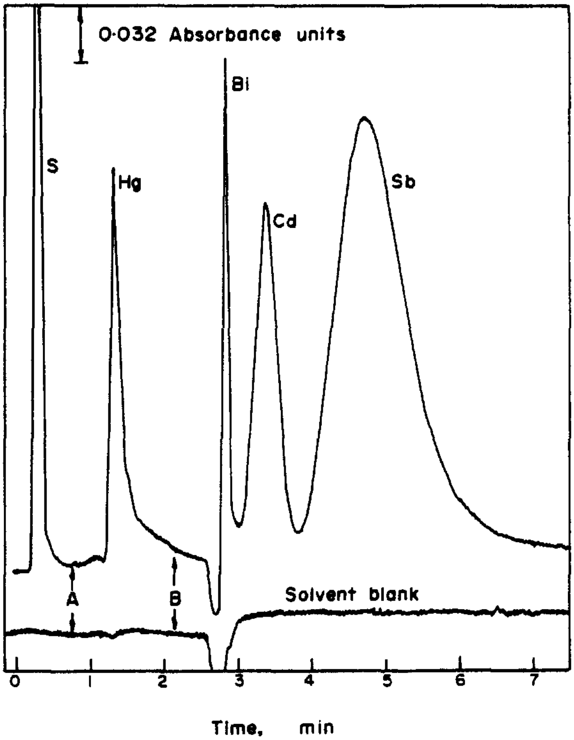

Fig. 6. Separation of 6·5 μg of Hg(II), 0·17 μg of Bi(III), 600 μg of Cd(II), and 23 μg of Sb(III) in 0·5*M* H_2SO_4.
Sample loop: 214 μl; column: 2·6 mm × 13 cm. Resin: Amberlyst 15, 250–325 mesh; flow-rate: 2·7 ml/min. Initial eluent: 0·05*M* H_2SO_4; *A*, change eluent to 0·05*M* HBr; *B*, change eluent to 0·5*M* HBr; *S*, solvent peak.

are retained. Mercury(II) is then eluted with 0·05*M* hydrobromic acid. On switching to 0·5*M* hydrobromic acid, bismuth(III), cadmium(II) and antimony(III) are then eluted in succession.

An interference study was carried out, using as much as a 1000-fold amount of each metal ion, relative to bismuth. The results of this study are given in Table 1. If the error was greater than 3%, the interference study was repeated for that particular interferent at a low level. In practically all cases, the relative error obtained by using peak height was less than the relative error obtained by using peak area. The relative standard deviation of repeated trials, each one obtained by comparison with the standard that immediately followed it, was 1·6%.

The only element that seriously interfered in the determination of bismuth was tin. When a 1000-fold amount was present, the value for bismuth was only 22% of what it should have been. In order to decrease the relative error to less than 3%, the amount of tin had to be less than 13-fold if area was used to determine concentration and less than 5-fold if height was used to determine concentration. It is possible that the tin(IV) on the column may hydrolyse and act as an inorganic ion-exchanger that retains bismuth.

The amount of antimony(III) that can be tolerated is limited. If 2·4 μmole of antimony(III) are injected onto the column previously described, it appears the column is overloaded in that the front edge of the elution peak is pushed forward enough to overlap with

Table 1. Determination of bismuth in the presence of other metals

Interferent (X)	Conc. of Bi^{3+}, μM	Molar ratio, X/Bi^{3+}	Solvent	Rel. error, % (area)	Rel. error, % (height)
Mo(VI)	4·78	100	0·1*M* HNO$_3$	+0·8	+2·1
Mo(VI)	4·78	1000	0·095*M* HNO$_3$	+9·2	+5·4
Mn(II)	4·78	1000	0·14*M* HNO$_3$	−2·3	−1·5
Zn(II)	4·78	1000	0·1*M* HNO$_3$	+0·3	−1·3
Cr(III)	4·78	100	0·1*M* HNO$_3$	+1·4	+1·6
Cr(III)	4·78	1000	0·1*M* HNO$_3$	−5·3	−4·8
Mg(II)	4·78	1000	0·1*M* HNO$_3$	+1·7	+0·6
Hg(II)	4·78	10	0·1*M* HNO$_3$	+8·3	+1·5
Hg(II)	4·78	100	0·1*M* HNO$_3$	+25·5	+9·9
Hg(II)	4·78	1000	0·14*M* HNO$_3$	+29·7	+8·7
Pb(II)	4·78	100	0·1*M* HNO$_3$	+1·6	+0·8
Pb(II)	4·78	1000	0·1*M* HNO$_3$	+5·2	+3·6
Sb(IV)	2·76	1000	0·17*M* HCl	+2·3	+1·4
Sb(III)	1·10	1000	0·24*M* HCl	−15·5	−3·1
Sb(III)	2·76	400	0·24*M* HCl	−0·6	−0·5
Tartrate	4·78	100	0·1*M* HNO$_3$	+2·2	+2·2
Tartrate	3·82	1000	0·1*M* HNO$_3$	−5·2	−3·7
K(I)	3·82	1000	0·1*M* HNO$_3$	−2·0	−2·7
Cu(II)	3·82	1000	0·1*M* HNO$_3$	−1·9	−1·1
Co(II)	3·82	1000	0·1*M* HNO$_3$	+1·5	+0·0
Cd(II)	3·82	1000	0·1*M* HNO$_3$	−1·6	−0·7
Fe(II)	3·82	1000	0·13*M* HNO$_3$	−1·9	−0·7
Fe(III)	4·78	100	0·10*M* HNO$_3$	+0·6	−0·6
Fe(III)	4·78	1000	0·14*M* HNO$_3$	−5·0	−7·5
Ba(II)	3·82	100	0·13*M* HNO$_3$	−4·1	−2·7
Ba(II)	4·78	1000	0·26*M* HNO$_3$	−15·6	−23·4
Al(III)	4·78	1000	0·12*M* HNO$_3$	−0·9	−0·8
Ca(II)	4·78	1000	0·1*M* HNO$_3$	+1·0	−0·6
Sn(IV)	2·76	2	0·13*M* HCl	−3·0	+1·1
Sn(IV)	2·76	10	0·13*M* HCl	−2·1	−5·8
Sn(IV)	2·76	25	0·13*M* HCl	−5·6	−8·0

Table 2. National Bureau of Standard certificate of analysis for sample NBS 53b

	%		%
lead	84·35	arsenic	0·042
antimony	10·28	nickel	0·006
tin	5·06	silver	0·003
copper	0·209	iron	0·002
bismuth	0·075	aluminium	0·0007

the bismuth peak. The rear edge of the antimony elution peak is not affected. If the amount of antimony(III) injected is reduced to 0·5 μmole the elution peak is normal and no difficulty is encountered.

An NBS standard sample (No. 53b, lead–base bearing metal, with certificate of analysis as shown in Table 2) was analysed as described. The amount of bismuth was found to be 0·0752% with a relative standard deviation of 1·4% for four trials. The certificate value is 0·075% bismuth.

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Zusammenfassung—Wismut(III) wird aus verdünnter Säure auf einer Kationenaustauschersäule zurückgehalten und dann von den meisten anderen Metallionen durch Elution mit 0,5*M* Bromwasserstoffsäure getrennt. Die Elutionskurve kann spektrophotometrisch gemessen und automatisch registriert werden. Dieses Abtrennverfahren geht rasch und ist für Wismut selektiv

Résumé—Le bismuth (III) est retenu sur une colonne échangeuse de cations à partir d'acide dilué, puis il est alors séparé de la plupart des autres ions métalliques par élution à l'acide bromhydrique 0,5*M*. La courbe d'élution peut être mesurée spectrophotométriquement ou enregistrée automatiquement. Cette méthode de séparation est rapide et est sélective pour le bismuth.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI)

(*Received* 20 *March* 1973. *Accepted* 26 *July* 1973)

Dithiol,[1] 5-phenylpyrazoline-1-dithiocarbonate,[2] 2,3-dimercaptopropionic acid,[3] 8-mercaptoquinoline,[4] thioglycollic acid[5] and disodium *cis*-1,2-dicyanoethylene[6] are some of the thio-compounds which have been used for the spectrophotometric determination of molybdenum. Molybdenum(VI) with potassium ethyl xanthate in 1·5–2*M* hydrochloric acid medium forms a complex which may be extracted into chloroform, carbon tetrachloride and petroleum ether–toluene.[7] The advantages of this reaction are its sensitivity and freedom from interference by tungsten(VI), titanium(IV), chromium(III) and vanadium(V). Molybdenum(VI) gives a red colour with ammonium thiocyanate in 5–8*M* hydrochloric acid medium. The reduction of molybdenum(VI) and determination with thiocyanate is widely used but the reduction is not quantitative.[1]

Molybdenum(VI) in 4–7*M* hydrochloric acid medium gives a red colour with potassium ethyl xanthate and ammonium thiocyanate, extractable into isoamyl alcohol or acetophenone. This may be recommended as a highly sensitive and selective mixed ligand method for the spectrophotometric estimation of Mo(VI).

EXPERIMENTAL

Reagents

Potassium ethyl xanthate. Prepared by shaking excess of carbon disulphide with a saturated solution of potassium hydroxide in absolute ethanol. It was recrystallized from a mixture of chloroform and ether. A 1% aqueous solution of the reagent was used.

Standard molybdenum solution. Analytically pure ammonium molybdate hydrate was dissolved in water containing a few drops of ammonia. The solution was standardized gravimetrically with 8-hydroxyquinoline.[8]

Ammonium thiocyanate solution, 5%.

Procedure

Place the molybdenum(VI) solution in a separating funnel and add 2–3 ml of 10*M* hydrochloric acid, 2 ml of potassium ethyl xanthate solution and 2 ml of ammonium thiocyanate solution, followed by 3 ml of acetophenone. Shake vigorously for 2 min. Transfer the deep orange–red acetophenone layer into a small beaker containing 0·5 g of anhydrous sodium sulphate. Extract twice more with 2-ml portions of acetophenone and combine the extracts (even a single extraction with about 5ml of acetophenone is enough to transfer molybdenum completely into the solvent layer). Transfer the combined extract to a 10ml volumetric flask and dilute to the mark with the solvent. Measure the absorbance in 1cm cells at 380 or 470 nm against a reagent blank prepared in a similar way.

Procedure for steel analysis

Dissolve an appropriate weight of the sample (1–2 g for 0·5% Mo, 0·1–0·2 g for 5% Mo) in 50 ml of sulphuric acid (1 + 6) in a 150ml Erlenmeyer flask and oxidize with conc. nitric acid. Boil the solution to expel oxides of nitrogen and filter if not clear. Cool to 25°, dilute to 100 ml and treat with sufficient ferrous ammonium sulphate to reduce chromium(VI) and vanadium(V). Take an aliquot of this solution and add 1 ml of saturated ascorbic acid. Then complete the determination by the procedure above.

RESULTS AND DISCUSSION

Spectral characteristics

The complexes of molybdenum(VI) with ethyl xanthate and with thiocyanate in 8–10*M* hydrochloric acid and with a mixture of thiocyanate and ethyl xanthate have absorption maxima at 310 and 505 (two), 460 and 460 nm respectively (Figs. 1 and 2). The acetophenone extract of the mixed complex has maxima at 380 and 470 nm (Fig. 3).

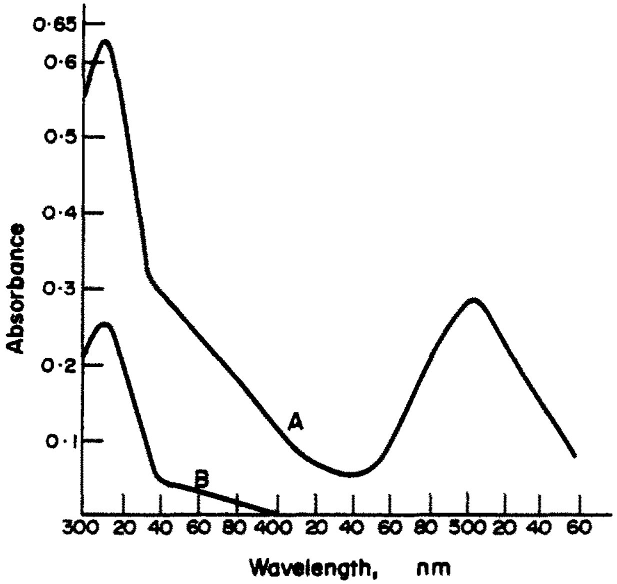

Fig. 1. Absorption spectra of (A) molybdenum xanthate complex, (B) reagent blank.

Reaction conditions

In the mixed ligand method the final solution (*ca.* 10 ml) should be 4–7*M* with respect to hydrochloric acid and contain 1·5–3·5 ml of ammonium thiocyanate solution and 1·75–3 ml of ethyl xanthate solution. The acetophenone extract of the mixed ligand complex is more intensely coloured and stable. The colour is stable for at least 40 hr. A change in temperature from 15° to 35° has no influence on the absorbance. Maximum colour development takes place instantaneously at room temperature.

The system obeys Beer's law over the range 1·2–13·8 ppm of Mo(VI), and the optimum concentration range as evaluated from a Ringbom plot is 2·4–10·2 ppm. The Sandell sensitivity indices are 0·0016 and 0·0068 ppm Mo/cm^2 at 380 and 470 nm respectively.

Ten determinations of 2·7 ppm Mo(VI) gave a mean absorbance value of 0·424 and an S.D. of $2{\cdot}8 \times 10^{-3}$. Six independent determinations of the reagent blank gave a mean absorbance of 0·024 and an S.D. of 2×10^{-3}.

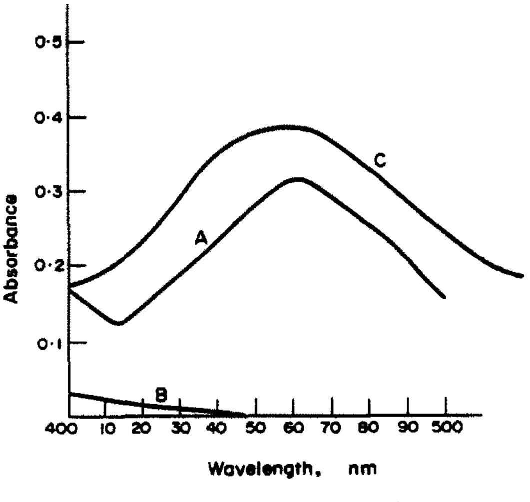

Fig. 2. Absorption spectra of (A) molybdenum thiocyanate complex, (B) reagent blank, (C) molybdenum thiocyanate xanthate mixed complex (methanol–water medium).

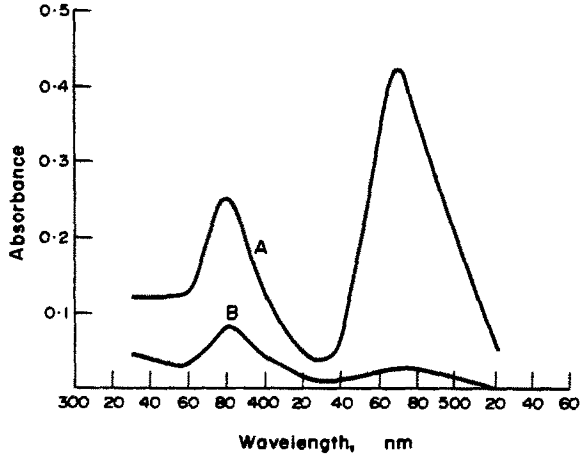

Fig. 3. Absorption spectra (acetophenone medium) of (*A*) molybdenum–thiocyanate–xanthate complex, (*B*) reagent blank.

Composition of the complex

Ammonium molybdate in 6–8*M* hydrochloric acid reacts with thiocyanate to give $MoO_2(SCN)_2$, which slowly decomposes, yielding yellow needle-shaped crystals of MoO_2Cl_2 (analysis for Cl, 35·2%; calc, 35·62%).

Molybdenum(VI) in hydrochloric acid with ethyl xanthate forms a pink complex $MoO_3(C_2H_5OCS_2H)_2$. In 4–7*M* hydrochloric acid, with thiocyanate and ethyl xanthate, molybdenum(VI) gives a red complex which may be formulated as $MoO_{(3-x)}\cdot(SCN)_{2x}(C_2H_5OCS_2H)_2$, where x is 1 or 2.

Interferences

The following cations do not interfere even in 1000-fold amounts: Na, K, Ba, Ca, Mg, Al, Ce(IV), La, Sn(II), Pb, Ti, Zr, As(III), Sb(III), Cr(III), Mn(II) and Fe(II). In nearly neutral solution, copper(II), cobalt(II) and nickel give colour reactions with potassium ethyl xanthate. The stability of each of these metal–xanthate complexes depends upon pH. In 4–7*M* hydrochloric acid, they are unstable and give no colour (15-fold amounts each). In 4–7*M* hydrochloric acid vanadium(V), tungsten(VI) and rhenium(VII) give colour reactions with ammonium thiocyanate and potassium ethyl xanthate. Ascorbic acid masks the interference of a 10-fold amount of vanadium and an 8-fold amount of tungsten, relative to molybdenum. Molybdenum can be separated from rhenium and determined as follows.

To the mixture of molybdenum and rhenium, add 0·2 ml of 10*M* hydrochloric acid and 0·5–1·0 ml of 1% aqueous potassium ethyl xanthate solution. Shake well, extract with acetophenone and separate the organic layer. To this organic layer, add 2·5–3 ml of hydrochloric acid, 1–2 ml of 1% aqueous xanthate reagent and 2–3 ml of 5% aqueous solution of ammonium thiocyanate. Shake for 5 min with acetophenone, separate the organic layer and measure its absorbance at 380 or 470 nm.

Thousandfold amounts of oxalate, borate, carbonate, citrate, nitrate, nitrite, bicarbonate, fluoride, phosphate, sulphate, chloride, bromide and iodide do not interfere.

Analysis of steels

The results of the analysis of two standard steels (mean of four determination) were 0·42–0·44% for Bureau of Analysed Samples Standard 60 B (certificate value 0·43%) and 4·9–5·0% for 64 B (4·95%).

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Summary—Molybdenum(VI) gives a red colour with ammonium thiocyanate in 5–8*M* hydrochloric acid medium, the Sandell sensitivity index being 0·018 ppm Mo(VI)/cm^2. Molybdenum(VI) in 4–7*M* hydrochloric acid medium forms a red complex with ethyl xanthate and ammonium thiocyanate and this can be extracted into acetophenone. Beer's law is obeyed over the range of 1·2–13·8 ppm, and the Sandell indices at 370 and 470 nm are 0·0016 and 0·0068 ppm/cm^2 respectively. The colour is stable for 40 hr. Most cations do not interfere.

Zusammenfassung—Molybdän(VI) gibt mit Ammoniumthiocyanat in 5–8*M* Salzsäure eine rote Farbe; der Empfindlichkeitsindex nach Sandell beträgt 0,018 ppm Mo/cm^2. In 4–7*M* Salzsäure bildet Molybdän(VI) mit Äthylxanthat und Ammoniumthiocyanat einen roten Komplex: dieser kann in Acetophenon extrahiert werden. Das Beersche Gesetz gilt im Bereich 1,2–13,8 ppm, die Sandell-Indices betragen bei 370 und 470 nm 0,0016 bzw. 0,0068 ppm/cm^2. Die Farbe ist 40 h lang stabil. Die meisten Kationen stören nicht.

Résumé—Le molybdène (VI) donne une coloration rouge avec le thiocyanate d'ammonium en milieu acide chlorhydrique 5–8*M*, l'index de sensibilité Sandell étant, 0,018 ppm Mo(VI)/cm^2. Le molybdène (VI) en milieu acide chlorhydrique 4–7*M* forme un complexe rouge avec le xanthate d'éthyle et le thiocyanate d'ammonium et celui-ci peut être extrait en acétophénone. La loi de Beer est suivie dans le domaine 1,2–13,8 ppm, et les indices de Sandell à 370 et 470 nm sont 0,0016 et 0,0068 ppm/cm^2 respectivement. La coloration est stable pendant 40 h. La plupart des cations ne gênent pas.

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DETERMINATION OF IODIDE WITH CHLORAMINE-T

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It is well known that addition of excess of potassium iodide to chloramine-T (CAT) solution in acid medium liberates iodine:

$$\{CH_3.C_6H_4SO_2NCl\}^-Na^+ + 2H^+ + 2I^- \rightarrow CH_3.C_6H_4SO_2NH_2 + I_2 + Na^+ + Cl^-.$$

This reaction is widely used for standardization of CAT solutions.[1,2] On addition of excess of 0·1 *M* CAT to approx. 0·01*M* iodide, we observed the incipient formation of a yellow colour due to iodine but then the solution soon became colourless, indicating further oxidation to iodate:

$$3\{CH_3.C_6H_4SO_2NCl\}^-Na^+ + I^- + 3H_2O \rightarrow 3CH_3.C_6H_4SO_2NH_2 + IO_3^- + 3Na^+ + 3Cl^-.$$

The yellow colour due to the intermediate formation of iodine disappeared fastest at pH 2·65–5. In presence of 0·2 *M* sulphuric acid, the disappearance of the iodine colour was slow at room temperature but was complete within 5 min at 50–60°. In presence of >0·3 *M* hydrochloric acid, oxidation of the iodide to iodate was found to be incomplete. Perhaps simultaneous increase in $[H^+]$ and $[Cl^-]$ retards the further oxidation. This inhibiting action of chloride was not observed when the hydrogen ion concentration was less than 0·2 *M*. The iodate formed could be determined if the excess of CAT was removed. Dimethyl sulphoxide (DMSO) was chosen to destroy CAT because of its known reaction[3] and because it has no reducing action on iodate in dilute aqueous solutions. The destruction of CAT by DMSO is complete within 5 min in presence of >1·0 *M* hydrochloric acid at room temperature and takes more time at pH 2·65–5. Heating the CAT–DMSO mixture to 50–60°, however, ensures complete destruction of CAT in all cases. The solution is then cooled and the iodate determined iodometrically as described in the procedure.

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EXPERIMENTAL

Reagents

Chloramine-T of initial purity 98·5% was thrice recrystallized from conductivity water before use. Dimethyl sulphoxide and analytical-grade potassium iodide were used as obtained. An approximately 0·01 *M* iodide solution was prepared, and standardized by the Volhard procedure.

Procedure

A 20ml portion of the 0·01*M* potassium iodide was pipetted into a glass-stoppered bottle. The pH was adjusted to 2–4 with sodium acetate–acetic acid buffer and 20 ml of 0·1 *M* CAT were added. To ensure complete oxidation, this solution was kept at 50–60° for about 5 min, then about 40 ml of 0·1 *M* DMSO and 20 ml of 2 *M* hydrochloric acid were added. The solution was kept at 50–60° for 5 min and then cooled to room temperature, 20 ml of 10% potassium iodide solution were added and the liberated iodine was titrated with 0·1 *N* sodium thiosulphate. From the second equation given above, one mole of iodide yields one mole of iodate and since the latter corresponds to six equivalents of iodine under the conditions used, the equivalent weight of the iodide is one-sixth of the atomic weight. Each ml of 0·1*N* thiosulphate therefore corresponds to 2·12 mg (i.e., 0·0167 mmole) of iodide. Six determinations were done in duplicate for different amounts of iodide and the results obtained (Table 1) were accurate to ±0·2%, based on the standard value obtained by Volhard's method.

Interferences

It was observed that when excess of CAT was added to 0·01 *M* bromide solutions at pH 2–4, a yellow colour due to bromine occurred initially, but faded in a few minutes, indicating oxidation to bromate. However, bromate was found to be reduced completely to bromide during the heating to 50–60° with DMSO and acid. Hence any bromate formed is eliminated at the same stage as excess of CAT and bromide does not interfere.

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Table 1. Experimental results of iodide determination

Iodide taken (based on Volhard's method), *mmole*	Iodide found, *mmole*
0·2119	0·2115
0·2226	0·2224
0·2332	0·2336
0·2438	0·2437
0·2544	0·2549
0·2650	0·2655

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Summary—A method is described for the estimation of iodide, based on its oxidation to iodate by the addition of excess of chloramine-T, destruction of the excess of chloramine-T with dimethyl sulphoxide and determination of the iodate iodometrically. In addition, the dimethyl sulphoxide eliminates any interference from bromide or bromate.

Zusammenfassung—Eine Methode zur Bestimmung von Jodid wird beschrieben; sie beruht auf seiner Oxidation zu Jodat durch Zugabe eines Überschusses von Chloramin-T, der Zerstörung des Überschusses von Chloramin-T mit Dimethylsulfoxid und jodometrischer Bestimmung des Jodats. Zusätzlich beseitigt das Dimethylsulfoxid jegliche Störung durch Bromid oder Bromat.

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Résumé—On décrit une méthode pour le dosage de l'iodure, basée sur son oxydation en iodate par l'addition d'un excès de chloramine-T, la destruction de l'excès de chloramine-T par le diméthyl sulfoxyde et le dosage iodométrique de l'iodate. De plus, le diméthyl sulfoxyde élimine toute interférence du bromure ou du bromate.

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TRACE ANALYSIS BY MICROWAVE EXCITATION OF SEALED SAMPLES—II
DETERMINATION OF 4–100 pg OF Cd, In AND Tl IN 0·5 ml OF AQUEOUS SOLUTIONS

(*Received* 21 *June* 1973. *Accepted* 8 *October* 1973)

In our first publication[1] we described the possibility of trace analysis by optical emission spectrometry based on microwave excitation of sealed samples. Because of the increasing interest in metal determinations at the picogram level, we tried to adapt the technique to that type of problem. When scaling down the amount of thallium to this level we found that the signal/background ratio decreased more than was expected from the results obtained for a few nanograms. The procedure was therefore changed in two respects. First, we used bismuth iodide as a matrix instead of zinc chloride because the background level is much lower (considerations similar to those given earlier[1] may be used to show that BiI_3 is suitable from the thermodynamic point of view). Even so, amounts below about 20 pg of Tl could not be detected, although detection should have been possible according to the signal obtained for larger amounts. This was thought to be caused by oxidation processes, and the difficulties were indeed solved by using hydrogen as a filler-gas. No further experiments were performed to prove the presence of oxidation processes. In our first publication we also described the presence of interfering band spectra. We have now found other band spectra, which were caused by contamination of the quartz used. We therefore have tested five types of quartz for their suitability.

EXPERIMENTAL

Apparatus

The vacuum apparatus is the same as described earlier.[1] The length of the electrodeless discharge lamps (EDL's) used was 22 mm, the outer diameter 9 mm and wall thickness 0·4 mm. A Hilger and Watts "Large Quartz Spectrograph" with photographic detection (slit 20 μm) was used for investigation of the band spectra. For quantitative measurements we used the monochromator (reciprocal dispersion 3·3 nm/mm, slit 25 μm) and the detector of the Techtron AA4 atomic-absorption spectrophotometer with mechanical modulation. To compare intensities over a wide range the relative gain of the amplifier was measured for each of the 20 different steps. The intensities are expressed in scale-deflections at the highest amplification. All values given were obtained by subtracting the background intensities, measured at a wavelength 0·4 nm longer than that of the line observed. The microwave equipment used was an EMS Microtron 200 with reflected-power meter (2450 MHz) and an EMS 216L ($\frac{1}{4}$-wave) cavity. Power values given in this paper are found by subtracting reflected power (generally about 10 W) from incident power.

Reagents

Germanium, 99·999% pure, (Koch-Light, England). BiI_3, prepared from "Specpure" Bi_2O_3, (Johnson and Matthey, England), dissolved in 30% hydrochloric acid and then treated with hydriodic acid (both acids "Suprapur", Merck, Germany), and diluted to give a final concentration of 0·02*M* for each acid. The metal iodides added were all of reagent grade. The hydrogen used was laboratory grade.

Preparation

First the EDL is degassed for 1 min under vacuum (about 0·05 mmHg) by heating with a propane–oxygen burner. Then 15–30 μg of solid Ge are added as a "getter". Next, about 100 μl of an aqueous solution containing both 2·5 μg of BiI_3 as a "matrix" and the metal iodides to be determined, are introduced. The solution is frozen to dryness. Finally hydrogen is added up to a pressure of 5 mmHg, the EDL is sealed off and is then ready for use. The complete preparation of six EDL's takes about 1 hr.

Résumé—On décrit une méthode pour le dosage de l'iodure, basée sur son oxydation en iodate par l'addition d'un excès de chloramine-T, la destruction de l'excès de chloramine-T par le diméthyl sulfoxyde et le dosage iodométrique de l'iodate. De plus, le diméthyl sulfoxyde élimine toute interférence du bromure ou du bromate.

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RESULTS

Influence of hydrogen pressure and power

The hydrogen pressure and the power supplied may be expected to influence the emission of an EDL. In some experiments to test these effects, the signal of 20 pg of thallium in the matrix described was measured as a function of time. In Fig 1*a* the influence of the hydrogen pressure at constant power is presented. The optimum hydrogen pressure is approximately 5 mmHg. In Fig. 1*b* the influence of the power at 5 mmHg hydrogen pressure is presented. The optimum power is about 50 W.

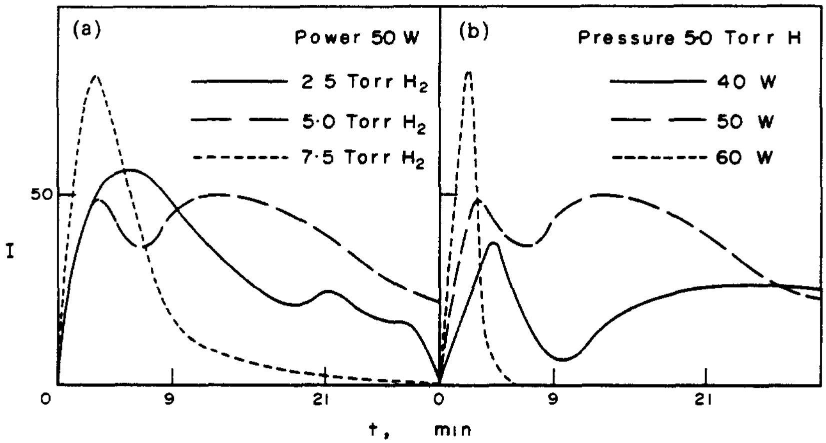

Fig. 1. (*a*) Effect of hydrogen pressure at constant power, and (*b*) effect of power at constant hydrogen pressure.

Because satisfactory results were obtained at a power of 50W and a hydrogen pressure of 5 mmHg, no other combinations were tested. It should be noted, however, that the optimum power is slightly dependent upon the dimensions of the EDL, but variations of about 20% in the volume of the EDL's caused no difficulties. No attempt is made to explain the influence of power and hydrogen pressure on the shape of the curves.

Quantitative measurements

The optical line-intensities for the metals introduced were measured at a fixed time after switch-on (In 5 min, Tl 6, Cd 7). In contrast to the first publication no internal standard was used, because this gave no increase in precision. The power was 50 W, the hydrogen pressure 5 mmHg, the volume introduced was nominally 100 µl. The log–log calibration curves for In, Tl and Cd are linear with a slope very close to the theoretical (for Cd a blank of 8 pg was found; in the calibration curve we corrected for this value).

No calibration curves could be made for Pb and Zn because of the high blank values (about 100 pg). The maximum volume that can be introduced is 500 µl. This gives the following detection limits (Table 1).

Table 1. Detection limits

	pg	*pg/ml*	Wavelength, *nm*
In	0·5	1	451·1
Tl	0·5	1	377·6
Cd	0·1	0·2	228·8

The detection limit given is a theoretical one. It was calculated, by extrapolation, as the concentration of metal required to give a signal twice as large as the background noise at the 4pg level. The precision of the method is better than 15% in most cases.

Influence of type of quartz

It was found that some types of quartz gave much better results than others. This effect appeared with both helium and hydrogen as filler-gas. A close correlation was found between the intensities of the band spectra emitted by a helium-filled EDL and the suitability of the quartz. (It should be noted that helium is more suitable than hydrogen for testing quartz, because with hydrogen as a filler-gas OH-bands and of course H-lines are found with all types of quartz used.) The spectra of helium-filled EDL's during the first 10 min after switch-on were compared. The spectra were obtained with the Hilger and Watts spectrograph. Water (or OH-groups) in quartz can be detected by measuring the infrared transmission at 2·72 μm (OH-band). From five types of quartz we compared the relative intensities of the bandheads of CO (297·7 nm), OH (306·4 nm), CN (388·3 nm), CH (431·2 nm), C_2 (469·8 nm), the hydrogen-line (486·1 nm) and the infrared transmission at 2·72 μm. (Table 2).

Table 2. Comparison of some types of quartz

Type	He	CO	OH	CN	CH	C_2	H	% i.r. transm.
Heraeus "Heralux"	—	M	S	M	S	S	S	35
Heraeus "Infralux"	S	—	M	—	M	—	M	100
Heraeus "OHF"	S	—	W	—	W	—	W	90
Quartz and Silice "Pursil 453"	S	W	M	M	M	S	M	90
Thermal Syndicate "Vitreosil"	—	S	S	M	S	S	S	30

— = Absent; W = weak; M = medium; S = strong.

It should be noted that two types of quartz, "Heralux" and "Vitreosil", do not give helium emission although helium is used as a filler-gas. Both types, in particular "Heralux", are not suitable for our purposes. Of the other three types, in further experiments we only used "Pursil 453", but the other two are also suitable. Possibly there is a connection between these differing properties of quartz and the great variation of procedures for degassing EDL's used in atomic-fluorescence spectroscopy, as noted in a review article[2] on preparation and use of EDL's in that technique.

Probably lower limits of detection or determination than given above may be obtained. Some of the limiting factors in our case are the sensitivity of the detection unit and the resolving power of the monochromator. Another difficulty is the lack of availability of reagents of sufficient purity. Another point is the possible interference of foreign compounds. Chemical conversions may therefore be required in many cases.

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Summary—Trace analysis by optical emission spectrometry by microwave excitation of sealed samples has been improved by use of H_2 as a filler-gas and of BiI_3 as a matrix. It was found that the selection of suitable quartz for the manufacture of the discharge lamps is important. Limits of determination of 4 pg in 0·5 ml may be obtained for In, Tl and Cd.

Zusammenfassung—Die Spurenanalyse durch optische Emissionsspektrometrie mit Mikrowellenanregung abgeschmolzener Proben wurde verbessert, indem H_2 als Füllgas und BiJ_3 als Matrix verwendet wurden. Die Auswahl geeigneten Quarzes zur Herstellung der elektrodenlosen Entladungsröhren ist jedoch von entscheidender Bedeutung. Für In, Tl und Cd kann man Nachweisgrenzen von 4 pg in 0,5 ml erreichen.

Résumé—On a amélioré l'analyse de traces par spectrométrie d'émission optique basée sur l'excitation par micro-ondes d'échantillons scellés par l'emploi de H_2 comme gaz de remplissage et de BiI_3 comme matrice, mais la sélection du quartz convenable pour la fabrication des tubes à décharge sans électrode est d'une importance fondamentale. Des limites de dosage de 4 pg dans 0,5 ml peuvent être obtenues pour In, Tl et Cd.

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ANNOTATION

THE EFFECT OF ORTHOPHOSPHATE ON THE GRAVIMETRIC DETERMINATION OF PYROPHOSPHATE

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Radionova and Hodakov[1] described a method for the gravimetric determination of pyrophosphate in the presence of orthophosphate and tripolyphosphate. According to them, precipitation must be done in the pH range 3·4–3·6, with zinc acetate. The method has found wide application.

A shortcoming of this method, however, is that in the presence of orthophosphate zinc might be expected[2] to react by:

$$3Zn^{2+} + 2H_2PO_4^- \rightleftharpoons Zn_3(PO_4)_2 + 4H^+.$$

In preliminary experiments with solutions containing pure orthophosphate it was found that 10 mg of KH_2PO_4 gave an immediate precipitate, 5 mg a precipitate after some hours, and 3 mg gave no precipitate at all. These results agree well with the equilibrium solubility of $Zn_3(PO_4)_2$ as a function of pH (Fig. 1). At pH 3·6 the solubility is about $10^{-2}M$ and it is clear why in the experiment with 3 mg of KH_2PO_4 there is no precipitation. In this case the concentration of the orthophosphate is about $3 \times 10^{-4}M$.

The aim of the present work is to investigate the effect of orthophosphate on the gravimetric determination of pyrophosphate.

EXPERIMENTAL

Reagents

Solutions of KH_2PO_4, $Na_4P_2O_7$ and $Zn(CH_3COO)_2$ (all *p.a.*) were prepared by dissolving appropriate amounts in distilled water.

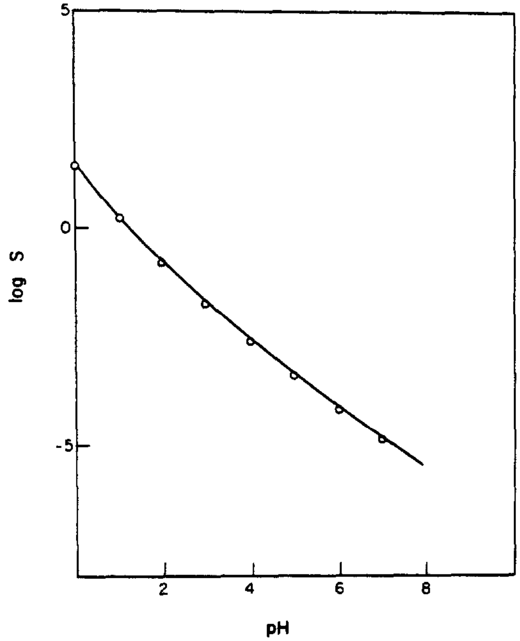

Fig. 1. The equilibrium molar solubility (S) of $Zn_3(PO_4)_2$ as a function of pH.

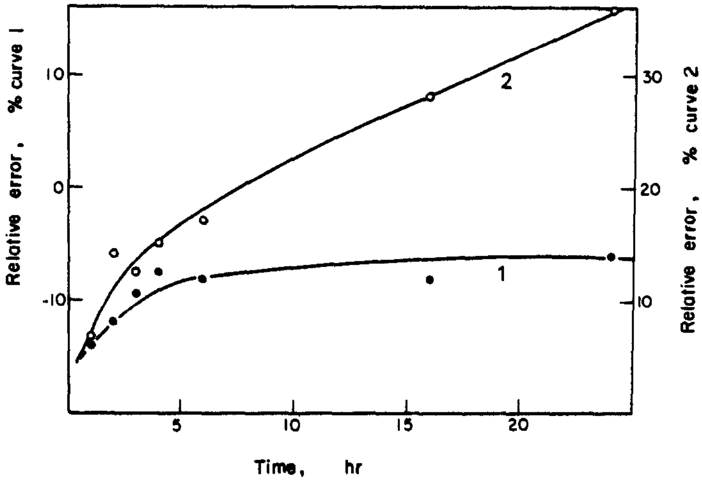

Fig. 2. Kinetics of precipitation. Curve 1.—400 mg of KH_2PO_4; Curve 2.—mixture of 200 mg of KH_2PO_4 and 328 mg of $Na_4P_2O_7 . 10\, H_2O$.

Precipitation technique

To 20–40 ml of the solution containing the phosphate (pyrophosphate or orthophosphate) were added 10 ml of 25% zinc acetate solution. Then hydrochloric acid (1 + 1) was very carefully added (in the presence of Methyl-Orange as guide) until the pH of the solution reached 3·2. More zinc acetate solution was then added to make the pH 3·4–3·6 (pH-meter). The final volume of the solution was about 70 ml. After 24 hr the precipitate was filtered off and washed with 0·3% zinc acetate solution at pH 3·6.

The solutions of pyrophosphate were prepared just before use, to avoid hydrolysis of the anion.

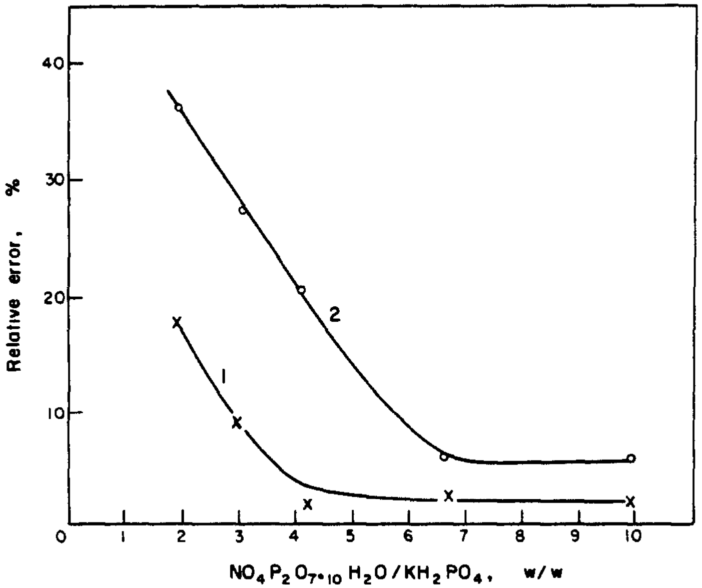

Fig. 3. The relative error as a function of weight ratio of $Na_4P_2O_7 . 10\, H_2O$ to KH_2PO_4. Curve 1.—$Na_4P_2O_7 . 10\, H_2O$ 190–158 mg; KH_2PO_4 100–16 mg. Curve 2.—$Na_4P_2O_7 . 10\, H_2O$ 95–79 mg; KH_2PO_4 50–8 mg.

RESULTS AND DISCUSSION

Figure 2 shows the kinetics of precipitation of pure orthophosphate (Curve 1), and of a mixture of orthophosphate and pyrophosphate (Curve 2). The relative error for the solution containing 0·4 g of KH_2PO_4 is −6% for 24 hr, *i.e.*, 94% of the orthophosphate will precipitate when the Radionova and Hodakov method is used. If the precipitation is done quickly enough, for example within 1 hr, then the error would still be −12%, that is 88% of the orthophosphate will precipitate. According to Curve 2 the error for the mixture is +35% for 24 hr, which is due to co-precipitation of the phosphate with pyrophosphate.

Considering the kinetics of precipitation and co-precipitation of $Zn_3(PO_4)_2$ by $Zn_2P_2O_7$, it is impossible to suggest improving the Radionova and Hodakov method by variation of the time of precipitation.

The relative error for analysis of solutions containing pyrophosphate and orthophosphate in various amounts is shown in Fig. 3. It is evident that the error depends not only on the ratio of pyrophosphate and orthophosphate but also on the absolute amount of orthophosphate. According to this figure the error is about +2% under the most favourable conditions. Although this error is rather large for gravimetric determination it may still be acceptable for control analysis purposes.

The reproducibility of the method in the absence of orthophosphate was estimated from the results of 6 sample solutions each containing 0·1659 g of $Na_4P_2O_7 . 10 H_2O$. The standard deviation was found to be $\pm 2{\cdot}5 \times 10^{-4}$ g and the relative error was ±0·25%.

As a result we may conclude that the method of Radionova and Hodakov for determination of pyrophosphate is not free from interference by orthophosphate. It still may be acceptable (with the error of +2%) if the concentration of orthophosphate in the solution is arranged to be below $10^{-2}M$. In any other case this method for determination of pyrophosphate in the presence of orthophosphate would not be reliable.

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Summary—The effect of orthophosphate on the precipitation of zinc pyrophosphate has been examined and it is shown that co-precipitation of the orthophosphate at pH 3·4–3·6 is serious if the orthophosphate concentration is >0·02*M*. Even with lower concentrations an error of up to +2% may occur

Zusammenfassung—Der Einfluß von Orthophosphat auf die Fällung von Zinkpyrophosphat wurde untersucht. Es wird gezeigt, daß bei pH 3,4–3,6 die Mitfällung von Orthophosphat ins Gewicht fallt, wenn die Orthophosphatkonzentration über 0,02*M* liegt. Selbst mit geringeren Konzentrationen kann ein Fehler bis zu +2% auftreten.

Résumé—On a examiné l'influence de l'orthophosphate sur la précipitation du pyrophosphate de zinc et il est montré que la coprécipitation de l'orthophosphate à pH 3,4–3,6 est sérieuse si la concentration de l'orthophosphate est >0,02*M*. Même avec des concentrations plus faibles, une erreur allant jusqu'à +2% peut se produire.

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COULOMETRIC TRACE DETERMINATION OF WATER BY USING KARL FISCHER REAGENT AND POTENTIOMETRIC END-POINT DETECTION

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Summary—A new approach to the determination of water *via* the Karl Fischer reaction is described. Iodine is coulometrically generated and the end-point, corresponding to a slight excess of iodine, is detected potentiometrically with a non-polarized platinum electrode. Samples of 1–500 μl containing 0·05–200 μg of water were analysed with a standard deviation of 0·015 μg in the range 0·05–20 μg of H_2O. A specially constructed electrolysis cell was used in combination with an LKB 16300 Coulometric Analyzer and the time for a complete analysis was 1–4 min, depending on sample size. The reagent composition has been optimized in order to enhance the rate of the main reaction and to minimize the extent of side-reactions. Decreasing the temperature reduced the extent of side-reactions. The displacement of end-point potential on dilution was studied and a correction is discussed.

Because of its specificity the Karl Fischer reagent has been widely used for the determination of water in a variety of organic and inorganic compounds since its introduction in 1935. Comprehensive reviews have been given by several authors.[1–3] In the standard procedure the reagent is added from a burette and the end-point is detected amperometrically with either a current or a voltage measuring device using two identical polarized Pt-electrodes. Recently a thorough examination of these "electrometric end-point" techniques was made by Beasley *et al.*[4] The non-linear behaviour of the diffusion current at low iodine concentration was suggested to depend on the formation of a large ionic complex, $C_5H_5N \cdot I_2 \cdot SO_2 \cdot NH_5C_5$, in equilibrium with $C_5H_5N \cdot I_2$ and $C_5H_5N \cdot SO_2$. The calculated slope of the titration curve between 5 and 25 μA was only 41% of the slope between 50 and 250 μA. Trace determinations of water down to 0·2 ppm have been reported.[5,6]

The coulometric generation of small amounts of iodine in a Karl Fischer medium eliminates the need for standardization of the reagent, as the stoichiometry is known.[7] Several commercial coulometric analysers using constant current and amperometric indication of the end-point have been developed.[8,9] They give an absolute standard deviation of approximately 2 μg of water for 1–5 g samples containing 10–100 μg of water.

The controlled-potential coulometric method proposed by Lindbeck[10] has the advantage of not being limited by the absolute error in the location of the end-point. Lindbeck determined 10–74 μg of water in 0·1 ml of methanol with an absolute standard deviation of 0·2 μg. He observed a drift corresponding to 0·53 ± 0·01 μg/min and noticed that this drift was independent of the concentration of iodine in the range 0–1 mM. He therefore produced a known excess of iodine in spent Karl Fischer reagent containing the sample, reduced the excess of iodine and determined the drift by repeating the procedure without adding any sample.

An important modification of the method proposed by Lindbeck was made by Karlsson and Karrman.[11] By using a rotating working electrode and a new cell design they could use a much larger reduction current. As a consequence, the time of analysis was decreased and so was the uncertainty of the drift correction. They reported titrations of 0·1–0·2 mg of water with an error of 0·15% and the time for one analysis was 3–12 min. The drift corrected for in their method corresponds to about 0·5 μg of water per min. Recently Karlsson[12] improved the method, including better electronic circuitry and design of the electrolysis cell. The lowest value reported, 0·6 μg, was determined with a standard deviation of 0·07 μg. In the range 500–5000 μg of water the relative standard deviation was 0·06–0·08% and the mean deviation from the calculated value was about 0·1%.

In the present work potentiometric end-point detection has been applied to the coulometric trace determination of water in a Karl Fischer medium. By increasing the rate of the main reaction at low iodine concentration (giving high sensitivity in the potentiometric indication) the time of analysis has been reduced significantly, especially for small sample sizes. This time reduction in combination with a lower drift has increased the sensitivity and precision of the coulometric method.

EXPERIMENTAL

Cell

A coulometric titration cell was made from glass with Teflon caps as shown in Fig. 1. It consists of three chambers, one for the auxiliary electrode, one for the sample, with generating and indicating electrodes, and one for the reference electrode. Electrolytic contacts were made *via* asbestos-filled liquid junctions. Asbestos (Hopkins & Williams) was plugged tightly with a hard tool into the connecting glass tubes. The generating electrode was placed close to the junction of the auxiliary electrode, and the indicating electrode close to the reference electrode junction, in order to minimize the interference with the indicating system by the generating electrode system. Further, the three compartments were arranged in line so that there should be geometric symmetry in the sample compartment. All electrodes were made from platinum; the generating electrode was a flat Pt-spiral, diameter 0·3 mm, with a total area of 0·5 cm^2, the auxiliary electrode was 36-mesh gauze, area 6 cm^2, the indicating electrode a 0·3 mm wire with a crimped Teflon insulation on the stem, and the reference electrode 5 cm^2 of 36-mesh gauze. The sample compartment was stirred with a magnetically driven glass bar. The caps were made from solid Teflon with an O-ring seal. Silicone rubber was inserted into holes bored in the Teflon caps, and the wires were inserted into the silicone rubber *via* hypodermic needles which were then removed. A silicone rubber septum for sample introduction was fitted into the Teflon cap of the sample compartment.

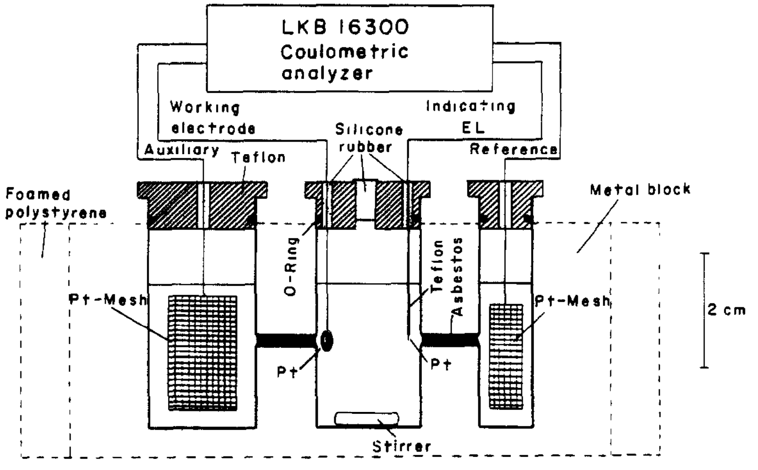


Fig. 1. Schematic diagram of the titration cell and the LKB Coulometric Analyzer.

The cell was fitted into a brass block insulated with polystyrene foam. Tap-water could be circulated through the block for cooling, a temperature of 7·0° being normally obtained

Reagents

A Karl Fischer reagent composition which has been shown[15] to give a fast reaction was used. It consisted of 1·0*M* pyridine (Mallinkrodt Analytical Reagent), 0·10*M* iodine (Merck *p.a.*), 0·60*M* sulphur dioxide (Fluka AG, >99·97% SO_2 in steel cans), dissolved in methanol (Merck p.a., max. 0·03% water).

Apparatus

Coulometric analyser. The electrodes were connected to an LKB 16300 coulometric analyser. The instrument contains a high impedance voltmeter which measures the voltage between the indicator and the reference electrodes. This voltage is compared with a preset voltage and any deviation amplified and used to control the current through the generating electrode system. Far from the end-point the generating current became about 12 mA with this cell. As the preset potential was approached the current was automatically decreased. The way in which the end-point was approached could be adjusted with the gain of the instrument so that it decreased rapidly at first and then asymptotically towards zero current.

The analyser showed the time integral of the current. The range used in this investigation was $\times 0{\cdot}1$ which corresponds to 10^{-9} equivalent or 0·5 nmole of water as the last digit in the reading.

Procedure

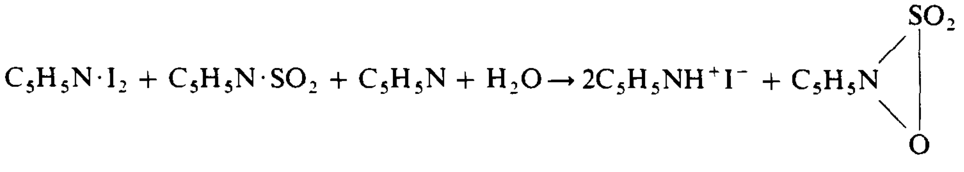
The sample compartment was filled with 4 ml of Karl Fischer reagent. The other cell chambers were filled to the same level with the reagent. A hypodermic needle was inserted into the caps for pressure equilibration, the caps were put into place, the needles were removed and the cell was turned upside down several times to remove moisture on the walls. The cell was so well sealed that introduction of samples caused a small overpressure which was released after addition of several samples.

Water was added with a 5 μl Hamilton syringe until a colour change occurred in the reagent. There was then a small excess of water. The end-point potential was set on the analyser, which was switched to the titration mode. The excess of water was titrated and a small well-defined iodine excess was present when the current ceased. The integrator was then reset and the system was ready for sample introduction. Samples were introduced with either a Hamilton syringe or an Agla micrometer syringe. When the sample had been introduced the titration started and when it was complete, after 1–4 min depending on sample size, the integrator was read. After resetting of the integrator a new sample could be introduced.

The reagent in the auxiliary compartment should be changed when the iodine excess is consumed, as indicated by the colour. With normal sample sizes about one change a day is necessary. The reagent in the reference electrode should also be changed when the colour changes, usually once a week. The reagent in the sample compartment should be changed when it becomes diluted with more than 1 ml of sample.

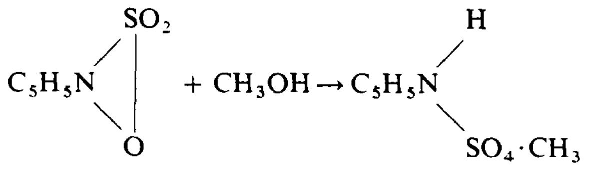
REACTIONS

The main Karl Fischer reaction according to Mitchell[1] is:



$$C_5H_5N\cdot I_2 + C_5H_5N\cdot SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5NH^+I^- + C_5H_5N\left\langle\begin{matrix}SO_2\\ \vert\\ O\end{matrix}\right. \qquad (1)$$

which in the presence of methanol proceeds to



$$C_5H_5N\left\langle\begin{matrix}SO_2\\ \vert\\ O\end{matrix}\right. + CH_3OH \rightarrow C_5H_5N\left\langle\begin{matrix}H\\ \\ SO_4\cdot CH_3\end{matrix}\right. \qquad (2)$$

which shows that one mole of water consumes one mole of iodine or two redox equivalents. There is no information regarding which species actually reacts at an electrode surface, but it is possible to write a reaction using only species known to exist in a partially spent reagent.

$$C_5H_5N\cdot I_2 + 2C_5H_5NH^+ + 2e^- \rightarrow 2C_5H_5NI^-H^+ + C_5H_5N \tag{3}$$

During a titration of the type described in this paper the pyridinium ion and pyridine concentrations remain constant. The electrode potential will then be given by equation (4) if the activity coefficients are assumed to be constant:

$$E = E' + \frac{RT}{2F}\ln\frac{[C_5H_5N\cdot I_2]}{[C_5H_5NHI]^2} \tag{4}$$

The electrode potential of this system proved to be very stable and therefore a half-cell with the Karl Fischer reagent was used as reference electrode, simplifying the cell design. As the concentrations in the reference electrode compartments remain constant during a titration, the electrode potential change of the indicating system will be a measure of the redox potential change in the sample compartments according to equation (4).

RESULTS

Rate of the electrode reaction

A number of micromoles of iodine complex, cf. equation (3), were rapidly generated and the potential of the indicating electrode was measured with an auxiliary digital voltmeter as a function of time. The quantity generated was read from the integrator and a plot of the resulting titration curve is shown in Fig. 2. The curve shows that the system approaches equilibrium slowly at low concentrations of the iodine complex but rapidly at higher concentration. Separate experiments in which the current direction was reversed allowed a similar titration to be made in which no water could be present, as it started from a solution with excess of iodine complex present. Provided that the iodine complex concentration was larger than $10^{-5}M$ the electrode response was rapid. The effect of the rate of the reaction between the reagent and water is reported in a separate paper.[15]

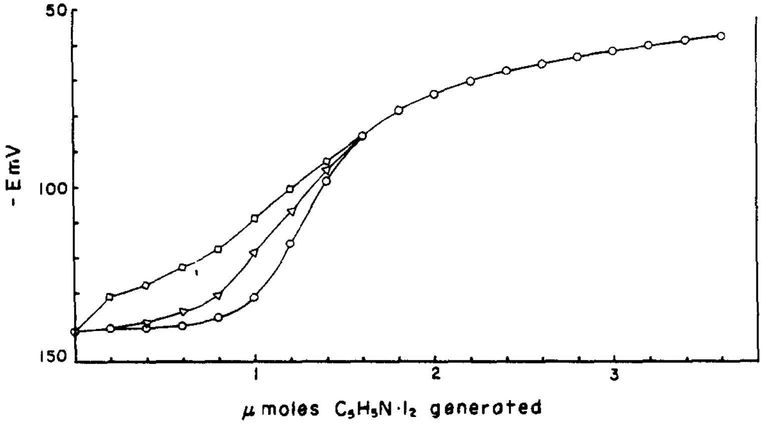


Fig. 2. Titration curve for 4·0 ml of spent Karl Fischer reagent of the following original composition: 0·10*M* iodine, 0·60*M* sulphur dioxide, 1*M* pyridine in methanol. (□) potential read after 15 sec, (△) 30 sec, (○) 60 sec.

Current efficiency

Barendrecht[13] studied the stoichiometry of the electrode reaction at various current densities and mass transfer efficiencies. A large electrode area, a high iodide concentration in the reagent and good stirring increased the maximum current that could be passed through the cell with 100% current efficiency for oxidation of iodide complex to iodine complex. Pribyl and Slovak[14] reported less than 100% current efficiency at low currents, <2 mA/cm^2 for 0·1*M* iodide complex. Karlsson[11,12] on the other hand obtained very accurate coulometric results with 0·2*M* iodide complex solution, with a current density down to 1 mA/cm^2. This raises the question whether Pribyl and Slovak made a sufficiently accurate correction for side-reactions in the case of low current densities, as the drift was of the same order of magnitude as the rate of generation.

A test of the current efficiency under the conditions described in this paper, *i.e.*, 0·2*M* iodide complex, was made and the result is shown in Table 1. A 50 μl portion of a solution of water in methanol was added with a Hamilton syringe. The recovery was, within experimental error, independent of current density.

Table 1. Recovery of water as a function of current density. Sample volumes 50 μl. Electrode area 0·5 cm^2

Current density, *mA/cm*^{2}	Taken, μg	Found, μg	Recovery, %
2	51·26	51·37	100·1
		51·51	100·5
		51·29	100·1
8·8	51·26	51·13	99·7
		51·22	99·9
24	51·26	51·20	99·9
		51·21	99·9

Dilution of the solvent

When a sample is added to the Karl Fischer reagent, it is diluted, which may affect the reaction rates[15] and the potential of the indicating electrode system. The present method required that the amount of iodine complex in the vessel after titration of a sample be identical to the amount in the vessel before sample addition. Dilution of a redox couple of the type given in equation (3) will theoretically result in a potential change of

$$\Delta E = \frac{RT}{2F} \ln \frac{V}{V + V_0} \tag{5}$$

if the activity coefficients and the liquid junction remain constant. V denotes the reagent volume and V_0 the volume added. At 25° a dilution from 4 to 5 ml should cause a change of $-2{\cdot}8$ mV. In practice the solution and the electrodes may be non-ideal.

To test the actual deviation a titration curve for 4·0 ml of reagent was recorded and another curve for 4·0 ml of reagent plus 0·5 ml of methanol was recorded in the same way. The iodine complex excess was determined by curve-fitting the experimental data until a plot of E *vs.* $-\log[C_5H_5N \cdot I_2]$ became a straight line with a slope of $RT/2F$, see Fig. 3. By using these lines as calibration, a plot of E *vs.* the amount of excess of iodine complex was made and these curves are also shown in Fig. 3. The significance of this plot can be

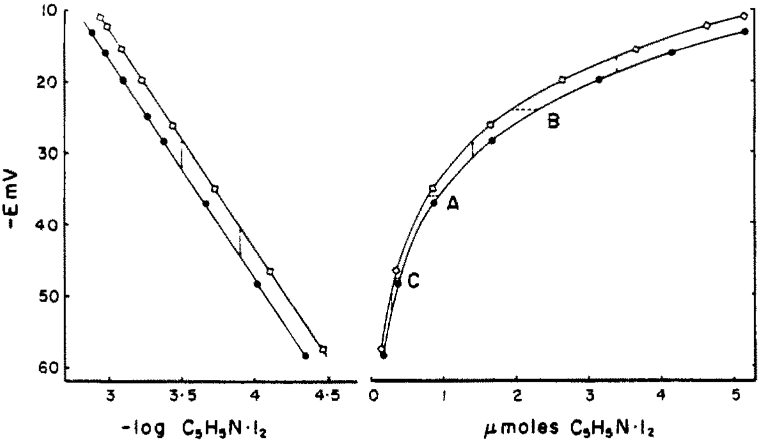


Fig. 3. The effect of diluting 4·0 ml of Karl Fischer reagent (0·10*M* iodine, 0·60*M* sulphur dioxide, 1·0*M* pyridine in methanol) with 0·5 ml of methanol. The curves to the left represent a plot of $-\log[C_5H_5N \cdot I_2]$ *vs.* *E* for (●) 4 ml of reagent, (□) 4·0 ml of reagent + 0·5 ml of methanol. The curves to the right show *E* as a function of the amount of iodine complex generated in (●) 4·0 ml of reagent, (□) 4·0 ml of reagent + 0·5 ml of methanol.

shown by an example. If the analyser were preset to −36 mV the 4·0 ml of reagent in the cell would contain an excess of 0·94 μmole of iodine complex. If 0·5 ml of methanolic sample were added and titrated to the same preset potential this diluted solution would contain an excess of 0·78 μmole of iodine complex. The diluted solution gives the same potential for a lower iodine excess than the undiluted solution. The difference appears as a systematic titration error of 0·78 − 0·94 = −0·16 μmole. Titration of 0·5 ml of methanol containing 5·20 μmole of water resulted in the following systematic errors. If the titration was made to the preselected potential *A*, Fig. 3, a deviation of −0·18 μmole was found which can be compared with the −0·16 μmole evaluated from the graph. At potential *B* a deviation of −0·39 μmole was found which compares well with −0·40 estimated from the graph.

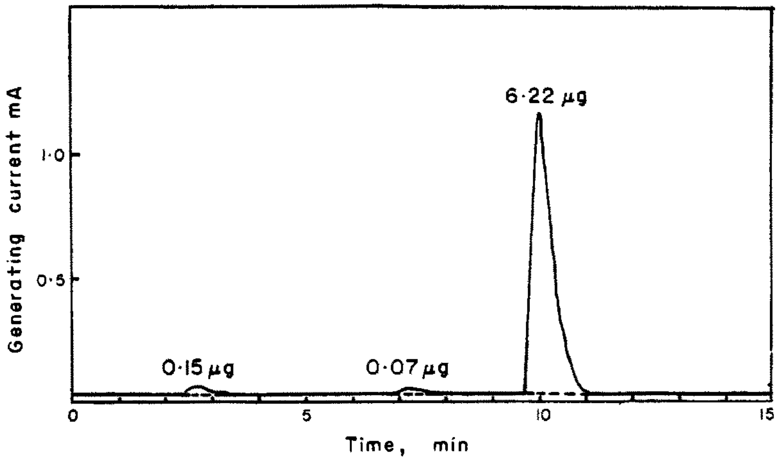


Fig. 4. Recorded current–time curves in the titration of some samples of water in methanol.

The size of this systematic error will thus depend on the selection of preset potential which in actual titrations corresponds to point C in Fig. 3. At this point dilution with 0·5 ml results in a deviation of $-0{\cdot}07$ μmole and a dilution with 100 μl in a deviation of $-0{\cdot}014$ μmole. A correction for these dilution effects can be made if necessary and then it should be possible to analyse a 100 μl sample correctly to within a few nmoles or less than 1 ppm water.

Equation (5) can be tested against the experiments by comparing the ΔE with the vertical displacement of the curves to the right in Fig. 3. For a dilution from 4·0 to 4·5 ml equation (5) gives $\Delta E = -1{\cdot}5$ mV and Fig. 3 gives $-2{\cdot}2$ mV. The difference represents the non-ideality of the electrodes and the solution.

Analytical results

Owing to side-reactions which are discussed in more detail in another paper,[15] the amount of iodine complex decreases with time. The rate of the decrease was independent of the iodine complex concentration in a solution with the composition given in this paper. At room temperature the decrease is equivalent to an addition of 0·22 μg of water/min and at 7° it is equivalent to 0·15 μg of water/min. All the results reported in this work were obtained at room temperature. The mean variation in the blank value was 0·005 μg of water/min. The decrease in iodine complex concentration with time was found to be proportional to the volume, as measured at 2·5 and 4·0 ml. The given blank values are for 4·0 ml of reagent. Before addition of a sample the integrator and a timer were started. When the titration was complete the time and the value of the integrator were noted, *e.g.*, every 30 sec. A blank correction was then calculated and subtracted from the results. When water amounts of about 0·5 mg was determined the blank correction was about 0·3%. The titration time was affected by the time taken by the analyser to decrease the current asymptotically to zero, typically 1 min for a small sample and the maximum generation current (which was 12 mA). At maximum speed about 65 μg of water could be titrated per minute.

Table 2. Determination of water in methanol

Sample volume, *μl*	Found		
	μmole	*μg*	% *v/v*
0·4*	0·004	0·07	0·018
	0·004	0·07	0·018
	0·005	0·09	0·023
1*	0·010	0·18	0·018
	$0{\cdot}008_5$	0·15	0·015
	$0{\cdot}009_5$	0·17	0·017
5†	0·052	0·94	0·0188
	0·051	0·92	0·0184
	0·051	0·92	0·0184
100§	1·015	18·29	0·0183
	1·016	18·31	0·0183
	1·016	18·31	0·0183

* Hamilton 1 μl.
† Hamilton 10 μl.
§ Agla micrometer syringe.

The end-point was selected so that the concentration of iodine complex in the reagent was $10^{-4}M$, point *C* in Fig. 3, which gives sufficiently rapid electrode and main reactions.[15] Too high a concentration results in a reduced sensitivity. The selected value represents a compromise and the slope for the indicating electrode was ~ 2 mV/μg of water. Such a slope requires an instrument with a very stable voltmeter. The performance of the system used can be seen from Fig. 4 which is a recording, with an auxiliary recorder, of the titration course when a few samples of various size were introduced into and analysed in the cell.

Table 2 shows the determination of water in Merck's p.a. methanol, on samples of different sizes. The results were corrected for the blank and the 100 μl samples were corrected by +0·014 μmole for dilution of the reagent. Table 3 shows that added water was quantitatively recovered.

The series show that the titration efficiency is very good and that water can be determined over a very wide range.

Table 3. Standard addition of water to various solvents

Solvent	Sample added, μl	Calculated, μg	Mean value found, μg	Rel. standard deviation, %	No. of detns.
Methanol	5	16·47	16·46	0·4	8
	30	98·82	98·90	0·1	3
	50	164·7	164·6	0·1	3
Acetic acid	25	24·82	24·73	0·2	3
Propan-Z-ol	25	24·82	24·87	0·2	5

DISCUSSION

True potentiometric end-point determination offers some advantages over the amperometric methods which have been the only methods in use previously. The reason is that there must be an excess of iodine complex if the electrode reaction is to proceed rapidly. The normal procedure using amperometric measurements is to wait about 30 sec between each addition of reagent and a similar waiting time should have been necessary with potentiometric indication under these conditions. In this paper another composition of the solution at the end-point is suggested and it is selected so that both the main reaction and the electrode reaction proceed rapidly. The end-point indicating system should be capable of locating this point with good precision. The potentiometric system is preferred as the only uncertainty lies in the reference electrode potential. In an amperometric method the value of the current would also be affected by stirring, temperature and electrode geometry.

The composition of the solution will affect the quantities measured by electroanalytical methods. In the potentiometric determination it will appear as a dilution effect, which can be neglected if the sample contains moderate or large amounts of water. An amperometric titration to a given value of the diffusion current would be still more sensitive to dilution effects.

In the present work the limit of detection has been decreased by a factor of ten, compared to earlier trace methods. Because of this the sample size can be decreased for samples containing larger amounts of water, which further reduces the dilution effect. The same reagent composition and operating conditions can thus be used to cover a wide range, from 0·5 ppm to 100% water, by working with sample volumes of 1–500 μl.

For routine applications there is much to be gained by using the present method. If the sample is introduced with a syringe an analysis will take 1–4 min, depending on the amount of water and up to 500 analyses can be performed in succession with the same reagent in the sample compartment. The reagent consumption would then be a few μl per sample provided that each sample contains less than a few % of water.

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Zusammenfassung—Ein neuer Weg zur Wasserbestimmung über die Karl-Fischer-Reaktion wird beschrieben. Jod wird coulometrisch erzeugt und der Endpunkt, der einem geringen Jodüberschuß entspricht, potentiometrisch mit einer nicht polarisierten Platinelektrode nachgewiesen. Proben (1–500 μl) mit 0,05–200 μg Wasser wurden im Bereich 0,05–20 μg H_2O mit einer Standardabweichung von 0,015 μg analysiert. Eine eigens dafür konstruierte Elektrolysezelle wurde in Verbindung mit einem coulometrischen Analysengerät LKB 16300 verwendet; die Gesamtzeit für eine Analyse beträgt je nach der Probengröße 1–4 min. Die Reagens-Zusammensetzung wurde optimal eingestellt, um die Geschwindigkeit der Hauptreaktion zu erhöhen und das Ausmaß der Nebenreaktionen möglichst klein zu halten. Ein Erniedrigen der Temperatur drängt die Nebenreaktionen zurück. Die Verschiebung des Potentials am Endpunkt mit der Verdünnung wurde untersucht; eine Korrektur wird diskutiert.

Résumé—On décrit un nouvel accès au dosage de l'eau par la réaction de Karl Fischer. De l'iode est engendré coulométriquement et le point de fin de dosage, correspondant à un léger excès d'iode, est déctecté potentiométriquement avec une electrode de platine non polarisée. On a analysé des échantillons (1–500 μl) contenant 0,05–200 μg d'eau avec un écart type de 0,015 μg dans le domaine 0,05–20 μg de H_2O. On a utilisé une cellule d'électrolyse spécialement construite en combinaison avec un Analyseur Coulométrique LKB 16300, et le temps pour une analyse complète est de 1–4 mn, dépendant de la taille de l'échantillon. La composition du réactif a été rendue optimale afin d'accroître la vitesse de la réaction principale et de minimiser l'importance de réactions secondaires. L'abaissement de la température réduit l'importance des réactions secondaires. L'abaissement de la température réduit l'importance des réactions secondaires. On a étudié le déplacement du potentiel du point final par dilution, et on discute d'une correction.

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RAPID DETERMINATION OF THE EQUIVALENCE VOLUME IN POTENTIOMETRIC ACID–BASE TITRATIONS TO A PRESET pH—I

THEORY AND APPLICATIONS

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Summary—A new approach to shorten the time needed for an acid–base titration has been made. The method developed is based on the equation for acid–base titrations derived by Ingman and Still. The equation is transformed into such a form that only one titration point is needed to calculate the equivalence volume when the titration is carried out to a preset pH which can be chosen according to the experimental conditions. The method is used for titration of acetic acid, $\log K^{H}_{HA} = 4{\cdot}65$, hydroxylammonium ion, $\log K^{H}_{HA} \sim 6{\cdot}2$, and boric acid, $\log K^{H}_{HA} \sim 9{\cdot}1$, with an error of 0·1–0·5%. In titration of hydrogen ascorbate ion, $\log K^{H}_{HA} \sim 11{\cdot}3$, the error obtained was about 0·3–2%.

The usual way to describe the course of a potentiometric acid–base titration is to plot the measured potential as a function of the volume of added titrant. However, the corresponding pH value, which is more concrete and gives more information about the course of the titration and all the equilibria of the system studied, is quite often plotted instead of the potential. The curve obtained is S-shaped and the equivalence point is located at the inflexion point of the curve, *i.e.*, at the potential jump.

Sørensen[1] transforms the S-shaped acid–base curve into two straight lines. He titrates a strong acid with a strong base and calculates antilog $(k_1 - \text{pH})$ of the points before the equivalence point and antilog $(k_2 + \text{pH})$ after the equivalence point. The constants k_1 and k_2 are arbitrarily chosen to yield numerical values that can be conveniently handled. Sørensen[1] also transforms the titration curve of a precipitation titration into two straight lines, *e.g.*, for titration of chloride with silver nitrate. The straight-line method has been further developed by Gran.[2] He takes account of the change in volume during titration and determines the equivalence point in complex-formation and oxidation–reduction titrations by transforming the corresponding titration curves into two straight lines. The method developed by Gran[2] is limited to the titration of weak acids with stability constants up to 10^7. The simplifications made by him when deriving his equations are no longer valid when $K^{H}_{HA} > 10^7$. Ingman and Still[3] have developed Gran's method so that weak acids with stability constants up to 10^{10} can be titrated. They assume that the titrated acid takes part in one equilibrium reaction only, *i.e.*, the dissociation equilibrium reaction of the acid. By introducing α-coefficients[7] into Ingman and Still's equation, more complicated titrations can be treated.

Ingman and Still[3] start by assuming that a weak acid HA is titrated with a strong base, *e.g.*, sodium hydroxide. The concentration of the acid is indicated by C_{HA} and the initial volume by V_0. The concentration of the strong base is denoted by C_{OH} and the volume added by V. The consumption of the strong base at the equivalence point is denoted by V_{eq}. The authors make the following three assumptions.

1. The law of mass action must hold for the reaction:

$$\mathrm{HA} \rightleftharpoons \mathrm{H} + \mathrm{A} \quad K^{\mathrm{H}}_{\mathrm{HA}} = \frac{[\mathrm{HA}]}{\{\mathrm{H}\}\,.\,[\mathrm{A}]} \tag{1}$$

For convenience, charges are omitted. The constant $K^{\mathrm{H}}_{\mathrm{HA}}$ is a mixed constant, *i.e.*, the activities of the hydrogen and hydroxide ions are used in conjunction with concentrations of other species.

The relationship between activity and concentration is defined according to equation (2):

$$\{\mathrm{G}\} = f_{\mathrm{G}}[\mathrm{G}] \tag{2}$$

where f_{G} is the activity coefficient of ion G at a certain ionic strength.

2. The electroneutrality rule for the solution is:

$$[\mathrm{H}] + [\mathrm{Na}] = [\mathrm{OH}] + [\mathrm{A}] \tag{3}$$

Equation (3) should also include concentrations of ions originating from the neutral salt added to adjust ionic strength. The salts used for this purpose, in this paper potassium nitrate and chloride, are completely dissociated, so the concentrations of the anion and cation are the same and cancel each other out in the equation.

The concentration of the sodium ion can be expressed by the following equation:

$$[\mathrm{Na}] = \frac{V\,.\,C_{\mathrm{OH}}}{V_0 + V} \tag{4}$$

3. The following equation should be valid at the equivalence point:

$$V_{eq}\cdot C_{\mathrm{OH}} = V_0\cdot C_{\mathrm{HA}} \tag{5}$$

This equation can be regarded as the definition of V_{eq}.

After elimination of certain terms and rearrangement of equations (1), (3), (4) and (5), the following equation is obtained:

$$V_{eq} - V = V\,.\,\{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}} + \frac{(V_0 + V)}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}])(1 + \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}}) \tag{6}$$

Equation (6) gives a straight line when $(V_{eq} - V)$ is plotted against V. The plot has a slope of -1 and intersects the V-axis at the point V_{eq}. By use of equation (6) the equivalence point can be located with a considerably greater accuracy than with the equations used by Sørensen[1] and Gran.[2] This is especially valid when very weak acids are titrated and the approximations assumed by Sørensen[1] and Gran[2] when deriving their equations are no longer valid.

THEORY

The chemical industry has begun to make extensive use of computers to regulate and control processes. This means that all the measurements carried out in the process must be performed quickly and automatically, and the values obtained must be sufficiently accurate. This is true of both physical measurements and chemical analyses, the results of which are required for control purposes. It follows that the analytical chemist has to develop methods of analysis which, in addition to being accurate, can also be rapidly carried out and easily automated.

The methods developed by Sørensen,[1] Gran,[2] and Ingman and Still[3] can easily be applied to automatic analyses. These methods use straight lines and the equivalence point can be determined by using at least two titration points. Johansson[4,5] has developed an automatic method of analysis using the Ingman–Still equation (6) in a modified form.

A method by which a potentiometric acid–base titration can be simplified so that the equivalence volume can be calculated from only one titration point, but nonetheless can be determined quite accurately, will be presented in this paper. The method is based on titration to a preset pH value.

From equation (6), we can, after a simple mathematical manipulation, obtain:

$$V_{\mathrm{eq}} = \left[\{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}} + \frac{1}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}])(1 + \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}}) + 1\right].V + \frac{V_0}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}])(1 + \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}}) \quad (7)$$

In titration to a certain pH value, the terms $\{\mathrm{H}\}$, $[\mathrm{H}]$ and $[\mathrm{OH}]$ are fixed. V_0 and C_{OH} are known and $K^{\mathrm{H}}_{\mathrm{HA}}$ can be found from tables of the stability constants of acids. Equation (7) is then simplified to:

$$V_{\mathrm{eq}} = B\,.\,V + A \quad (8)$$

where

$$A = \frac{V_0}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}])(1 + \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}}) \quad (9)$$

$$B = \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}} + \frac{1}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}])(1 + \{\mathrm{H}\}\,.\,K^{\mathrm{H}}_{\mathrm{HA}}) + 1 \quad (10)$$

A and B are constants that can be calculated in advance for any pH value, different acids, different values of $K^{\mathrm{H}}_{\mathrm{HA}}$, and varied values of V_0 and C_{OH}. From equation (8) it is easily seen that in titration to a certain pH value for which the constants A and B have been calculated in advance, just one titration point, one value of V, has to be known before V_{eq}, the equivalence volume, can be determined. The titration point needed is naturally the volume of added titrant to give the required pH value. It is not always necessary to carry out the titration to the same pH value, and the value to be used can be chosen according to the experimental conditions. The constants A and B have then to be recalculated for the new pH value.

Titration to a given pH has been used earlier. The pH has been chosen to be as near as possible that at the equivalence point. Goldman and Meites[8] have considered the end-point errors in this type of titration. The error function given by them is not useful when very weak acids, *e.g.*, boric acid, are titrated. According to the earlier method the volume of added standard base needed to give the desired pH is considered as the equivalence volume. In the method proposed, on the contrary, the pH is chosen from an earlier stage of the titration and the equivalence volume is calculated from the volume of added standard base.

In this paper the titration of weak acids with a strong base is studied. The method described can also be applied to titration of a weak base with a strong acid. All the equations used have then to be derived from the equation given by Ingman and Still[3] for the titration of a weak base with a strong acid.

In Fig. 1 the constant A for different acids has been plotted against pH. The acids used are those titrated later on in this paper, acetic acid, hydroxylammonium ion, boric acid and hydrogen ascorbate ion. The calculations are based on the values determined by the experimental conditions under which the titrations are carried out: V_0 = 100·0 ml, C_{OH} = 0·05984M sodium hydroxide, μ = 0·1 (KNO_3) and T = 25° at which $\log f_H$ = −0·08 and $\log f_{OH}$ = −0·12 according to Kielland,[6] and the stability constant,[7] $\log K^H_{HA}$, is for acetic acid 4·65, for hydroxylammonium ion 6·2, for boric acid 9·1 and for hydrogen ascorbate ion 11·3. The ionic product of water is $K_w = 10^{-14}$.

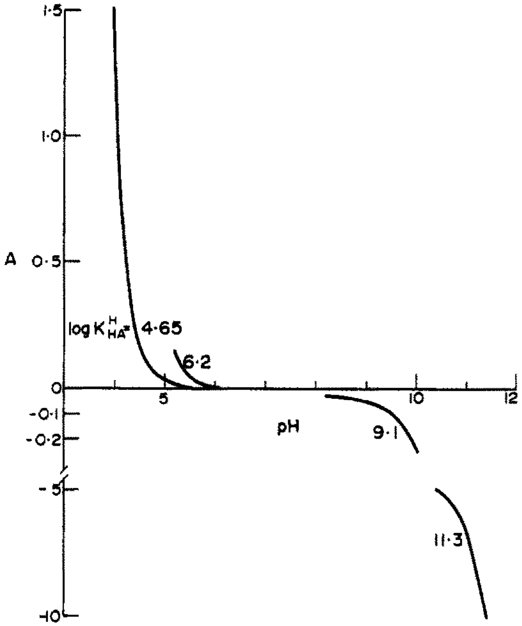

Fig. 1. Constant A, equation (9), as a function of pH for acetic acid, $\log K^H_{HA}$ = 4·65, hydroxylammonium ion, $\log K^H_{HA}$ = 6·2, boric acid, $\log K^H_{HA}$ = 9·1, and hydrogen ascorbate ion, $\log K^H_{HA}$ = 11·3. V_0 = 100·0 ml, C_{OH} = 0·05984M, $\log f_H$ = −0·08 and $\log f_{OH}$ = −0·12, T = 25° and μ = 0·1 (KNO_3).

As can be seen from Fig. 1. the constant A is almost zero near the neutral point, but increases on the acid side and assumes increasingly negative values on the alkaline side. Only the parts of the curves having practical significance have been plotted. On studying equation (9), the expression for A, it will be realized that when pH = 7 is reached the term ([H] − [OH]) and the constant A will be zero. From Fig. 1 it can also be seen that when hydrogen ascorbate ion is titrated, the constant A is quite large and thereby will have a greater influence in equation (8) than it does for the other titrations to be presented.

In Fig. 2, the constant B, according to equation (10), is plotted as a function of pH for the same acids and same pH intervals as the constant A in Fig. 1. The same values are used for stability constants, activity coefficients, V_0 and C_{OH} as for Fig. 1.

As seen from Fig. 2, all the curves have approximately the same shape and tend to approach the value 1. This is easily realized from studying the expression for B, equation (10). With increasing pH all the variable terms in equation (10) decrease and the value of the constant B approaches 1.

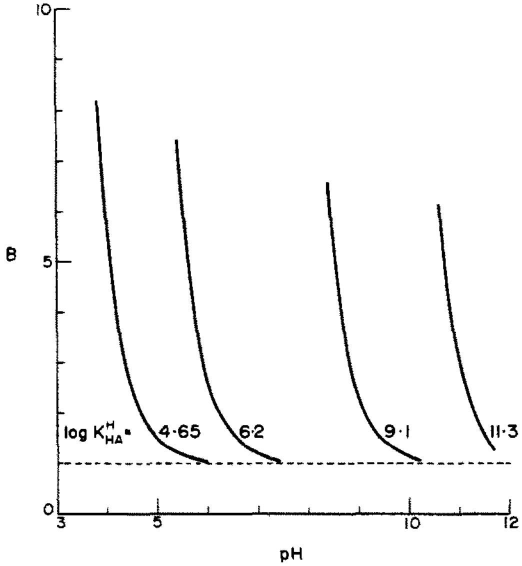

Fig. 2. Constant B, equation (10), as a function of pH for acetic acid, hydroxylammonium ion, boric acid and hydrogen ascorbate ion (conditions as for Fig. 1).

Let us consider the titration of acetic acid, and equation (8). From Figs. 1 and 2 it is noticed that if the titration is carried out to the equivalence point, the pH being a little higher than 8, $A = 0$ and $B = 1$. This is easily realized by substituting these values in equation (8), because at the equivalence point $V = V_{eq}$. The same deduction can be used in the case of hydroxylammonium ion. The value of B at the equivalence point is strongly dependent on the term $\{H\}.K^{H}_{HA}$ in equation (10). If the difference between the pH of the equivalence point and log K^{H}_{HA} is not very great, as in the case of weak acids, *e.g.*, boric acid and hydrogen ascorbate ion, the constant B has a value greater than 1 at the equivalence point. From Fig. 1 it can be seen that for titration of boric acid and hydrogen ascorbate ion, the constant A is negative. This means that according to equation (8), the constant B should have values over 1 when these acids are titrated to the equivalence point, $V = V_{eq}$.

DISCUSSION

When equation (8) is used to determine the equivalence volume V_{eq} and it is desirable to find the error in it caused by the error in measuring the added volume of titrant V, equation (8) can be differentiated:

$$dV_{eq} = B.dV \tag{11}$$

According to equation (11) the constant B determines to what extent an error in V influences the error in determining V_{eq}. As seen from Fig. 2, the plots of B against pH are quite steep at the beginning and B is quite large. With increasing pH B decreases rapidly and around the pH value corresponding to log K^{H}_{HA} the curves become less steep and with further increase in pH approach 1. This means that if the pH to which the titration is carried out is much lower than the value of log K^{H}_{HA} for the acid considered, the error in V_{eq} will be much larger than the error made in measuring V. Also the relative error in measuring V will be largest at the beginning and decrease during the titration. At a pH near log K^{H}_{HA} the error in V_{eq} would be only twice that of measuring V. In that pH region the buffer index of the solution is highest, resulting in an increase of the volume error, the magnitude of which depends on the discrimination of the pH-meter. By moving away from pH = log K^{H}_{HA} to a region of lower buffer index, the volume error, constant B, and hence the error in V_{eq}, can all be decreased. On the other hand, a titration to pH about log K^{H}_{HA} can easily be performed exactly to the chosen pH at which the calculated value of constant B is valid. This fact increases the usefulness of this pH region. When choosing a pH much higher than log K^{H}_{HA} in order to move to a region of lower buffer index it may be difficult to stop the titration exactly at the desired pH and an erroneous value of constant B may then be used.

If the titration is taken to the equivalence point the constant B will be 1 for acetic acid and hydroxylammonium ion and therefore the equivalence volume V_{eq} can be determined with the same accuracy as the volume of added titrant can be measured. When titrating very weak acids, *e.g.*, boric acid and hydrogen ascorbate ion, to the equivalence point, the constant B has values greater than 1. The error in V_{eq} is always larger than the error made in measuring V if V_{eq} is determined by equation (8).

These surveys of titration error are valid when the reference pH values used are lower than, or the same as, that at the equivalence point. If the acids are titrated to pH values after this point the hydroxide ion concentration [OH] is so high that the constant B, equation (10), can have values less than 1. Titrations to such high pH values have not been studied in this paper.

It is apparent from equations (9) and (10) that when the titration is carried out to pH values higher than log K^{H}_{HA}, small variations in the stability constant of the acid will not affect the values of A and B to any great degree. This means that the pH value to which titration is performed should not be too low on the scale, in order that an acceptable degree of accuracy may be obtained.

If the literature values for the stability constants[7] of hydroxylammonium ion, boric acid and hydrogen ascorbate ion were used to calculate A and B, the titration error would be so large that the method could not be used, not even if the titration were performed to pH values not far away from that at the equivalence point, in order to minimize the influence of the incorrect value of the stability constant on the value of B. A variation of even ±0·1 logarithmic units in the value of the stability constants would cause an error of about 10% in determining the equivalence volume if the reference pH values were those used in Tables 2 and 3. Such a variation in reported stability constants is not unusual.

This dependence on reliable values for the stability constants can be avoided if B is eliminated from equation (8). The value of A can be calculated with the literature values for the stability constants[7] because small variations in log K^{H}_{HA} do not effect A appreciably. B is eliminated by measuring its value in a calibration titration under exactly the same conditions as the analysis is performed. To emphasize the difference between the constant

B and that determined by calibration titration, the latter constant may be called B_{ex} and expressed by equation (12):

$$B_{ex} = \frac{V_{eq} - A}{V} \quad (12)$$

In the calibration titration the initial concentration of the acid and hence V_{eq} are accurately known. In titration to different pH values B_{ex} can be calculated for each pH value. Equation (8) can be rewritten, using the constant B_{ex}:

$$V_{eq} = B_{ex}.V + A \quad (13)$$

If the value of A, however, is appreciably changed although $\log K^{H}_{HA}$ is only slightly altered, equations (12) and (13) cannot be used. This is true when very weak acids, *e.g.*, hydrogen ascorbate ion, are titrated. The constant A can be eliminated by performing another calibration titration to the chosen pH. The following pair of equations is then obtained:

$$\begin{cases} V_{eq_1} = B.V_1 + A \\ V_{eq_2} = B.V_2 + A \end{cases} \quad (14)$$

When (14) is solved and an expression A_{ex} similar to B_{ex} is applied, the following equations are obtained:

$$\begin{cases} A_{ex} = \dfrac{V_{eq_2}.V_1 - V_{eq_1}.V_2}{V_1 - V_2} & (15) \\[2ex] B_{ex} = \dfrac{V_{eq_1} - V_{eq_2}}{V_1 - V_2} & (16) \end{cases}$$

and equation (8) can be rewritten:

$$V_{eq} = B_{ex}.V + A_{ex} \quad (17)$$

APPLICATIONS

Titration of a weak acid having a known and reliable value for the spability constant

Results obtained from titration of acetic acid with sodium hydroxide are given in Table 1. Various reference pH values were used in conjunction with equations (8) for calculation of V_{eq} and (9) and (10) for A and B. The various pH values give equally good results and the analyst can choose a value best suited to his experimental conditions.

Table 1. Titration of acetic acid, CH_3COOH. $C_{OH} = 0{\cdot}05984M$ NaOH, $V_0 = 100{\cdot}0$ ml, $T = 25{\cdot}0°$, $\mu = 0{\cdot}1$ (KNO_3), $\log f_H = -0{\cdot}08$, $\log f_{OH} = -0{\cdot}12$ and $\log K^{H}_{HA} = 4{\cdot}65$. The theoretical value of $V_{eq} = 9{\cdot}43$ ml

pH	A, *ml*	B	V, *ml*	$B.V$, *ml*	V_{eq}, *ml*	Error, %
4·00	1·150	5·478	1·51	8·272	9·42	−0·1
4·20	0·507	3·823	2·34	8·946	9·45	+0·2
4·50	0·161	2·414	3·85	9·294	9·45	+0·2
4·60	0·112	2·123	4·40	9·341	9·45	+0·2
4·70	0·079	1·892	4·95	9·365	9·44	+0·1
5·00	0·030	1·447	6·50	9·406	9·44	+0·1

Titration of weak acids with unknown values for stability constants

Calibration results for hydroxylammonium ion, boric acid and hydrogen ascorbate ion are given in Table 2.

Table 2. Titration of hydroxylammonium ion, $\overset{+}{N}H_3OH$, boric acid, $B(OH)_3$, and hydrogen ascorbate ion, $C_6H_7O_6^-$, with 0·05984*M* NaOH, V_0 = 100·0 ml, T = 25·0°, μ = 0·1 (KNO_3), log f_H = −0·08 and log f_{OH} = −0·12.

$\overset{+}{N}H_3OH$ Theoretical V_{eq} = 13·06 *ml*				$B(OH)_3$ Theoretical V_{eq} = 9·70 *ml*			
pH	*V*, *ml*	*A*, *ml*	B_{ex}	pH	*V*, *ml*	*A*, *ml*	B_{ex}
5·80	4·62	0·011	2·824	8·50	1·78	−0·034	5·469
6·00	6·13	0·005	2·130	8·70	2·54	−0·040	3·835
6·10	6·91	0·004	1·889	9·00	3·99	−0·050	2·444
6·20	7·66	0·003	1·705	9·10	4·52	−0·055	2·158
6·30	8·38	0·002	1·558	9·20	5·09	−0·063	1·918
6·40	9·05	0·001	1·443	9·50	6·67	−0·097	1·469

$C_6H_7O_6^-$ Theoretical V_{eq_1} = 14·04 ml V_{eq_2} = 7·01 *ml*

pH	V_1, *ml*	V_2, *ml*	A_{ex}, *ml*	B_{ex}
11·00	4·65	3·39	−11·904	5·579
11·20	7·17	5·34	−13·504	3·842
11·30	8·88	6·70	−14·596	3·225
11·40	11·03	8·42	−15·669	2·693
11·45	12·28	9·47	−16·682	2·502
11·50	13·70	10·58	−16·829	2·253

In Table 3 results are given for two titrations of hydroxylammonium ion, boric acid and hydrogen ascorbate ion performed to the same pH values as titrations of the same acids in Table 2.

As seen from Table 3, hydroxylammonium ion, boric acid and hydrogen ascorbate ion have been titrated to such a degree of accuracy that the method described in this paper may be regarded as satisfactory. Naturally the method can also be applied when titrating other acids. Even hydrogen ascorbate ion has been titrated with considerable accuracy considering its high stability constant. The difference between the accuracy obtained in titrations (*a*) and (*b*) of hydrogen ascorbate ion is quite understandable and not unusual when titrating such weak acids. It may be noticed from Table 3 that when the titration is performed to a pH much lower than the value of log K_{HA}^{H} for the acid, the error is larger than when a pH near to or greater than log K_{HA}^{H} is used, in accord with the discussion in the theoretical part.

DISCUSSION

The method proposed has several advantages over conventional procedures. First it is fast, since only one titration point is needed. The numerical calculations are easily performed. The equivalence volume can be obtained by multiplication and addition or sub-

Table 3. Titration of hydroxylammonium ion, $\overset{+}{N}H_3OH$, boric acid, $B(OH)_3$, and hydrogen ascorbate ion, $C_6H_7O_6^-$. C_{OH} = 0·05984*M* NaOH. V_0 = 100·0 ml, T = 25·0 and μ = 0·1 (KNO_3)

$\overset{+}{N}H_3OH$

Theoretical $V_{eq(a)}$ = 8·87 ml $V_{eq(b)}$ = 16·28 *ml*

pH	B_{ex}	*A*, *ml*	$V_{(a)}$, *ml*	$V_{eq(a)}$, *ml*	Error, %	$V_{(b)}$, *ml*	$V_{eq(b)}$	Error, %
5·80	2·824	0·011	3·17	8·96	1·0	5·86	16·56	+1·7
6·00	2·130	0·005	4·17	8·89	+0·2	7·71	16·43	+0·9
6·10	1·889	0·004	4·69	8·86	−0·1	8·67	16·38	+0·6
6·20	1·705	0·003	5·20	8·87	0·0	9·60	16·37	+0·6
6·30	1·558	0·002	5·69	8·87	0·0	10·51	16·38	+0·6
6·40	1·443	0·001	6·14	8·86	−0·1	11·33	16·35	+0·4

$B(OH)_3$

Theoretical $V_{eq(a)}$ = 11·35 ml $V_{eq(b)}$ = 9·84 *ml*

pH	B_{ex}	*A*, *ml*	$V_{(a)}$, *ml*	$V_{eq(a)}$, *ml*	Error, %	$V_{(b)}$, *ml*	$V_{eq(b)}$, *ml*	Error, %
8·50	5·469	−0·034	2·10	11·45	+0·9	1·81	9·86	+0·3
8·70	3·835	−0·040	2·97	11·35	0·0	2·58	9·85	+0·1
9·00	2·444	−0·050	4·67	11·36	+0·1	4·05	9·85	+0·1
9·10	2·158	−0·055	5·31	11·40	+0·5	4·62	9·91	+0·8
9·20	1·918	−0·063	5·95	11·35	0·0	5·18	9·87	+0·3
9·50	1·469	−0·097	7·82	11·39	+0·4	6·82	9·92	+0·8

$C_6H_7O_6^-$

Theoretical $V_{eq(a)}$ = 9·56 ml $V_{eq(b)}$ = 13·86 *ml*

pH	B_{ex}	A_{ex}, *ml*	$V_{(a)}$, *ml*	$V_{eq(a)}$, *ml*	Error, %	$V_{(b)}$, *ml*	$V_{eq(b)}$, *ml*	Error, %
11·00	5·579	−11·904	3·85	9·58	+0·2	4·60	13·76	−0·7
11·20	3·842	−13·504	6·01	9·59	+0·3	7·11	13·81	−0·3
11·30	3·225	−14·596	7·55	9·75	+2·0	8·82	13·85	−0·1
11·40	2·693	−15·669	9·37	9·56	0·0	11·00	13·95	+0·7
11·45	2·502	−16·682	10·50	9·59	+0·3	12·25	13·97	+0·8
11·50	2·253	−16·829	11·73	9·60	+0·4	13·60	13·81	−0·3

traction according to equations (8) or (13) or (17). The error is comparable to that of other methods.

The method can be used in chemical industry, *e.g.*, in control laboratories where fast and reliable analysis is required. In processes where flowing acids or bases are continuously analysed an automatic titrator using the method could be directly connected to a data-logger conveying titration data to a process computer.

One of the advantages of the method is that the equivalence volume can be determined even at pH values lower than that at the equivalence point, and disturbing equilibria and reactions which may occur at high pH, *e.g.*, if the strong base is not free from carbonate, can be avoided.

EXPERIMENTAL

Apparatus

A digital pH-meter (Beckman "Digital", discrimination 0·003 pH units) was used with a Beckman glass electrode (pH 0–14, factory-guaranteed) and calomel electrode. The pH measuring system was calibrated with standard potassium hydrogen phthalate buffer, pH = 4·01 at 25°, for pH < 7 and standard borax buffer, pH = 9·18 at 25°, for pH > 7. This calibration is essential to obtain reproducible results.

Reagents

The sodium hydroxide solution was prepared from reagent grade "Titrisol" (Merck), special care being taken to ensure that the solution was free from carbonate. All other chemicals were also of Merck reagent grade. Metrohm piston burettes (5 and 10 ml) were used, and the initial volume was measured by pipette. The titration beaker temperature was thermostatically controlled at 25·0 ± 0·1°. Weight burettes were used for determining the initial concentrations of the acids from which the theoretical consumptions were calculated.

Procedure

The titrations were performed in a closed beaker under a nitrogen atmosphere if the reference pH value was higher than 7, and before the titration nitrogen was passed through the solution for 15 min in order to remove dissolved carbon dioxide. The titration solutions were continuously stirred with a magnetic stirrer.

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Zusammenfassung—Ein neuer Weg zur Verkürzung der zu einer Säure-Basen-Titration benötigten Zeit wurde beschritten. Die entwickelte Methode beruht auf der von Ingman und Still abgeleiteten Gleichung für Säure-Basen-Titrationen. Die Gleichung wird in eine solche Form gebracht, daß zur Berechnung des Äquivalentvolumens nur ein Titrationspunkt benötigt wird, wenn man die Titration bis zu einem festgelegten pH-Wert führt, der den Versuchsbedingungen entsprechend gewählt werden kann. Das Verfahren wird zur Titration von Essigsäure, log K^{H}_{HA} = 4,65, Hydroxylammonium-Ion, log K^{H}_{HA} ~ 6,2, und Borsäure, log K^{H}_{HA} ~ 9,1, mit einem Fehler von 0,1–0,5% verwendet. Bei der Titration des Hydrogenascorbat-Ions, log K^{H}_{HA} ~ 11,3, betrug der Fehler 0,3–2%.

Résumé—On a effectué un nouveau progrès pour diminuer le temps nécessaire à un titrage acide-base. La méthode développée est basée sur l'équation pour les titrages acide–base établie par Ingman et Still. L'équation est transformée dans une forme telle qu'un point de titrage seulement est nécessaire pour calculer le volume équivalent quand le titrage est mené à un pH fixé qui peut être choisi selon les conditions expérimentales. La méthode est utilisée pour le titrage de l'acide acétique, log K^{H}_{HA} = 4,65, de l'ion hydroxylammonium, log K^{H}_{HA} ~ 6,2 et de l'acide borique, log K^{H}_{HA} ~ 9,1, avec une erreur de 0,1–0,5%. Dans le titrage de l'ion hydrogène ascorbique, log K^{H}_{HA} ~ 11,3, l'erreur obtenue est d'environ 0,3–2%.

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RAPID DETERMINATION OF THE EQUIVALENCE VOLUME IN POTENTIOMETRIC ACID–BASE TITRATIONS TO A PRESET pH—II*

STANDARDIZING A SOLUTION OF A STRONG BASE, GRAPHIC LOCATION OF EQUIVALENCE VOLUME, DETERMINATION OF STABILITY CONSTANTS OF ACIDS AND TITRATION OF A MIXTURE OF TWO WEAK ACIDS

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Summary—A newly proposed method of titrating weak acids with strong bases is applied to standardize a solution of a strong base, to graphic determination of equivalence volume of acetic acid with an error of 0·2%, to calculate the stability constants of hydroxylammonium ion, boric acid and hydrogen ascorbate ion and to analyse a mixture of acetic acid and ammonium ion with an error of 0·2–0·7%.

This paper presents further applications of the method described in Part I.[1]

STANDARDIZING A SOLUTION OF A STRONG BASE

In Part I, the constants *A* and *B* used for determining equivalence volumes were calculated according to equations (1) and (2). Careful choice of the pH to which the titration is to be performed simplifies these equations to a certain degree.

$$A = \frac{V_0}{C_{OH}}([H] - [OH])(1 + \{H\} \cdot K^{H}_{HA}) \tag{1}$$

$$B = \{H\} \cdot K^{H}_{HA} + \frac{1}{C_{OH}}([H] - [OH])(1 + \{H\} \cdot K^{H}_{HA}) + 1 \tag{2}$$

When acetic acid is titrated, the value of the constant *A* decreases with increasing pH,[1] and the middle term in equation (2) influences the value of the constant *B* less and less as the pH is increased. If acetic acid is titrated to pH values over 5 the constant *A* and the middle term in equation (2) can be disregarded and equation (7) from Part I is simplified to

$$V_{eq} = (\{H\} \cdot K^{H}_{HA} + 1) \cdot V \tag{3}$$

Equation (3) does not include the term C_{OH}, *i.e.*, the equivalence volume can be determined without knowing the concentration of the titrant base. Equation (3) is useful when an unknown solution of a strong base is to be standardized. Data from such a titration are given

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* Part I: *Talanta*, 1974, **21**, 377

Table 1. Standardizing a solution of KOH against acetic acid. Taken: 47·0 mg of CH_3COOH, $V_0 = 50{\cdot}0$ ml, $T = 25{\cdot}0°$, $\mu = 0{\cdot}1$ (KCl) and $\log K^{H}_{HA} = 4{\cdot}65$

pH	$\{H\}.K^{H}_{HA} + 1$	V, *ml*	V_{eq} *ml*	C'_{OH}, *M*	C_{OH}, *M*
5·30	1·224	6·35	7·772	0·1007	0·1006
5·40	1·178	6·60	7·775	0·1007	0·1006
5·50	1·141	6·82	7·782	0·1006	0·1006

in Table 1. A solution of potassium hydroxide is standardized against a known amount of acetic acid. V_{eq} in the fourth column is calculated according to equation (3). The corresponding concentration of the base is denoted by C'_{OH}. If a high degree of accuracy is sought, the constants A and B can be calculated according to equations (1) and (2) with the value of C'_{OH}. A more accurate value of the equivalence volume can then be determined by equation (4), which is (8) in Part I,[1]

$$V_{eq} = B \cdot V + A \tag{4}$$

and the concentration more exactly obtained. The C_{OH} values calculated by using such an iteration are also given.

The same potassium hydroxide solution was also standardized six times against potassium hydrogen phthalate by conventional titration methods. The value obtained was $C_{OH} = 0{\cdot}1004 \pm 0{\cdot}0002\,M$. The value given in Table 1 agrees well with this one.

GRAPHIC DETERMINATION OF THE EQUIVALENCE VOLUME

Equation (4) describes a straight line when V_{eq} is plotted against V. The line has a slope of B and intersects the V_{eq}-axis at A. Different reference pH values give lines with different values for A and B. A series of such lines can be plotted for different acids. The direct ratio between A and V_0/C_{OH} is seen in equation (1). In the expression for B, equation (2), the middle term has only a slight influence on the value of B, especially if points with pH <4 and >10 or very low values of C_{OH} are avoided. A slight variation in the value of C_{OH} does not change the value of B to any great degree. It therefore follows that if lines for different reference pH values are plotted according to equation (4) for certain values of V_{OH} and C_{OH}, lines for the same pH value can be constructed for other values V''_0 and C''_{OH} obtained by using

$$B'' \sim B \tag{5}$$

$$A'' = \frac{V''_0}{C''_{OH}} \cdot \frac{C_{OH}}{V_0} A \tag{6}$$

In Fig. 1 the data in Table 1 in Part I[1] for titration of acetic acid, are treated graphically. The lines according to equation (4) are plotted for different values of pH, the values of A and B valid for $V_0 = 100{\cdot}0$ ml and $C_{OH} = 0{\cdot}05984\,M$ being used. From these lines new ones are constructed for another titration of acetic acid where $V_0 = 50{\cdot}25$ ml and $C_{OH} = 0{\cdot}1004\,M$ and are also shown in Fig. 1. The data from this titration are given in Table 2.

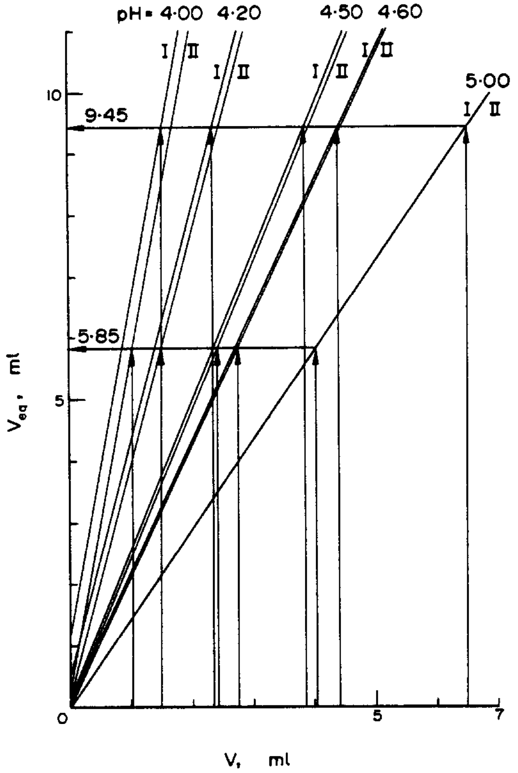

Fig. 1. Graphic determination of equivalence volumes in the titrations of acetic acid given in (**I**) Table 1 of Part I and (**II**) Table 2 of this Part. The lines **II** corresponding to the titration given in Table 2 are constructed from the lines **I**. In titration **I** $V_0/C_{OH} = 10^{0\cdot22}$ l.^{2}/mole and in **II** $V_0/C_{OH} = 10^{-0\cdot30}$ l.^{2}/mole. Theoretical $V_{eq_I} = 9{\cdot}43$ ml and $V_{eq_{II}} = 5{\cdot}84$ ml.

As seen in Fig. 1 the equivalence volume can easily be determined if lines drawn according to equation (4) are plotted in advance (even one of them will suffice). The lines can be replotted for other values of V_0 and C_{OH} and quite accurate results are obtained even then (Fig. 1). It may be noted, furthermore, that with increasing pH the difference between the two lines for the same pH, *i.e.*, two different values of V_0/C_{OH}, decreases. The difference between the two lines when pH = 4·6 is very small, and when pH = 5·0 they cannot be plotted separately in spite of the large difference between the ratios of V_0/C_{OH}. It may be concluded that when acetic acid is titrated to pH over 4·6, although V_0 and C_{OH} vary slightly from one titration to another, only one line is needed for determining the equivalence volumes in routine analysis. With increasing pH the slope of the lines in Fig. 1 decreases and approaches 1 as discussed in Part I.[1]

Table 2. Titration of acetic acid with 0·1004 *M* KOH, $V_0 = 50{\cdot}25$ ml, $T = 25{\cdot}0^\circ$ and $\mu = 0{\cdot}1$ (KCl). Theoretical $V_{eq} = 5{\cdot}84$ ml

pH	4·00	4·20	4·50	4·60	5·00
V, ml	1·01	1·49	2·40	2·74	4·04

DETERMINATION OF THE STABILITY CONSTANTS OF ACIDS

The method formulated in this series of papers for titrating weak acids can also be used to determine their stability constants. The value of B_{ex} given in Table 2 of Part I[1] can be used. The expression for B_{ex} is actually the same as for the constant B:

$$B_{ex} = \{H\} \cdot K^{H}_{HA} + \frac{1}{C_{OH}}([H] - [OH])(1 + \{H\} \cdot K^{H}_{HA}) + 1 \tag{7}$$

By performance of a calibration titration in order to obtain the constant B_{ex}, the stability constant of the acid under the conditions of the experiment is determined. Equation (7) can be solved for K^{H}_{HA}:

$$K^{H}_{HA} = \frac{B_{ex} - 1 - \frac{1}{C_{OH}}([H] - [OH])}{\{H\}[1 + \frac{1}{C_{OH}}([H] - [OH])]} \tag{8}$$

When the values of B_{ex} given in Table 2 of part I[1] are used and K^{H}_{HA} is calculated for the corresponding pH, the values in Table 3 are obtained. These values are in reasonable agreement with the literature values,[2] the difference for hydrogen ascorbate ion being not unusual for work with very weak acids.

Table 3. Mixed stability constants of hydroxylammonium ion, $\overset{+}{N}H_3OH$, boric acid, $B(OH)_3$, and hydrogen ascorbate ion, $C_6H_7O_6^+$, determined at $T = 25{\cdot}0°$, $\mu = 0{\cdot}1$ (KNO_3) and according to equation (8)

	$\overset{+}{N}H_3OH$		$B(OH)_3$		$C_6H_7O_6^+$	
	pH	log K^{H}_{HA}	pH	log K^{H}_{HA}	pH	log K^{H}_{HA}
	5·80	6·06	8·50	9·15	11·00	11·67
	6·00	6·05	8·70	9·15	11·20	11·67
	6·10	6·05	9·00	9·16	11·30	11·68
	6·20	6·05	9·10	9·16	11·40	11·67
	6·30	6·05	9·20	9·16	11·45	11·67
	6·40	6·05	9·50	9·17	11·50	11·65
Literature value[2]		6·2		9·1		11·3

It should be emphasized that the values given in Table 3 are determined on the basis of one titration, which explains the small dispersion between individual values.

TITRATION OF A MIXTURE OF TWO WEAK ACIDS

The method described in this series of papers can also be applied to titration of two acids in the same solution. The titration is first performed to a pH value at which the weaker of the acids is not dissociated. The volume of titrant added is used to titrate part of the stronger acid and the equivalence volume can be determined according to equation (4) or (9) [equation (13) of Part I[1]].

$$V_{eq} = B_{ex} \cdot V + A \tag{9}$$

The titration is then continued to a pH suitable for analysing the weaker acid. Subtraction of the previously determined equivalence volume of the stronger acid from the value of

V obtained for the second pH gives the volume of titrant consumed in titrating part of the weaker acid. By using equation (4) or (9) or (10) [equation (17) in Part I[1]],

$$V_{eq} = B_{ex} \cdot V + A_{ex} \tag{10}$$

depending on the particular case, the equivalence volume of the weaker acid can be determined. If the stronger acid has not been completely titrated at the second pH the value of V used for determining the equivalence volume of the weaker acid will be too large and lead to a false result. The second pH therefore must be higher than the pH corresponding to the equivalence volume of the stronger acid. This drawback means that the method can only be applied if the difference between the constants of the acids is at least four orders of magnitude.

The feasibility of this method has been tested by titrating a solution containing acetic acid and ammonium ion. As has been emphasized in Part I[1], the titration error can be quite large if the chosen pH is much lower than the value of log K^{H}_{HA} of the acid. The titration may first be performed to a pH near the value of log K^{H}_{HA} of acetic acid, *e.g.*, pH = 4·60, and then to pH = 9·40, *i.e.*, approximately the value of log K^{H}_{HA} of ammonium ion. A calibration titration was carried out in order to determine the constant B_{ex} for ammonium ion at this pH. The data from that titration as well as the corresponding B_{ex} determined according to equation (12) of Part I[1] are given in Table 4. In calculating the constant A an approximate value of log K^{H}_{HA} = 9·4 was used.

Table 4. Determination of B_{ex} for ammonium ion at pH = 9·40, C_{OH} = 0·1004 M KOH, V_0 = 51·0 ml, T = 25·0° and μ = 0·1 (KCl). Theoretical V_{eq} = 9·30 ml

pH	A, *ml*	V, *ml*	B_{ex}
9·40	−0·034	4·83	1·933

Calculation of log K^{H}_{HA} according to equation (8) from the value of B_{ex} given in Table 4 gave a value of log K^{H}_{HA} = 9·37. This is precisely the value given in the literature.[2]

Data from two titrations of a solution of acetic acid and ammonium ion with a strong base are given in Table 5. For calculating the equivalence volume of acetic acid according to equation (4) the value of B given in Table 1 of Part I was used. The constant A was recalculated to allow for the new ratio V_0/C_{OH}. For calculation of the equivalence volume for the ammonium ion, the values of A and B_{ex} given in Table 4 are used with equation (9).

The error in the equivalence volume of acetic acid is rather too large, but the ammonium ion can be titrated with quite a good degree of accuracy. The result of the whole titration depends on the accuracy with which the equivalence volume of the stronger acid is determined, since any error will influence the calculation of the equivalence volume of the weaker acid. In the titrations given in Table 5 the error in V_{eq} of acetic acid has probably been compensated by another error when pH = 9·40, or the ammonium ion would not have been determined so accurately.

The method described can hardly be used when more than two acids have to be determined in the same solution. In titration of a mixture of three acids the difference between

Table 5. Titration of a mixture of two weak acids, acetic acid (1) and ammonium ion (2), with 0·1004 M KOH, $V_0 = 51{\cdot}2$ ml, $T = 25{\cdot}0^{\circ}$ and $\mu = 0{\cdot}1$ (KCl)

Theoretical	(a) (b)	$V_{eq_1} = 3{\cdot}60$ *ml* $V_{eq_1} = 5{\cdot}45$ *ml*			$V_{eq_2} = 4{\cdot}77$ *ml* $V_{eq_2} = 3{\cdot}15$ *ml*	
pH	V, *ml*	B	A, *ml*	V_{eq_1}, *ml*	Error, %	
(a) 4·60	1·70	2·123	0·034	3·64	+1·1	
(b)	2·57			5·49	+0·7	
pH	V, *ml*	$(V - V_{eq_1})$, *ml*	B_{ex}	A, *ml*	V_{eq_2}, *ml*	Error, %
(a) 9·40	6·13	2·49	1·933	−0·034	4·78	+0·2
(b)	7·14	1·65			3·16	+0·3

the constants of the strongest and the weakest acids has to be at least 8 orders of magnitude before the method can be applied. Its feasibility in such cases is therefore questionable and such an analysis could succeed only with certain acids.

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Zusammenfassung—Ein neu vorgeschlagenes Verfahren der Titration schwacher Säuren mit starken Basen wird zur Einstellung einer Lösung einer starken Base, zur graphischen Bestimmung des Äquivalentvolumens von Essigsäure mit einem Fehler von 0,2%, zur Berechnung der Stabilitätskonstanten des Hydroxylammonium-Ions, der Borsäure und des Hydrogenascorbat-Ions sowie zur Analyse eines Gemisches von Essigsäure und Ammoniumionen mit einem Fehler von 0,2–0,7% benutzt.

Résumé—On utilise une méthode nouvellement proposée de titrage d'acides faibles avec des bases fortes pour étalonner une solution d'une base forte, pour une détermination graphique du volume d'équivalence de l'acide acétique avec une erreur de 0,2%, pour calculer les constantes de stabilité de l'ion hydroxylammonium, de l'acide borique et de l'ion hydrogène ascorbique, et pour analyser un mélange d'acide acétique et d'ion ammonium avec une erreur de 0,2–0,7%.

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AUTOMATIC CLASSIFICATION OF CHEMICAL BEHAVIOUR BY SEQUENTIAL HYPOTHESIZATION, MULTIPARAMETRIC CURVE-FITTING, AND DEVIATION-PATTERN RECOGNITION—I

FULLY COMPUTERIZED EVALUATION OF THE FUNCTIONALITY OF A BASE FROM TITRATION-CURVE DATA

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Summary—A completely automatic procedure is described for evaluating the functionality j of a base from the potentiometric titration curve obtained on titration with standard acid. It involves successive hypotheses that $j = 1, 2, \ldots$, fits to the corresponding titration-curve equations, and scrutiny of the resulting deviation patterns. Logical decisions are based on both the existence and position of a region in which the deviations are much larger than the estimated standard error of measurement.

It is often necessary to classify a substance or its behaviour on the basis of numerical data, and much scientific work would be facilitated if this could be done automatically. There are three common possibilities. In the simplest, the classification is binary and consists of deciding whether the substance behaves in a certain way or not. In another, the classification might be termed "linear" and is equivalent to seeking the value of some physically significant cardinal number, which might be the number of successive complexes formed by adding ligand groups to a metal ion or the number of acidic or basic functional groups in a molecule. In the third, which might be termed "branched", there is no *a priori* way of arranging all the successive hypotheses in order and the nature of the systematic errors associated with one hypothesis may influence the selection of one or another alternative as the next to be tested.

This paper describes an example of linear classification based on deviation-pattern recognition and effected without human intervention. The problem considered, the evaluation of the functionality of a base with the aid of potentiometric titration-curve data, has been discussed in detail by Meites and Barry,[1] who outlined the deviation-pattern recognition-scheme employed here. The automated decision-making procedure outlined here should be applicable to any linear classification.

Procedures for elucidating the formulas and dissociation constants of hydroxo and other complexes in solution are well known and some have been more or less completely automated.[2-4] A linear classification procedure in which decisions are based on the signs of the formation constants calculated on the bases of successive hypotheses has been described by Piljac, Grabarić, and Filipović[5] for elucidating the number of successive complexes between a ligand and a metal ion, a problem that has received much attention for many years. Classical statistics prescribes comparing the standard deviations obtained from regression on the various equations describing the models considered, but may not give unambiguous answers; when this was done for the present data the balance of probability appeared to be that acetate ion is difunctional, succinate ion trifunctional, and citrate ion about equally likely to be tetra- or pentafunctional. None of these conclusions was accompanied by a confidence level exceeding 0·7, but all are chemically absurd. The present procedure takes the natures of the deviations as well as their magnitudes into account and, when properly used, yields the correct results.

The problem may be stated as follows: if a potentiometric neutralization curve shows only a single point of maximum slope and if no other information is available, how many acidic or basic functional groups does the substance contain? There may be only one, or there may be two or more for which the acidic or basic dissociation constants are so nearly equal that inflections at all of the successive equivalence points, excepting only the last, are either impossible to discern or non-existent. For a difunctional substance Roller[6] showed that there is only one point of maximum slope if K_1/K_2 is less than 27.

EXPERIMENTAL

Data were obtained from titrations of acetate, succinate, and citrate with standard hydrochloric acid. The data for acetate were obtained by Mrs. D. M. Barry in titrations of 0·0993M potassium acetate with 1·057M hydrochloric acid. Solutions containing accurately weighed amounts of disodium succinate (0·05M) or trisodium citrate (0·03M) and having accurately known initial volumes were titrated in exactly the same way and under exactly the same conditions. Every solution contained enough potassium chloride to bring its ionic strength to 3·00M, and all of the experimental conditions were identical with those described by Barry and Meites.[7] Usually about 20 data points, evenly spaced along the volume axis between 5 and 120% of the volume of acid required to reach the point of maximum slope, were employed.

COMPUTATIONS

All the computations were performed on a Digital Equipment Corp. (Maynard, Massachusetts) PDP8/I computer operated in an early version of EduSystem 25 BASIC and in a multi-user configuration that provided 4096 words of user area for this work. This sufficed for operation with about 40 data points in the worst case, where the tetrafunctional hypothesis is examined *en route* to the final conclusion.

The programme* embodies the main elements of a general multiparametric curve-fitting programme,[8] from which flexibility unnecessary in the present application was removed. Input to it includes the co-ordinates of the data points, the estimated standard error of measurement (σ) of a single pH-value, and the value of the apparent activity coefficient of hydrogen ion in the titration medium employed. The last of these is obtained from prior titrations of known bases in the same medium;[7] provision may be made for evaluating it in each successive fit but at the expense of consuming much more computer time.

Preliminary estimates of C_b^0, the initial concentration of base titrated, and K_a, the conditional dissociation constant of its conjugate acid, are first obtained, assuming the base to be monofunctional, from the location of the point of maximum slope and the interpolated pH-value halfway to that point. A preliminary test of the monofunctional hypothesis

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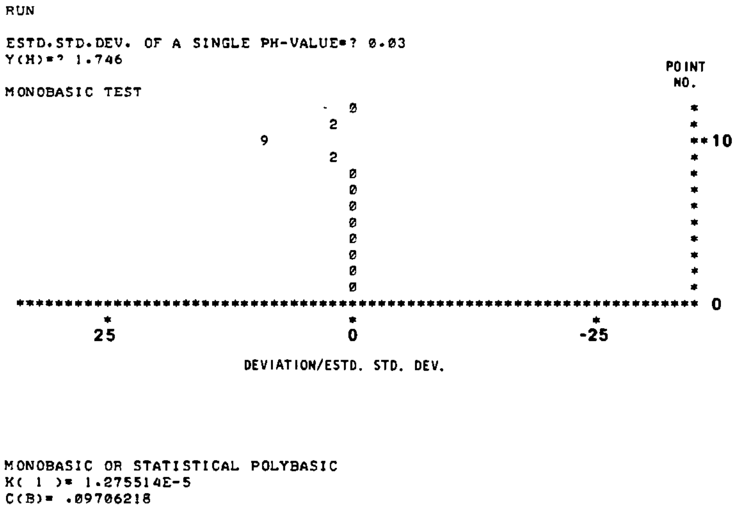
* Punched paper-tape and hard-copy listings of the programme BASTEC, with brief directions for use, may be obtained by remitting $4.00, to defray the costs of duplication and postage, to the Computing Laboratory of the Department of Chemistry of Clarkson College of Technology, Potsdam, New York 13676. A copy of the parent curve-fitting programme CFT3, accompanied by a 112-page manual of explanation and instruction, and with listings in POLYBASIC and FORTRAN-IV, may be obtained in addition for a remittance of $8.00.

is made by using these values to compute the pH at each experimental point and thence the quantity R defined by

$$R = (\mathrm{pH}_{\mathrm{meas}} - \mathrm{pH}_{\mathrm{calc}})/\sigma$$

To provide a visual indication of the progress of the computation, R is plotted against the ordinal number of the data point; with points evenly spaced along the volume axis, this plot has the same shape as the deviation pattern. A typical plot for acetate, assuming $\sigma = 0{\cdot}03$ pH-unit, is shown in Fig. 1.



```
RUN

ESTD.STD.DEV. OF A SINGLE PH-VALUE=? 0.03
Y(H)=? 1.746

MONOBASIC TEST
```

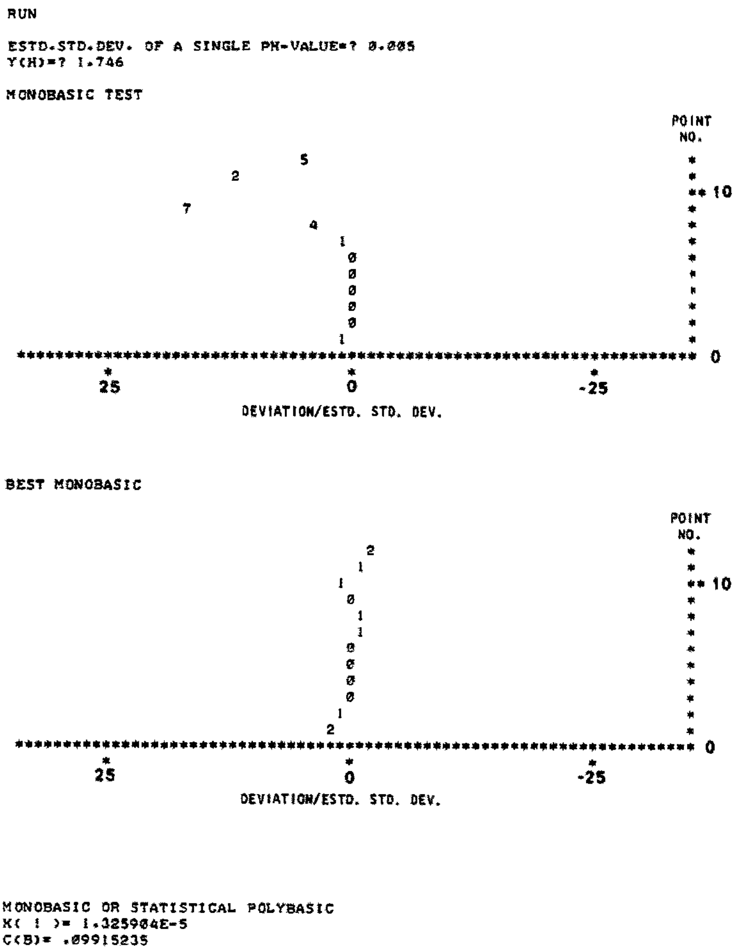
```
MONOBASIC OR STATISTICAL POLYBASIC
K( 1 )= 1.275514E-5
C(B)= .09706218
```

Fig. 1. Print-out obtained with data from a typical titration of acetate with $\sigma = 0{\cdot}03$ pH-unit. Each number appearing on the deviation-pattern plot is the units digit of the absolute value of R, so that a "5" corresponds to $R = \pm 5$, ± 15, or ± 25.

One of two things must be true: either there are deviations that are both large and systematic, or there are not. Large and systematic deviations are considered to be present if there are n consecutive points for which $|R|$ exceeds 3 and for which R has the same sign: the required number n is arbitrarily taken as int(N1/10) + 1, where N1 is the number of data points. If the preliminary estimates of C_{b}^{0} and K_{a} were exact and if there were no systematic error involved in the monofunctional hypothesis, the probability of occurrence of large systematic deviations (as defined above), which is $\mathrm{N1}(\mathrm{erfc}\ R)^{n}/2^{n-1}$, would be only about 3×10^{-5} even if n were only 2, as it would be if there were only 10–15 data points.

The probability that large systematic deviations will appear at this stage, even though the base is monofunctional, far exceeds the result of this calculation because neither of the preliminary estimates is likely to be exact. In Fig. 1 there is a deviation of 9σ at point number 10, which is the nearest one to the equivalence point, because the preliminary estimate of C_{b}^{0} is in error by about 2%. Nevertheless it is often possible to identify a base as monofunctional at this point, especially when σ is fairly large, which of course means that the monofunctional hypothesis will account for any titration curve if the data are sufficiently imprecise.

When, for the same data, σ is assigned any value between 0·0025 and 0·025 unit, the preliminary estimates do not produce an acceptable fit to the monofunctional hypothesis,



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RUN

ESTD.STD.DEV. OF A SINGLE PH-VALUE=? 0.005
Y(H)=? 1.746

MONOBASIC TEST
```

```
BEST MONOBASIC
```

```
MONOBASIC OR STATISTICAL POLYBASIC
K( 1 )= 1.325904E-5
C(B)= .09915235
```

Fig. 2. Print-out obtained from the data in Fig. 1 with $\sigma = 0{\cdot}005$ pH-unit. The values of K_a and C_b^0 given at the bottom of this figure were obtained from the best fit to the monofunctional hypothesis, whereas those in Fig. 1 are the initial crude estimates based on the same hypothesis.

as is shown by the upper half of Fig. 2. A two-parameter fit to the appropriate titration-curve equation is initiated to refine the estimates of C_b^0 and K_a. The refined values are used to obtain a new deviation pattern like the one in the lower half of Fig. 2, and this is scrutinized both to identify the existence of a group of points corresponding to large systematic deviations as defined above, and to find the location of the earliest such group.

There are now four possibilities. If (1) there is no such group of points, the monofunctional hypothesis is accepted, the values of C_b^0 and K_a obtained from the fit are printed, and execution terminates. If there is, the first such group may (2) occur at or near the beginning of the titration and R may be positive, (3) occur at or near the beginning of the titration and R may be negative, or (4) occur only after half or two-thirds of the equivalent volume of acid has been added. Case (2) corresponds to a polyfunctional base for which the ratios of successive dissociation constants exceed the statistical values,[9] case (3) corresponds to a polyfunctional base for which these ratios are smaller than the statistical values, and case (4) corresponds to a logical contradiction that is discussed in a later paragraph.

In cases (2) and (3) the monofunctional hypothesis is replaced by the difunctional one. New estimates of C_b^0 and of K_1 and K_2 (based on the interpolated pH-values at points three-quarters and one-quarter, respectively, of the way from the start of the titration to the point of maximum slope) are made and used to construct a preliminary deviation pattern based on the equations that describe the titration of a difunctional base. If this does not contain large systematic deviations the difunctional hypothesis is accepted; if it does, the estimates of C_b^0, K_1, and K_2 are refined by a three-parameter fit, and so on.

Although the process could be continued for as many successive hypotheses as could be manipulated in the user area available, there are so few tetra- and higher-functional bases for which the successive stages of neutralization overlap too much to be resolved by any less stringent analysis that the programme ends at the point where the trifunctional hypothesis has been either accepted or definitely rejected.

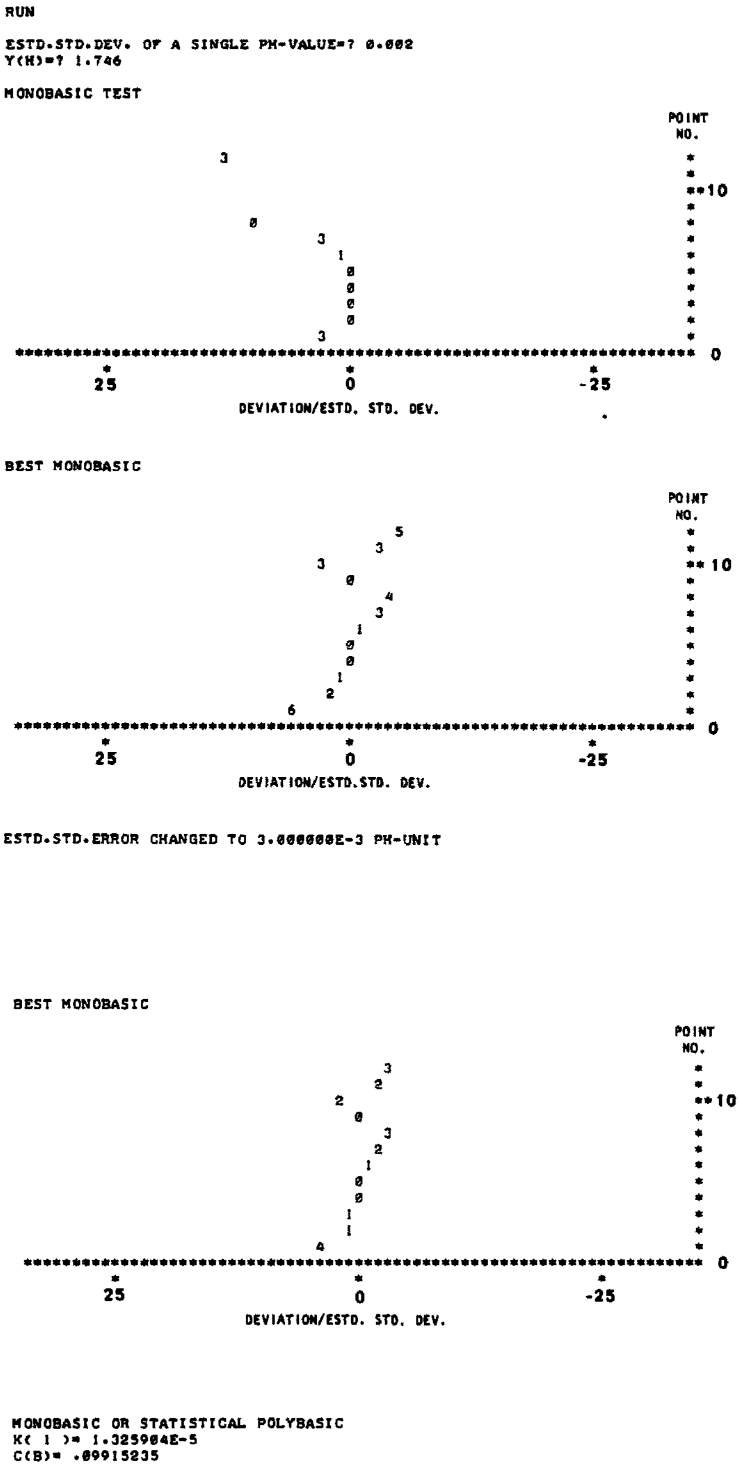
RESULTS AND DISCUSSION

The standard error of measurement of a single pH-value was believed to be approximately 0·003 pH-unit. With that value of σ, or any other between 0·001 and 0·0075 pH-unit, acetate, succinate, and citrate were correctly classified with data from every titration performed.

Acetate could not be wrongly classified with any value of σ down to 0·0005 pH-unit, but Occam's razor was less forgiving with the other bases. Succinate was classified as monobasic if σ was assigned any value above 0·06 pH-unit, while citrate was classified as monofunctional if σ equalled or exceeded 0·15 pH-unit and as difunctional if σ lay between 0·008 and 0·1 pH-unit. In all automatic classification schemes, branched as well as linear, an erroneous overestimate of the standard error of measurement will entail the danger of accepting a hypothesis simpler than the truth.

One might expect an erroneous underestimate to have the opposite effect, but this danger can be minimized by establishing two different criteria for the rejection of a hypothesis. The aim is to raise the possibility of a logical contradiction like the one illustrated by Fig. 3. Here the data and input were identical with those for Figs. 1 and 2 except that the standard error of measurement was deliberately assigned an erroneously low value. The best fit to the monofunctional hypothesis now gives deviations as large as 6σ. Hence the monofunctional hypothesis cannot be accepted, but neither can any polyfunctional one because it would give rise to large systematic deviations near the start of the titration and these are not observed. This is the situation identified above as case (4), and the two criteria by which it is recognized are (1) the existence of a group of aberrant deviations (2) in a region that cannot be accounted for by any subsequent hypothesis. It may be resolved by increasing the estimated value of σ and retesting the prior hypotheses, beginning with the first. Occasional misclassifications are still possible if the original underestimate of σ is gross: in some titrations citrate was classified as tetrafunctional if σ was assigned a value as small as 0·0005 pH-unit, but the more usual course resembles that shown in Fig. 3 and produces both a reasonable estimate of σ and the correct classification.

This is a useful result and one that can probably be obtained in any linear-classification scheme, but several dangers must be emphasized. The programme's library of hypotheses must not only be complete but must contain one hypothesis beyond the last acceptable one. There must be no appreciable systematic deviations, of either chemical or instrumental origin, from the correct hypothesis. Any revision of the estimate of σ, if that estimate



```
RUN

ESTD.STD.DEV. OF A SINGLE PH-VALUE=? 0.002
Y(H)=? 1.746

MONOBASIC TEST

BEST MONOBASIC

ESTD.STD.ERROR CHANGED TO 3.000000E-3 PH-UNIT

BEST MONOBASIC

MONOBASIC OR STATISTICAL POLYBASIC
K( 1 )= 1.325904E-5
C(B)= .09915235
```

Fig. 3. Print-out obtained from the data in Fig. 1 with $\sigma = 0{\cdot}002$ pH-unit.

has been knowledgeably and carefully made, should prompt a thorough re-examination of the chemistry of the system and the instrumentation and technique employed, and an unacceptably large final value must be understood to mean either that the system obeys some equation not included in the programme or that some essential experimental condition has not been met.

Although automated data-acquisition is now taken for granted, the notion that any classification more complex than a binary one can be effected without human intervention is more difficult to accept. Nevertheless, the success of the present scheme in discriminating among titration curves that are indistinguishable on visual inspection leads us to believe that this general approach is potentially a very powerful aid in the interpretation of scientific data.

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Zusammenfassung—Ein vollautomatisches Verfahren zur Ermittlung der Wertigkeit j einer Base aus der durch Titration mit eingestellter Säure erhaltenen potentiometrischen Titrationskurve wird beschrieben. Dabei wird nacheinander angenommen, daß $j = 1,2,\ldots$, beträgt, die entsprechenden TTitrationskurvenGleichungen werden an die Meßdaten angepaßt und die Abweichungen, die sich ergeben, systematisch untersucht. Logische Entscheidungen werden darauf aufgebaut, daß und wo ein Gebiet existiert, in dem die Abweichungen wesentlich größer sind als die geschätzte Standard abweichung der Messung.

Résumé—On décrit une technique entièrement automatique pour évaluer la fonctionnalité j d'une base à partir de la courbe de titrage potentiométrique obtenue par titrage avec un acide étalon. Elle comprend les hypothèses successives que $j = 1,2,\ldots$, s'adapte aux équations de courbe de titrage correspondantes, et l'examen minutieux des diagrammes de déviation qui en résultent. Les décisions logiques sont basées à la fois sur l'existence et la position d'une région dans laquelle les déviations sont beaucoup plus grandes que l'erreur de mesure type estimée.

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APPLICATIONS OF ENZYME-CATALYSED REACTIONS IN TRACE ANALYSIS—VII*

DETERMINATION OF LEAD AND INDIUM BY THEIR INHIBITION OF ISOCITRATE DEHYDROGENASE

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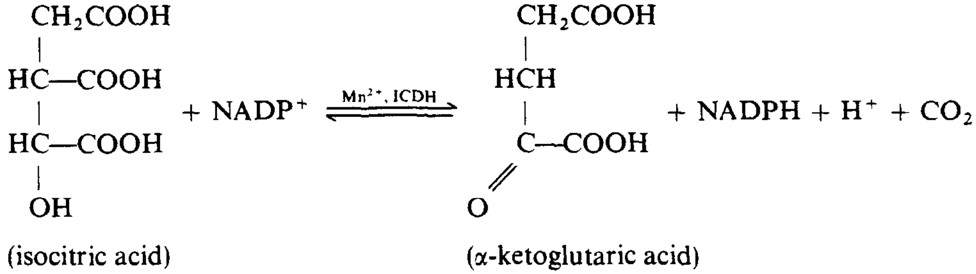
Summary—The inhibition of isocitrate dehydrogenase by lead, indium and calcium has been studied. Methods for the determination of 0·024–1 μg of lead and indium, based on this inhibition, are outlined. Lead may be separated from some interfering ions by extraction with tributyl phosphate in isobutyl methyl ketone, before application of the enzymic reaction.

Isocitrate dehydrogenase [isocitrate:NADP oxidoreductase (decarboxylating), EC. 1.1.1.42], ICDH, catalyses the oxidative decarboxylation of isocitrate to α-ketoglutarate. A nicotinamide nucleotide is the co-enzyme used as the oxidant and a doubly-charged cation such as Mg^{2+} or Mn^{2+} is required to activate the enzyme:



(isocitric acid) (α-ketoglutaric acid)

The reaction proceeds from isocitrate to α-ketoglutarate through an enzyme-bound oxalosuccinate intermediate.[1]

There are two isocitrate dehydrogenases.[2] One requires NADP as its co-enzyme whereas the other requires NAD. The enzyme used in the present study is the purified NADP-linked enzyme, obtained from pig's heart,[3-5] molecular weight 61 × 10^3. It is inhibited by a wide range of metal ions,[6] and is activated by manganese(II), magnesium, cobalt(II) and zinc ions.[6] The enzyme has been used to determine μg amounts of magnesium in blood serum[7] and ng amounts of manganese,[8] by means of their activation property. An interesting method of titrating a sequence of metal ions (including Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+}) with EDTA, using the activation and inhibition effects to follow the progress of the titration, has also been developed, using this enzyme.[6]

Earlier workers showed that ICDH was inhibited by ng amounts of a number of metal ions. This paper reports an investigation of the inhibitory effects of lead, indium and calcium on ICDH, with a view to developing sensitive methods for the determination of these

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* Part VI: *Talanta*, 1970, 17, 299

elements. As many other ions would interfere in such determinations, either by inhibiting or activating the enzyme, attempts are made to utilize chemical separation techniques to improve selectivity.

In the discussion that follows, all metal ion concentrations refer to the final solution in which the enzyme-catalysed reaction takes place, unless otherwise indicated.

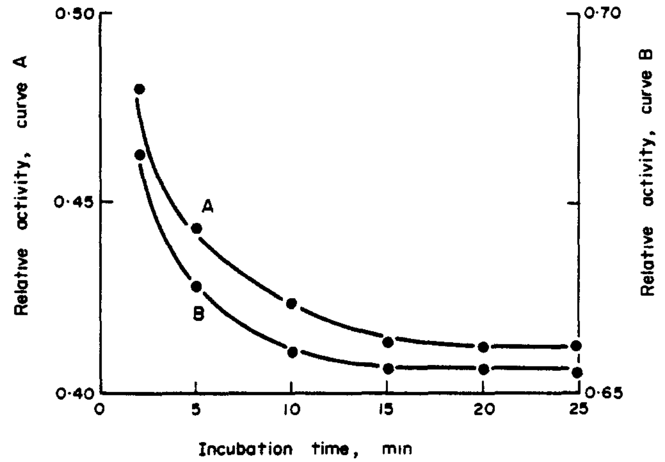

Fig. 1. Effect of incubation time of ICDH with (*A*) 20 ng of Pb^{2+} per ml in pH 8·5 tris buffer and (*B*) with 20 ng of In^{3+} per ml in unbuffered water.

INVESTIGATION OF EXPERIMENTAL CONDITIONS

Effect of manganese(II) ions and pH on the activity of ICDH

NADP-linked isocitrate dehydrogenase is active only in the presence of an activating metal ion. It is most effectively activated by manganese(II) ions[6] and these were used in the present investigation. It was necessary to establish the manganese(II) concentration and contact time with the enzyme required to induce maximal enzyme activity, under the conditions used for the metal ion determinations. On incubation of the enzyme with 6×10^{-5} *M* manganese(II) at 0° in 0·05*M* Tris buffer (pH 7·5) or water, the activity increases slightly at first but there is no further increase in activity after 10 min. As maximal inhibition of the enzyme by lead or indium is achieved after 15 min incubation of inhibitor with ICDH (Fig. 1), this incubation time was used for both activator and inhibitor in all subsequent experiments.

The effect of manganese(II) concentration on enzyme activity, after incubation in pH 7·5 Tris buffer solution for 15 min, is shown in Fig. 2. Under these conditions, which are those recommended for the determination of indium (see below), greatest enzyme activity is stimulated by $10^{-5}M$ manganese(II). The same concentration of manganese(II) was found to be necessary to give maximal activation under the conditions recommended for the determination of lead (pH 8·5 Tris buffer, *ca.* 0·13 units of enzyme per ml of reaction mixture).

The change in enzyme activity with pH (Fig. 3) shows that maximal activity occurs at pH 7·4.

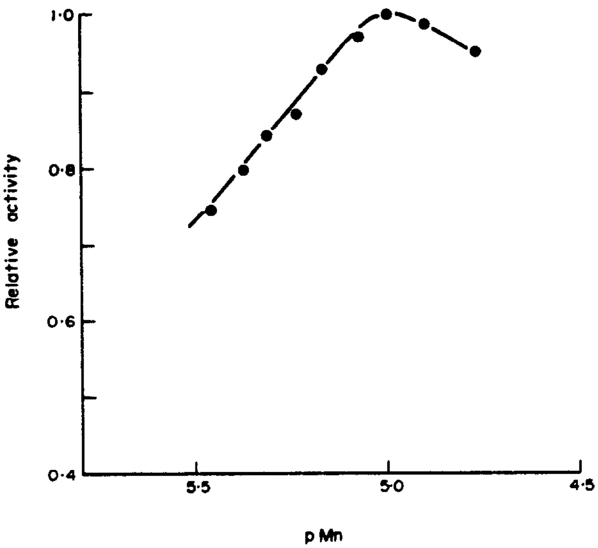

Fig. 2. Effect of Mn^{2+} concentration on ICDH activity after 15 min incubation in pH 7·5 Tris buffer.

Inhibition by lead

As indicated above, inhibition by lead is maximal after 15 min at 0°, and is extensive even after 1 min. Incubation is best done at 0°, because the enzyme slowly loses activity at 25°. Figure 3 shows that inhibition is greatest at pH 8·5. Thus, combination of these conditions gives the greatest sensitivity to lead, reproducible inhibition being obtained over the range 2–70 ng of lead per ml (Fig. 4).

Kratochvil *et al.*[6] have reported that NADP-linked ICDH is inhibited by traces of many metal ions. The effect on enzyme activity of incubating the enzyme with lead (20 ng/ml) and other ions (2 μg/ml) in pH 8·5 0·05*M* Tris buffer was studied. The results are summarized in Table 1. All the ions investigated interfered, by inhibition (high results) or activation

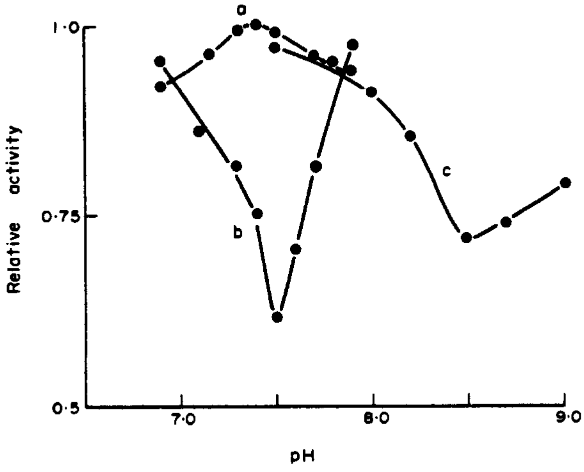

Fig. 3. Effect of pH on (*a*) ICDH activity; (*b*) inhibition by 40 ng of In^{3+} per ml; (*c*) inhibition by 20 ng of Pb^{2+} per ml.

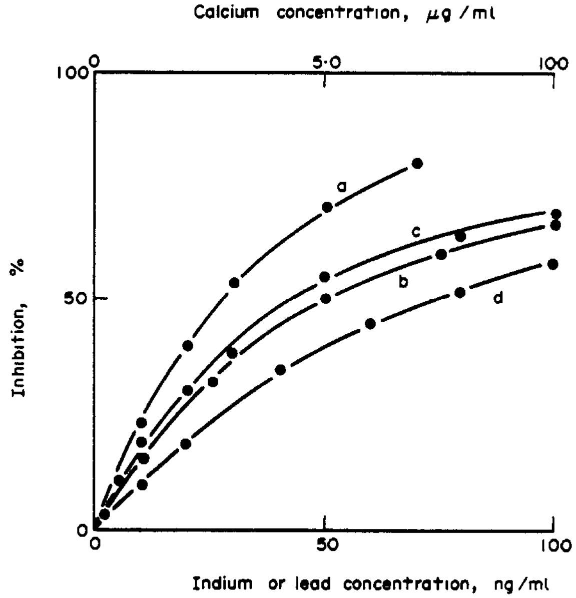

Fig. 4. Inhibition of ICDH by various concentrations of (*a*) Pb^{2+}, (*b*) Ca^{2+}, under the recommended conditions, and of In^{3+} after incubation in (*c*) unbuffered water; (*d*) pH 7·5 Tris buffer solution.

(low results) except for Al^{3+}. Complete inhibition of the enzyme was observed in the presence of Hg^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+} and Cd^{2+}. Most of these results are in agreement with the effects noted previously.[6]

In an attempt to develop a selective method for lead, the extraction method of Yadav and Khopkar[9] was investigated. Tributyl phosphate (TBP, 30% solution in isobutyl methyl ketone) is reported to separate lead selectively from a wide range of metal ions[9] in a medium that is 3*M* in hydrochloric acid and 2*M* in lithium chloride. The most probable composition of the extractable lead species is $PbCl_2{\cdot}2TBP$.[9] Lead can readily be stripped from the organic phase with water, for enzymic determination. The final aqueous extracts were flushed with a slow stream of nitrogen to get rid of the last traces of isobutyl methyl ketone, which was found to inhibit the enzyme. With use of this method lead (45 μg) could be determined in the presence of up to 4·5 mg of Bi^{3+}, Ba^{2+}, and Ca^{2+}, 2·25 mg of Hg^{2+}, and 1·1 mg of Ag^{+}. These are the maximum tolerance limits as reported by Yadav and Khopkar,[9] and greater ratios were not investigated. The results are shown in Table 2.

Inhibition by indium

Conditions for maximal inhibition of ICDH by indium were found in a similar manner to those for lead. With incubation in unbuffered water for at least 15 min, and the enzyme reaction carried out at pH 7·5, fairly reproducible inhibition was achieved over the range

Table 1. Direct determination of lead (20 ng/ml) in the presence of other ions (2 μg/ml)

Other ions	—	—	Al^{3+}	Ni^{2+}	Co^{2+}	Ba^{2+}	Mg^{2+}	Ca^{2+}	V^{5+}	Fe^{3+}	Cr^{3+}	Hg^{2+}	Ag^{+}	Zn^{2+}	Cu^{2+}	Cd^{2+}
Pb^{2+} found, *ng/ml*	20	20	20	48	29	24	12	60	6	17	11	>100	>100	>100	>100	>100

Table 2. Determination of lead after extraction with 30% tributyl phosphate in isobutyl methyl ketone (Pb^{2+} taken = 15 ng/ml)

Other cations, (*μg/ml*)	—	Bi^{3+} (1·6)	Ba^{2+} (1·6)	Ca^{2+} (1·6)	Hg^{2+} (0·8)	Ag^{+} (0·4)
Pb^{2+} found, *ng/ml*	15	13	16	13	13	16
		16	13	16	16	13

2–100 ng of indium per ml (Fig. 4). Results for the determination of indium in pure solution are shown in Table 3.

When the enzyme was incubated with indium in pH 7·5 buffer solution for 15 min, the inhibition was slightly less sensitive (Fig. 4), allowing 3–100 ng indium per ml to be determined. Determinations were more reproducible, however (Table 3).

In order to eliminate the interference of other metal ions, an attempt was made to determine indium after solvent extraction separation. The procedure of Khosla and Rao[10] using extraction by *N*-benzylaniline in chloroform from a hydriodic acid medium was investigated. The extraction procedure is simple and the separation of the organic and aqueous phases is very rapid. Indium is later stripped from the organic phase with 2*M* hydrochloric acid. When a 9% w/v solution of *N*-benzylaniline in chloroform, reported by Khosla and Rao[10] to separate indium from most metal ions, was used, some benzylaniline appeared in the final aqueous solution, resulting in the complete inactivation of the enzyme. To overcome this problem the effect of smaller benzylaniline concentrations was investigated. It was found that the concentration had to be decreased to 1% to prevent inhibition by the extractant. However, when a 100-fold amount (by weight) of some other ions was present with 60 μg of indium, and the 1% extractant solution was used, high results for indium were obtained (Table 4). Complete inhibition was observed after extraction when mercury and cadmium ions were present in 100-fold amount.

Inhibition by calcium

The incubation of the enzyme with calcium was done in unbuffered water for 15 min. The pH of the reaction solution was the same as for the determination of indium. The method allowed the determination of 0·5–10 μg calcium per ml in the absence of interfering ions (Fig. 4).

Stability of the enzyme–inhibitor complexes

The reaction between a cationic inhibitor (M^{x+}) and an active site of an enzyme, (E), can be represented by the equation

$$E + nM^{x+} \rightleftharpoons M_n^{x+}.E \qquad (1)$$

where *n* is the number of metal ions bound per active site.[11]

Table 3. Determination of indium

No buffer	Taken, *ng/ml*	2	5	10	30	80	
	Found, *ng/ml*	3	7	13	36	85	
0·05*M Tris buffer, pH* 7·5	Taken, *ng/ml*	10	20	40	60	80	100
	Found, *ng/ml*	11	23	40	61	77	100

Table 4. Determination of indium after extraction with 1% *N*-benzylaniline in chloroform. (Indium taken = 20 ng/ml; other ions = 2 μg/ml)

Other cations	—	—	Pb^{2+}	Ca^{2+}	Co^{2+}	Al^{3+}	Zn^{2+}	Ni^{2+}	Mg^{2+}	Ba^{2+}	Cd^{2+}	Hg^{2+}
In^{3+} found, *ng/ml*	20	19	47	89	47	39	89	58	28	39	>200	>200

An equilibrium constant, K, is given by

$$K = \frac{[E][M^{x+}]^n}{[M_n^{x+}.E]} \tag{2}$$

The relative activity, RA, is proportional to the concentration of free enzyme sites, [E]. Therefore, the concentration of inhibited enzyme, $[M_n^{x+}.E]$, is proportional to $(1-RA)$ so

$$\frac{1-RA}{RA} = \frac{[M_n^{x+}.E]}{[E]} \tag{3}$$

where RA is the fractional enzyme activity relative to that of the uninhibited enzyme under the same conditions.

A combination of equations (2) and (3) gives

$$\frac{1-RA}{RA} = \frac{[M^{x+}]^n}{K} \tag{4}$$

or

$$\log \frac{1-RA}{RA} = n \log [M^{x+}] - \log K \tag{5}$$

A plot of $\log (1-RA)/RA$ *vs.* $\log [M^{x+}]$ should therefore give a straight line of slope n and intercept $\log K$. The results of such plots for lead, indium and calcium are summarized in Table 5. All three plots give straight lines and the values of n are all approximately unity, indicating that one ion per active site is responsible for the inhibition. The equilibrium constants confirm that the strength of binding by the enzyme increases in the order $Ca^{2+} \ll In^{3+} < Pb^{2+}$.

Table 5. Equilibrium constants for the enzyme–inhibitor complexes

Inhibitor	Incubation, pH	n	K, *mole/l.*
In^{3+}	7·5	1·15	$6{\cdot}4 \times 10^{-7}$
		1·20	$6{\cdot}0 \times 10^{-7}$
	H_2O*	0·91	$3{\cdot}4 \times 10^{-7}$
		0·96	$4{\cdot}3 \times 10^{-7}$
		0·90	$2{\cdot}4 \times 10^{-7}$
Pb^{2+}	8·5	1·04	$1{\cdot}1 \times 10^{-7}$
		1·16	$1{\cdot}3 \times 10^{-7}$
		1·20	$1{\cdot}3 \times 10^{-7}$
		0·94	$1{\cdot}5 \times 10^{-7}$
		1·04	$1{\cdot}4 \times 10^{-7}$
Ca^{2+}	H_2O*	1·07	$1{\cdot}2 \times 10^{-4}$

* Unbuffered.

Adsorption of metal ions on glassware

Traces of metals are readily adsorbed by glass surfaces.[12, 13, 14] During these investigations, it was confirmed that lead is adsorbed by glass, which could lead to serious errors when ng amounts of this metal ion were being measured. This source of error could be eliminated, however, by putting the enzyme solution into the incubation flask first, followed by the lead solution. The lead was preferentially bound by the enzyme, and no significant amount was lost on the glass surface. To minimize any possible contamination from adsorbed lead or other metal ions, however, all glassware was soaked before use for several hours in a saturated aqueous solution of disodium EDTA, and rinsed thoroughly with water. Adsorption was also minimized by leaving metal ion solutions in contact with the glass for as short a time as possible.

As polyethylene is not so susceptible to these adsorption effects,[15] all stock metal ion solutions were stored in polyethylene bottles.

Conclusions

The methods described allow the reproducible determination of ng amounts of indium and lead, and rather larger amounts of calcium. As the enzyme studied is also inhibited by a wide range of other metal ions, means of prior separation of indium and lead from potential interferences were sought. Solvent extraction was successfully applied for the separation of lead, provided no significant amount of extractant found its way into the presence of the enzyme. Isobutyl methyl ketone and *N*-benzylaniline both inhibited ICDH, but whereas the ketone could readily be eliminated from the final aqueous solution, and thus did not interfere in the determination of lead, *N*-benzylaniline could not be prevented from finding its way into the final aqueous solution, if its concentration was to be sufficient to separate indium from other metals.

EXPERIMENTAL

The enzymic reactions were monitored in 10 mm silica cuvettes in a Beckman DB spectrophotometer by measuring at 340 nm the rate of formation of NADPH at constant temperature (25·0 ± 0·1°).

Reagents

Water distilled from an all-glass apparatus was used throughout.

Enzyme. Highly purified pig's heart isocitrate dehydrogenase in 50% glycerol (Sigma Chemical Co.) of activity 5 μmole. mg^{-1}. min^{-1} was stored at 4°. A standard solution was prepared from this stock enzyme daily before use by diluting, with 0·05*M* Tris buffer of the required pH, 20-fold v/v for indium and calcium determinations (pH 7·5) and 10-fold for lead determinations (pH 8·5). The standard enzyme solutions were kept in an ice-bath during use.

Tris(hydroxymethyl)methylamine (Tris) buffer solution, 0·05*M*. Tris (3·03 g) was dissolved in about 400 ml of water, adjusted to the required pH with 0·1*M* analytical-grade hydrochloric acid and diluted to exactly 500 ml with water The solution was kept in a thermostat at 25° before use.

Substrates. A reaction mixture consisting of 30 mg of analytical-grade trisodium DL-isocitrate dihydrate (ICA) and 17 mg of the monosodium salt of nicotinamide adenine dinucleotide phosphate (Sigma Chemical Co.) in 25 ml of 0·05*M* Tris buffer solution of the required pH was used. This mixture was kept in an ice-bath during use and kept frozen when not in use. When frozen it was stable for weeks.

Metal ion solutions. Stock solutions of indium and lead (200 μg/ml), calcium (120 μg/ml) manganese ($5{\cdot}0 \times 10^{-3}M$) and possible interfering ions (*ca.* 1 mg/ml) were prepared from analytical-grade reagents and stored in polyethylene bottles. More dilute solutions were prepared immediately before use by appropriate dilution of the stock solutions.

Procedures

Determination of lead (24–840 *ng*). To a 2 ml volumetric flask add Tris buffer (pH 8·5, *ca.* 1·0 ml) and exactly 0·1 ml (0·1 mg of protein ≡ 0·5 units) of enzyme solution previously cooled in ice. Mix gently and add

$1{\cdot}2 \times 10^{-3}M$ manganese solution (exactly 0·1 ml). Mix the contents of the flask again and add <0·5 ml of lead solution, at 0°, containing 24–840 ng of lead. Make up to the mark with pH 8·5 Tris buffer at 0°, mix thoroughly and place in ice for 15 min. Add exactly 0·5 ml of this solution to a mixture of ICA–NADP in pH 8·5 Tris buffer (0·5 ml), pH 8·5 Tris buffer (1·0 ml) and water (1·0 ml) all at 25·0°. After exactly 15 min at this temperature, measure the absorbance (A_i) at 340 nm in a 10 mm cuvette against water. Repeat the experiment in the absence of the inhibitor to obtain the absorbance (A_u) resulting from the uninhibited reaction and calculate the percentage inhibition ($\%I = 100(A_u - A_i)/A_u$). Plot a calibration curve of $\%I$ *vs.* lead concentration for the results obtained from standard lead solutions taken through the procedure. A new calibration curve should be made daily.

Liquid–liquid extraction of lead with tributylphosphate. This was investigated as follows. To 1 ml of solution containing 45 μg of lead were added (4 ml of solution containing ≤ 4·8 mg of Bi^{3+}, Ba^{2+} or Ca^{2+}, 2·4 mg of Hg^{2+} or 1·2 mg of Ag^{+}). To this solution, in a 100 ml separating-funnel, 12*M* hydrochloric acid (5 ml) and 4*M* lithium chloride (10 ml) were added, to make their respective concentrations 3*M* and 2*M* in a total volume of 20 ml. The mixture was extracted with 10 ml of 30% tributyl phosphate in isobutyl methyl ketone by shaking briskly for 5 min. The layers were allowed to separate, the aqueous layer carefully removed, and lead stripped from the organic phase by shaking with water (two 10 ml portions). The aqueous lead solutions were quantitatively transferred to a 25 ml volumetric flask and made up to volume with water. Isobutyl methyl ketone was removed from the aqueous solution by passage of a slow stream of nitrogen for 15 min. Aliquots of this aqueous solution (0·1 ml contained 0·18 μg of lead) were used for the enzymic determination of lead.

Determination of indium (24–1200 *ng*). Use the procedure described for lead, but incubate the enzyme (0·1 ml containing 50 μg of protein ≡ 0·25 units) in water instead of tris buffer solution and add ≤0·5 ml of solution containing 24–1200 ng of indium. Carry out the enzyme-catalysed reaction in pH 7·5 Tris buffer solution at 25·0 ± 0·1°. Plot a calibration graph of $\%I$ *vs.* indium concentration. A new calibration curve should be made daily.

Separation of indium by solvent extraction with N-*benzylaniline.* The investigation was made as follows. In a 50 ml separatory funnel distilled water (6 ml), indium solution (1 ml containing 60 μg of indium) and 5 ml of a solution containing 6 mg of interfering ion were mixed. Solid potassium iodide (3·735 g) and 10*M* sulphuric acid (3 ml) were added, to make the solution 1·5*M* in potassium iodide and 2*M* in sulphuric acid, in a total volume of 15 ml. The contents of the funnel were mixed to dissolve the potassium iodide, and then extracted for 2 min with a 1% *N*-benzylaniline solution in chloroform (two 5 ml portions). The mixture was swirled gently and the chloroform layer separated. The organic phases were combined and indium stripped by shaking for 2 min with 2*M* hydrochloric acid (15 ml). The aqueous layer was transferred to a 25 ml volumetric flask and concentrated ammonia solution was added dropwise until a turbidity appeared, which was cleared with a few drops of 2*M* hydrochloric acid, and the solution was then diluted to volume with water. A 0·1 ml aliquot of this neutral extract (containing 0·24 μg of indium) was used for the determination of indium.

Determination of calcium (6–120 *μg*). Use the procedure for indium, but add 0·1 ml of solution containing 6–120 μg of calcium. Plot a calibration curve of $\%I$ *vs.* calcium concentration. A new calibration curve should be made daily.

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Zusammenfassung—Die Inhibierung von Isocitrat-Dehydrogenase durch Blei, Indium und Calcium wurde untersucht. Es werden Methoden skizziert, wie man auf Grund dieser Inhibierung 0,02 –1 μg Blei und Indium bestimmen kann. Blei kann vor der Enzymreaktion durch Extraktion mit Tributylphosphat in Isobutylmethylketon von einigen störenden Ionen abgetrennt werden.

Résumé—On a étudié l'inhibition de la déshydrogénase isocitrique par le plomb, l'indium et le calcium. On indique des méthodes pour le dosage de 0,024–1 μg de plomb et d'indium, basées sur cette inhibition. On peut séparer le plomb de quelques ions gênants par extraction au phosphate de tributyle en isobutylméthylcétone, avant application de la réaction enzymatique.

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SOLVENT EXTRACTION AND SEPARATION OF GALLIUM, INDIUM AND THALLIUM WITH *N*-BENZYLANILINE

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Summary—A simple and rapid method is proposed for the separation of tervalent gallium, indium and thallium by solvent extraction with *N*-benzylaniline in chloroform from different concentrations of hydrochloric acid. Thallium and gallium are extracted from $1M$ and $7{\cdot}0$–$7{\cdot}5M$ hydrochloric acid respectively. Indium is finally extracted from hydriodic acid. These metals in the final extracts are determined complexometrically. Interference from some cations can easily be eliminated by reduction with sulphite, followed by selective oxidation of thallium(I) to thallium(III) with saturated bromine water, and from others by the use of thioglycollic acid as a masking agent in the extraction of gallium and indium. Most common anions cause no interference. Log–log plots of distribution coefficients *vs.* concentration of amine for gallium, indium and thallium indicate a 2:1 limiting mole ratio of amine to these metals.

A variety of techniques have been reported in the literature for the mutual separation of gallium, indium and thallium. These techniques are based on precipitation, solvent extraction, ion-exchange and chromatographic procedures. These metals have been separated by precipitation with hexa-amminecobalt(III) chloride.[1] The solvent extraction methods are predominantly based on extraction from different concentrations of hydrochloric or hydrobromic acids. Methods for the separation of gallium, indium and thallium have been reviewed by Korkisch.[2] Irving and Rossotti[3] have reviewed the extraction of these metals with diethyl ether. These metals have also been separated with tri-n-butyl phosphate[4] in benzene from different concentrations of hydrochloric acid. Gallium, indium and thallium can also be extracted with *N*-benzoyl-*N*-phenylhydroxylamine[5] into chloroform by adding an acetate buffer and adjusting the pH to appropriate values. Recently Fritz, Frazee and Latwesen[6] have reported the column extraction chromatographic separation of these metals from their aqueous solutions in hydrobromic acid. A fairly good separation can be effected by reverse-phase chromatography on Whatman No. 1 paper, treated with bis-(2-ethylhexyl)phosphoric acid in cyclohexanone, by elution with 1 or $8M$ hydrochloric acid.[7]

We have recently described the selective extraction of indium with *N*-benzylaniline in chloroform from hydriodic acid media.[8] In the present work, conditions have been worked out for quantitative solvent extraction of tervalent gallium, indium and thallium with *N*-benzylaniline in chloroform from different concentrations of hydrochloric acid. Thallium is extracted from $1M$ hydrochloric acid, followed by extraction of gallium from $7{\cdot}0$–$7{\cdot}5M$ hydrochloric acid, and indium is finally extracted from hydriodic acid. Thallium, gallium and indium are easily stripped from the organic phase, with acetate buffer, water and $2M$ hydrochloric acid respectively. The metals in the final extracts are determined complexometrically. Interference from vanadium(V), cerium(IV), chromium(VI), ruthenium(VII), osmium(VIII) and manganese(VII) can be eliminated by reduction with sulphite, followed by selective oxidation of thallium(I) to thallium(III) with saturated bromine water, and from some other ions by masking with thioglycollic acid in the extraction of gallium and indium. Most common anions cause no interference. The proposed method is very simple and rapid, and effects a clean-cut separation of these metals from many cations.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-grade reagents. Aqueous solutions were prepared with doubly distilled water.

Gallium(III) solution. Prepared by dissolving 1·0 g of gallium nitrate octahydrate in 100 ml of $0{\cdot}2M$ nitric acid and standardized complexometrically.[9] Indium(III) solution was prepared by dissolving 1·782 g of pure indium metal in 15 ml of concentrated nitric acid, boiling to expel nitric oxides and diluting to 200 ml. More dilute solutions were prepared by accurate dilution.

Thallium(III) solution. Prepared by dissolving 6·66 g of thallous nitrate in a minimum quantity of water, followed by evaporation to dryness three times, after addition of 50, 25 and 25 ml of *aqua regia* respectively. Finally the residue was taken up in 120 ml of nitric acid (1 + 1) and the solution diluted to 500 ml. The solution was standardized by precipitation of thallous chromate after reduction with sulphur dioxide. More dilute solutions were prepared by accurate dilution.

Thorium solution, $0{\cdot}01M$. Prepared by dissolving the required amount of thorium nitrate tetrahydrate in $0{\cdot}001M$ nitric acid, and standardized against EDTA (Xylenol-Orange indicator), and diluted as required.

N-*Benzylaniline.* Prepared by dissolving 9·0 of purified reagent[10] (m.p. 36°, b.p. 180°/16 mbar) in 100 ml of chloroform.

Buffer solution.

Prepared by dissolving 27·2 g of sodium acetate trihydrate in 400 ml of water, adding 17 ml of glacial acetic acid, and diluting to 1 litre.

Procedure

Extraction of thallium(III). To an aliquot of solution containing not more than 10 mg each of gallium, indium and thallium, add sufficient sodium sulphite to reduce ions such as vanadium(V), chromium(VI) and cerium(IV), which hinder the extraction of thallium(III). Boil off excess of sulphur dioxide. Now gradually add saturated bromine water to the hot solution till the thallous precipitate completely dissolves and a yellow colour persists. Heat the solution at just below the boiling point until the colour of bromine disappears. Cool the solution to room temperature and add enough dilute hydrochloric acid and water to give $1M$ acid concentration in a volume of 15 ml. Extract thallium(III) by shaking the solution for 1 min with 10 ml of extractant mixture (5 ml of *N*-benzylaniline solution and 5 ml of chloroform). Swirl the separating funnel slightly and separate the chloroform layer. Repeat the extraction with 10 ml of extractant mixture. Retain the aqueous phase and combine the organic layers. Strip the thallium from the organic phase with two 35 ml portions of the buffer solution, and transfer these aqueous phases to a 250 ml conical flask. Add excess of $0{\cdot}01M$ EDTA, 7 drops of 0·1% Xylenol-Orange indicator and back-titrate with $0{\cdot}001$–$0{\cdot}01M$ thorium nitrate.

Extraction of gallium. To the aqueous phase, after separation of thallium, add 3–4 ml of 80% thioglycollic acid solution to mask interfering elements, and sufficient concentrated hydrochloric acid and water to give $7{\cdot}0$–$7{\cdot}5M$ acid concentration in a volume of 40–45 ml. Extract gallium(III) by shaking for 1 min with 15 ml of extractant mixture (5 ml of *N*-benzylaniline solution and 10 ml of chloroform). Swirl the separating funnel slightly and separate the chloroform layer. Repeat the extraction with 15 ml of extractant mixture. Retain the aqueous phase for the determination of indium. Combine the organic layers and strip the gallium by shaking for 1 min with two 30 ml portions of water. Combine these extracts in a 250 ml conical flask, add dilute ammonia solution until a turbidity appears and then clear it with a few drops of $1M$ hydrochloric acid. Now add excess of $0{\cdot}01M$ EDTA and adjust the pH to 2·5 ± 0·5 with $1M$ ammonia solution (narrow-range pH-paper or pH-meter). Add 7 drops of 0·1% Xylenol-Orange indicator and back-titrate with $0{\cdot}001$–$0{\cdot}01M$ thorium nitrate.

Extraction of indium. Evaporate the aqueous solution left after the separation of thallium and gallium, to about 5 ml to remove excess of hydrochloric acid. Add 3–4 ml of thioglycollic acid to mask interfering elements, and enough solid potassium iodide and $9M$ sulphuric acid to make the solution $1{\cdot}5M$ in potassium iodide and $2M$ in sulphuric acid in a volume of 30 ml. Transfer the solution to a separating funnel and extract indium by shaking for 2 min with 10 ml of extractant mixture (5 ml of *N*-benzylaniline solution and 5 ml of chloroform). Swirl the separating funnel slightly and separate the chloroform layer. Repeat the extraction with 10 ml of extractant mixture. Combine the organic layers and strip the indium by shaking for 2 min with 30 ml of $2M$ hydrochloric acid. Combine these aqueous extracts in a 250 ml conical flask and dilute to 75–80 ml with water. Add dilute ammonia solution until a turbidity appears and then clear it with a few drops of $1M$ hydrochloric acid. Add excess of $0·01M$ EDTA, adjust the pH to 2·5 ± 0·5 with $1M$ ammonia solution, add 7 drops of 0·1% Xylenol-Orange indicator and back-titrate with $0·001$–$0·01M$ thorium nitrate.

RESULTS AND DISCUSSION

Effect of foreign ions

Several ions were examined for interference (Table 1). The tolerance limit was set at the amount required to cause a relative error of not more than 1·5%. Vanadium(V), chromium(VI), cerium(IV), ruthenium(VII), osmium(VIII) and manganese(VII) hindered the extraction of thallium(III), but did not interfere after reduction with sodium sulphite in dilute acid; the solution was boiled to remove excess of sulphur dioxide; thallium(I) was selectively re-oxidized to thallium(III) with saturated bromine water. Palladium(II) was co-extracted but remained in the organic phase during stripping. Tungsten(VI), antimony(V), niobium(V), tantalum(V), zirconium(IV) and hafnium(IV) were kept in solution in the presence of tartaric acid. Bismuth was more than 50% extracted from $1M$ hydrochloric acid and thus strongly interfered in the extraction of thallium.

Mercury(II), antimony(III), silver, arsenic(III), lead(II), tin(II,IV), copper(II), cadmium, tellurium(IV) and platinum(II,IV) caused interference in the extraction of gallium, but this could easily be eliminated by masking them with thioglycollic acid. Molybdenum(VI), in the presence of thioglycollic acid, was partially extracted along with gallium, but caused no interference in the recommended titration of gallium.

Cadmium, antimony, tin, aluminium and platinum were extracted from hydriodic acid with *N*-benzylaniline in chloroform. Indium(III), however, could easily be separated from these ions by shaking the organic layer with $2M$ hydrochloric acid, whereby indium only was stripped.

Common anions such as phosphate, tartrate, citrate, nitrate, sulphate and fluoride did not interfere in the extraction of gallium, indium or thallium. The results obtained for various synthetic samples are given in Table 2.

Table 1 Ions without effect on extraction of gallium, indium and thallium

Foreign ion	Amount, *mg*	Foreign ion	Amount, *mg*	Foreign ion	Amount, *mg*	Foreign ion	Amount, *mg*
Co(II)	50	Ir(IV)	5	Mg(II)	100	U(VI)	50
Ni(II)	50	Mo(VI)	20	Sr(II)	100	Ce(IV)	30
Zn(II)	30	W(VI)*	20	Pb(II)	10	La(III)	27
Fe(III)	30	Cr(VI)	30	Al(III)	27	Eu(III)	30
Mn(II)	30	V(V)	30	Be(II)	30	Dy(III)	30
Cu(II)	30	Ti(IV)	30	Te(IV)	30	Sm(III)	30
Cd(II)	26	Re(VII)	10	Ge(IV)	30	Tartrate	1000
Hg(II)	10	Zr(IV)*	30	Pd(II)	10	Citrate	1000
Sn(IV)	10	Hf(IV)*	30	Pt(IV)	10	Phosphate	2000
Sb(III)*	20	Nb(V)*	14	Rh(III)	30	Nitrate	1000
As(III)	20	Ta(IV)*	14	Os(VIII)	30	Sulphate	500
As(V)	20	Sc(III)	25	Ru(VII)	30	Fluoride	100
Ca(II)	100	Y(III)	30				

* In the presence of tartaric acid.

Table 2. Analysis of synthetic mixtures of gallium, indium and thallium

Taken, *mg*			Found, *mg*		
Ga	In	Tl	Ga	In	Tl
3·44	8·92	9·92	3·44	8·89	9·92
1·72	4·46	4·96	1·72	4·46	4·96
6·88	3·57	2·48	6·91	3·55	2·48
8·60	1·78	1·98	8·63	1·77	1·98
9·46	9·81	9·92	9·50	9·78	9·92

Extraction conditions

The concentration of hydrochloric acid was varied from 0·5 to 6*M*, while the concentration of thallium(III) and the extractant were kept constant. The volume ratio of the aqueous to organic phase was 2·0. The results (Table 3) show that thallium(III) is quantitatively extracted from 1–3*M* hydrochloric acid. The procedure gives quantitative extraction of up to 80 mg of thallium(III). A plot of log *D vs.* log *C* (*C* = *N*-benzylaniline concentration) for 1*M* hydrochloric acid medium gave a slope of 1·70, indicating that the extracted species is probably $HTlCl_4 \cdot 2N$-benzylaniline. Similar experiments show (Table 3) that with a 3:1 volume-ratio of aqueous to organic phase extraction of up to 10 mg of gallium is quantitative from 6·5–7·5*M* hydrochloric acid, and that the same type of complex is extracted (slope of log *D vs.* log *C* is 1·90).

Table 3. Degree of extraction of thallium(III) and gallium(III). (Thallium 19·83 mg and gallium 1·72 mg; conditions as in the procedure except for acidity)

	Extraction, %	
[HCl], *M*	Tl	Ga
0·5	98·0	—
1·0–3·0	100·0	—
3·5	—	6·3
4·0	96·7	—
4·5	—	58·3
5·0	93·4	—
5·5	—	78·2
6·0	88·9	91·7
6·5–7·5	—	100·0
8·0	—	96·0

The conditions for indium extraction had already been established.[8] A log *D vs.* log *C* plot had a slope of 1·70, again indicating extraction of a 1:2 complex. Variation of the extraction-time over the range 1–10 min showed that equilibration for 1 min sufficed for thallium and gallium, and 2 min for indium.

Reproducibility

For ten runs with 19·8, 1·72 and 8·91 mg of thallium(III), gallium(III) and indium(III) respectively, the average recovery was 99·8 ± 0·2% with a standard deviation of 1·0%.

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Zusammenfassung—Ein einfaches und schnelles Verfahren zur Trennung von dreiwertigem Gallium, Indium und Thallium durch Extraktion mit N-Benzylanilin in Chloroform aus verschieden konzentrierter Salzsäure wird vorgeschlagen. Thallium und Gallium werden aus $1M$ bzw. 7,0–$7.5M$ Salzsäure extrahiert, Indium schließlich aus Jodwasserstoffsäure. Die Metalle in den Extrakten werden komplexometrisch bestimmt. Störungen durch einige Kationen können leicht durch Reduktion mit Sulfit beseitigt werden, wonach Thallium(I) selektiv mit gesättigtem Bromwasser zu Thallium(III) oxidiert wird; andere Storungen durch die Verwendung von Thioglycolsäure als Maskierungsmittel bei der Extraktion von Gallium und Indium. Die meisten gewöhnlich vorkommenden Anionen stören nicht. Doppeltlogarithmische Auftragung der Verteilungskoeffizienten gegen die Aminkonzentration zeigt bei Gallium, Indium und Thallium ein Grenzverhältnis von 2 : 1 (Amin : Metall).

Résumé—On propose une méthode simple et rapide pour la séparation du gallium, de l'indium et du thallium trivalents par extraction par solvant avec la N-benzylaniline en chloroforme à partir de différentes concentrations d'acide chlorhydrique. Le thallium et le gallium sont extraits d'acide chlorhydrique $1M$ et 7,0–$7.5M$ respectivement. L'indium est finalement extrait de l'acide iodhydrique. On dose ces métaux dans les extraits finaux complexométriquement. L'interférence de quelques cations peut être éliminée aisément par réduction avec le sulfite, suivie d'oxydation sélective du thallium (I) en thallium (III) par l'eau de brome saturée, et celle d'autres cations par l'emploi d'acide thioglycolique comme agent de dissimulation dans l'extraction du gallium et de l'indium. La plupart des anions communs ne causent pas d'interférence. Les tracés log–log des coefficients de partage par rapport à la concentration en amine pour le gallium, l'indium et le thallium indiquent un rapport molaire limite 2: 1 de l'amine à ces métaux.

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DETERMINATION OF MICROGRAM QUANTITIES OF SILVER IN ALUMINIUM-, IRON-, AND NICKEL-BASE ALLOYS

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Summary—Trace quantities of silver in commercial nickel and its alloys are quantitatively extracted from 10% hydrochloric acid medium containing 2% ascorbic acid and 9% potassium iodide by a 5% solution of tri-n-octylphosphine oxide in 4-methylpentan-2-one (MIBK). The MIBK-extract containing the silver is then nebulized directly into an atomic-absorption flame. The sensitivity for the determination of silver in MIBK is about 6 times that for aqueous media. The proposed technique is accurate, rapid, and has a standard deviation of ± 0·025 ppm at the 1 ppm level. The limit of detection is 0·2 ppm of silver. The method is also applicable to a number of elements in aluminium- and iron-base alloys.

There are many methods for determining trace quantities of silver, but no simple, generally accepted method, which is applicable to a variety of alloy systems and to a variety of trace elements. Many techniques are known for the determination of silver around the 10 ppm level: emission spectrography,[1] X-ray spectroscopy,[2] spectrophotometry (*via* silver rhodanate),[3] neutron activation,[4] and atomic absorption.[5, 6, 7] Silver has been accurately determined directly in plant liquors by atomic absorption. Considerable errors occur when the level of nickel exceeds 10 g/l.[8] An extraction procedure for bismuth and lead[9, 10] has also been applied to the extraction of silver from nickel and its alloys, as well as iron- and aluminium-base alloys. A non-aqueous atomic-absorption method has been reported for silver,[11] but it could not be applied to the analysis of alloys in acid solution because the silver di-n-butylammonium salicylate complex would not form and thus could not be extracted. Tri-iso-octylthiophosphate (TOTP) in MIBK has been shown to be a good extractant for silver from 4–8M nitric acid[12] and used to remove silver from geological materials. The procedure is specific for silver and mercury.[13] Silver diethyldithiocarbamate has been extracted before determination by atomic absorption.[14]

The mixed solvent proposed for the quantitative extraction of antimony, bismuth, lead, and tin[9] has been tested as an extractant for ppm levels of silver. The group extractant is a 5% solution of tri-n-octylphosphine oxide (TOPO) dissolved in 4-methylpentan-2-one (MIBK).

EXPERIMENTAL

Apparatus

A Perkin–Elmer Model 303 atomic-absorption spectrophotometer with a premix chamber and triple-slot Boling burner head was used with a Perkin–Elmer silver hollow-cathode lamp and a Sargent Model SRG recorder.

The silver resonance line at 328·1 nm was used, and the band-pass was 7 Å. When MIBK solutions were aspirated, the air pressure was 30 psig with a flow-rate of 24 l./min and the acetylene pressure was 8 psig with a flow-rate of 2 l./min.

Reagents

Standard stock solution of silver, 1000 $\mu g/ml$. Weigh 1·000 g of silver metal (99·9999% purity) and dissolve it in 10 ml of nitric acid (1 + 1) with heating, boil gently, cool, and dilute to 1 litre with water. Mix, then transfer to and store in a polyethylene bottle.

Standard stock solution of silver, 5 $\mu g/ml$. Transfer 5 ml of the 1000 μg/ml stock solution to a 1 litre volumetric flask, add 200 ml of hydrochloric acid (1 + 1), dilute to volume and mix. Store in a polyethylene bottle.

Working standard solution of silver, 1 $\mu g/ml$. Transfer 20 ml of the 5 μg/ml stock solution into a 100 ml volumetric flask, add 20 ml of hydrochloric acid (1 + 1) and dilute to volume. Prepare this solution fresh daily, to avoid loss by adsorption.[15]

5% TOPO in MIBK.

Iodide reagent. Prepare daily a solution of 30% w/v potassium iodide and 10% w/v ascorbic acid in 10% v/v hydrochloric acid.

All chemicals used were reagent grade. The hydrochloric and nitric acids were found to contain less than 0·05 ppM (parts per milliard) silver and the formic acid 0·1 ppM silver.

Class-A volumetric glassware was used.

Procedure

Calibration curve. Transfer 0, 0·5, 1, 2, 5, and 10 ml of working standard silver solution to six acid-washed separatory funnels. To each of the solutions add 15 ml of the iodide reagent and dilute to 50 ± 5 ml with hydrochloric acid (1 + 9). Pipette 10 ml of the 5% TOPO reagent into the separatory funnel, shake the funnel for 30 sec, allow the phases to separate, and drain off and discard the lower aqueous layer. Transfer the organic phase to a glass-stoppered vial for measurement.

Analysis. Weigh a sample (to the nearest 1 mg) which contains 0·5–10 μg of silver. Prepare a reagent blank. Dissolve 1 g samples in a covered acid-washed 150 ml beaker with appropriate acids. Use a 600 ml beaker for 10 g samples. Evaporate the solution to dryness.

Remove the beaker from the hot-plate, cool, and moisten the salts with 5 ml of water per g of sample. Add 10 ml of hydrochloric acid per g of sample and heat to boiling. Add 88% formic acid dropwise until no more oxides of nitrogen are evolved and evaporate to incipient dryness. Dissolve the salts in 20 ml of hydrochloric acid (1 + 1) and heat gently to complete the dissolution. Add ascorbic acid to those samples containing iron. The disappearance of the dark yellow colour due to iron(III) indicates the complete reduction to iron(II). Transfer the solution to a 125 ml separatory funnel and extract silver according to the procedure given for the calibration curve.

After its extraction, determine the silver by atomic adsorption, with direct aspiration of the organic phase into the acetylene–air flame. Obtain the requisite data for the calibration curve and samples and calculate the amount of silver.

DISCUSSION AND RESULTS

The TOPO solvent-extraction technique is a general method for the isolation of metals which form anionic complexes, such as $HFeX_4$. The method was initially developed for antimony, bismuth, lead, and tin,[9] and has also been shown to be applicable to thallium,[16] cadmium and copper.[17]

Silver chloride ($K_{sp} = 2{\cdot}8 \times 10^{-10}$) is appreciably soluble in hydrochloric acid because it forms soluble complex ions such as $AgCl_2^-$ or $AgCl_3^{2-}$. For example, the solubility of silver chloride in 10% hydrochloric acid is 74 mg/l at 21°. This solubility is adequate for the determination of microgram quantities of silver in hydrochloric acid. Silver iodide ($K_{sp} = 8{\cdot}6 \times 10^{-17}$) is considerably more insoluble than the chloride. A precipitate has been obtained from 0·2M potassium iodide in 2·3M hydrochloric acid containing 40 μg of silver per ml.[18] No precipitation of silver was observed at the concentrations of silver and iodide used in this study. Silver iodide is soluble in solutions of potassium iodide owing to the formation of complex ions: AgI_2^-, AgI_3^{2-}, and AgI_4^{3-}.

The results in Table 1 substantiate the proposed method. A 100 μg quantity of silver in 50 ml of aqueous phase was treated with 10 ml of various extractants. The level of silver

Table 1. Variation of extraction parameters for the separation of 100 μg of silver

Test	Extractant	Aqueous phase, 10% HCl plus	D*	E%†
1	5% TOPO in cyclohexane	—	0·8	14
2	5% TOPO in cyclohexane	4·5% KI, 1·5% ascorbic acid	150	97
3	100% MIBK	—	0·3	0·6
4	100% MIBK	4·5% KI, 1·5% ascorbic acid	4·6	48
5	5% TOPO in MIBK	—	7·7	61
6	5% TOPO in MIBK	4·5% KI, 1·5% ascorbic acid	997	99·5

* A single 60-sec extraction was used to obtain the distribution coefficient, $D = [Ag]_o/[Ag]_{aq}$.

† Extraction = $100\,D/(D + 5)$%.

remaining in the aqueous phase was ascertained by means of a second extraction, after addition of iodide, with 10 ml of 5% TOPO in MIBK. Test 6 shows that this is valid since the distribution coefficient, D, for the iodide–TOPO–MIBK system is nearly 1000. The organic phase was analysed for silver after dilution to 100 ml. Examination of the extraction results for tests 1, 3, and 5 shows a low D value when the extraction is performed from hydrochloric acid alone, regardless of the extractant. A similar distribution coefficient has been obtained[19] with TOPO in an inert solvent, and 2–6M hydrochloric acid. A value of about 10 was obtained with 100% tri-*n*-butylphosphate (TBP) and 1M hydrochloric acid.[20] The extracted species[21] was $HAgCl_2(TBP)_3(H_2O)_2$ and when an iodide medium was used the AgI_2^- complex ion was found in the TBP phase.[22] A similar species is probably formed with TOPO and accounts for the efficient extraction of silver. No attempt was made to identify the extracted species.

Organic solvents have been widely used in atomic-absorption because they increase the efficiency of the process of introducing molecules into the flame.[23, 24] The primary use of the organic solvent in this study was to separate and concentrate silver. One slight disadvantage with MIBK, as a solvent for TOPO, is its slight solubility in water (2%)[25] and dilute hydrochloric acid. The analytical results are not affected by this solubility because a calibration curve is prepared in the same manner. This is an important step to avoid errors[26] arising from the volume changes occurring when 10 ml of MIBK are equilibrated with 50 ± 5 ml of aqueous phases.

Solvents such as 2,6-dimethyl-4-heptanone (DMH) or cyclohexane have solubilities in water of less than 0·06%. Neither solvent forms emulsions or third phases, both burn in the acetylene–air flame, dissolve TOPO, and efficiently extract silver and at first sight seem attractive alternatives to MIBK. The calibration curves shown in Fig. 1 illustrate the variation in sensitivity as a function of the solvent and the sensitivity for silver in DMH and cyclohexane is seen to be less than for MIBK. Also, the burning characteristics and/or nebulization properties are not as ideal as those of MIBK. Attempts to improve the sensitivity by adjustment of the nebulization rate for each system were not successful. Silver is quantitatively extracted by the 5% TOPO–DMH and 30% TOTP–MIBK systems. Lower sensitivity was observed for silver with the TOTP system.

The calibration curves given in Fig. 1 were obtained by using the appropriate solvent to zero the instrument, *e.g.*, cyclohexane was aspirated as the reference solvent when the silver–cyclohexane solutions were being analysed. The normal working range for silver in aqueous media is from 0·5 to 5 μg/ml and in MIBK from 0·05 to 1 μg/ml. The curves were drawn on the special paper described by Green.[27] The intercepts of the calibration curves

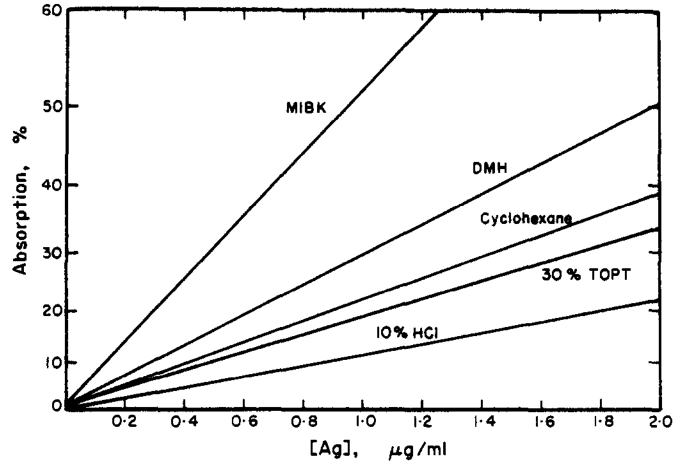

Fig. 1. Comparison of atomic-absorption calibration curves for 10% HCl, three non-aqueous solvents containing 5% TOPO, and 30% TOPT in MIBK.

shown in Fig. 1 give an indication of the blank as well as background observed. The amount of silver found in the acids and reagents is negligible; therefore, the blank due to contamination by silver can normally be ignored. Attempts to eliminate the background by purification of the reagents failed. Similar statements could be made for the determination of lead by the TOPO method.[9] Aspiration of MIBK–TOPO solutions equilibrated with aqueous solutions gave absorption values for the blank ranging from 3 to 7% at the 217·0 nm lead line. This effect is not as serious at the higher wavelength used for silver. The background for the silver 328·1 nm resonance line is about 1% absorption; a background correction is required. When MIBK is used as a solvent for the extraction of silver it also extracts some water, hydrochloric acid, and inorganic salts. The presence of these materials in the MIBK extract produces light scatter or molecular absorption. This effect is more important at shorter wavelengths and is not appreciably reduced by filtration or drying of the organic phase.

The TOPO method is capable of determining silver under a wide variety of conditions. Minor operator-errors will not affect the accuracy. Quantitative extraction of 10 μg of silver was obtained when the concentration of hydrochloric acid was varied from 0·1 to 20% v/v, the level of potassium iodide from 0·3 to 15% w/v, or the amount of ascorbic acid from 0·1 to 10 g. A 30 sec extraction period has been recommended but complete extraction is obtained for any equilibration period greater than 5 sec. The effect of these four variables was determined with all other factors kept constant. Nitric acid remaining after the dissolution step causes the formation of free iodine in the TOPO phase, and gives low results. Evaporation of the sample to dryness and treating the subsequent hydrochloric acid solution with formic acid effectively eliminates nitric acid.

Standard materials containing a certified level of silver in a nickel matrix are not available. A synthetic standard was prepared with 1 g of 99·999% pure nickel, spiked with 1 μg of silver. Twenty synthetic standards were similarly prepared and carried through the proposed procedure. This set had a mean of 1·002 and standard deviation ±0·025 ppm. The relative standard deviation for a 95% confidence level is 5%. The relative error of the average is 0·2%. These data were obtained for sets of 10 on separate days.

Table 2. Determination of silver in various standard alloys by the *TOPO* method

Designation	Description*	Ag found *ppm*
INCO-CC	Electronickel	<0·05
INCO-CO	Nickel Pellets	<0·05
INCO-CO	Nickel 123	<0·05
INCO-CO	Nickel 270	<0·05
NBS 111b	Ni-Mo Steel	0·3
NBS 126a	Ni36 Steel	0·7
NBS 348	Ni26-Cr15 Steel	0·8
NBS 838	Mo High Speed Tool Steel	0·5
NBS 55e	Ingot Iron	0·3
NBS 82a	Nickel-Chromium Iron	0·2
NBS 341	Ductile Iron	0·8
NBS 57	Refined Silicon	0·2
NBS 87a	Aluminum-Silicon Alloy	0·2
NBS 168	Cobalt-Base Alloy	0·9
NBS 169	Ni77-Cr20 Alloy	0·2
NBS 349	Waspaloy†	0·2
NBS 671	Nickel Oxide	0·6
NBS 672	Nickel Oxide	0·2
NBS 673	Nickel Oxide	0·1
NBS 1194	A-286	0·7
NBS 1195	Discaloy 24†	0·4
NBS 1205	Alloy 713-C	0·6
NBS 361	AISI-4340 Steel (4)	4
NBS 362	AISI-94B17 Steel Modified (10)	11
NBS 363	Cr-V Steel Modified (30)	31
NBS 365	Electrolytic Iron (~0·02)	0·08
BCS 310/1	NIMONIC 90†	<0·05
BCS 387	NIMONIC 901 Alloy†	0·2
BCS 371	Commercial Nickel	0·5
BCS 149/3	High Purity Iron	0·05
BCS 260/3	High Purity Iron	<0·05
BCS 242/1	Ferro Tungsten	21
BCS 243/1	Ferro Titanium	9
BCS 312	Permanet Magnet Alloy	3
BCS 365	Alcomax II†	2

* Values in parentheses are Ag contents (ppm) reported on the provisional certificate as the results by a single laboratory.

† Trademarked products: Waspaloy—United Aircraft Corp.: Discaloy—Westinghouse Electric Corp.: NIMONIC—The International Nickel Co., Inc.; Alcomax—Aluminum Company of America.

Results given in Table 2 show the amount of silver found in a number of typical materials. The first four materials are various types of commercial nickel. They all contain less than 0·05 ppm of silver and are not the source of silver found in various alloys. The normal low calibration point corresponds to 0·5 μg of silver and an absorbance of about 0·02 above background. The detection of less than 0·5 ppm of silver is easily attained by using sample weights greater than 1 g. A limit of detection of 0·05 ppm has been obtained with a 10 g sample. This method was used to analyse the first four samples of nickel in Table 2.

The working range of the method can also be lowered by reducing the volume of the organic phase from 10 to 2 ml. A calibration curve is prepared, using 3 ml of the TOPO solution, which would leave about 2 ml of organic phase after equilibration. For 0·1 μg of silver, the silver level would be 0·01 μg/ml for 10 ml of extractant or 0·05 μg/ml for 2

Table 3. Application of the TOPO atomic-absorption method for the determination of 1 μg of silver added to various materials

Designation	Description	Ag found, μg*
NBS 126a	Ni26-Cr15 Steel	0·95
NBS 168	Cobalt-base Alloy	1·1
NBS 169	Ni77-Cr20 Alloy	1·0
NBS 349	Waspaloy†	1·1
BCS 310/1	NIMONIC 90†	1·1
BCS 387	NIMONIC 901 Alloy†	0·8
BCS 371	Commercial Nickel	0·8
BCS 149/3	High-purity Iron	1·1

* Corrected for silver originally present.
† See Table 2 for identification of trademarks.

ml. This method was used to analyse a 4 g sample of NBS 365. This sample weight gives a silver concentration of 0·04 μg/ml in 2 ml. The limit of detection could also be lowered by using scale expansion.

A few of the iron-base materials have been analysed for silver by another technique. Neutron-activation analysis gave the parenthesized values listed for NBS 361–363 and the spark-source mass spectrograph for NBS 365.[28]

In order to verify further the accuracy of the proposed method several representative materials were spiked with 1 μg of silver, dissolved, and carried through the procedure with 1 g of the alloy. The recovery of silver from nickel, iron, a steel, a cobalt alloy and several nickel-base alloys is shown in Table 3. A correction was made for any silver which may have originally been present. The results indicate that silver can be determined by the proposed method without interference.

The proposed technique is not applicable to alloys which are predominantly composed of metals which are also extracted along with silver. Normally, it cannot be used for the determination of trace quantities of silver in antimony, bismuth, cadmium, copper, gold, mercury, the platinum metals, gallium, indium, tin, thallium, or zinc. The method has not been evaluated for the extraction of milligram quantities of silver, lead, *etc.* It is possible to separate trace quantities of silver in the presence of up to 50 mg of an element which is also extracted, *e.g.*, copper. Additional potassium iodide must be added to dissolve copper(I) iodide. The BCS standard 180/1 (67Cu–30Ni) is not certified for silver. Analysis by a controlled-potential method[29] indicated 25 ppm and the TOPO method showed 23 ppm for a 0·1 g sample.

Other ions which are likely to be obtained by dissolution of superalloys and which will be extracted are iron(III), chromium(VI), manganese(VII), and molybdenum(VI). There are provisions in the procedure to prevent extraction of the first three of these elements by reduction to a lower reduction state, *e.g.*, iron(II) is not extracted. Molybdic oxide is formed in the dissolution step and does not interfere.

The process of removing nitric and hydrofluoric acids from a sample will cause the formation of insoluble oxides for metals such as molybdenum, tungsten, tantalum, *etc.* The presence of 0·5–2 g of boric acid or 1 g of molybdic or tungstic oxide did not affect the recovery of 10 μg of silver.

The TOPO method can be used for group extraction and each determination completed by atomic absorption. There is no optical interference nor effect due to the simultaneous extraction of a number of trace elements.

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Zusammenfassung—Silberspuren in handelsüblichem Nickel und seinen Legierungen kann man quantitativ aus 10% Salzsäure, die 2% Ascorbinsäure und 9% Kaliumjodid enthält, mit einer 5%-igen Lösung von Tri-*n*-octylphosphinoxid in 4-Methylpentan-2-on (MIBK) extrahieren. Der das Silber enthaltende MIBK-Extrakt wird dann direkt in eine Atomabsorptions-Flamme zerstäubt. Die Empfindlichkeit der Bestimmung von Silber in MIBK ist etwa 6-mal so groß wie in wäßrigen Medien. Das vorgeschlagene Verfahren ist genau, geht schnell und hat eine Standardabweichung von ±0,025 ppm im 1 ppm-Bereich. Die Nachweisgrenze beträgt 0,02 ppm Silber. Die Methode läßt sich auch auf eine Anzahl von Elementen in Legierungen mit Aluminium oder Eisen als Hauptbestandteil anwenden.

Résumé—Des quantités d'argent à l'état de traces dans le nickel commercial et ses alliages sont extraites quantitativement à partir d'un milieu à 10% en acide chlorhydrique contenant 2% d'acide ascorbique et 9% d'iodure de potassium par une solution à 5% d'oxyde de tri-n-octylphosphine en 4-méthyl-pentane 2-one (MIBK). L'extrait MIBK contenant l'argent est alors nébulisé directement dans une flamme d'absorption atomique. La sensibilité pour le dosage de l'argent en MIBK est environ 6 fois celle pour les milieux aqueux. La technique proposée est précise, rapide, et a un écart type de ±0,025 ppm au niveau de 1 ppm. La limite de détection est de 0,02 ppm d'argent. La méthode est aussi applicable à un certain nombre d'éléments dans des alliages à base d'aluminium et de fer.

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PROPERTIES AND ANALYTICAL APPLICATION OF CHLORPROMAZINE PICRATE

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Summary—In neutral medium, picric acid (PA) reacts with chlorpromazine (CPM) hydrochloride with the formation of an orange compound, sparingly soluble in water, of molar ratio PA:CPM = 1:1. The compound is thermally stable up to a temperature of about 200°C. The m.p. (178°C) can be used for identification of picric acid as well as of chlorpromazine hydrochloride. Chlorpromazine picrate is extracted quantitatively with benzene, and the extract can be used for colorimetric determination of chlorpromazine hydrochloride. Beer's law is obeyed in the CPM concentration range 10–60 μg/ml.

As pointed out in our earlier work,[1-4] phenothiazine derivatives, which occur in aqueous solution as large organic cations, react with anionic complexes of a number of metals with the formation of compounds, sparingly soluble in water, of general formula $(PDH)_m[MeX_n]$, where: X = Cl, Br, I, SCN; $m = 1$–3; $n = 4$–6; Me = metal; PD = phenothiazine derivative.

We have also found that phenothiazine derivatives react with some organic compounds (*e.g.*, picric and picrolonic acids, trinitrobenzene) to form coloured highly crystalline compounds. In the present work the preparation, structure and properties of chlorpromazine picrate, and its application to extractive colorimetric determination of chlorpromazine hydrochloride are described. Chlorpromazine hydrochloride—a typical representative of phenothiazine compounds—has found wide application in medicine. It exhibits relatively low toxicity, high physiological activity and many-sided pharmacological action. Owing to these properties it is often the subject of extensive pharmacological studies.

In the first ten years after the discovery of its therapeutic properties more than 10,000 papers were devoted to this compound.

EXPERIMENTAL

Reagents

Chlorpromazine hydrochloride [*2-chloro-10-(3-dimethylaminopropyl) phenothiazine hydrochloride*], *0·02M and 0·02% aqueous solutions*. Standardized gravimetrically by means of silicotungstic acid.[5]

Picric acid (*PA*), *0·02 M and 0·1% aqueous solutions.*

Preparation and composition of chlorpromazine picrate

Chlorpromazine picrate was precipitated by mixing 0·02*M* picric acid and chlorpromazine hydrochloride in the ratio 1 : 1. The precipitate was washed with water, dried at room temperature and crystallized from methanol. Large orange crystals, consisting of spheroid aggregates of elongated plates, were obtained.

The composition of the compound was established by means of the method of continuous variations and spectrophotometric titration. Suitable volumes of PA and CPM solutions were transferred to 50 ml separatory-funnels, and shaken with benzene. The yellow extracts were transferred to 10 ml flasks and diluted to volume with benzene and the absorbances measured at 405 nm (*i.e.*, at the absorption maximum). The graph of absorbance *vs.* mole fraction of PA gave a maximum corresponding to a 1 : 1 molar ratio, and this was confirmed by spectrophotometric titration.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectrum of chlorpromazine picrate (Fig. 1, curve 3) is similar to that of picric acid (curve 2), all three bands characteristic of picric acid being preserved, but intensity of band I is slightly increased, since the spectra of the reagents (PA and CPM) overlap. From the viewpoint of mechanism of complex formation it is interesting to note: (*a*) a slight shift (~7 nm) towards longer wavelength of band II in the spectrum of the compound as compared to the PA spectrum; (*b*) an increase in the intensity of band III, (*c*) appearance of a new band IV. The slight shift of band II can be explained by an increase in the electron-donor properties of the oxygen atom of the hydroxyl group of picric acid. This can only take place if this group acts as a proton donor in the formation of a hydrogen bond. The increase in the intensity of band III and appearance of the new band IV can be assigned to intermolecular charge-transfer. An electron in a non-bonding orbital of the amino-nitrogen atom of chlorpromazine passes to free orbitals of the nitro groups of picric acid.[6,7]

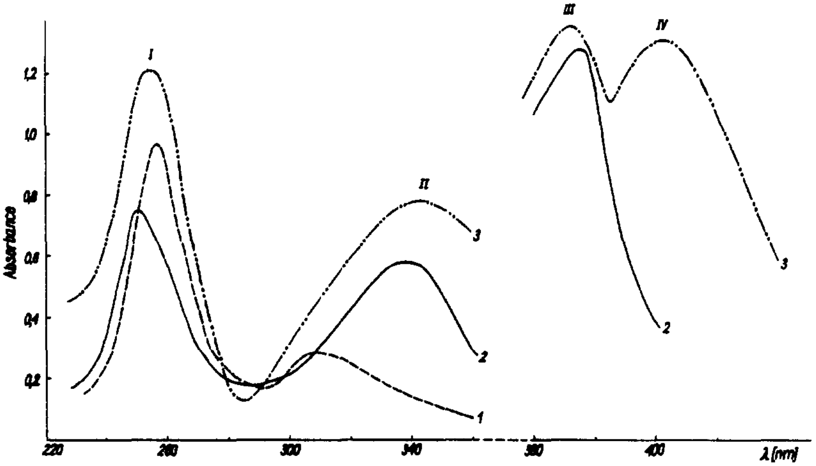


Fig. 1. Absorption spectra of chloroform solutions: *1*—chlorpromazine hydrochloride, $C = 10$ $\mu g/ml$; 2—picric acid, (U.V.) $C = 30$ $\mu g/ml$, (VIS) $C = 500$ $\mu g/ml$; 3—chlorpromazine picrate, (U.V.) $C = 30$ $\mu g/ml$, (VIS) $C = 80$ $\mu g/ml$; 1 cm cells.

The characteristic bands and corresponding electronic transitions, as well as λ_{max} and the molar absorptivity, are given in Table 1.

Infrared spectra

Infrared examination (KBr discs) in the region 650–5000 cm^{-1} was performed with the aid of a Unicam SP 200 spectrophotometer (Fig. 2). The spectrum of CPM picrate in the region 650–1700 cm^{-1} is essentially the sum of the spectra of the reagents, with

Table 1. λ_{max} and log ϵ of chloroform solutions of picric acid and its compound with chlorpromazine

Picric acid		Chlorpromazine picrate			
λ_{max}	log ϵ*	λ_{max}	log ϵ*	Band	Electron transition
249	3·75	256	4·42	I	$\pi_{ring} \rightarrow \pi^*_{NO_2}$
338	3·65	345	4·20	II	$n_{OH} \rightarrow \pi^*_{NO_2(pair)}$
375	2·78	374	4·08	III	$\pi_{NO_2} \rightarrow \pi^*_{NO_2}$
—	—	405	3·99	IV	$n_{N(CPM)} \rightarrow \pi_{NO_2(PA)}$ charge-transfer

* Units of ϵ are l.mole^{-1}.cm^{-1}.

that of PA predominating, there being only an insignificant shift ($\sim$15 cm^{-1}) and decrease in intensity of $\nu_{as(NO_2)}$ and $\nu_{s(NO_2)}$ bands in the PA spectrum at 1540 and 1350 cm^{-1}. The significant differences in the spectra occur in the region 2300–3700 cm^{-1}. The wide band in the region 2300–2600 cm^{-1} in the CPM spectrum, characteristic[8] of the hydrogen atom in the ion-pair $R_3HN^+ - Cl^-$ is shifted to higher frequencies in the chlorpromazine picrate spectrum, its intensity decreasing. The intensity of the complex band resulting from the overlap of $\nu_{(=CH)}$ and $\nu_{(O-H)}$, which occurs at 3150 cm^{-1} in the PA spectrum, is decreased. A new band with a maximum at about 3500 cm^{-1} appears, characteristic of intermolecular hydrogen bonding.

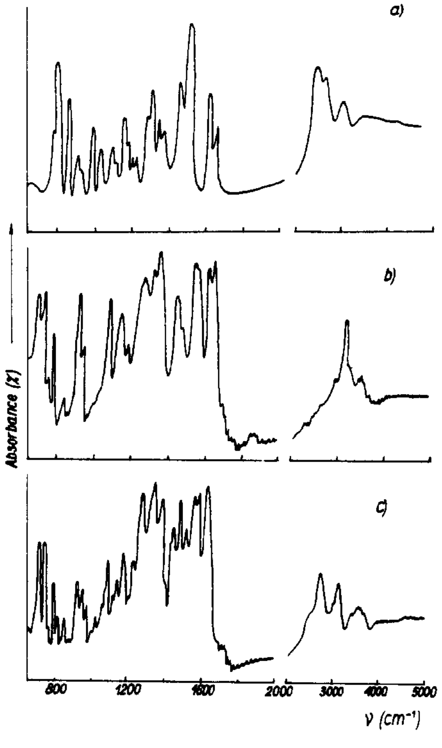
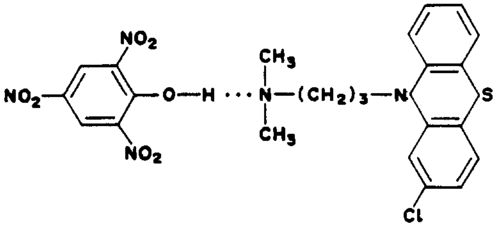


Fig. 2. Infrared absorption spectra: *a*—chlorpromazine hydrochloride, *b*—picric acid, *c*—chlorpromazine picrate.

On the basis of these spectroscopic results it can be concluded that the OH group of PA and the aliphatic amino-nitrogen of chlorpromazine are responsible for the formation of chlorpromazine picrate:



The complex results from the strongly polar hydrogen bonding and the effect of charge transfer to the nitro-group π-orbitals.

This interpretation of the spectra is in fair agreement with the results of examination of picric acid complexes with other aliphatic and aromatic amines.[9] [12]

Derivatograph studies

A Paulik, Paulik and Erdey "Derivatograph" was used. Chlorpromazine picrate is thermally stable up to 200°C (Fig. 3). The insignificant weight loss indicated on the TG

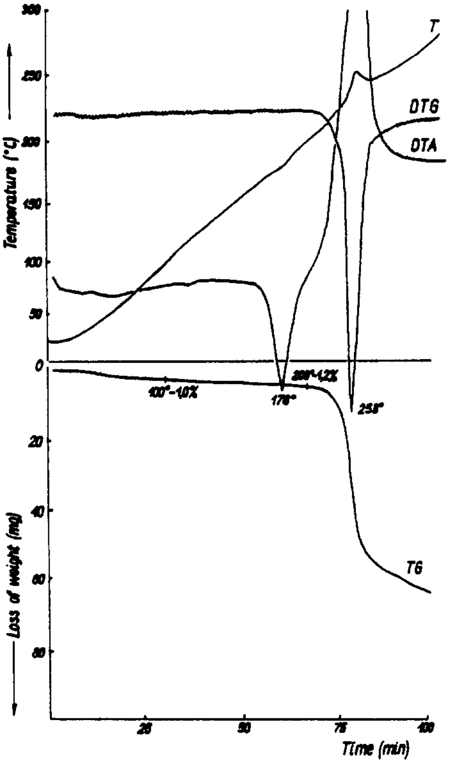


Fig. 3. Derivatograph curves of chlorpromazine picrate.
Sample 0·2018 g, air-atmosphere in furnace, comparison sample Al_2O_3, heated at 300° at 3°/min; relative sensitivity, 1/2 for DTA, 1/5 for DTG.

curve up to 200°C (~ 1·2%) is due to the loss of traces of moisture adsorbed on the surface.

The DTA curve of chlorpromazine picrate shows two thermal effects: an endothermic effect with transition maximum at 178°C, and an exothermic one with a maximum at 253°C. The endo-effect is characteristic of melting of the chlorpromazine picrate crystals, while the exo-effect is due to chemical decomposition of the compound and accompanied by a weight loss of about 45%, as indicated by the TG curve. The minimum at a temperature of 253°C indicates violent decomposition of the compound, which is accompanied by evolution of gaseous products. Qualitative analysis of these products showed the presence of carbon and nitrogen oxides and water vapour.

Solubility in water and organic solvents

The solubility of chlorpromazine in water, determined spectrophotometrically,[13] is low and amounts to $8{\cdot}2 \times 10^{-7}$ *M*. On the other hand the solubility in organic compounds[14] is relatively high, *e.g.*, acetone 0·093*M*, chloroform 0·043*M*, benzene 0·019*M*, ethyl acetate 0·017*M*, methanol 0·0036*M*.

Extraction constant

The extraction constant of chlorpromazine picrate was determined spectrophotometrically by the modified method of isomolar series.[15,16] The following formula was used:

$$K_E = [(m+n)/k]^{(m+n-1)} m^{-m} n^{-n} y_{\max}(1-y_{\max})^{-(m+n)} \qquad (1)$$

where K_E = extraction constant, *m*, *n* = stoichiometric coefficients of the reaction, *k* = total concentration of reagents ($C_{PA} + C_{CPM}$), $y_{\max}$ = a magnitude determined experimentally from absorbance measurements. This magnitude can be found from a plot of the function $y = A/A_{0,\max} = f(x)$, where *A* is the measured absorbance of the solution, and $A_{0\,\max}$ is the absorbance corresponding to PA completely combined in the complex. The latter is determined separately by absorbance measurements on solutions containing a large excess of chlorpromazine:

$$x = C_{PA}/(C_{PA} + C_{CPM}).$$

The mean value of log K_E was $5{\cdot}02 \pm 0{\cdot}05$, indicating good extraction with benzene.

Extractive colorimetric determination of chlorpromazine hydrochloride

The extraction of chlorpromazine picrate into benzene has been used for the colorimetric determination.

Procedure. Place the chlorpromazine hydrochloride solution (1–4 up to 150 μg/ml) in a 50-ml separatory funnel. Add 2 ml of 0·1% PA solution and dilute to 10 ml with water. Extract with two successive portions (>5 ml each) of benzene, transferring the extracts to a 10 ml volumetric flask and diluting to the mark with benzene. Measure the absorbance at 405 nm, in 10 mm cells, using benzene as reference.

Beer's law is obeyed over the CPM concentration range from 10 to 60 μg/ml in the benzene extract. The error does not exceed ± 2·0%. The time for a determination is about 20 min. The method has been applied successfully to the determination of chlorpromazine hydrochloride in "Fenactil" tablets.

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Zusammenfassung—In neutralem Medium reagiert Pikrinsäure (PA) mit Chlorpromazin-(CPM-) hydrochlorid zu einer nur wenig wasserlöslichen orangefarbigen Verbindung mit dem Molverhältnis PA:CPM = 1:1. Die Verbindung ist bis etwa 200°C thermisch stabil. Ihr Schmelzpunkt (178°C) kann zur Identifizierung von Pikrinsäure und von Chlorpromazin-hydrochlorid dienen. Chlorpromazin-pikrat läßt sich quantitativ mit Benzol extrahieren; der Extrakt kann zur colorimetrischen Bestimmung von Chlorpromazin-hydrochlorid verwendet werden. Das Beersche Gesetz gilt für 10–60 μg CPM pro ml.

Resume—En milieu neutre, l'acide picrique (PA) reagit avec le chlorhydrate de chlorpromazine (CPM) avec formation d'un compose orange, faiblement soluble dans l'eau, de rapport molaire PA:CPM = 1:1. Le composé est thermiquement stable jusqu'à une température d'environ 200°C. Le point de fusion (178°C) peut être utilisé pour l'identification aussi bien de l'acide picrique que du chlorhydrate de chlorpromazine. Le picrate de chlorpromazine est extrait quantitativement par le benzène, et l'extrait peut être utilisé pour le dosage colorimétrique du chlorhydrate de chlorpromazine. La loi de Beer est suivie dans le domaine de concentration 10–60 μg/ml en CPM.

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UNTERSUCHUNGEN AN REAGENZIEN ZUR PHOTOMETRISCHEN ZINNBESTIMMUNG*

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Zusammenfassung—Mit photometrischen Methoden wurde die Komplexbildung von Zinn(IV) mit einfachen ortho-Diphenolen und ortho-Hydroxychinonen untersucht. Es konnte nachgewiesen werden, daß einfache ortho-Hydroxychinone nicht mit Zinn(IV) reagieren. Chloranilsäure bildet SnR_2-Komplexe, ortho-Diphenole reagieren zu SnR_3-Komplexen. Im Hinblick auf eine analytische Bestimmung von Zinn wurde die Komplexbildung mit Hydroxyxanthenfarbstoffen untersucht. Die pH-Beständigkeit, die Lichtabsorptionseigenschaften, die Löslichkeiten, die Zusammensetzung der Komplexe sowie deren Komplexkonstanten wurden ermittelt. Analysenverfahren zur Bestimmung von Zinn wurden entwickelt und hinsichtlich Präzision, Empfindlichkeit sowie Einfluß von Störungen überprüft. Als Reagenzien können Gallein und Oxyhydrochinonphthalein empfohlen werden.

Für die photometrische Zinnbestimmung wurden in den letzten Jahren zahlreiche Reagenzien vorgeschlagen. Größere Bedeutung haben davon Quercetin,[2] Hämatoxylin[3] bzw. Hämatein,[4] Brenzcatechinviolett,[5] Phenylfluoron[6] und dessen Derivate[7,8] sowie Gallein[9] erlangt. Alle genannten Reagenzien enthalten orthoständige Sauerstoffdonatorgruppen im Molekül. Es ist aber noch weitgehend unbekannt, ob die ortho-Hydroxychinongruppierung oder die ortho-Diphenolgruppierung als analytisch funktionelle Gruppe für Zinn wirksam wird. Zur Klärung dieses Problems wurden zunächst Reaktionen des Zinns mit einfachen Verbindungen, die diese funktionellen Gruppen im Molekül enthalten, untersucht. Im Hinblick auf eine analytische Anwendung sind aber bei den Verbindungen mit einem umfangreichen Kohlenstoffgerüst bessere Ergebnisse zu erwarten. Es wurden deshalb durch systematische Untersuchungen Struktur, Löslichkeit, Stabilität und optisches Verhalten der Zinnkomplexe von Hydroxyxanthenfarbstoffen aufgeklärt.

EXPERIMENTELLER TEIL

Die photometrischen Messungen wurden mit den Spektralphotometern VSU 1 (VEB Carl Zeiss Jena) und DK 2 A (Beckman) ausgeführt

Die Zinnlösungen wurden aus Ammoniumhexachlorostannat(IV) hergestellt. Zur Verhinderung von Hydrolysereaktionen enthalten alle Zinnlösungen einen zehnfachen molaren Überschuß an Weinsäure. Die Ionenstarken der Lösungen wurden mit Natriumperchlorat auf *ca.* 0,1*M* und die pH-Werte mit verdünnter Perchlorsäure, Essigsäure bzw. Natriumhydroxidlösung eingestellt.

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* Gilt als Mitteilung Nr. 258 aus der Akademie der Wissenschaften der DDR, Forschungsinstitut für Aufbereitung, Freiberg.[1]

Tiron (VEB Berlin Chemie), Chloranilsäure (Chemapol, Prag), Phenylfluoron (Merck, Darmstadt) und Pyrogallolrot (VEB Berlin Chemie) sind handelsübliche Reagenzien. Brenzcatechin wurde in frisch sublimiertem Zustand verwendet. Synthetisiert wurden Tribromhydroxy-*p*-chinon,[10] 2-Hydroxynaphthochinon[11] sowie die Hydroxyxanthenverbindungen durch Kondensation eines Phenylmethanderivates mit der doppelten Molzahl eines Phenols unter Ausschluß von Luftsauerstoff.[12] Die Dibromderivate wurden durch Bromierung der Hydroxyxanthenverbindungen in Eisessig als Lösungsmittel hergestellt. Die einheitliche Zusammensetzung der Reagenzien wurde durch Papierchromatographie unter Verwendung von Fließmitteln aus Wasser n-Butanol/Eisessig nachgewiesen.

Komplexbildung mit einfachen ortho-Hydroxychinonen und ortho-Diphenolen

Brenzcatechin und Tiron als ortho-bzw. peri-Diphenole sowie Tribromhydroxychinon, Chloranilsäure und 2-Hydroxynaphthochinon als ortho- Hydroxychinonverbindungen wurden für die Untersuchungen zur Feststellung der analytisch funktionellen Gruppe für Zinn herangezogen. In Vorversuchen wurde festgestellt, daß die anwesende Weinsäure keinen Einfluß auf das Komplexbildungsgleichgewicht hat, da die Bedingungen nach Cheng[13]

$$(\mathrm{p}M_1)^2/\mathrm{p}M_2 > 7$$

erfüllt wird ($\mathrm{p}M_1$ = Metallionenexponent bei Reaktion mit Hauptkomplexbildner und $\mathrm{p}M_2$ = Metallionenexponent bei Reaktion mit Hilfskomplexbildner).

Für die Komplexbildung sind die Aciditäten der Donatorgruppen von großer Bedeutung. Es wurden deshalb die Dissoziationskonstanten der Verbindungen überprüft. Da sich die Dissoziationsprodukte der Reagenzien in ihren Lichtabsorptionseigenschaften unterscheiden, können die p*K*-Werte aus den Extinktions–pH-Kurven (λ = const.) abgeleitet werden. Die erhaltenen Ergebnisse stimmen gut mit den in der Literatur angegebenen Werten überein.[14 18]

Zur Ermittlung der Reaktionsfähigkeit der einzelnen Verbindungen wurde untersucht, ob in Abhängigkeit vom pH-Wert der Lösungen eine Veränderung der Lichtabsorption eintritt, wenn zu deren Lösungen Zinn(IV) hinzugefügt wird. Bei Tribromhydroxychinon und 2-Hydroxynaphthochinon konnte auch bei unterschiedlichen Verhältnissen der Reaktionspartner in der Lösung keine Veränderung der Lichtabsorption nachgewiesen werden.

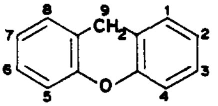
Mit Brenzcatechin, Tiron und Chloranilsäure erfolgt eine deutlich Reaktion. Das pH-Gebiet maximaler Komplexbildung liegt für Brenzcatechin bei pH = 6,5–7,0, für Tiron bei pH = 5,0–5,5 und für Chloranilsäure bei pH = 1,0–1,5. Die Absorptionsmaxima der Komplexe liegen bei 285 nm für Brenzcatechin, 304 nm für Tiron sowie 340 und 540 nm für Chloranilsäure. Auch mit versciedenen Verhältnissen von Zinn zu Reagens blieb das Absorptionsmaximum der Komplexe konstant. Dies deutet darauf hin, daß in den Systemen nur ein Komplex gebildet wird. Die Zusammensetzung der Komplexe wurde mit der Job-Methode[19] ermittelt. Chloranilsäure bildet einen Komplex der Zusammensetzung von Reagens zu Zinn wie 2:1 und Brenzcatechin sowie Tiron reagieren zu Komplexen mit einem Verhältnis von 3 : 1.

Bemerkenswert ist es, daß von den ortho- Hydroxychinonen nur Chloranilsäure Zinnkomplexe bildet. Eine Erklärung für diese Erscheinung liefern die mesomeren Grenzstrukturen dieser Verbindungen. Bei den ortho-Hydrohydroxychinonen erfolgt Mesomerie zwischen ortho- und para-Chinonstruktur. Bei den Verbindungen mit nur einer ortho-Hydroxychinongruppe im Molekül werden hierdurch Elektronen von den Sauerstoffatomen abgezogen, und es ist somit keine funktionelle Gruppe zur Komplexbildung mit Zinn mehr vorhanden. Bei der Untersuchung der Komplexbildung von

Germanium mit ortho-Hydroxynaphthochinon konnte ebenfalls keine Reaktion nachgewiesen werden.[18] Die Chloranilsäure enthält zwei ortho-Hydroxychinongruppen mit unterschiedlichen Eigenschaften ($pK_1 = 0{,}73$; $pK_2 = 3{,}08$). Durch die Ausbildung der ortho-Chinonstruktur nach Dissoziation der einem Hydroxylgruppe wird an der anderen ortho-Sauerstoffgruppe ein Zustand ähnlich dem in den ortho-Diphenolen erreicht. Hierdurch wird eine Komplexbildung mit Zinn möglich.

Komplexbildung mit Hydroxyxanthenfarbstoffen

Aus der Reihe der polycyclischen Verbindungen, die ortho-Hydroxychinongruppierungen enthalten und die sich sowohl in der Stellung der Sauerstoffdonatorgruppen als auch weiterer Substituenten unterscheiden, wurden folgende Verbindungen auf ihre Eigenschaften als Zinn-Reagenzien geprüft:



Xanthen

Phenylfluoren (PF) [2,6,7-Trihydroxy-3-oxo-9-phenylxanthen].

Bromphenylfluoron (BrPF) [4,5-Dibrom-2,6,7-trihydroxy-3-oxo-9-phenylxanthen].

Oxyhydrochinonphthalein (OP) [2,6,7-Trihydroxy-3-oxo-9-(phenyl-*o*-carbonsäure)-xanthen].

Bromoxyhydrochinonphthalein (BrOP) [4,5-Dibrom-2,6,7-trihydroxy-3-oxo-9-(phenyl-*o*-carbonsäure)xanthen].

Gallein (G) [4,5,6-Trihydroxy-3-oxo-9-(phenyl-*o*-carbonsäure)xanthen].

Bromgallein (BrG) (2,7-Dibrom-4,5,6-trihydroxy-3-oxo-9-(phenyl-*o*-carbonsäure)-xanthen].

Pyrogallolrot (PR) [4,5,6-Trihydroxy-3-oxo-9-(phenyl-*o*-sulfonsäure)xanthen].

Brompyrogallolrot (BrPR) [2,7-Dibrom-4,5,6-trihydroxy-3-oxo-9-(phenyl-*o*-sulfonsäure)-xanthen].

Die Absorptionswellenlängen und die Absorptionsintensitäten der gelösten Verbindungen verändern sich in Abhängigkeit vom pH-Wert der Lösungen. Aus der pH-Abhängigkeit der Extinktion (λ = const.) wurden die pK-Werte der Säuredissoziation ermittelt. Tabelle 1 enthält die für die Komplexbildung in neutraler und saurer Lösung wichtigen pK-Werte der ersten beiden Dissoziationsstufen.

Tabelle 1. pK-Werte der Säuredissoziation von Hydroxyxanthenverbindungen (pK_0-Dissoziation der protonisierten Verbindung, pK_1-Dissoziation der ersten Hydroxylgruppe)

	pK_0	pK_1
PF	2,2	6,4
PF[20]	2,21	6,37
BrPF	1,0	4,4
OP	2,5	6,0
BrOP	1,1	4,2
G	1,8	6,3
BrG	1,1	5,3
PR	2,6	6,1
BrPR	0,9	5,2

Gegenüber den einfachen Phenolen sind die pK-Werte für die Dissoziation der ersten phenolischen Hydroxylgruppe erniedrigt. Die Ursache dafür liegt in der elektronenanziehenden Wirkung des Ringsystems. Da Bromsubstitution diesen Effekt verstärkt, sind die Säurekonstanten der Bromderivate auch um ein bis zwei Größenordnungen größer als die der unsubstituierten Verbindungen. Substitution am Benzolring hat nahezu keinen Einfluß auf die pK-Werte der sauren Gruppen am Xanthengerüst.

Wird zu Lösungen der betrachteten Verbindungen Zinn(IV) hinzugefügt, dann wird insbesondere in schwach saurer Lösung eine Veränderung der Farbe beobachtet. Die Absorptionsmaxima sind außerdem noch vom Verhältnis Zinn(IV) zu Reagens in den Lösungen abhängig, wobei sowohl große Zinnüberschüsse als auch Reagensüberschüsse zu konstanten Wellenlängen der Absorptionsmaxima führen. Die Absorptionsmaxima der Komplexe, die bei Reagensüberschuß gebildet werden, sind in Tabelle 2 aufgeführt. Diese Tabelle enthält auch die pH-Werte maximaler Beständigkeit der Komplexe. Gemessen wurde hierbei gegen Reagenslösungen gleicher Konzentration und gleichen pH-Wertes, da die Absorptionsspektren der Reagenzien vom pH-Wert abhängig sind.

Die Komplexkonstanten wurden unter der Annahme des Gleichgewichtes:

$$\mathrm{AB}_n \rightleftharpoons \mathrm{A} + n\mathrm{B}$$

berechnet. Die Konstante K stellt in diesem Falle die globale scheinbare Dissoziationskonstante, die für konstanten pH-Wert und konstante Ionenstärke gilt, dar. Für den Gleichgewichtszustand gilt:

$$K = \frac{[\mathrm{A}][\mathrm{B}]^n}{[\mathrm{AB}_n]} = \frac{\left|a - \frac{m'_\lambda}{\varepsilon'_{\lambda\mathrm{AB}_n}}\right| \left|b - \frac{nm'_\lambda}{\varepsilon'_{\lambda\mathrm{AB}_n}}\right|^n}{\left|\frac{m'_\lambda}{\varepsilon'_{\lambda\mathrm{AB}_n}}\right|} \tag{1}$$

a, b = Ausgangskonzentration der Komponenten A bzw. B; m'_λ = Extinktionsmodul* der Lösung des Komplexes, gemessen gegen Reagenslösung gleicher Konzentration und gleichen pH-Wertes.

Die Berechnung des Extinktionskoeffizienten der Komplexverbindung $\varepsilon'_{\lambda\mathrm{AB}_n}$ ist aus dem waagerechten Teil der Kurve $m'_\lambda = f(b)$ möglich, da hier vollständige Komplexbildung angenommen werden kann. Hierfür gilt:

$$\varepsilon'_{\lambda\mathrm{AB}_n} = \frac{m'_\lambda}{a} \tag{2}$$

Die Ermittlung der Zusammensetzung der Komplexe und damit von n ist z.B. mit dem Verfahren von Job[19] möglich. Die Werte für n und $\varepsilon'_{\lambda\mathrm{AB}_n}$ sind dann richtig, wenn für verschiedene Wertepaare a, b und m_λ mit Gleichung (1) konstante Werte für K erhalten werden.

Aus Job-Kurven mit äquimolaren Lösungen wurden bei einer Zusammensetzung von $a : b = 1 : 2$ für alle untersuchten Systeme Maxima der Extinktion gefunden. Die Messung erfolgte im Absorptionsmaximum der bei Reagensüberschuß gebildeten Komplexe. Die bei Zinnüberschuß gebildeten Komplexe zeigen nur eine geringfügige Verschiebung in Richtung der Zusammensetzung 1 : 1. Dies deutet auf eine weitaus größere Beständigkeit der SnR_2-Komplexe hin.

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* Die auf eine Küvetten-Schichtdicke von 1 cm bezogene Extinktion.

In Tabelle 2 sind die Extinktionskoeffizienten der Komplexe, die p*K*-Werte der Komplexkonstanten sowie zum Vergleich die Extinktionskoeffizienten der Reagenzien angeführt.

Tabelle 2. Komplexkonstanten

	λ_{max}, *nm*	pH_{max}	$\varepsilon'_{\lambda AB_2}$ 10^3 *l. mol*$^{-1}$	$\varepsilon_{\lambda B}$. *cm*$^{-1}$	log, p*Ks*	$\varepsilon'_{\lambda AB_2}$ (extrah.) 10^3 *l. mol*$^{-1}$.*cm*$^{-1}$
PF	510	2,5	49	8,0	10,95	96
BrPF	515	1,6	32	6,0	10,83	72
OP	510	2,4	58	4,5	10,70	108
BrOP	515	1,5	35	4,5	10,61	76
G	495	2,3	29	3,0	11,07	42
BrG	498	1,8	24	5,0	10,89	41
PR	483	2,5	10	16	11,16	—
BrPR	493	1,7	20	12	11,12	—

Wellenlängen der Absorptionsmaxima der Komplexe = (λ_{max}), pH-Werte maximaler Komplexbildung = (pH_{max}), Extinktionskoeffizienten der Komplexe = ($\varepsilon'_{\lambda AB_2}$) und der Reagenzien = ($\varepsilon_{\lambda B}$), p*K*-Werte der Komplexkonstanten, $\varepsilon'_{\lambda AB_2}$ in Cyclohexanon.

Die höchsten Werte der Extinktionskoeffizienten erreichen die Zinnkomplexe des Phenylfluorons und des Oxyhydrochinonphthaleins. Bemerkenswert ist hierbei der vergleichweise niedrige Extinktionskoeffizient der entsprechenden Dibromderivate.

Obwohl sicherlich die Art und die Stellung der Substituenten maßgebend sein wird, kann bis jetzt noch keine befriedigende theoretische Erklärung für diese Unterschiede gegeben werden.

Der Vergleich der p*K*-Werte der einzelnen Komplexe zeigt, daß nur geringe Stabilitätsunterschiede bestehen. In der Regel sind die Komplexe der Bromderivate etwa instabiler als die der vergleichbaren unsubstituierten Verbindungen. Substitution am Benzolring hat, wie erwartet, keinen Einfluß auf die Stabilität der Komplexe.

Loslichkeit der Komplexe und Extraktion

Die Komplexe von Phenylfluoron und Bromphenylfluoron sind in Wasser schwer löslich. Dies macht sich dadurch bemerkbar, daß die Extinktionen der Lösungen nach *ca.* 30 min abnehmen und Niederschläge auftreten. Bei den Komplexen von Oxyhydrochinonphthalein, Gallein und deren Bromderivaten sind ähnliche Erscheinungen, allerdings erst nach etwa einem Tag, zu beobachten. Die Komplexe von Pyrogallolrot und Brompyrogallolrot sind bei den untersuchten Konzentrationen von $<10^{-4}M$ in Wasser löslich.

Die Schwerlöslichkeit der Komplexe beeinträchtigt die photometrischen Messungen erheblich. Durch Schutzkolloide können die Ausfällungen verhindert werden, allerdings wird hierbei die Komplexbildung in starkem Maße zeitlich verzögert. Geeigneter ist die Extraktion der Komplexe, die außerdem eine Abtrennung von Störelementen, eine Anreicherung sowie unter Umständen eine Entfernung von überschüssigem Reagens ermöglicht.

Eine gute Extraktion eines Teils der untersuchten Zinnkomplexe ist mit Ketonen, Alkoholen und Phosphorsäureestern möglich. Komplexe mit Liganden, die stark hydrophile Sulfogruppen enthalten, werden nur teilweise extrahiert. Die Art des Lösungsmittels hat nur geringen Einfluß auf die Lage der Absorptionsmaxima der Komplexe. Die Absorptionsintensitäten sind dagegen unterschiedlich, wobei zu bemerken ist, daß die Extinktionskoeffizienten meist größer als in wäßriger Lösung sind. Die Ursache für diese Erscheinung liegt darin, daß in den organischen Lösungsmitteln eine echte Lösung der Komplexe und in wäßriger Lösung je nach Vorhandensein von hydrophilen Gruppen eine echte bis kolloidale Lösung der Komplexe erfolgt. Als günstigstes Extraktionsmittel erwies sich Cyclohexanon. Die in diesem Lösungsmittel erreichten Extinktionskoeffizienten sind ebenfalls in Tabelle 2 angeführt.

Photometrische Bestimmung von Zinn in reiner Lösung

Gallein und Oxyhydrochinonphthalein wurden als für eine photometrische Zinnbestimmung geeignete Reagenzien ausgewählt. Wegen der unterschiedlichen Extinktionskoeffizienten der Komplexe ergeben sich zwei Anwendungsbereiche. Mit Gallein können Zinngehalte bis maximal 30 μg in 20 ml Lösung und mit Oxyhydrochinonphthalein bis maximal 6 μg in 20 ml Lösung bestimmt werden. Das Grundverfahren ist für beide Reagenzien gleich.

Arbeitsvorschrift

Zinneichlösung. Ammoniumhexachlorostannat(IV) wird in einer Lösung von Weinsäure aufgelöst. Es wird ein zehnfacher molarer Überschuß an Weinsäure als Hilfskomplexbildner verwendet.

Pufferlösung. Chloressigsäure (0,5*M*) wird mit Natronlauge auf pH = 1,5 eingestellt.

Reagenslösung. Gallein (100 mg) bzw. 20 mg Oxyhydrochinonphthalein werden in 100 ml Äthanol gelöst.

Die Eichung des Verfahrens erfolgt mit Aliquoten der Zinneichlösung, die im 50 ml Scheidetrichter gegen Phenolphthalein neutralisiert werden und danach mit 5 ml Chloracetatpufferlösung auf einen pH-Wert von 1,8–1,9 gebracht werden. Nach Zugabe von 1 ml Reagenslösung und Ergänzung mit Wasser auf 25 ml wird nach einer Reaktionszeit von 30 min mit genau 10 ml Cyclohexanon 30 sec extrahiert. Wasserspuren werden durch Zentrifugieren aus dem Extrakt entfernt. Die Extinktionen der Lösungen werden bei $\lambda = 496$ nm für Gallein bzw. $\lambda = 510$ nm für Oxyhydrochinonphthalein in Küvetten von 1 cm Schichtdicke gemessen. Als Vergleichslösung dient Cyclohexanon.

Durch Regressionsanalyse der erhaltenen Meßwerte[21] wurden folgende Eichfunktionen erhalten:

$$E = (0{,}167 \pm 0{,}025) + (0{,}0366 \pm 0{,}0014)c_{\mathrm{Sn}}\ \mu\mathrm{g}^{-1}$$

für Gallein als Reagens, und

$$E = (0{,}392 \pm 0{,}010) + (0{,}1049 \pm 0{,}0027)c_{\mathrm{Sn}}\ \mu\mathrm{g}^{-1}$$

für Oxyhydrochinonphthalein als Reagens: c_{Sn} ist die Menge (in μg) des Zinns im Aliquot.

Die Nachweisgrenzen liegen bei den angegebenen Verfahren bei 1,55 μg für die Galleinmethode und 0,212 μg für die Oxyhydrochinonphthaleinmethode.

Störungen

Störungen der Zinnbestimmung sind durch Komplexbildungsreaktionen anderer Lösungsbestandteile, Zerstörung der Reagenzien durch z.B. starke Oxydationsmittel und durch Zinnadsorption an in der wäßrigen Lösung gebildeten Niederschlägen zu erwarten. Unter Anwendung des Grundverfahrens wurde überprüft, welchen Einfluß bestimmte Lösungsbestandteile auf die Bestimmung von 10 μg Zinn mit Gallein bzw. von 2,5 μg Zinn mit Oxyhydrochinonphthalein haben. Dabei wurde festgestellt, daß starke Oxydationsmittel, z.B. Peroxide, Fe(III), Mn(VII), V(V), Cr(VI), Ce(IV) stören, und es wurde deshalb in allen weiteren Versuchen Ascorbinsäure (25 mg) als Reduktionsmittel hinzugefügt.

Die Zinnbestimmung wird nicht gestört durch: Alkalien, Erdalkalien, Pb, Zn, Cd, Ni, Fe im Überschuß von 1000 : 1: B, Al, Tl, Si, As, Sb(V), Bi, La, Ce, Ti, Zr, V, Cr, Mo, W, Mn, Co, Cu, Hg im Überschuß von 100 : 1; Sb(III), Se, Te, Th, Ag im Überschuß von 10 : 1. Störungen durch Germanium sind nicht zu beseitigen. In Tabelle 3 sind die wesentlichen Störungen zusammengefaßt.

Tabelle 3. Einfluß von Lösungsbestandteilen auf die Bestimmung von 10 μg Zinn bei Verwendung von Gallein und von 2,5 μg Zinn bei Verwendung von Oxyhydrochinonphthalein

Lösungsbestandteile und Bemerkungen	Verhältnis des Lösungsbestandteils zu Zinn	gefundene Zinnmenge, μg	
		Gallein	OP
Ge	1 : 1	11,1	2,8
Sb(III)	100 : 1	12,0	3,0
Se	100 : 1	9,0	2,2
Te	100 : 1	11,0	2,7
Fe(III) ohne Ascorbinsäure	10 : 1	7,5	1,8
V(V)		9,0	2,3
Cr(VI)		2,0	0,6
Mn(VII)		3,5	0,8
Ce(IV)		8,5	2,1
F^-	100 : 1	7,9	2,5
F^- und Zr(IV)	100 : 1	10,0	—
$ZrO(H_2PO_4)_2$	100 : 1	5,0	—
Kieselsäure	1000 : 1	9,1	2,0
$PbSO_4$	100 : 1	9,5	2,4
$BaSO_4$	100 : 1	9,7	2,2
AgCl	100 : 1	8,9	2,5

Anwendungsbeispiel

Die vorgeschlagenen Zinnbestimmungsverfahren wurden bei der Analyse von Erzen und Aufbereitungsprodukten erprobt. Diese Materialien haben meist eine komplizierte Zusammensetzung. Der sehr schwer lösliche Zinnstein wird durch den Aufschluß mit Natriumperoxid in Lösung gebracht. Nach Beendigung des Aufschlusses wird die Schmelze mit Wasser aufgenommen und zur Zerstörung von Peroxiden aufgekocht. Die Suspension der Oxide und Hydroxide wird mit Säure behandelt. Da hierbei insbesondere beim Überschreiten des neutralen pH-Gebietes Zinnoxidhydrate ausfallen können, wird vor dem Ansäuern Weinsäure als Hilfskomplexbildner hinzugefügt. Es empfiehlt sich ebenfalls, die zur Zerstörung der Oxydationsmittel notwendige Ascorbinsäure bereits zuzusetzen. Die Aufschlußlösung wird hierdurch sehr viel schneller klar. Die Menge an Maskierungsreagens und Säure muß so bemessen sein, daß nach dem Auffüllen im Meßkolben Konzentrationen von 5 g/l an Weinsäure, 2,5 g/l an Ascorbinsäure und 0,5N an H^+ eingestellt werden. Als Säure sind Salzsäure und Schwefelsäure geeignet.

Von der auf diese Weise vorbereiteten Aufschlußlösung werden Aliquote je nach dem Zinngehalt für die photometrische Bestimmung abgenommen. In Analogie zum bereits beschriebenen Grundverfahren erfolgt die Neutralisation, die Zugabe der Pufferlösung und der Reagenslösung sowie die Extraktion mit Cyclohexanon. Nach der Entfernung von Wasser aus dem Extrakt wird die Extinktion bei 495 nm bei Gallein bzw. 510 nm bei Oxyhydrochinonphthalein gemessen. Die Schichtdichte der Küvetten richtet sich nach der Zinnkonzentration, die bestimmt werden soll. Der als Verunreinigung in den verwendeten Reagenzien vorhandene Zinngehalt wird durch eine Vergleichsanalyse ohne Einsatz von Zinnerz erfaßt.

Mit dem Verfahren wurde der Zinngehalt von Erzen und Aufbereitungsprodukten Altenberger Erztypen bestimmt. Der Analysenfehler betrug 3–5% (relativ) bei Gehalten zwischen 0,1 und 1% Sn.

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Summary—The formation of complexes between tin(IV) and *o*-diphenols, and *o*-hydroxyquinones, has been studied spectrophotometrically. Simple *o*-hydroxyquinones do not react with tin(IV), chloranilic acid gives an SnR_2 complex, and *o*-diphenols give SnR_3 complexes. The reactions of tin(IV) with hydroxyxanthene dyes to give coloured products were considered for their possible analytical utility: the pH range, absorption spectrum, solubility and composition of the complexes were investigated, and the stability constants determined. Analytical procedures have been developed for tin and checked for precision and sensitivity: gallein and hydroxyhydroquinonephthalein (dihydroxyfluorescein) are to be recommended.

Resume—On a etudie spectrophotometriquement la formation de complexes entre l'etain (IV) et les *o*-diphenyles et *o*-hydroxyquinones. Les *o*-hydroxyquinones simples ne reagissent pas avec l'ètain (IV), l'acide chloranilique donne un complexe SnR_2, et les *o*-diphénols donnent des complexes SnR_3. Les reactions de l'etain (IV) avec les colorants de l'hydroxyxanthene pour donner des produits colorés ont été considérées pour leur utilité analytique possible: on a étudié les domaines de pH, spectre d'absorption, solubilité et composition des complexes et determine les constantes de stabilite. Des techniques analytiques ont ete developpees pour l'ètain et contrôlées pour la précision et la sensibilité: la galléine et l'hydroxyhydroquinonephthaleine (dihydroxyfluoresceine) doivent etre recommandees.

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EXTRACTIVE SEPARATION OF MOLYBDENUM AS Mo(V) XANTHATE FROM IRON, VANADIUM, TUNGSTEN, COPPER, URANIUM AND OTHER ELEMENTS

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Summary—A simple and selective extraction of molybdenum is described. Tungsten is masked with tartaric acid and molybdenum(VI) is reduced in 2*M* hydrochloric acid by boiling with hydrazine sulphate. Iron, copper and vanadium are then masked with ascorbic acid, thiourea and potassium hydrogen fluoride respectively. The molybdenum(V) is extracted as its xanthate complex into chloroform, from 1*M* hydrochloric acid that is 0·4*M* potassium ethyl xanthate. The complex is decomposed by excess of liquid bromine, and the molybdenum is stripped into alkaline hydrogen peroxide solution. The molybdenum is then determined by standard methods. Large amounts of Cu(II), Mn(II), Fe(III), Ti(IV), Zr, Ce(IV), V(V), Nb, Cr(VI), W(VI), U(VI), Re(VII) and Os(VIII) do not interfere. Several synthetic samples and ferromolybdenum have been rapidly and satisfactorily analysed by the method.

The extraction of molybdenum as xanthate by organic solvents[1] has been mainly used[2,a] to prevent its interference in rhenium determination with thiocyanate. The reaction has not found application for the determination of molybdenum, as the coloured species is not stable.[2b] Although the complex is supposed to be formed with the Mo(V) produced by the reduction of Mo(VI) by xanthate itself in acid solution,[2c] the procedures insist on starting from Mo(VI) and alkaline solution to avoid formation of molybdenum blue which does not react with the reagent.[3] Such conditions do not permit the suppression of extraction of other elements by their reduction and complexation. Starting from Mo(V), the method presented below makes possible a selective extraction of molybdenum xanthate and its subsequent determination by standard methods. There are very few such methods[4 9] for milligram amounts of molybdenum which are satisfactory.[7 9]

EXPERIMENTAL

Reagents and solutions

Molybdenum solution. 10 mg of Mo per ml. Prepared from sodium molybdate dihydrate, standardized by the oxine method,[10] and diluted as required.

Potassium ethyl xanthate solution, 2M. Prepared fresh daily by dissolving 32·05 g of the salt[11] in water to give 100 ml of solution.

Test samples. Known amounts of molybdenum solutions were mixed with solutions of other elements to give the desired compositions (Table 4) in the aliquot taken for analysis.

Ferromolybdenum. A finely powdered 0·1-g sample was dissolved[12] by warming with 2·5 ml of concentrated hydrochloric acid and 0·2 ml of concentrated nitric acid. The resulting solution was neutralized with 8*M* sodium hydroxide and adjusted to 2*M* with respect to hydrochloric acid for analysis by the procedure.

Separation procedure

A 10-ml sample solution containing up to 100 mg of molybdenum was adjusted to be 2*M* in hydrochloric acid and boiled with excess of hydrazine sulphate (1 mg/mg of reducible ions) for 2–3 min, in a 5 ml covered beaker. The solution was cooled with tap-water and transferred to a 150 ml separatory funnel already containing 4 ml of xanthate solution and enough water to make the final volume 20 ml. The solution was shaken for 2 min with 20 ml of chloroform to extract the violet-red molybdenum(V)-xanthate complex. The chloroform layer was transferred to another separatory funnel. If necessary, another 2 ml of the xanthate solution were added and a second extraction was done with 20 ml of chloroform.

For each 100 mg of tungsten present, 3 g of tartaric acid were added before acidification of the sample solution. For each 100 mg of iron(III), copper(II) and vanadium(V) present, 0·6 g of ascorbic acid, 2 g of thiourea and 1 g of potassium hydrogen fluoride respectively were added, after the reduction of molybdenum.

Back-extraction of molybdenum. The combined solvent phases were shaken with liquid bromine which was added dropwise till the solution was clear red. Sodium hydroxide, 8*M*, was then added dropwise till the solvent turned yellow. The funnel was cooled in ice and then shaken first with 30 ml of just alkaline water containing 2–3 ml of 6% hydrogen peroxide and then with two 20 ml portions of this mixture, each time for 2 min. The combined aqueous phase was boiled for 5 min with excess of hydrogen peroxide and filtered through Whatman No. 41 paper to remove the hydroxides of co-extracted elements. The molybdenum in the filtrate was then determined.[10,13]

To study the variables the following parameters were held constant, except when these parameters themselves were the subject of study: 20 ml of aqueous phase, containing 20 mg of molybdenum, 1*M* in hydrochloric acid, 0·4*M* in xanthate, and extraction once with an equal volume of solvent. The amount of molybdenum extracted was obtained by difference between that taken and that left in the aqueous phase.

Determination of the elements. Molybdenum in < 5 mg amounts was determined spectrophotometrically by the tribenzylamine-thiocyanate method,[7] and in > 5 mg amounts either gravimetrically[10] with oxine or titrimetrically[13] by hydrazine reduction and cerimetry. Appropriate standard methods[10] were used for other elements. Extraction of elements in traces was confirmed by sensitive tests.[10]

Table 1. Extraction by some solvents

Solvent	Mo extraction*, %
Chloroform	100·0
Benzene	100·0
Carbon tetrachloride	99·9
Diethyl ether	99·1
Isopentyl acetate	98·3
Isopentyl alcohol	97·9
Methyl isobutyl ketone	95·4
Tributyl phosphate	93·3

* From 0·5*M* hydrochloric acid.

RESULTS AND DISCUSSION

When tungsten is masked with just enough tartaric acid, molybdenum(VI) is conveniently reduced to molybdenum(V) with hydrazine in 2*M* hydrochloric acid.[2d,13] Molybdenum blue is not formed as it is when xanthate is used for the reduction.[3] Consequently in the proposed procedure all of the xanthate is used for complex formation and the oxidation state of the molybdenum is known with certainty. Slightly lower extraction is obtained if the reduction is carried out from < 2*M* hydrochloric acid. Ascorbic acid and thiourea suppress the extraction of iron and copper, respectively, under these conditions. Vanadium(V) is also reduced to vanadium(IV) and is extracted to a lesser degree. Further suppression is achieved by complexation with fluoride. Any chromium(VI) is reduced to chromium(III) which is not extracted.

Effect of varying experimental conditions

Molybdenum extraction is ⩾ 99·9% from 0·4*M* xanthate and 0·2–1·5*M* hydrochloric acid and 99·9–98·9% from 0·4*M* xanthate in 0·2–1·5*M* sulphuric acid, and is independent of molybdenum concentration from 0·05 to 5 mg/ml. Chloroform is the best organic solvent (Table 1). Equilibrium is attained in 1–2 min. Complexing agents suppress the

Table 2. Effect of anions on Mo–xanthate extraction

Salt added*	Mo extraction, % 0·5M HCl	Mo extraction, % 1M HCl
None	100·0	99·9
Sodium chloride (1)†	99·9	
Sodium sulphate (5)†	99·0	
Sodium acetate (4)	98·8	
Potassium hydrogen fluoride (3)	5·3‡	78·0
Sodium tartrate (2)	4·3§	99·5
Sodium oxalate (0·8)	2·1	
Disodium salt of EDTA (0·5)	1·5	41·0
Potassium phosphate (2·5)	0·5	
Sodium citrate (3·5)	0·0	

* Amount of the salt added (g) after Mo reduction, in brackets.

† Added before Mo reduction.

‡ 85%, § 87·5%, if 1 g of the salt is added.

extraction more at lower acidity. The procedure given utilizes the optimum conditions for 99·9% extraction. More than 100 mg of molybdenum can be handled by the procedure, if the concentration of xanthate and the volume of chloroform are increased.

Effect of diverse ions

When added after reduction of molybdenum, nearly saturated solutions of sodium acetate decrease the extraction by 1% whilst EDTA, tartrate, oxalate, citrate, phosphate and fluoride almost completely suppress the reaction (Table 2). At lower concentrations of the complexing agents, the extraction is still high and can be further increased by raising the acidity of the solution but more than two extractions may be necessary. Sodium chloride and sulphate have negligible effect.

Table 3 Extraction of various elements under conditions of the method

Element*	Extraction, %
Cu(II)	100·0, 0·01§
Sb(III)	100·0
Bi(V)	100·0
Pd(II)†	100·0
Sn(II)	98·0
Ni(II)	85·7
Pb(II)	55·0
Co(II)	52·2
Fe(III)	45·6, 0·15¶
V(V)	15·1, 0·02‖
Ru(III)†	0·3
Pt(IV)†	0·2
U(VI)	0·01
Ti(IV)†, Cr(VI), Mn(II), Nb(V)†, W(VI)**, Re(VII)‡, Os(VIII)†, Zr(IV), Ce(IV)	Nil

* 5 mg/ml: initial oxidation state in brackets.

† 1·5 mg/ml and ‡ 5 μg/ml of aqueous phase.

§ 2 g of thiourea, ¶ 0·6 g of ascorbic acid and ‖ 1 g of KHF, per 20 ml, added after hydrazine reduction.

** Kept in solution by 3 g of tartaric acid.

Under the proposed conditions, Ti, Zr, Ce, Nb, Cr, W, Mn, Re and Os are not extracted at all (Table 3). Uranium and (in presence of the appropriate masking agents) copper, iron and vanadium, are extracted in traces. Of these, copper can be stripped by shaking the extract with 1*M* hydrochloric acid containing thiourea. At higher acidities, the extraction of iron, cobalt and nickel (in the absence of masking agents) decreases to a few per cent but so does that of molybdenum. Differential stripping of other extracted elements is not effective as the molybdenum complex is similarly affected.

Stripping and determination of molybdenum

Molybdenum cannot be stripped completely from the solvent with concentrated hydrochloric or nitric acid, permangante solution or complexing agents and hydrogen peroxide in acid or alkaline solution. The molybdenum xanthate must first be decomposed and this is achieved with liquid bromine. For quantitative stripping, the resulting chloroform solution should be shaken with aqueous sodium hydroxide till it turns yellow. Hydrogen peroxide is added to further oxidize the xanthate decomposition products. Filtration of the hydroxides of co-extracted traces of copper and iron does not entail any loss of molybdenum.[14] Traces of vanadium may remain in the filtrate without causing appreciable error in the determination of molybdenum.

The filtrate is acidified and boiled with excess of hydrogen peroxide to decompose the bromide completely. The molybdenum can then be determined by standard gravimetric or colorimetric methods.[10] The decomposition of bromide may be omitted if it does not interfere. Titrimetric determination by cerimetry[13] can be done after oxidizing the filtrate with nitric acid and evaporating the resulting solution to fuming with a little sulphuric acid. Otherwise, low results are obtained owing to incomplete reduction and an uncertain end-point in the titration.

Applications

The method is useful for the separation of μg–mg amounts of molybdenum. Separation

Table 4. Analysis of samples by the proposed method

Sample composition*		
Matrix	Mo	Mo found†
Mn(60) Fe(15) Cu(30) U(25)	48·8 mg	48·75 mg
Fe(50) Cu(20) V(12) Cr(35) Re(0·5)	39·0 mg	39.1 mg
Fe(42)	58·5 mg	58·5 mg
W(45)	29·3 mg	29·2 mg
V(60)	19·55 mg	19·6 mg
U(75)	34·1 mg	34·2 mg
Cr(20) Ce(8) Nb(15) Os(5) Zr(25) Ti(10) Nb(5) V(15) W(10) U(8)	68·25 mg	68·3 mg
Fe(10) Cr(15)	14·6 mg	14·6 mg
Mn(15) Zr(10) Ti(5) Fe(40) Cr(20)	48·0 μg	47·8 μg
V(25) W(15) U(30) Re(0·5)	20·0 μg	19·9 μg
Fe(6·6) W(1·7) Cr(1) C(0·35)§	250·0 μg	248·0, 249·0 μg
Ferromolybdenum	58·9 %	59·0, 58·8 % 58·84, 58·9 %‡

* Number in brackets gives the amount in mg.

† Milligram amounts by oxinate method[10] and μg amounts by TBA–SCN method.[7]

‡ By cerimetry.[13]

§ Analogous to cristite.

from large amounts of otherwise difficultly separable elements, *viz.*, Fe, W, V, Cr, Cu, U, Ti, Nb, is possible in about 20 min. Satisfactory analyses (Table 4) of several complex synthetic samples and ferromolybdenum show the wide applicability of the method.

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Zusammenfassung—Eine einfache und selektive Methode zur Extraktion von Molybdän wird beschrieben. Wolfram wird mit Weinsäure maskiert und Molybdän(VI) in 2*M* Salzsäure durch Kochen mit Hydrazinsulfat reduziert. Eisen, Kupfer und Vanadium werden dann mit Ascorbinsäure, Thioharnstoff bzw. Kaliumhydrogenfluorid maskiert. Das Molybdän(V) wird als Xanthat-Komplex aus 0,4*M* Kaliumäthylxanthat enthaltender 1*M* Salzsäure in Chloroform extrahiert. Der Komplex wird durch einen Überschuß von flüssigem Brom zersetzt und das Molybdän in alkalische Wasserstoffperoxidlösung zurückextrahiert. Molybdän wird dann in bekannter Weise bestimmt. Große Mengen Cu(II), Mn(II), Fe(III), Ti(IV), Zr, Ce(IV), V(V), Nb, Cr(VI), W(VI), U(VI), Re(VII) und Os(VIII) stören nicht. Mehrer selbst gemischte Proben und Ferromolybdän wurden auf diese Weise rasch und zufriedenstellend analysiert.

Resumé—On décrit une extraction simple et sélective du molybdène. Le tungstène est dissimulé par l'acide tartrique et le molybdène (VI) est réduit en acide chlorhydrique 2*M* par ébullition avec le sulfate d'hydrazine. Les fer, cuivre et vanadium sont alors dissimulés par l'acide ascorbique, la thiourée et le fluorure acide de potassium respectivement. Le molybdène (V) est extrait à l'état de complexe xanthique en chloroforme, d'acide chlorhydrique 1*M* qui est 0,4*M* en éthylxanthate de potassium. Le complexe est décomposé par un excès de brome liquide, et le molybdène est réextrait dans une solution alcaline de peroxyde d'hydrogène. Le molybdène est alors dosé par les méthodes normales. De grandes quantités de Cu(II), Mn(II), Fe(III), Ti(IV), Zr, Ce(IV), V(V), Nb, Cr(VI), W(VI), U(VI), Re(VII) et Os(VIII) ne gênent pas. Plusieurs échantillons synthétiques et le ferromolybdène ont été analysés rapidement et de manière satisfaisante par la méthode.

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DETERMINATION OF TRACES OF Mo IN SOILS AND GEOLOGICAL MATERIALS BY SOLVENT EXTRACTION OF THE MOLYBDENUM–THIOCYANATE COMPLEX AND ATOMIC ABSORPTION

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Summary—Comprehensive studies of the extraction of the molybdenum–thiocyanate complex with methyl isobutyl ketone have resulted in an improved method for the determination of traces of molybdenum in soils and geological materials by atomic-absorption spectroscopy. The method is applicable in the range 1–500 ppm Mo, with 1-g samples, giving relative standard deviations not exceeding about 8% at a level of 1 ppm. The limit of detection is 0·1 ppm. There are few interferences, and large quantities of iron are without effect.

Molybdenum as a trace element in waters, geological materials, plants and animals has been extensively studied for over 30 years. Mo in soils has been the subject of many investigations since 1939 when Arnon and Stout[1] first showed it was essential to higher plants. The average abundance of Mo in soils is given as 2·5 ppm by Andrews-Jones[2] but soils can have Mo contents ranging from less than 1 ppm in deficient soils, to several hundred ppm in soils over molybdenum-rich rocks. The average abundance of Mo in geological materials is given[2] as: crust 2·3 ppm, sediments 2·0 ppm, igneous rocks 1·7 ppm, but as with soils, the Mo contents of geological materials can range from less than 1 to several hundred ppm and even larger amounts in ores. Mo is also a valuable pathfinder element in geobotany and biogeochemistry studies in mineral exploration.[3]

Numerous methods are available for the chemical determination of Mo in soils and geological materials. Early work by David[4] examined factors affecting the determination of Mo by atomic-absorption spectroscopy (AAS), as applied to superphosphate and steel samples. More recently Purushottom, Naidu and Lal[5] used phosphoric acid for the suppression of interferences in the determination of Mo in steel and ferromolybdenum in the range 0·02–70 %. The recent method of Hutchison[6] uses complexation and extraction with α-benzoinoxime in chloroform followed by AAS determination of Mo as ammonium molybdate in ammonium chloride–perchloric acid solution. The method is applicable in the range 0·5–250 ppm Mo with relative standard deviations (RSD) ranging from approximately 3 % for the higher concentration ranges to 35% in the lower ranges. However, the method is time-consuming.

Table 1 lists some solvent extraction methods with direct aspiration for the determination of Mo by AAS. None of the methods is entirely suitable for the determination of traces of Mo in soils and geological materials, particularly in the lower ranges, because of limitations with regard to sensitivity, accuracy, simplicity and freedom from interferences. The last method listed in Table 1 has certain similarities to our method but is not applicable to low concentrations of Mo in steel and consequently is not suitable for

Table 1. Solvent extraction of Mo for AAS

Extraction System	Sample	Extraction conditions		Limitations	Ref.
MIBK-Aliquat 336	Geological material	10% H_3PO_4-2% H_2O_2	$N_2O-C_2H_2$	Poor precision, > 30 ppm Mo	7
MIBK-Oxine	Lake water	pH 2–2·4	$N_2O-C_2H_2$	Extraction sensitive to pH variation	8
MNAK-Oxine	Water, plants, silicates, soils	pH 1·5–2·5	Air–C_2H_2	Inferior solvent; poor flame; Fe interferes	9
$CHCl_3$-MIAK-Oxine	Fertilizers	pH 1·6	$N_2O-C_2H_2$	Inferior solvent; pH critical	10
BuOH-butylamine-Oxine	Nb, Ta alloys	pH 4·5	$N_2O-C_2H_2$	Inferior solvent; unsuitable low Mo ranges	11
MIBK-APDC	Brine	pH 4(25% NaCl)	Air–C_2H_2	Poor flame; variable recovery; specificity poor	12
MIBK-Dithiol	Brine	HCl + KI	Air–C_2H_2	Poor reagent stability; main applic. to brines	13
Isoamyl alcohol-SCN-Sn(II)	Fertilizers	< 1*M* HCl	Air–C_2H_2	Inferior solvent; Fe interferes; > 2·5 ppm Mo	14
Butyl acetate or MIBK-SCN-Sn(II)	Steels, organic compounds	2*M* HCl	$N_2O-C_2H_2$	Unsuitable soils and geological materials; applic. to % Mo; Fe interferes	15

MIBK—Methyl isobutyl ketone. MNAK—Methyl n-amyl ketone. MIAK—Methyl isoamyl ketone. Aliquat 336—Methyltricaprylammonium chloride. APDC—Ammonium pyrrolidine dithiocarbamate. Oxine—8-hydroxyquinoline. Dithiol—4-methyl-1,2-dimercaptobenzene (toluene-3,4-dithiol).

soils and geological materials. Although butyl acetate was preferred to methyl isobutyl ketone in this method, the latter could have been used by using a lean flame before aspiration of the solvent.

Various photometric methods have been used for traces of Mo in the range of materials studied. A recommended method for minerals[16] involves extraction of the thiocyanate complex into butyl acetate and measurement of the absorbance at 520 nm. A somewhat similar official method for plants[17] involves extracting the same complex into isoamyl alcohol and measuring the absorbance at 465 nm. These methods are not generally applicable at concentrations below 5 ppm Mo and are also prone to several interferences.

Emission spectroscopy has been extensively used in survey work for the determination of Mo in plants, soils and geological materials.[3] The detection limit is approximately 5 ppm with an RSD of 10–15% in the lower ranges. This method may be adequate for most survey work but is not satisfactory for Mo-deficient areas or for other studies of concentrations below 5 ppm.

A comprehensive review of the analytical chemistry of molybdenum is available in a recent book by Elwell and Wood.[18]

Our studies of the extraction of the thiocyanate complex with MIBK have revealed that it can form the basis of an improved method for the determination of traces of Mo in soils and geological materials. The method uses a mixture of perchloric and hydrofluoric acids for dissolution of samples, followed by development of the complex after addition of ascorbic acid and stannous chloride. The final stage involves solvent extraction and direct aspiration of the solvent phase into the nebulizer-burner system of an atomic-absorption spectrophotometer.

EXPERIMENTAL

Reagents

Stock solution of 1000 ppm Mo. Prepared by dissolving 1·84 g of analytical grade ammonium heptamolybdate tetrahydrate in distilled water and diluting to 1000 ml. The stock solution was further diluted to 10 ppm.

Tin(II) chloride solution, approx. 10% w/v. Prepared by warming 20 g of analytical-grade reagent ($SnCl_2.2H_2O$) and a small piece of analytical-grade tin metal in 20 ml of 10*M* hydrochloric acid until the solution was clear, cooling, and diluting to 200 ml with distilled water, filtering if necessary, and adding a small piece of tin metal.

Potassium thiocyanate solution, approx. 10% w/v.

MIBK. Redistilled, and fraction boiling at 116–118° collected.

All the other reagents used were of analytical grade.

Apparatus

Instrument: Techtron AA5 atomic-absorption spectrophotometer.
Indicator: DI-30 digital indicator.
Source: ASL molybdenum hollow-cathode lamp.
Wavelength: 313·3 nm.
Current: 5 mA.
Bandpass: 0·10 nm.
Height of light-path above burner: 6 mm.
Fuel: acetylene; flowmeter setting 6·5–7 (approx. 7 l./min).
Support gas: nitrous oxide, delivery pressure 15 psig; flowmeter setting 6 (approx. 6·5 l./min).
Burner: 5-cm AB50 (high-temperature); slot 0·5 mm wide.
Flame: 1–1 5 cm red cone before aspiration of organic solvent.
Aspiration rate: 2·3 ml/min

Calibration

Prepare a stock 5 ppm molybdenum solution by taking 500 μg of Mo in 50 ml of 1*M* hydrochloric acid, adding 2 ml of 10% thiocyanate solution and 3 ml of 10% tin(II) chloride solution, extracting with four successive 10-ml portions of MIBK and diluting the combined extracts to 100 ml with MIBK in a volumetric flask. Dilute aliquots of this solution with MIBK to cover the molybdenum concentration range 0·1–2·0 ppm.

Procedure

Moisten a 1 g sample of the soil or rock (100–200 mesh) with water in a 100 ml Teflon beaker, add 4 ml of 70% perchloric acid and 10 ml of 40% hydrofluoric acid. Evaporate the solution on a hot-plate at about 200° until white fumes of perchloric acid appear, add another 10 ml of 40% hydrofluoric acid and evaporate to dryness. Wash down the walls of the beaker with 1*M* hydrochloric acid and add about 20 ml more, cover with a watch-glass and boil gently for a short time to dissolve the residue. Cool and transfer the solution into a 100 ml separating-funnel, washing the cover and the beaker with 1*M* hydrochloric acid to give a final volume of 40–50 ml. Add 1 ml of 10% thiocyanate solution and solid ascorbic acid (or a solution) until the red colour of the ferric thiocyanate complex disappears (0·2 g of ascorbic acid is needed for 100 mg of ferric iron). At this stage, if a white suspension appears because titanium is present, add 0·5 g of sodium fluoride and shake. Add 2 ml of 10% tin(II) chloride solution and 5 ml of MIBK and shake vigorously for 2 min. Let the phases separate. Drain the aqueous phase into a second separating-funnel and the organic phase into a 10 ml volumetric flask. Wash the first funnel with 4·5 ml of MIBK and transfer the washings into the second funnel. Shake for 1 min. Discard the aqueous solution and add the organic phase to the volumetric flask. Wash the funnel with MIBK to fill the flask to the mark. Determine the absorbance of the extract, using MIBK as blank, by aspirating into the nebulizer–burner system of an atomic-absorption spectrophotometer, under the specified conditions.

For a higher amount of Mo, which can be judged by the red colour of the molybdenum–thiocyanate complex, a larger volume of MIBK can be used. Interference caused by the presence of large amounts of iron and titanium can be removed by additions of ascorbic acid and sodium fluoride respectively.

RESULTS AND DISCUSSION

Comparison of some organic solvents

Aliquots of the MIBK stock solution of molybdenum were diluted exactly 50-fold with various organic solvents and the atomic absorption of each solution was measured relative to that of the solvent alone. The contribution of the MIBK in the mixture was considered negligible. The results are shown in Table 2. Ethyl acetate and MIBK were both found superior but MIBK was selected because of the volatility of ethyl acetate and its high solubility in water, together with the high purity of redistilled MIBK and its low cost.

Effects of acids and other reagents

The effect of 0·5–2·0*M* hydrochloric or sulphuric acid on the extraction of 5 μg of molybdenum as the Mo–SCN complex was investigated. The molybdenum was added

Table 2. Atomic absorption of Mo–SCN complex in various organic solvents (flame conditions optimized to correspond to those obtained for MIBK)

Organic solvent	Absorbance (at 313·3 nm)
Di-isobutyl ketone	0·135
Methyl n-amyl ketone	0·140
Methyl isobutyl ketone	0·400
Isobutyl alcohol	0·102
n-Butyl alcohol	0·120
Isoamyl alcohol	0·098
n-Butyl acetate	0·256
Ethyl acetate	0·405

to 50 ml of the acid in an 80 ml culture tube and 1 ml of 10% thiocyanate solution and 2 ml of 10% tin(II) chloride solution were added, followed by 5 ml of MIBK. After shaking for 20 min in a mechanical shaker, the organic phase was separated and its atomic absorption measured. There were no significant differences between the acids over the range tested. Hydrochloric acid (1*M*) was preferred because it was more suitable for use in the dissolution procedure, and avoided possible interference by sulphate and the hydrolysis of tin(II,IV) chlorides which occurs at hydrochloric acid concentrations below about 0·5*M*. Grosz,[15] using a somewhat similar system, found constant extraction of molybdenum from 2–6*M* hydrochloric acid but there is little advantage in using these higher concentrations, which may also cause increased extraction of interfering ions. Also, in 1*M* hydrochloric acid, iron is easily masked with ascorbic acid.

Similar studies with varied amounts of thiocyanate and tin(II) showed no marked differences, and the recommended amounts need variation only for high molybdenum and iron contents. With large quantities of iron, any deficiency of reducing agent can be readily recognized from the red colour of iron(III) thiocyanate. If necessary a 20% tin(II) chloride solution can be used.

Extractability of the Mo–SCN complex into MIBK

The Mo–oxine–MIBK system has been recommended for the determination of microgram quantities of Mo in lake waters.[8] A comparison was made between this system and ours by taking 1 μg of Mo in 100 ml of water, adjusting to the respective extraction conditions (pH 2–2·2 and 1*M* hydrochloric acid) and extracting (mechanical shaking for 1 hr) with 10 ml of 1% oxine solution in MIBK, or with MIBK according to our procedure. The absorbances under identical flame conditions were 0·057–0·081 (mean 0·071) for the Mo–oxine–MIBK extract (4 determinations), and 0·084–0·091 (mean 0·088) for our method (4 determinations). It is considered that the wider spread for the first method is due to the criticality of pH control. Our method would therefore seem well suited to water analysis.

Recovery of Mo

Successive extractions with 10 ml of MIBK showed that extraction was quantitative with the first 10 ml for up to 200 μg of molybdenum.

Standard extracts covering the range 0·1–1·0 ppm Mo and kept in glass-stoppered bottles faded in colour within some hours but gave unchanged atomic-absorption readings over a period of 4 weeks.

Interference studies

A wide range of cations and anions likely to be present in soils and geological materials, or introduced by various dissolution methods, was tested for interference. The results are shown in Tables 3 and 4. In each case the extraction conditions were based on 50 ml of 1*M* hydrochloric acid containing 5 μg of Mo together with the specified interfering element, followed by a single extraction with 5 ml MIBK.

The major interferences were from iron and titanium. Iron up to the 1000 mg level is easily masked by addition of 0·2 g of ascorbic acid for each 100 mg of iron, before the tin(II) chloride solution, the ascorbic acid complexing the iron(II) produced. Ascorbic acid alone does not reduce the Mo quantitatively. Titanium up to the 3 mg level is also

Table 3. Effect of cations on Mo absorbance

Cation (salt used)	Amount of cation added, *mg*	Absorbance
No addition	—	0·54
Li (LiCl)	1000	0·51
	2000	0·46
Na (NaCl)	100	0·52
	1000	0·46
	2000	0·44
K (KCl)	100	0·52
	1000	0·49
	2000	0·48
NH_4 (NH_4Cl)	100	0·51
	1000	0·49
Mg ($MgCl_2$)	100	0·54
	500	0·53
Ca ($CaCl_2$)	100	0·51
	1000	0·48
Ba ($BaCl_2$)	100	0·54
	1000	0·51
Ni ($NiCl_2$)	0·1	0·52
	0·5	0·52
	1·0	0·52
Pb [$Pb(NO_3)_2$]	1·0	0·50
	5·0	0·52
	10·0	0·52
Cu ($CuCl_2$)	1·0	0·53
	5·0	0·54
	10·0	0·54
Cd ($CdCl_2$)	0·1	0·52
	0·5	0·52
Mn ($MnCl_2$)	0·1	0·54
	5·0	0·54
W (Na_2WO_4)	0·1	0·55
	0·2	0·54
Cr ($K_2Cr_2O_7$)	0·1	0·54
	5·0	0·54
V (V_2O_5 in HCl)	0·1	0·54
	0·2	0·54
Ce [$Ce(NH_4)_2(SO_4)_3$]	1·0	0·54
	2·0	0·53
Zr [$Zr(SO_4)_2$]	1·0	0·53
	2·0	0·54
Fe [$FeNH_4(SO_4)_2$]*	25·0	0·53
	50·0	0·53
	100·0	0·18
	150·0	0·10
	200·0	0·08
	250·0	0·05
Al ($AlCl_3$)	5·0	0·53
	10·0	0·53
	20·0	0·52
Zn (ZnO in HCl)	1·0	0·52
	5·0	0·53
As (As_2O_3 in HCl)	1·0	0·52
	2·0	0·53
Sb (Sb_2O_3 in HCl)	1·0	0·53
	2·0	0·53
Bi (Bi_2O_3 in HCl)	1·0	0·51
	5·0	0·52
	10·0	0·52
Co ($CoCl_2$)	1·0	0·52
	2·0	0·52
Ti (Ti in HCl)	1·0	0·38
	2·0	0·19
Re ($KReO_4$)	0·05	0·52
	0·10	0·52
Pt (PtO)†	1·0	0·52
Rh (Rh sponge)†	1·0	0·52
Pd (PdI_2)†	1·0	0·52

* Used in place of $FeCl_3$, which contained Mo.

† HF-$HClO_4$ dissolution procedure used.

Table 4. Effect of anions on Mo absorbance

Anion (salt used)	Amount of anion added, *mg*	Absorbance	Anion (salt used)	Amount of anion added, *mg*	Absorbance
No addition	—	0·52	Oxalate [$(NH_4)_2C_2O_4$]	500	0·52
				1000	0·52
Phosphate (Na_2HPO_4)	1	0·52	Sulphate (Na_2SO_4)	5	0·52
	5	0·52		700	0·51
	500	0·52		1000	0·51
Nitrate ($NaNO_3$)	5	0·51	Fluoride (NaF)	500	0·53
	700	0·51		1000	0·52
	1000	0·50	Tetrafluoroborate (KBF_4)	500	0·54
Silicate (Na_2SiO_3)	500	0·53		1000	0·53
	1000	0·53	Acetate ($NaC_2H_3O_2$)	500	0·50
Borate (H_3BO_3)	1000	0·53		1000	0·52
	2000	0·54			

easily masked, by the addition of 0·5 g of sodium fluoride before the tin(II) chloride solution.

Dissolution of samples

Several dissolution methods are available for soils and geological materials. More recent methods include: decomposition with hydrofluoric acid at 110–120° in a Teflon-lined decomposition vessel and use of a fluoboric–boric acid matrix;[19] decomposition with hydrofluoric acid by heating on a water-bath[20] and in some cases with a hydrofluoric–perchloric acid mixture by a bomb technique;[20] and fusion with lithium metaborate.[21] Earlier fusion methods with fluxes such as the carbonates or borates of sodium, potassium or lithium may give incomplete attack on the samples, losses caused by reduction and alloying with the crucible material, and limited solubility of some metal ions in the particular flux. In addition these methods lead to high salt concentrations, which is a considerable disadvantage in AAS. Simpler methods than bomb-dissolution or lithium metaborate fusion were preferred for this study. In our method, the presence of silica causes difficulties in the extraction step if alkaline fusion is used, owing to the formation of colloidal silicic acid upon acidification. For this reason silica is removed with hydrofluoric acid.

Comparative dissolution studies on 1 g soil samples showed that decomposition in a Teflon beaker with hydrofluoric–perchloric acid mixture was simple, rapid and well suited to the extraction system. Three variations of the dissolution method were tested on 1 g samples (200 mesh) of a soil containing 2·5 ppm Mo.

Method A. The sample was weighed into a platinum crucible and moistened with a few drops of water followed by a few drops of concentrated sulphuric acid. Then 10 ml of 40% hydrofluoric acid were added and evaporated on a steam-bath, followed by a further addition of 10 ml of hydrofluoric acid and evaporation, then heating on a hot-plate to expel sulphuric acid, followed by addition of 4 g of sodium carbonate and fusion at 950°. The fused cake was digested with hot water, the hydroxides were filtered off and the solution was evaporated to about 40 ml, then 10 ml of concentrated hydrochloric acid were added (to adjust the acidity to approximately 1*M*) and the extraction method and determination of Mo applied.

Method B. Same procedure as for method *A* but without filtering off the hydroxides. The fused cake was dissolved with 10 ml of 10*M* hydrochloric acid and the solution diluted to 50 ml, ready for extraction.

Method C. Hutchison's procedure:[6] 10 ml of hydrofluoric acid were added to the sample in a Teflon beaker and evaporated to dryness, then 10 ml of a mixture of perchloric and nitric acids (1 : 3) were added and evaporated to dryness. The dry residue was dissolved by boiling with 1*M* hydrochloric acid, then the extraction and determination of Mo were applied.

Method D. The recommended method.

All four methods gave results of 2·5 ± 0·1 ppm Mo. Method *D* was chosen mainly for speed and convenience, although any of the methods would do.

Amount of sample

The recommended procedure was applied to 1-, 2- and 3 g amounts of a soil containing 1·2 ppm Mo. For each additional 1 g of soil above the recommended 1 g, the recovery of Mo dropped by approximately 10%. The reason is not known. The other constituents of this soil, as determined by emission spectroscopy, were approximately Si, 40%, Al 10%, Fe 3%, Ca 0·3%, Mg 0·5%, Na < 0·1%, K < 0·1%, Mn 0·1%, Ti 0·1%, Cu 0·05%, Ag 0·001%.

Working curves

Working curves were prepared covering the ranges 0·1–1·0, 1–10 and 10–50 ppm Mo and were linear up to approximately 30 ppm of Mo in MIBK (corresponding to 300 ppm Mo in soil) and then curved slightly. Instrument scale expansions of 1–10 could be used where appropriate. Before each measurement the signal was adjusted to zero with pure MIBK. The reagent blank was zero. With the higher concentrations of molybdenum and increased volumes of MIBK, some hydrochloric acid can be extracted in the form of an ion-pair with the stoichiometric composition $HCl.5H_2O.4MIBK$.[22] For this reason additional hydrochloric acid can be added to maintain the acidity of the aqueous phase for maximum extraction efficiency. Sometimes the red colour of $KSCN–SnCl_2–MIBK$ can be confused with that of Mo(V)–SCN–MIBK, although they can be differentiated with experience.

Analysis of soils and geological materials

A range of soils and geological materials was analysed for Mo by the recommended procedure. Where possible, samples were selected which had been analysed by an independent laboratory. The results are given in Table 5. Table 6 gives the approximate matrix composition of the samples as determined by emission spectroscopy.

CONCLUSION

An improved method is described for the determination of traces of Mo in soils and geological materials by atomic-absorption spectroscopy. The method is applicable in the range 1–500 ppm Mo, on 1 g samples, with relative standard deviations not exceeding about 8% at the 1 ppm level. The detection limit is 0·1 ppm. Interferences by iron and titanium can be removed. The method should also be applicable to the determination of trace Mo in waters, steels and other materials.

Table 5. Analysis of soils and geological materials

Sample	No. of detns.	Mean Mo, *ppm*	RSD,* %	Indep. lab. value
Open Cut, Rye Park, N.S.W.	3	99·1	1·2	—
Rye Park Soil, N.S.W.	4	3·7	2·6	—
Sunny Corners Soil (Creek), N.S.W.	13	2·5	4·0	—
Sunny Corners Soil (Dump), N.S.W.	4	1·2	8·1	—
Sunny Corners Soil (Road), N.S.W.	4	1·2	8·1	—
N.S.W. Mine's Dept. (3023)	4	3·4	5·7	3
N.S.W. Mine's Dept. (Mo)	5	117·0	0·7	—
U.S.G.S. Gossan	3	6·3	0·9	6
CRAE 142434	3	1·2	4·9	<2
CRAE 101932 (3100)	3	22·1	1·6	22
CRAE 10600 (3063)	4	5·7	1·7	6

* Calculated from range if less than 10 replicates.

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Zusammenfassung—Eine umfassende Untersuchung der Extraktion des Molybdän-Thiocyanat-Komplexes mit Methylisobutylketon ergab eine verbesserte Methode zur Bestimmung von Molybdanspuren in Böden und geologischem Material durch Atomabsorptionsspektrometric. Das Verfahren arbeitet bei 1–500 ppm Mo mit 1 g-Proben; die relativen Standardabweichungen übersteigen 8 % bei 1 ppm nicht. Die Nachweisgrenze ist 0,1 ppm. Es gibt nur wenige Störungen; große Mengen von Eisen sind ohne Einfluß.

Résumé—Des études approfondies de l'extraction du complexe thiocyanate de molybdène avec la méthylisobutylcétone ont conduit à une méthode améliorée pour le dosage de traces de molybdène dans les sols et les substances géologiques par spectroscopie d'absorption atomique. La méthode est applicable dans le domaine 1–500 p.p.m. de Mo, avec des échantillons de 1 g, donnant des écarts types relatifs n'excédant pas environ 8% au niveau de 1 p.p.m. La limite de détection est 0,1 p.p.m. Il y a peu d'interférences, et de grandes quantités de fer sont sans influence.

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SIMULTANEOUS DETERMINATION OF *N*-UNSUBSTITUTED AND *N*-SUBSTITUTED NITROAZOLES AND CRITERIA FOR THEIR IDENTIFICATION—II

CHROMATOGRAPHIC SEPARATION AND POLAROGRAPHIC DETERMINATION OF NITROPYRAZOLES

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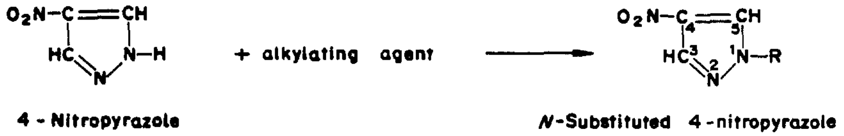
Summary—The *N*-unsubstituted nitropyrazoles have an imino hydrogen atom, in contrast to the *N*-substituted derivatives, and react with hydroxide to give nitropyrazole anions. The strongly negative shift of $E_{1/2}$ for these anions makes possible simultaneous polarographic determination of any pair of compounds, one of which is an *N*-unsubstituted nitropyrazole and the other a corresponding *N*-substituted derivative. Simultaneous polarographic determination of three compounds [3(5)-, 3- and 5-nitropyrazoles] is also possible with 0·1*M* sodium hydroxide as supporting electrolyte, but only when $\Delta E_{1/2}$ between the *N*-substituted isomers is at least 100 mV. In this case adequate $\Delta E_{1/2}$ is caused by the different electron densities of the nitro-groups of isomers. In the medium mentioned it is possible to determine simultaneously even four compounds [1-, 3(5)-, 3- and 5-nitropyrazoles], because the $E_{1/2}$ value of 1-nitropyrazole does not change with pH, contrary to other nitropyrazoles. Developers for the chromatographic separation are proposed. Some criteria are given for the distinction of the *N*-unsubstituted- and the corresponding *N*-substituted nitropyrazoles. The structures of two new compounds have been determined. Methods are recommended for the simultaneous identification and determination of the compounds appearing together in the reaction mixtures during the substitution of the imino hydrogen atom, or during the rearrangements of the 1-nitropyrazoles to the *N*-unsubstituted ones.

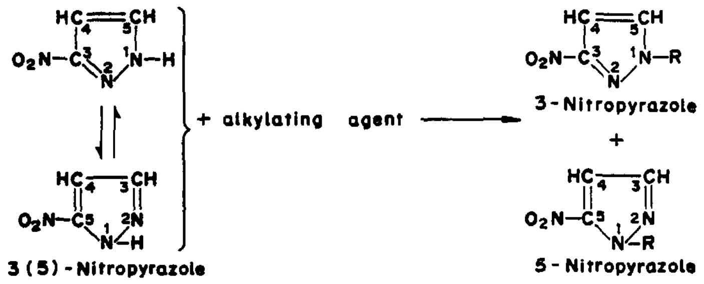
The polarographic method for simultaneous identification and determination of nitroimidazoles appearing together in reaction mixtures during the substitution of the imino hydrogen atom, is based on the different behaviour of *N*-unsubstituted and *N*-substituted nitroimidazoles in 0·1*M* sodium hydroxide.[1–3] The strong negative shift of $E_{1/2}$ which characterizes the anions of *N*-unsubstituted nitroimidazoles, makes possible simultaneous polarographic determination of any pair of compounds, one of which is an *N*-unsubstituted nitroimidazole and the other a corresponding *N*-substituted derivative. When the starting compound is tautomeric, two *N*-substituted derivatives are formed during the substitution of the imino hydrogen atom. Simultaneous polarographic determination of all three compounds is possible, but only in the sodium hydroxide supporting electrolyte, the $E_{1/2}$ values of the *N*-substituted derivatives being differentiated by the effect of the nitro-group in the 4- or 5-position.

The similar physicochemical properties of nitroimidazoles and nitropyrazoles led us to use the same methods for nitropyrazoles as for nitroimidazoles.[1–3] Here, we also wanted to investigate two reaction schemes. According to the first, in which the nitro-group of the starting compound is in a position symmetrical with respect to both nitrogen atoms (position 4), and positions 3 and 5 are unsubstituted or substituted with identical substituents, only one *N*-substituted derivative is formed (Scheme 1). According to the



Scheme 1

second, where the nitro-group of the starting compound is in position 3 or 5 with respect to both nitrogens, two *N*-substituted derivatives are obtained during the substitution of the imino hydrogen atom (Scheme 2).



(R = alkyl)

Scheme 2

However, until very recently[4–6] it was generally considered that the nitration of pyrazoles occurs only in position 4. The only exception was the nitration of *N*-unsubstituted pyrazoles in acetic acid with nitric acid and acetic anhydride, when 1-nitropyrazoles were obtained. [7,8,15,16] As the 3(5)-nitropyrazole, which we wanted to use as a starting material for the preparation of 3- and 5-nitropyrazole isomers, had not been synthesized when we started the work, we could only confirm our assumption for the reaction scheme 1 (Fig. 1).

During 1970 and 1971, three different groups of authors prepared 3(5)-nitropyrazole, in three different ways.[7,9,10] We used one of these procedures[7] to synthesize the starting compound for reaction scheme 2. The processes according to the schemes described earlier for nitroimidazoles[3] and scheme 1 are well known. For scheme 2 we could not find any information, although more recently,[11–14] it has been shown that certain 4-substituted pyrazoles can be nitrated to their 3- or 5-nitro derivatives, but they were prepared from the *N*-substituted pyrazoles. We wished to prepare a reaction mixture for which we could follow the existence of three similar nitropyrazoles. The possibility for that lay in the alkylation reaction, and when 3(5)-nitropyrazole was methylated three compounds were polarographically confirmed. Their structures were deduced from their $E_{1/2}$ values. We expected the $E_{1/2}$ of 1-methyl-3-nitropyrazole to be at a more negative potential than that of the 5-nitro isomer, because of the proximity of the nitro-group to the electron-donor system, as in the case of 4-nitroimidazoles.[3] Accordingly, the structure of 1-methyl-3-nitropyrazole was assigned to the *N*-substituted nitropyrazole having the

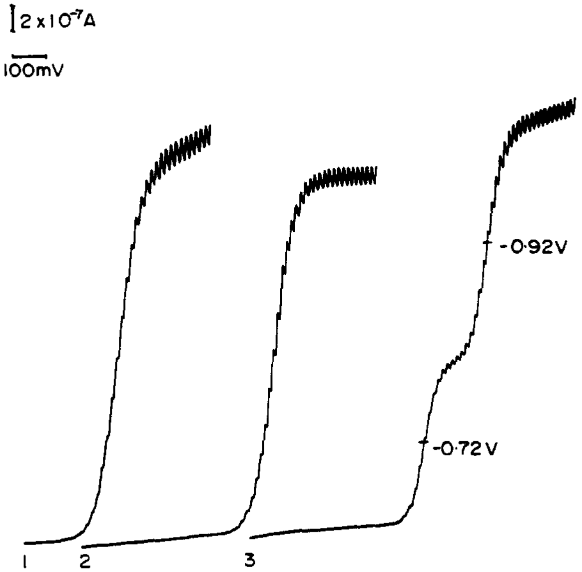


Fig. 1. Equimolar mixtures of 1-methyl-4-nitropyrazole and 4-nitropyrazole polarographed at different pH values. (These compounds appear together in the reaction mixture according to Scheme 1.)
1—pH 2·40; *2*—pH 7·00 (Britton-Robinson buffers); *3*—0·1*M* NaOH. Concentration of each compound $10^{-4}M$. Curves *1* and *2* start at 0 V *vs.* S.C.E. Curve *3* starts at −0·2 V *vs.* S.C.E.

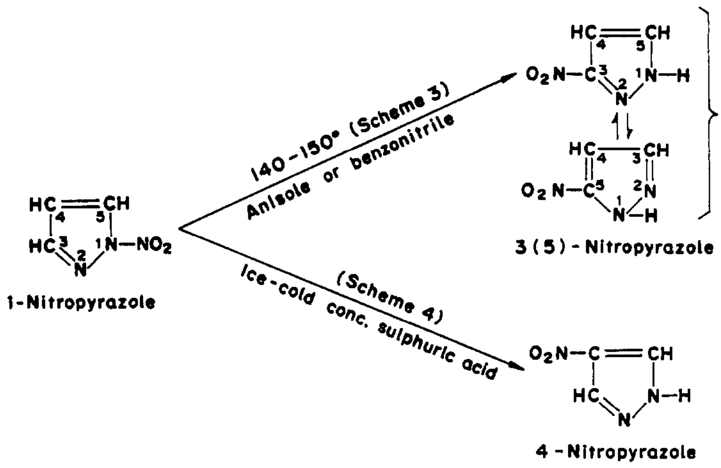
more negative $E_{1/2}$ value, whereas the structure of 1-methyl-5-nitropyrazole was assigned to the compound with the more positive $E_{1/2}$ value. The structures of the newly synthesized compounds were confirmed by infrared, NMR and mass spectroscopy.

It is of importance that the polarographic behaviour was as expected, even for the hitherto unknown reaction scheme 2. Furthermore, the compounds synthesized were identified polarographically directly in the reaction mixture.

Owing to this method, it is possible to isolate 1-methyl-5-nitropyrazole, by choosing the most suitable conditions for its isolation. While searching for these, we observed that under certain experimental conditions a new polarographic wave appeared, which we later identified as belonging to 1-nitropyrazole. This rearrangement had not previously been noted in the literature, though the rearrangement of 1-nitropyrazole to 3(5)-nitropyrazole[7,15,16] (Scheme 3) or to 4-nitropyrazole[8] (Scheme 4) were known. In our case, 3(5)-nitropyrazole was rearranged under certain conditions to 1-nitropyrazole, hence four nitropyrazole compounds could be present in a mixture.

During the rearrangements according to schemes 3 and 4 there are only two compounds in the reaction mixture, of which one is an *N*-substituted nitropyrazole and the other an *N*-unsubstituted nitropyrazole. The possibilities of simultaneous polarographic identification and determination during these and the above-mentioned processes were examined.

In this work six nitropyrazoles have been investigated. Two of them are newly synthesized. The nitropyrazoles investigated, in which the nitro-group was in every position possible for the pyrazole ring [1-, 3(5)-, 3-, 4- and 5-], are examples of compounds appearing together in the reaction mixtures during the substitution of the imino hydrogen



atom (Schemes 1 and 2), during the rearrangements (Schemes 3 and 4), or during the isolation of 1-methyl-5-nitropyrazole.

We describe the chromatographic and polarographic behaviour of these nitropyrazoles, and recommend conditions for their simultaneous identification and determination directly in the reaction mixtures. The structures of the new compounds are discussed and determined, and criteria for distinction between the *N*-unsubstituted nitropyrazole and the *N*-substituted derivatives are proposed.

EXPERIMENTAL

Compounds

All nitropyrazoles studied were prepared in the research department for synthetic chemistry of the Pharmaceutical and Chemical Factory "Galenika", Zemun. The nitropyrazoles had melting points and properties reported in the literature and were prepared according to the references cited. 1-Nitropyrazole, m.p. 92–93°.[8] 4-nitropyrazole, m.p. 161–162°;[17] 1-methyl-4-nitropyrazole, m.p. 91–92°;[17] [19] 3(5)-nitropyrazole, m.p. 174–175°.[7] The newly synthesized compounds were: 1-methyl-3-nitropyrazole, white crystals, m.p. 85°; 1-methyl-5-nitropyrazole, pale yellow liquid, b.p. 83–84°/15 mm, n_D^{25} 1·5310.

RESULTS AND DISCUSSION

The structures of the new nitropyrazoles have been established by NMR and mass and infrared spectrometry. In the NMR spectra both 1-methyl-3-nitropyrazole and 1-methyl-5-nitropyrazole show singlets for methyl-protons, at 4·07 and 4·25 ppm respectively. The difference of 0·18 ppm is due to anisotropy of the nitro-group, which is nearer to the methyl-group in 5- than in 3-nitropyrazole.[13] The other two protons give two doublets at 6·97 and 7·57 ppm in the spectrum of 1-methyl-3-nitropyrazole and at 7·05 and 7·48 ppm in the spectrum of 1-methyl-5-nitropyrazole.

The mass spectra of the isomers studied are more characteristic. In the mass spectrum of the 1-methyl-3-nitropyrazole the intensities of the fragment ions are very low, as in the case of aromatic compounds. M–16 (O) and M–30 (NO) fragments are characteristic for aromatic nitro-compounds. The relative intensities of these two peaks are 3 and 23%, respectively. Fragment ions of the 1-methyl-5-nitropyrazole were M–17 (OH) (44%) and M–29 ($CH_3N \leftrightarrow CH_2NH$) (55%). The OH fragment is possible only if the methyl group is in the neighborhood of the nitro-group.

The infrared spectra of 1-methyl-3-, and 1-methyl-5-nitropyrazole are also consistent with their structures. The bands arising from *asym* and *sym* stretching vibrations of the nitro-group of 1-methyl-3-nitropyrazole are at 1530 and 1373 cm^{-1}, and of 1-methyl-5-nitropyrazole at 1510 and 1345 cm^{-1}. ν_{N-CH_3} is 1280 cm^{-1} (1-methyl-3-nitropyrazole) and 1255 cm^{-1} (1-methyl-5-nitropyrazole). The difference in the position and intensity between these two bands is remarkable. In the spectrum of 1-methyl-5-nitropyrazole the band at 1255 cm^{-1} is the most intensive. One could say that the N–C bond in 1-methyl-5-nitropyrazole is rather polarized.

Chromatographic separations

For all the reaction mixtures we recommend two developers. Thin-layer chromatography was done on unactivated 0·25 mm thick layers of silica gel HF_{254} in an atmosphere saturated with the vapour of the developer. After separation on the adsorbent, the spots visible under short-wave ultraviolet illumination (254 nm) are marked with a needle.

Table 1. Chromatographic separations

Compound	Reaction scheme	R_F values Benzene/methanol (90 : 5)	R_F values Diethylamine	Colour
4-Nitropyrazole	1	0·11	0·10	yellow
1-Methyl-4-nitropyrazole		0·47	0·59	yellow
3(5)-Nitropyrazole	2	0·15	0·12	yellow
1-Methyl-3-nitropyrazole		0·36	0·55	yellow
1-Methyl-5-nitropyrazole		0·78	0·85	reddish
1-Nitropyrazole	*	0·72	0·77	colourless or pale yellow

* 1-Nitropyrazole together with 3(5)-nitropyrazole–reaction Scheme 3, and with 4-nitropyrazole—reaction Scheme 4.

The same plate is then visualized by spraying the chromatogram with tin(II) chloride solution [1·5 ml of 15% tin(II) chloride solution mixed with 7·5 ml of conc. hydrochloric acid, and diluted with 90 ml of water; this solution is freshly prepared before use], dried with hot air and then sprayed with *p*-dimethylaminobenzaldehyde solution (1 g of reagent is dissolved in a mixture of 100 ml of ethanol and 3 ml of conc. hydrochloric acid). After 10 min, coloured spots appear for all the compounds except 1-nitropyrazole. R_F values and colours are given in Table 1.

Polarographic investigation

The polarographic behaviour of all the compounds was examined in 0·5*M* sulphuric acid, acetate buffer (pH 4·68), phosphate buffer (pH 6·85), borate buffer (pH 9·23), 0·1*M* sodium hydroxide and Britton–Robinson buffers over the pH range 1·83–9·30.

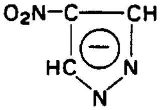
The stock solutions ($10^{-3}M$) of the compounds studied were prepared with water. All measurements, except those designed to investigate the effect of concentration, were carried out with low concentrations of the depolarizers ($2 \times 10^{-4}M$). The solutions examined were prepared by mixing 2 ml of aqueous stock solution with 8 ml of the buffer solution, or 2 ml of the aqueous stock solution with 3 ml of water and 5 ml of 1*M* sulphuric acid, or 2 ml of aqueous stock solution with 3 ml of water and 5 ml of

0·2M sodium hydroxide. The buffer solutions were twice as concentrated as in the original prescriptions, for the reason given in the previous work.[3]

1-Nitropyrazole was studied polarographically by Laviron and Fournari.[20] According to them the first reduction wave corresponds to a two-electron reduction. The mechanisms of reduction for the first and the second wave can be seen in their paper.

4-Nitropyrazole and 1-methyl-4-nitropyrazole give two reduction waves in acidic and neutral media, and only one in alkaline ones. 1-Methyl-3-nitropyrazole also gives two reduction waves in acidic media (pH <4), and a single one at higher pH values. 3(5)-Nitropyrazole and 1-methyl-5-nitropyrazole give one reduction wave over the whole pH range investigated.

The half-wave potentials for the first wave of the compounds investigated, as a function of pH, are given in Table 2. From Table 2 it can be seen that 3(5)-nitropyrazole and 1-methyl-3-nitropyrazole have similar $E_{1/2}$ values over all the pH range (except in 0·1M sodium hydroxide). It shows that 3(5)-nitropyrazole mainly has the 3-nitro form. However, in 0·1M sodium hydroxide N-unsubstituted nitropyrazoles [4-nitropyrazole, 3(5)-nitropyrazole] have more negative $E_{1/2}$ values, because they react with hydroxide, giving the anions I and II, respectively. The high electron-density of their nitro-groups causes a strong negative shift of $E_{1/2}$. The $E_{1/2}$ values of the 1-methyl-3-nitropyrazole are more negative than these of the 5-nitro isomer, because the nitro-group is located in the vicinity of the electron-donor system. The values of $\Delta E_{1/2}/\Delta$pH for the first reduction wave of nitropyrazoles in the pH range 1·83–9·30 are collected in Table 3.



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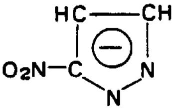

II

From the $E_{1/2}$ values as a function of pH it can clearly be seen that the simultaneous polarographic determination of two (scheme 1, Fig. 1), three (scheme 2, Fig. 2) or four nitropyrazoles (Fig. 3) is only possible if 0·1M sodium hydroxide is used as supporting electrolyte.

As the $E_{1/2}$ values of 1-nitropyrazole remain practically independent of pH ($\Delta E_{1/2}/\Delta\text{pH} = -0{\cdot}005$ V), contrary to the other nitropyrazoles, simultaneous polarographic determination of two compounds (scheme 3) is possible at any pH higher than 6 (Fig. 4), or higher than pH 5 (scheme 4, Fig. 5). Buffers of pH between 6 and 9 are preferred.

The heights of the first wave (investigated separately for each nitropyrazole) are a linear function of the depolarizer concentration over the range from 5×10^{-5} to $2 \times 10^{-3}M$, but when the concentration of one of the compounds is varied in the presence of one or more others which are at constant concentration ($2 \times 10^{-4}M$) the linear relationship is no longer valid over the whole range. Accordingly, the polarographic determination for reaction mixtures should be carried out only over the range where a linear relationship exists (5×10^{-5}–$5 \times 10^{-4}M$).

In this paper we do not intend to draw any definite conclusions concerning the nature of the polarographic current, the number of electrons the nitro-groups consume during the electrode processes, nor give any theoretical explanation for the observed polarographic phenomena. We hope to answer all these questions later, giving here only

Table 2. $E_{1/2}$ as a function of pH

		$E_{1/2}$ V *vs.* S.C.E.													
							pH (Britton-Robinson buffer)								
Compound	Reaction scheme	0·5M H_2SO_4	Acetate buffer pH = 4·68	Phosphate buffer pH = 6·85	Borate buffer pH = 9·23	0·1M NaOH	1·83	2·23	3·20	4·20	5·03	6·06	7·04	8·22	9·30
4-Nitropyrazole	1	−0·14	−0·43	−0·64	−0·73	−0·92	−0·24	−0·25	−0·33	−0·40	−0·47	−0·56	−0·63	−0·70	−0·73
1-Methyl-4-nitropyrazole		−0·14	−0·38	−0·58	−0·68	−0·72	−0·21	−0·22	−0·29	−0·35	−0·42	−0·53	−0·57	−0·65	−0·69
3/5/-Nitropyrazole		−0·09	−0·33	−0·53	−0·61	−0·83	−0·18	−0·20	−0·25	−0·31	−0·37	−0·44	−0·56	−0·58	−0·62
1-Methyl-3-nitropyrazole	2	−0·08	−0·31	−0·49	−0·61	−0·65	−0·17	−0·18	−0·23	−0·29	−0·33	−0·42	−0·49	−0·55	−0·61
1-Methyl-5-nitropyrazole		−0·03	−0·23	−0·39	−0·48	−0·51	−0·09	−0·11	−0·15	−0·20	−0·26	−0·31	−0·39	−0·47	−0·49
1-Nitropyrazole	*	−0·17	−0·26	−0·24	−0·25	−0·24	−0·21	−0·21	−0·22	−0·23	−0·25	−0·25	−0·25	−0·26	−0·25

* 1-Nitropyrazole together with 3(5)-nitropyrazole-reaction scheme 3, and with 4-nitropyrazole—reaction scheme 4.

$E_{1/2}$ values are corrected by comparison with the half-wave potential of thallium in 0·1M KCl.

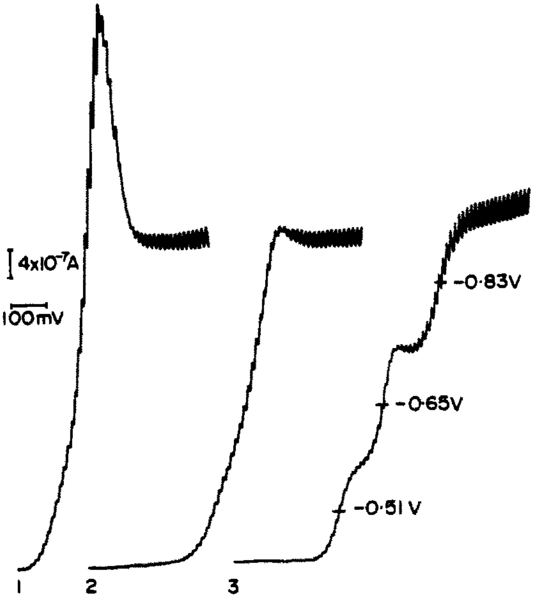

Fig. 2. Equimolar mixtures of 1-methyl-5-nitropyrazole, 1-methyl-3-nitropyrazole and 3(5)-nitropyrazole polarographed at different pH values. (These compounds appear together in the reaction mixture according to scheme 2.)
1—pH 2·23; *2*—7·04 (Britton–Robinson buffers); *3*—0·1*M* NaOH. Concentration of each compound $10^{-4}M$. Curves *1* and *2* start at 0 V *vs.* S.C.E. Curve *3* starts at −0·2 V *vs.* S.C.E.

the correct procedure for simultaneous polarographic determination of nitropyrazoles in reaction mixtures.

Simultaneous polarographic determination

Since the reaction conditions and the composition of the solutions vary during the syntheses, the isolation steps and the rearrangements, calibration curves cannot be used for the evaluation of the polarograms. Instead, the method of standard addition is used.

Procedure

Weigh a sample from the reaction mixture, dissolve it in distilled water and make up to 100 ml, so that the concentration of all polarographically active compounds is about $10^{-3}M$. Transfer a 2 ml portion to a polarographic cell and add water (3 ml) and 0·2*M* sodium hydroxide (5 ml). Deaerate the solution with nitrogen for 5 min and then record the polarogram over the range from −0·1 to −1·2 V *vs.* S.C.E.

Transfer another 2 ml portion of the sample solution to a polarographic cell, add 1 ml of $10^{-3}M$ standard solution of each compound present in the sample examined, add water to 5 ml, if necessary, and 5 ml of 0·2*M* sodium hydroxide, and proceed as before. Evaluate the polarograms by using the equation:

$$\% = (100hc)/(h'w)$$

Table 3. The $\Delta E_{1/2}/\Delta pH$ of nitropyrazoles

Compound	$\Delta E_{1/2}/\Delta pH$, *V*
4-Nitropyrazole	−0·066
1-Methyl-4-nitropyrazole	−0·064
3(5)-Nitropyrazole	−0·059
1-Methyl-3-nitropyrazole	−0·059
1-Methyl-5-nitropyrazole	−0·054
1-Nitropyrazole	−0·005

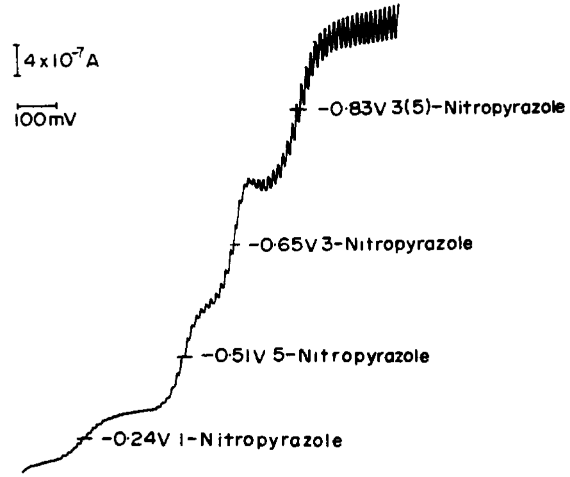

Fig. 3. Equimolar mixture of 1-nitropyrazole, 1-methyl-5-nitropyrazole, 1-methyl-3-nitropyrazole and 3(5)-nitropyrazole.
Supporting electrolyte 0·1*M* NaOH. Concentration of each compound $10^{-4}M$. The curve starts at −0·1 V *vs.* S.C.E.

where % = amount of compound present in the mixture, h = wave-height for the sample, c = weight of the standard added (g), w = weight of the sample in the cell (g), h' = wave-height for the standard (*i.e.*, increase in wave-height when standard is added).

This method of determination is used when it is necessary to know the exact amount of each compound. During the substitution of the imino hydrogen atom it is important to follow the reaction rates and to determine the end of the reaction. In such cases the exact amounts of the compounds present need not to be known, but only their ratio. Such a procedure is very fast. One or two drops from a reaction mixture are added to 0·1*M* sodium hydroxide, deaerated with nitrogen for 5 min, and the polarogram recorded over the range from −0·1 to −1·2 V *vs.* S.C.E. The total wave-heights are taken as equivalent to 100%, and the individual amounts calculated by simple proportion.

The criteria for distinction between N-unsubstituted nitropyrazoles and their N-substituted derivatives

N-unsubstituted nitropyrazoles, because of their pseudo-acidic character, have lower R_F values than the *N*-substituted derivatives in diethylamine. 1-Methyl-5-nitropyrazole is a

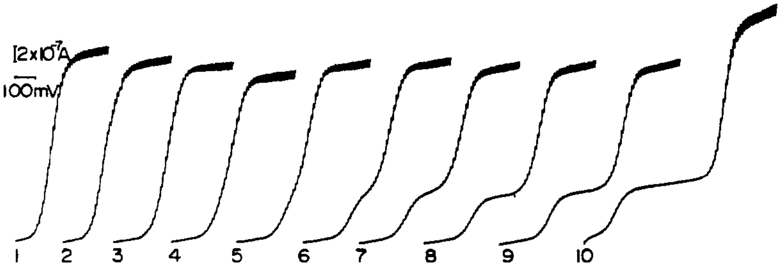

Fig. 4. Equimolar mixtures of 1-nitropyrazole and 3(5)-nitropyrazole polarographed at different pH values. (These compounds appeared together during the rearrangement according to Scheme 3.)
1—pH 1·83; *2*—pH 2·23; *3*—pH 3·20; *4*—pH 4·20; *5*—pH 5·05; *6*—pH 6·06; *7*—pH 7·04; *8*—pH 8·22; *9*—pH 9·30 (Britton-Robinson buffers); *10*—0·1*M* NaOH. Concentration of each compound $10^{-4}M$. Starting potential for all curves is 0 V *vs.* S.C.E., except for the last curve, where it is −0·1 V *vs.* S.C.E.

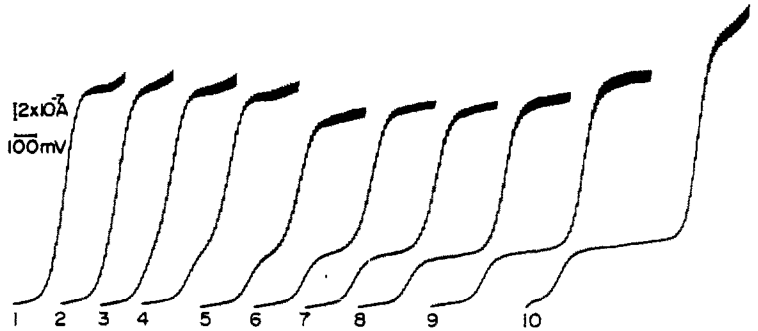

Fig. 5. Equimolar mixtures of 1-nitropyrazole and 4-nitropyrazole polarographed at different pH values. (These compounds appear together during the rearrangement according to Scheme 4.) *1*—pH 1·83; *2*—pH 2·23; *3*—pH 3·20; *4*—pH 4·20; *5*—pH 5·05; *6*—pH 6·06; *7*—pH 7·04; *8*—pH 8·22; *9*—pH 9·30 (Britton–Robinson buffers); *10*—0·1*M* NaOH. Concentration of each compound $10^{-4}M$. Starting potential for all curves is 0 V *vs.* S.C.E., except for the last curve, where it is −0·1 V *vs.* S.C.E.

stronger base than the 3-nitro isomer and hence has in the same developer the highest R_F value. The nitropyrazoles studied, except 1-methyl-5-nitropyrazole and 1-nitropyrazole, give a yellow colour with the spray reagent on silica gel thin-layers. The same treatment applied to 1-methyl-5-nitropyrazole gives a reddish colour, and to 1-nitropyrazole no colour or a pale yellow.

N-unsubstituted nitropyrazoles in alkaline media (*i.e.*, 0·1*M* sodium hydroxide) show a strong negative shift of $E_{1/2}$ value compared to the *N*-substituted derivatives. 4-Nitropyrazole and 1-methyl-4-nitropyrazole or 3(5)-nitropyrazole and 1-methyl-3-nitropyrazole have almost the same $E_{1/2}$ values over a wide pH range (except in 0·1*M* alkali). The $E_{1/2}$ values of 1-methyl-5-nitropyrazole are more positive.

CONCLUSIONS

In an earlier study of 19 nitroimidazoles[3] (8 reaction mixtures) it could be seen that the influence of different alkyl substituents in the 1- or 2-position was without great effect on the $E_{1/2}$ values. Accordingly, the method was recommended for simultaneous polarographic determination of nitroimidazoles in the reaction mixtures during the substitution of the imino hydrogen atom, irrespective of the nature of the substituents.

Based on the present study (2 alkylation reaction mixtures and 2 rearrangements), although the influence of only one alkyl substituent was examined, we think that we could recommend this method of simultaneous determination for any alkylation or rearrangement process involving nitropyrazoles.

Furthermore, since the structures assumed from the $E_{1/2}$ values were confirmed spectroscopically, we can recommend this polarographic method for the determination of the structures, directly in the reaction mixtures.

The nitropyrazoles investigated represent a group of compounds only recently discovered, where the rearrangement phenomena add further difficulty, and we hope that our method will be of special use in syntheses and studies of these compounds.

We wish only to add, that to obtain information about the compounds present in a reaction mixture, all that is needed is a drop of the solution and 10 min of time.

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Zusammenfassung—N-Unsubstituierte Nitropyrazole haben im Gegensatz zu ihren N-substituierten Derivaten ein Imino-Wasserstoffatom und reagieren mit Hydroxid zu Nitropyrazol-Anionen. Die starke Verschiebung von $E_{1/2}$ dieser Anionen zu negativeren Werten ermöglicht die gleichzeitige polarographische Bestimmung jedes Paares von Verbindungen aus N-unsubstituiertem Nitropyrazol und dem entsprechenden N-substituierten Derivat. Auch die gleichzeitige polarographische Bestimmung dreier Verbindungen (3(5)-, 3-und 5-Nitropyrazol) ist mit 0,1*M* Natriumhydroxid als Trägerelektrolyt möglich, aber nur, wenn $\Delta E_{1/2}$ zwischen den N-substituierten Isomeren wenigstens 100 mV beträgt. In diesem Fall wird ein brauchbares $\Delta E_{1/2}$ durch die verschiedenen Elektronendichten an den Nitrogruppen der Isomeren hervorgerufen. In dem erwähnten Medium kann man sogar vier Verbindungen (1-, 3(5)-, 3- und 5-Nitropyrazol) gleichzeitig bestimmen, da sich der $E_{1/2}$-Wert von 1-Nitropyrazol mit dem pH nicht ändert, im Gegensatz zu anderen Nitropyrazolen. Entwickler für die chromatographische Trennung werden vorgeschlagen. Es werden einige Kriterien für die Unterscheidung N-unsubstituierter und der entsprechenden N-substituierten Nitropyrazole angegeben. Die Strukturen zweier neuer Verbindungen wurden ermittelt. Es werden Methoden empfohlen, um die Verbindungen gleichzeitig zu identifizieren und zu bestimmen, die in den Reaktionsgemischen gemeinsam vorliegen, die man bei der Substitution des IminoWasserstoffatoms oder während der Umlagerung von 1-Nitropyrazolen zu den N-unsubstituierten erhält.

Résumé—Les nitropyrazoles non substitués à l'azote ont un atome d'hydrogène imino, à l'opposé des dérivés N-substitués, et réagissent avec l'hydroxyde pour donner des anions nitropyrazole. Le déplacement fortement négatif de $E_{1/2}$ pour ces anions rend possible le dosage polarographique simultané de n'importe quelle paire de composés, dont l'un est un nitropyrazole non substitué à l'azote et l'autre un dérivé N-substitué correspondant. Le dosage polarographique simultané de trois composés [3(5)-, 3- et 5-nitropyrazoles] est aussi possible avec la soude 0,1*M* comme électrolyte support, mais seulement quand $\Delta E_{1/2}$ entre les isomères N-substitués est d'au moins 100 mV. Dans ce cas le $\Delta E_{1/2}$ convenable est causé par les densités électroniques différentes des groupes nitro des isomères. Dans le milieu mentionné il est possible de doser simultanément même quatre composés [1-, 3(5)-, 3- et 5-nitropyrazoles], parce que la valeur de $E_{1/2}$ du 1-nitropyrazole ne change pas avec le pH, contrairement aux autres nitropyrazoles. On propose des révélateurs pour la séparation chromatographique. On donne quelques critères pour la distinction entre les nitropyrazoles non substitués à l'azote et les composés N-substitués correspondants. On a déterminé les structures de deux nouveaux composés. On recommande des méthodes pour l'identification et le dosage simultanés des composés apparaissant ensemble dans les mélanges réactionnels pendant la substitution de l'atome d'hydrogène imino, ou pendant des réarrangements des 1-nitropyrazoles en nitropyrazoles non-substitués à l'azote.

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APPLICATION OF FLOW-MICROCALORIMETRY TO ANALYTICAL PROBLEMS—II

UREA–UREASE SYSTEM

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Summary—A discussion of the importance of the kinetic parameters, particularly the Michaelis constant K_m, in designing an analytical kinetic technique is given. The magnitude of K_m is shown to affect only the range of substrate concentrations accessible and not the sensitivity of the method. The limitations and advantages of the microcalorimetric method in the determination of K_m are outlined. The microcalorimetric technique and the principles discussed were tested by application to the urea–urease system.

Several recent communications have described the utility of modern flow-microcalorimeters for the determination of enzyme activities[1–4] and of enzyme–inhibitor concentrations. The LKB flow-microcalorimeter[3] measures the average rate of heat output ($d\bar{q}/dt$) from a small cell, volume V_c, through which a reacting solution is flowing (flow-cell mode) or in which two streams of liquid meet and react (mixing-cell mode). The relations between the observable quantity and the instrumental and reaction parameters have been worked out for reactions with zero- and first-order kinetics[4] with particular reference to the kinetics of enzyme-catalysed reactions. It was shown that both the kinetic and thermodynamic parameters of a reaction, in principle, can be obtained from measurements with a flow-microcalorimeter, in addition to the determination of both enzyme activities and substrate concentrations. Experimental confirmation of some of the theoretical conclusions has also been reported.[5,6]

The design of a successful analytical method for the measurement of enzyme activity and particularly of substrate concentration depends markedly on the properties of the particular enzyme–substrate reaction, since the conditions used must depend upon the kinetics of the reaction. It is the purpose of this paper to illustrate the type of kinetic information required, to show how it may be obtained from flow-calorimetry, and to indicate the extent to which successful methods can be developed from it. The urea–urease system was chosen for an initial study because of the ease with which the enzyme can be obtained commercially, and the fairly extensive studies of the kinetics of the urea–urease system which have already been made[7–10] in a range of buffers. The use of this enzyme for the microcalorimetric assay of urea in urine samples has already been described but few details were given.[5]

THEORETICAL CONSIDERATIONS

The rate of an enzyme-catalysed reaction can generally be expressed in terms of the Michaelis–Menten equation:[10]

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{ke_0[\mathrm{S}]}{K_m + [\mathrm{S}]} \tag{1}$$

where [S] is the substrate concentration, e_0 the enzyme activity, k a constant, and K_m the Michaelis constant. At high substrate concentrations, with $[\mathrm{S}] \gg K_m$, the reaction is zero-order:

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = ke_0. \tag{2}$$

When $[\mathrm{S}] \ll K_m$, the reaction becomes first-order:

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{ke_0[\mathrm{S}]}{K_m}. \tag{3}$$

The instrument response (I) from the flow-calorimeter (flow-cell mode) has been shown[4] to take the following forms in the two limiting cases.

(*a*) *Zero order*

$$I \equiv I_z = \beta ke_0 V_c \Delta H_{\mathrm{R}} \tag{4}$$

where ΔH_{R} is the reaction enthalpy and β is an instrument calibration factor.

This output is independent of time and flow-rate, provided that heat produced by degradation of the mechanical energy of the flowing liquid can be ignored. This is true for normal operating conditions.

(*b*) *First order*. Let the liquid flow-rate be R, and define an average residence time τ such that $\tau = V_c/R$. From equation (3), the first-order rate constant k_1 is equivalent to ke_0/K_m, and if the initial substrate concentration is denoted by $[\mathrm{S}^0]$:

$$I = \beta R[\mathrm{S}^0]\Delta H_{\mathrm{R}}[1 - \exp(-k_1\tau)]\exp(-k_1 t). \tag{5}$$

When $k_1\tau$ is small,

$$1 - \exp(-k_1\tau) \simeq k_1\tau = k_1 V_c/R = \frac{ke_0 V_c}{RK_m}. \tag{6}$$

Hence, when this condition is fulfilled,

$$I = \beta[\mathrm{S}^0](ke_0/K_m)V_c \Delta H_{\mathrm{R}} \exp(-k_1 t). \tag{7}$$

The output I decays exponentially with time and the slope of a plot of $\log I$ against time gives k_1 or (ke_0/K_m). The intercept at zero time, I_0, of such a plot should vary linearly with $[\mathrm{S}^0]$ and, from (7),

$$\begin{aligned} I_0/[\mathrm{S}^0] &= (\beta ke_0 V_c \Delta H_{\mathrm{R}})/K_m \\ &= I_z/K_m. \end{aligned} \tag{8}$$

In principle, this provides a method for finding the Michaelis constant K_m without the necessity for measuring β, V_c, ΔH_{R}, k and e_0.

It follows from equation (4) that the value (I_z) of I in the presence of excess of

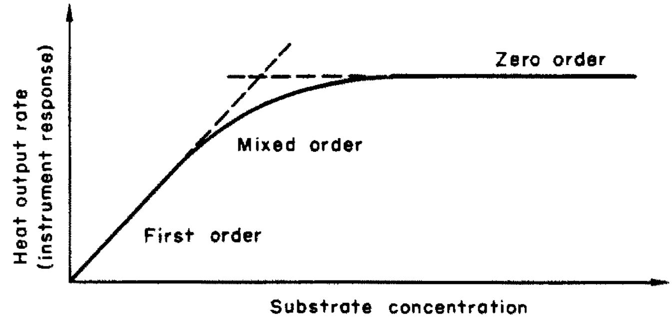

Fig. 1. Theoretical form of variation of heat output-rate with substrate concentration at a constant arbitrary time after initiation of reaction.

substrate gives a relative measure of the enzyme activity. I_z should vary linearly with e_0 and be independent of [S] provided this is large, and there is no inhibition by substrate. Since I_z is time-independent, the interpretation of the data is particularly simple. The substrate concentration can be obtained in principle by measuring the instrument output as a function of time and extrapolating to zero time, provided $[S^0] \ll K_m$. However this extrapolation may be difficult in practice. Alternatively, equations (5) and (7) show that at a fixed time I is linearly proportional to $[S^0]$. It can also be shown[4] that for first-order kinetics the integral

$$\int_{t_1}^{t_2} I \, dt,$$

i.e., the area under the curve on a plot instrument output against time, is linearly proportional to $[S^0]$. When the reaction is of intermediate order ($[S^0] \sim K_m$) these relations will not hold exactly, and the instrument output at fixed time, or the integrated output at fixed time, or the integrated output between fixed time-limits, should vary with substrate concentration in the manner shown in Fig. 1. Once this calibration curve is established, substrate analysis of an unknown becomes possible.

Factors affecting the applicability of the method

The optimum experimental conditions for the successful application of the method in enzyme and substrate analyses will depend on the kinetic parameters k and K_m, and on ΔH_R. The instrument response in the presence of excess of substrate [equation(4)] depends on the product $ke_0 \Delta H_R$. The rate of an enzyme reaction varies with pH because of the effect of pH on ke_0, but changes in pH can also affect ΔH_R if the products or reactants of the enzyme reaction show acid–base properties in the appropriate pH range. It is first necessary to determine the pH which gives the maximum value of $ke_0 \Delta H_R$. This will not necessarily be the pH at which the reaction proceeds most rapidly (ke_0 maximum). For the urea–urease system, and probably for many others, $ke_0 \Delta H_R$ changes rapidly with pH. Since flow-cell experiments require the reacting mixture to be studied for some time, the buffer used must have sufficient capacity for the effect of changes in pH on $ke_0 \Delta H_R$ to be negligible during this period.

If substrate concentrations are to be determined, the value of the Michaelis constant is of importance. When it is low, the accessible range of substrate concentration is also low. Equation (7) is only applicable when $[S^0] \ll K_m$ and from (7) and (4) it follows that under these conditions:

$$I = \frac{[S^0]}{K_m} I_z \exp(-k_1 t). \tag{9}$$

Thus the instrument response may be small in substrate analyses, unless I_z (effectively the enzyme activity) can be increased. In principle, for first-order kinetics to be obeyed with reasonable accuracy, $[S^0]/K_m$ should be about 0·01, but in practice[6] quite good "first-order" plots are obtained even when this ratio approaches 0·2. A reasonably linear calibration curve of instrument response at a fixed time, or of

$$\int_{t_1}^{t_2} I \, dt$$

between fixed limits, plotted against [S], may therefore be expected for substrate concentrations up to about $0{\cdot}2K_m$. The value of the Michaelis constant for the urea–urease system depends upon the overall composition of the buffer because the enzyme is inhibited by both potassium and sodium ions and activated by phosphate ions.[8] In concentrated phosphate buffers $K_m \sim 0{\cdot}05M$,[7–9] whereas in "tris" sulphate buffer,[10] where the buffer components have no effect on the enzyme, $K_m = 0{\cdot}004M$. Thus the value of K_m determines the practicable range of substrate concentrations which can be determined but does not affect the sensitivity of the procedure.

EXPERIMENTAL

Apparatus

The LKB flow-microcalorimeter was housed in a room maintained at 25° ± 0·5° and was operated at 25°. The flow-through mode[3,4] was employed. Solutions were pumped through the calorimeter by peristaltic pumps (LKB Perpex, 55 ml/hr).

Materials

$Na_2HPO_4 . 12H_2O$ and $NaH_2PO_4 . 12H_2O$ (analytical-reagent grade) at a total phosphate concentration of $0{\cdot}75M$, constituted the buffer solution (pH 7·0). Urea (analytical-reagent grade) was used without further treatment. Urease (Sigma London Chemical Co., Type III prepared from jack bean) was stored at 0° until required; fresh solutions in buffer were prepared daily.

Procedure

The general procedure for the operation of the calorimeter has been described previously.[2,4] An instrumental base-line was established by pumping substrate solution (50 ml initially) through the calorimeter. After precisely 10 min, 4·55 ml of enzyme solution (1 mg/ml in buffer) was added rapidly with vigorous stirring and the change in instrument output with time recorded. All solutions presented to the calorimeter were maintained at 25° in a water-bath. The amplifier setting was equivalent to 10 μV for full-scale deflection.

RESULTS

The effect of pH

A phosphate buffer was chosen for the work because the high value of K_m ($\sim 0{\cdot}05M$) permitted a convenient range of substrate concentrations to be studied by using the flow-cell mode. Preliminary studies showed that a sufficiently high buffer capacity could only be obtained by using a total phosphate concentration of $0{\cdot}75M$. Even so, the pH only remained constant with time over a narrow range in the vicinity of pH = 7·0, and it was only in this range that the instrument output was time-independent in the presence of excess

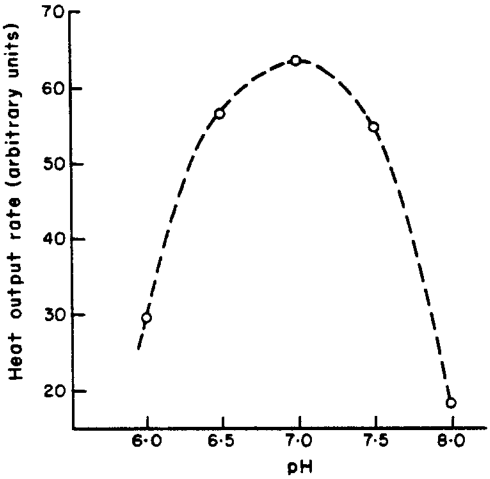

Fig 2. Variation of heat output-rate (30 min after the initiation of the reaction) with pH in 0·75M phosphate buffer.

of substrate as required by equation (4). Figure 2 shows the variation of instrument output 30 min after the start of reaction, against pH in this buffer. The maximum instrument output occurs at pH = 7·0, where the buffer capacity is fortunately high enough for pH changes with time to be negligible. Optimum pH values for the urea–urease system in phosphate buffer have been reported[7] [12] to range from 6·2 to 8·0.

Determination of enzyme activity

The relationship between enzyme activity and instrument response was found to be linear for enzyme concentrations between 0·25 and 2·0 mg/ml. The least-squares line passed through the origin within experimental error and gave a regression coefficient of 0·9985.

The determination of substrate concentration

All substrate analyses were performed as described above, the instrument response being monitored for at least 30 min after initiation of the reaction by addition of enzyme to the buffered substrate solutions. Substrate concentrations up to 1M were studied.

At low substrate concentrations (below 0·025M) the instrument response at a fixed time (30 min) after initiation of the reaction was linear with respect to substrate concentration. A least-squares analysis of data for experiments with substrate concentrations between 5×10^{-4} and $250 \times 10^{-4} M$ gave the following relationship between substrate concentration [S] and instrument response I:

$$[S] = 2{\cdot}57 \times 10^{-4} I - 1{\cdot}39 \times 10^{-4} \text{ mole/l.} \qquad (10)$$

Table 1 shows the values of I (mean of two or three independent values in each case) for substrate concentrations in the range stated, on which equation (10) was based, together with calculated values of [S] based on equation (10). The differences between calculated and observed values are obviously very small. The viability of the

Table 1. Thermometric assay of urea solutions by use of urease in phosphate buffer

Instrument response, % *of full scale*	Substrate conc., *M* Actual	Found, [eq. (10)]
96·3	0·0250	0·0246
76·5	0·0200	0·0195
71·1	0·0180	0·0181
63·3	0·0160	0·0161
44·1	0·0120	0·0112
29·4	0·0075	0·0074
22·5	0·0060	0·0056
20·2	0·0050	0·0050
$17{\cdot}2_5$	0·0040	0·0041
11·6	0·0030	0·0028
7·3	0·0020	0·0018
5·3	0·0010	0·0012
$2{\cdot}3_4$	0·0005	$0{\cdot}0004_6$

method for the determination of urea in biological fluids was tested by analysing a sample of urine by dilution with phosphate buffer and carrying out the thermometric assay in the manner described. The urea concentration in the original sample was found to be 0·20*M* by this method. A conventional assay (Nessler) carried out by the clinical biochemistry department of a London hospital on the same sample gave a urea concentration of 0·19*M*.

At urea concentrations much greater than 0·025*M*, equation (10) ceased to apply, and the experimental curve of instrument response against substrate concentration was similar to that shown in Fig. 1. At a urea concentration of 0·30*M* the instrument output was 64·0 μV, at 0·35*M* 64·2 μV, at 0·4*M* 64·0 μV. All these were independent of time within the duration (up to about 1 hr) of the experiment. At a still higher concentration (1·0*M*) the output was 65·4 μV, again constant with time over a fairly long period. From equation (4) the instrument response should be independent of [S] if [S] is high. The variation in I_z is attibuted to inhibition by substrate.

Estimation of Michaelis constant from flow-calorimetry data

If the system obeys Michaelis–Menten kinetics over the whole range of substrate concentrations, equation (8) provides a possible method of estimating K_m. For this purpose it is necessary to find $I_0/[S^0]$ for the range of substrate concentrations where the reaction shows first-order kinetics, and also I_z, the limiting instrument response at high substrate concentrations, when the reaction is zero-order. I_0 is the extrapolated value of I at zero time derived from the first-order kinetic plot of log I against time.

For the urea–urease–phosphate system at urea concentrations up to 0·012*M* the instrument output has been found to vary exponentially with time[6] when the reacting system is passed through the flow-cell. Table 2 shows apparent first-order rate-constants derived from these plots together with extrapolated values of I_0.

If the reaction remained first-order over the range of substrate concentrations shown, $I_0/[S^0]$ should be independent of $[S^0]$. This was clearly not the case in spite of the excellent linearity of the first-order plots obtained in each case (*cf.* reference 6). A first

Table 2. Urea–urease–phosphate system. Apparent first-order rate-constants and I_0 values at low concentrations

$[S^0]$, *mmole/l.*	I_0, *μV*	$I_0/[S^0]$, *mV.l.mole*$^{-1}$	Apparent first-order rate-constant, *min*$^{-1}$
3	3·36	1·12	0·0333
3	3·48	1·16	0·0360
4	4·17	1·04	0·0260
5	5·27	1·05	0·0295
7·5	7·84	1·06	0·0279
12·0	11·80	0·985	0·0290

estimate of K_m can be found by assuming the limiting value of $I_0/[S^0]$ at low substrate concentrations is 1·10 mV.l.mole^{-1} and that I_z is 65·0 μV. From equation (8) and these data $K_m = 0{\cdot}059M$, and even at $[S^0] = 0{\cdot}003M$ the condition that $K_m \gg [S^0]$ is not fulfilled very well. In addition there is some uncertainty about I_z since substrate inhibition of urease is known to occur.

A more accurate form of equation (8) is

$$I_0 = \frac{I_z[S^0]}{K_m + [S^0]}. \tag{11}$$

Consequently

$$1/I_0 = K_m/I_z[S^0] + 1/I_z. \tag{12}$$

This equation is analogous to the well-known Lineweaver–Burk plot and could be used in principle to calculate both K_m and I_z. It gives a linear plot for the data in Table 2. Regression lines have been calculated as follows.

(*a*) For all points.

$$1/I_0 = 8{\cdot}343 \times 10^{-4}/[S^0] + 0{\cdot}019\ \mu V^{-1} \tag{13}$$

Regression coefficient 0·996; standard deviations 0·37 × 10^{-4} (slope), 0·009 (intercept).

(*b*) Omitting points at $[S^0] = 3 \times 10^{-3}M$.

$$1/I_0 = 9{\cdot}362 \times 10^{-4}/[S^0] - 0{\cdot}004\ \mu V^{-1} \tag{14}$$

Regression coefficient 0·9997; standard deviations 0·16 × 10^{-4} (slope), 0·003 (intercept).

The intercept is small and uncertain because of the small range of substrate concentrations covered, and it is impossible to get a reasonable estimate of I_z from these data. Using $I_z = 65{\cdot}0$ μV, the directly observed value, as a minimum estimate, it follows that $K_m = 0{\cdot}054M$ [case (*a*)] or $0{\cdot}061M$ [case (*b*)]. These are minimum estimates from the observed slopes of the two regression lines and will increase if the observed I_z is too low. In spite of their uncertainty they are consistent with earlier values for this system in phosphate buffers, as follows.

pH	Buffer concentration, *M*	K_m, *M*	Reference
7·0	0·067	0·027	13
7·0	0·158	0·026	9
7·0	0·267	0·05	9
6·9	0·75	0·06	this work

Data obtained by using a flow-cell are not suitable for use with equations (11) and (12) over a wider range of concentration than that used in this work because I_0 cannot be easily obtained when the reaction departs appreciably from first-order kinetics. Use of the mixing-cell would give a good estimate of I_0 without any need for extrapolation to zero time at any value of $[S^0]$. The method is then exactly comparable to more conventional methods of studying the kinetics of enzyme reactions, with the advantage of providing a simple general technique for following the reaction.

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Zusammenfassung—Die Bedeutung der kinetischen Parameter, besonders der Michaelis-Konstanten K_m, für die Planung eines kinetischen Analysenverfahrens wird diskutiert. Es wird gezeigt, daß die Größe von K_m nur Einfluß auf den erfaßbaren Konzentrationsbereich an Substrat hat und nicht auf die Empfindlichkeit der Methode. Vorteile und Grenzen der mikrokalorimetrischen Methode zur Bestimmung von K_m werden skizziert. Das mikrokalorimetrische Verfahren und die diskutierten Grundsätze wurden durch Anwendung auf das System Harnstoff-Urease überprüft.

Résumé—On présente une discussion sur l'importance des paramètres cinétiques, particulièrement la constante de Michaelis K_m, dans la conception d'une technique cinétique analytique. On montre que la grandeur de K_m affecte seulement le domaine de concentrations de substrat accessible et non la sensibilité de la méthode. On indique les limitations et avantages de la méthode microcalorimétrique dans la détermination de K_m. La méthode microcalorimétrique et les principes discutés ont été essayés par application au système urée-uréase.

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QUANTITATIVE REFLECTOMETRY—II*

PRECISION AND INTERFERENCES

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Summary—A detailed assessment of the precision of direct reflectance measurements has been made, using commercially available test-strips for nickel. The overall relative precision is 3·2–4·6% for the concentration range 10–100 ppm. The effect of interfering ions has been studied and the mechanism of interference discussed in terms of diffusion. Non-commercial test-strips have been prepared and compared with the commercial product.

The feasibility of using direct reflectance measurements for quantitative analysis was examined in the first paper of this series[1] and it was shown that the relative precision is 2–4% for 10–100 ppm of nickel. A more detailed assessment of the precision has now been made by an analysis of variance,[2] and interferences have been investigated.

During the course of the current work, nickel test-strips were prepared with a larger surface area than those available commercially. The principal advantage of such "home-made" strips is the ability to make reflectance measurements with an attachment fitted to a spectrophotometer. Although spectrophotometric measurements using the commercial strips had been made during the earlier work, a rather tedious routine of mounting six strips on a card was necessary to provide adequate instrumental response. The properties of the larger test-strips have been compared with those of the commercial product.

EXPERIMENTAL

The reagents and apparatus were those described earlier,[1] with the addition of plastic TLC plates coated with silica gel (with binder) or cellulose (no binder).

Groups of up to five test-strips were mounted in a large cork which was then clamped in position for the strips to be immersed simultaneously (no stirring) in the appropriate sample solution (for 2·0 min ± 1 sec). The strips were then rinsed briefly with distilled water and dried for 3 min with a hot-air blower. For the statistical evaluation of precision, sets of five strips were developed for nickel concentrations of 10, 25, 50, 75 and 100 ppm.

The procedures and conditions for reflectance measurements with the "Chromoscan" and SP 800 instruments were as previously described.[1] The SP 800 spectrophotometer was used only for the non-commercial strips, which were large enough to be mounted directly in the SP 890 reflectance attachment

Study of interfering ions

The effects of K, Ca, La, Fe(III), Cu(II), Co(II) and Hg(II) on a 100 ppm nickel standard were investigated at levels up to 20,000 ppm. Each metal was added as the nitrate and the pH of the sample solution adjusted to between 5 and 7 with sodium acetate if necessary. In the case of Fe(III), tartrate was also added to prevent precipitation of the hydrated oxide. Interference from Cu(II) at high levels was masked with sodium thiosulphate, from Fe(III) with potassium fluoride and from Hg(II) with sodium chloride.

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* Part I: *Talanta*, 1972, **19**, 1563.

Preparation of non-commercial test-strips

Plastic silica-gel and cellulose TLC plates were each cut into strips approximately 2 × 0·75 in. and the adsorbent layer removed from one end so as to leave a test area of about 1 × 1·75 in. Each strip was immersed briefly in a 1 : 1 mixture of saturated solutions of dimethylglyoxime and anhydrous sodium acetate in methanol. After rinsing in methanol to remove excess of reagent, the strips were allowed to dry in air.

RESULTS AND DISCUSSION

Assessment of precision

In the development of an analytical procedure, it is of interest to know the precision that can be expected from a "batch" of measurements made with a given set of reagents and within a given working period, and the overall precision of measurements made in a number of such periods. The overall precision may be affected by the use of different sets of reagents and by gross changes in laboratory conditions. In the present work a "batch" is a set of measurements made with test-strips taken from one particular box of 100, during one working session. Good estimates of "within-box", "between-box" and "overall" precision can be made by statistical analysis of variance on data from sets of five replicates from each of four boxes. This has been done for solutions containing 10, 25, 50, 75 and 100 ppm of nickel, the optimum range of concentration being indicated by linearity in the Kubelka–Munk and Ringbom plots.[1] The precision of repeated measurements on a set of prepared standards over a long period (10 weeks) has been assessed similarly.

Table 1. Analysis of variance formulae

Source of variability	Sums of squares, S_i	Degrees of freedom	Mean squares
Between boxes	$S_1 = \sum B^2/n - (\sum B)^2/mn$	$N_1 = m - 1$	$M_1 = S_1/N_1$
Within boxes	$S_0 = \sum X^2 - \sum B^2/n$	$N_0 = m(n-1)$	$M_0 = S_0/N_0$
Total	$S_t = \sum X^2 - (\sum B)^2/mn$	$N_t = mn - 1$	

X = reflectance measurement; B = sum of a set of n replicates; m = number of boxes or number of sets of measurements made on a set of standards over a period of time: $M_0 = s_W^2$ and $M_1 = ns_B + s_W$ where s_B and s_W are estimates of the "within-box" and "between-box" standard deviations.

The formulae used in the analysis of variance are shown in Table 1. If "between-box" variations are significantly greater than "within-box" variations, then the following relationships are valid:

$$s_W = \sqrt{M_0}$$

$$s_B = \sqrt{\left(\frac{M_1 - M_0}{n}\right)}$$

$$s_T = \sqrt{(s_W^2 + s_B^2)}$$

where s_W, s_B and s_T are estimates of "within-box", "between-box" and "overall" standard deviations respectively, the other symbols being defined in Table 1.

This will hold only if M_1 is significantly greater than M_0 as indicated by application of the statistical F-test, and was found to be the case at all the concentrations studied except the 10 ppm level, which was anomalous in that M_1 was significantly less than M_0

Table 2. Relative precision of reflectance measurements in the determination of nickel

[Ni], *ppm*	Within boxes	Relative precision, % Between boxes	Overall
10	3·2	—	—
25	2·0	3·1	3·7
50	1·4	2·9	3·3
75	1·4	2·9	3·2
100	1·5	4·3	4·6
	Single day	*Over 10 weeks*	*Overall*
100	1·3	1·3	1·8

so that only "within-box" precision could be calculated at that level. The source of the anomaly, which may have been an undetected but determinate error, has not been investigated further.

The calculated precisions are given in Table 2 and are in general agreement with the results obtained in the preliminary study.[1]

Interferences in reflectometry

The colour of test-strips immersed for 2 min in a nickel solution intensifies appreciably during this period even though the solution is unstirred. The process clearly involves diffusion since nickel ions at the surface of the test-strip are removed from the solution by the chromogenic reaction, thereby creating a concentration gradient, nickel ions then diffusing from the bulk solution to the surface until all the reagent is consumed. If the chromogenic reaction is fast, diffusion will be the rate-controlling process. The lower reflectance (increased reading) for test-strips immersed in stirred solutions, where mechanical convection augments diffusion, can be adduced as evidence to support this assumption.[1] It is also of interest to note from the earlier results that the effect of stirring is greater at the 10 ppm level, where a relatively small concentration gradient is established, than at the 50 ppm level where the gradient is much larger. The higher rate of diffusion expected in the 50 ppm solution is proportionately less affected than that prevailing at the lower concentration.

The rate of diffusion of an ionic species can also be altered by the formation of an electrical double-layer at the surface of the test-strip. In general, electrical double-layers form at any interface between a solid and an electrolyte solution. The double-layer, consisting of a monolayer of adsorbed ions, or an ionized surface, and a more diffuse layer of counterions extending into the bulk solution, behaves like a condenser in that a potential gradient is established normal to the surface. Other electrolytes in the sample solution can have a profound effect on the magnitude of the potential gradient, and if at high enough concentrations, may reduce the bulk diffusion rate of the ions of interest (in this case, nickel). Non-electrolytes may have a similar effect solely by increasing solution viscosity. High concentrations of ionic species which do not react with dimethylglyoxime but which result in a negatively-charged surface with an outer layer of positive counter-ions will therefore inhibit the diffusion of nickel ions to the surface of the test-strip. For a given immersion time, an increased reflectance (lower reading) will be observed, although the colour of the strip will not be visibly affected. These conclusions are supported by the results given in Table 3 which show the effects of

Table 3. Effect of K, Ca and La on the reflectance of a 100-ppm nickel standard

Interfering ion	Concentration, *ppm*	Reflectance (mean of 5 replicates)	Relative precision, %
none	—	9·80	1·6
K^+	2,000	7·16	1·5
	20,000	6·93	1·1
Ca^{2+}	2,000	7·20	1·7
	20,000	5·50	1·4
La^{3+}	2,000	5·60	1·3
	20,000	5·60	1·6

K^+, Ca^{2+} and La^{3+}, all added as nitrates and none of which reacts with the reagent. The precision of these measurements, also given, does not differ significantly from that of those made with pure nickel solutions.

There is some indication from the results shown in Table 3 that the degree of interference is related to the formal charge on the cation, tervalent lanthanum causing very serious interference even at the 2000 ppm level. At the 20,000 ppm level, La^{3+} and Ca^{2+} have an effect comparable to but more pronounced than that of K^+, but at such a high concentration of electrolyte the inhibition of bulk diffusion may be the dominant factor. It is possible that interference of this type could be correlated with other parameters such as charge density, but further work would be necessary. It can be assumed that any electrolyte present in addition to nickel salts constitutes an interference, the threshold concentration at which reflectance is measurably affected being determined by the nature of the electrolyte. For analytical purposes, the situation may be regarded as a matrix effect which can be obviated by use of standards with a composition similar to that of the sample.

If the interfering ion also reacts with the reagent to form a coloured complex, additional changes in reflectance will occur. This is because of the competition for the reagent between nickel and the interfering ion at the surface of the test-strip. If there is a considerable excess of the interfering ion present, it is likely that there will be a significant reduction in the amount of nickel complex formed in addition to the effect caused by a slower rate of diffusion. Likely interfering ions of this type, *viz.* Cu(II), Fe(III), Co(II) and Hg(II), have been investigated at concentration levels between 50 and 5000 ppm. These concentration levels and suitable masking reactions were based on data provided with the commercial test-strips. The results are summarized in Table 4 and show that Cu(II) can be tolerated up to at least 1000 ppm but at 5000 ppm the test-strip is discoloured by a green deposit and the reflectance increases. Although the addition of sodium thiosulphate prevents formation of the green discolouration and prevents the copper from competing for the reagent, the diffusion of nickel is still significantly inhibited. Interference by Fe(III) at both the 1000 and 5000 ppm levels can be minimized by complexing the iron with tartrate or fluoride but the diffusion of nickel is nevertheless impaired. At 5000 ppm of Fe(III), a slight brown discolouration of the test-strip is noticeable. Interference by Co(II) is serious and is observed even at 50 ppm, the reflectance decreasing owing to formation of a brown cobalt complex. Bathing the strips in aqueous ammonia (1 + 20) after immersion in the sample solution dissolves some cobalt complex but leaves only a very pale pink colour due to nickel and results in a higher reflectance. Up to at least 5000 ppm of Hg(II) can be masked successfully

Table 4 Effect of Cu(II), Fe(III), Co(II) and Hg(II) on the reflectance of a 100 ppm nickel standard

Interfering ion	Concentration, *ppm*	Reflectance (mean of 5 replicates)	Masking agent	Relative precision, %
None	—	10·00	—	1·4
Cu^{2+}	1,000	10·30	—	1·7
	5,000	7·10	—	4·7
	5,000	8·41	$Na_2S_2O_3$	3·1
Fe^{3+}	1,000	9·48	tartrate or fluoride	1·4
	5,000	8·46		1·7
Co^{2+}	50	10·60	—	2·6
	1,000	not measured	—	—
	1,000	8·30	aqueous ammonia	6·6
Hg^{2+}	1,000	not measured	—	—
	1,000	10·03	NaCl	2·0
	5,000	9·34	NaCl	3·1

with sodium chloride, the test-strips showing a deep red–brown colour in the absence of the masking agent. It should be noted that in many cases, especially at high concentrations of the interfering ion, the relative precision is significantly reduced.

Assessment of non-commercial test-strips

Strips prepared from plastic TLC plates coated with silica gel or cellulose were impregnated with dimethylglyoxime, and sodium acetate as a buffer to enable them to be used down to pH 2–3. Comparison with the commercial strips showed that the colour intensity produced at a given nickel concentration was greater for both types of "home-made" strips. However, the silica gel coating tends to flake off during immersion in the sample solution, and the precision at the 25- and 100 ppm levels (5 replicates) is not as good as that of the commercial product (Table 5). The cellulose layers are mechanically stronger, give a very even colour and a precision somewhat better than that of the commercial product (Table 5). The reflectance spectrum of the developed cellulose-coated strips is similar to that of the commercial strips except that the maximum is slightly less broad and is shifted from 547 ± 1 nm to 538 ± 1 nm. This hypsochromic shift is to be expected from the finer and more even particle size of the powdered cellulose used in the manufacture of the plates as compared to the coarse, fibrous structure of paper. As in the case of the commercial strips, the Kubelka–Munk law is obeyed up to about 100 ppm of nickel and the optimum range for quantitative measurements indicated by a Ringbom plot is 10–100 ppm.

Table 5. Comparison of commerical and non-commercial test-strips

Strip	[Ni], *ppm*	Reflectance (mean of 5 replicates)	Relative precision, %
Commercial product	25	4·80	2·2
	100	10·05	1·6
Cellulose TLC plates	25	5·32	1·5
	100	11·14	0·7
SiO_2 TLC plates	25	5·03	7·4
	100	10·95	3·1

CONCLUSIONS

An analysis of variance at several concentrations between 10 and 100 ppm of nickel has confirmed that the overall relative precision of direct reflectance measurements on commercial test-strips lies in the range 3·2–4·6%. Within a single working session and with one particular box of test-strips, a relative precision of 1·4–3·2% can be expected. Larger strips, prepared from cellulose-coated TLC plates, give a more even colour and marginally better precision, but similarly-prepared silica gel coated strips are not satisfactory.

Interfering ions which do not react with the chromogenic reagent do not appear to affect the precision significantly, but the colour produced is reduced in intensity (the reflectance is increased). The degree of such interference may be related to formal charge or charge density and is considered to be caused by changes in the rate of diffusion of nickel ions to the surface of the strip during the immersion period. Cobalt at the 50 ppm level interferes by reacting with the reagent, but iron, copper and mercury interference can be minimized by using suitable masking agents. In such cases, the precision may be adversely affected. For quantitative analysis, samples and standards should have as similar a composition as possible.

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Zusammenfassung—Mit Hilfe handelsüblicher Testreifen für Nickel wurde die Genauigkeit direkter Reflexionsmessungen im enzelnen abgeschätzt. Im Konzentrationsbereich 10–100 ppm ist die relative Genauigkeit insgesamt 3,2–4,6%. Der Einfluß störender Ionen wurde untersucht und der Mechanismus der Störung im Sinne der Diffusion diskutiert. Es wurden selbst Teststreifen hergestellt und mit den käuflichen verglichen.

Résumé—On a fait une appréciation détaillée de la précision de mesures de pouvoir réflecteur direct, en utilisant des lames-essai commercialement accessibles pour le nickel. La précision globale relative est 3,2–4,6% pour le domaine de concentration 10–100 ppm. On a étudié l'influence d'ions gênants et discuté du mécanisme d'interférence en fonction de la diffusion. On a préparé des lames-essai non commerciales et les a comparées au produit commercial.

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USE OF DATA-PROCESSING IN MODERN RAPID METHODS OF ELEMENTAL ANALYSIS*

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Summary—Automated methods for the rapid determination of carbon, hydrogen, nitrogen, and oxygen have been developed for use in conjunction with modern data processing equipment. Details as to the methods, apparatus, programming of procedures, and evaluation of the results are presented.

The personnel costs in a large laboratory for elemental analysis make automation of individual methods essential for economic operation. The degree of automation cannot stop at, say, furnaces with automatic programming, but must be such that almost every human activity, including control of the analysis, is replaced by computer. In this field automation is no longer a hollow slogan but a stark necessity.

Carbon, hydrogen, nitrogen and oxygen are the elements which are most frequently determined. Automatic methods for these elements were most urgently required. Two approaches were therefore considered:

(*a*) determination of several elements in one weighed sample,
(*b*) rapid separate determinations of each element.

The first approach is the basis for many familiar methods for the simultaneous determination of carbon, hydrogen, and nitrogen. Almost all these methods are only partially automated: the analyst is tied to the apparatus until the determination is completed. Time is saved only because three elements are measured in one procedure. Most methods for semi-automatic determination of carbon, hydrogen, and nitrogen have two major disadvantages: first, most of them are more or less ultramicro in scale, and secondly, they tend to give results that are dependent on the sample structure. This latter difficulty results, perhaps, from the inherent impossibility of selecting optimum pyrolysis and combustion conditions when several elements are to be determined simultaneously.

We in BASF's Analytical Laboratories deliberately chose the second approach in preference to the first, and developed individual rapid methods for determining carbon and hydrogen, nitrogen, and oxygen. Each of these methods can be automated to the fullest extent and yields results in digital form for processing in a computer.

To avoid dependence on physical calibrations we chose methods for the end-determinations that yield physical values strictly proportional to amount of substance. Volumetric titrimetry and gas volumetry seemed to fulfil this condition most closely; the pressure and temperature corrections for the latter are of course quite unambiguous.

These rapid methods[1–4] will now be described and the advantages of electronic data-processing for elemental microanalysis in general will be discussed.

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* Paper presented at the Symposium on Microchemical Techniques, Penn State University, 19–24 August 1973.

NITROGEN

Our work on nitrogen determination was carried out first, and the automatic apparatus we developed has proved itself in routine use over the last five years.

Principle

The determination is based on the Dumas method. This classical method has two basic faults: (*a*) thermally stable compounds decompose incompletely, giving low values; (*b*) volatile pyrolysis products may be incompletely oxidized and cause high values. However, both sources of error may be eliminated by the use of pure oxygen during the combustion.

Pyrolysis and oxidation are achieved in a very short time by almost explosive combustion in a rapid stream of oxygen in an adequately-dimensioned vertical tube. The combustion products are swept out with carbon dioxide, which carries them through successive heated beds of copper oxide and copper. Finally the volume of nitrogen is measured in an automated nitrometer, and the value is either printed out or fed to a calculator. With this modification we gain an absolutely universal method.

The method is, of course, only fully automatic when the sample weight is measured by an electronic microbalance with an output signal which can be coded and fed to the calculator.

For micro-samples 30 sec is required for combustion and 2 min for purging. For materials which are more difficult to pyrolyse, the oxygen stream can be maintained for a longer time. Combustion can also be prolonged for larger samples, but so far we have not encountered a substance that requires more than 2 min for a 20 mg sample. For trace analysis in samples weighing 50 mg or more the method must be modified slightly: the oxygen stream is maintained for as long as necessary, and complete oxidation of pyrolysis is ensured by an additional oxidation stage.

The method thus covers the determination of both constitutional and trace nitrogen.

Apparatus

The apparatus is available commercially from W. C. Heraeus GmbH in modular form under the designation Rapid N. It consists of the two gas sources, the combusion unit with the combustion tube and reduction tube, the nitrometer unit with a counter and appropriate control electronics, and a printer or calculator. The combustion unit itself (Fig. 1) consists of a sample-entry stop-cock (*1*) a vertical com-

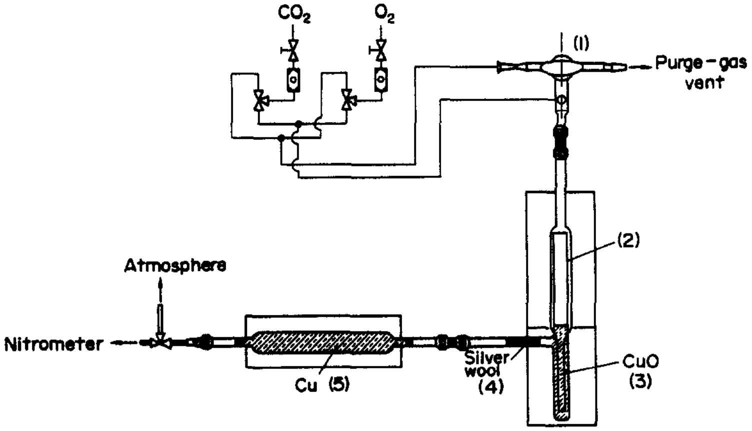


Fig. 1. Rapid N apparatus.

bustion tube with copper oxide as oxygen donor (*2*)-(*4*), and a horizontal reduction tube filled with copper (*5*). The combustion tube is made in one piece but has three distinct sections:

(1) the upper section (*2*), the combustion chamber, is lined with a quartz sleeve to protect it against the locally very high internal temperatures;

(2) the lower section (*3*) is filled with copper oxide; it is double-walled to form a longer path for the pyrolysis products;

(3) the side outlet (*4*) is filled with silver wool; it is connected to the reduction tube by a metal screw coupling.

Furnaces maintain the combustion chamber at 900–950°C, the oxidation zone at 850°C, and the reduction tube at 500°.

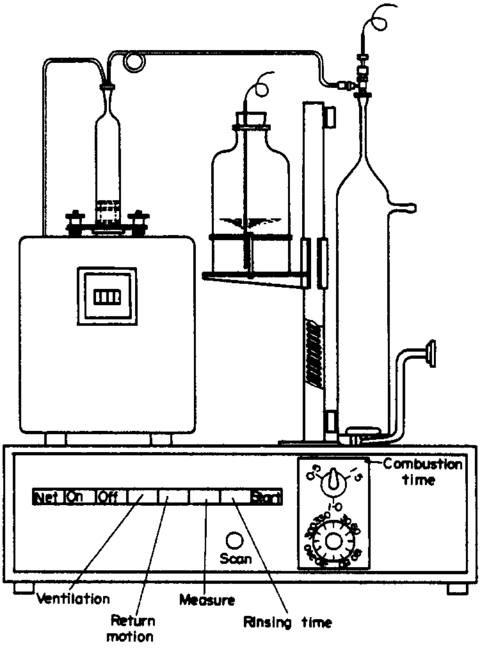


Fig. 2. Automatic nitrometer.

The unit in which the nitrogen volume measured is fitted with a motor-driven piston burette. The gas-absorption vessel was specially developed to allow a long series of determinations to be carried out without changing the potassium hydroxide absorption solution. The measuring system (Fig. 2) works entirely automatically, including raising and lowering of the levelling bottle and re-zeroing of the piston burette. Quantitative absorption of carbon dioxide is ensured by a magnetic stirrer in the absorption vessel; this rotates during the combustion and purging periods, and distributes the gas in fine bubbles. The volume of the nitrogen is measured by drawing the gas into the piston burette, the motor of which switches off when the conductive potassium hydroxide solution reaches an electrical contact. The gas volume is measured twice for safety's sake, in case the solution forms bubbles, and the value is only printed or coded for data processing when it has been thus confirmed by the second measurement.

Programme

Once the start-button has been pressed, each operation is performed automatically in accordance with a preset programme. The sequence is shown in the block diagram (Fig. 3), the dashed lines representing the measuring circuits. The various gas valves, for example those which disconnect the supply of oxygen and the supply of carbon dioxide to the combustion tube, are actuated magnetically.

The sample-entry stop-cock is a large glass three-way plug valve joined by a metal connector. The sample, wrapped in tinfoil boats if it is solid or held in a phosphate–glass capillary if it is liquid, is placed in the bore of the plug and purged free from air before being dropped into the combustion tube. The sides of the boats are folded over with tweezers before the sample is placed in the entry stop-cock.

The sample can, of course, be introduced automatically with the help of a suitable electromagnetic device; in this case it is advantageous to use a multi-chamber arrangement.

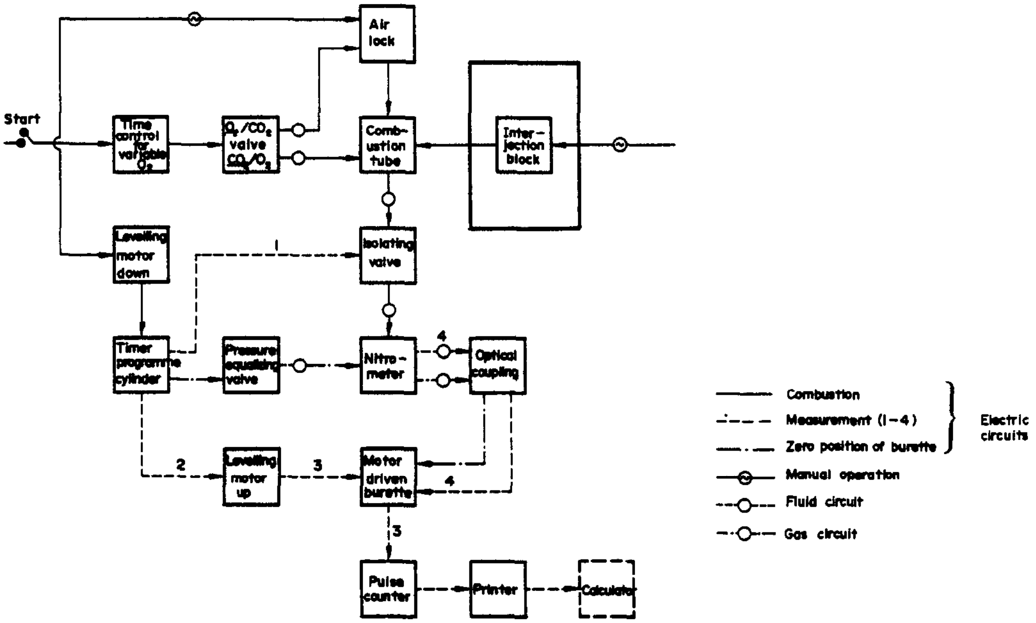


Fig. 3. Block diagram of automated nitrogen analyser.

The fully-automated version of the equipment can be loaded with up to 50 weighed samples and left to run without supervision—overnight for instance. The masses of the samples can be coded and recorded on punched tape or fed direct to the calculator. Barometric pressures and temperatures are measured intermittently and used to correct the nitrogen volumes. After correcting the volume the calculator works out the mass fraction of nitrogen in the sample and prints out the value. The additional cost of the fully-automated version is more than compensated for by the improved utilization of the equipment.

Results

Table 1 shows the accuracy and precision of the microdeterminations carried out on test substances. The same high accuracy was obtained even at very low and high nitrogen

Table 1. Nitrogen determination in standards with the Rapid-N apparatus

Substance	Nitrogen, %		
	Theory	Found*	s†
Acetanilide	10·36	10·36	0·10
1-Chloro-2,4-dinitrobenzene	13·82	13·75	0·13
Azobenzene	15·37	15·36	0·08
Copper phthalocyanine	19·46	19·40	0·13
2,4-Dinitrophenylhydrazine	28·28	28·26	0·10
Urea	46·66	46·64	0·14
Melamine	66·63	66·59	0·08
"Lupolen" (polythene)	0·20	0·24	0·08
N,N,N′,N′,-Tetramethyl-ethylenediamine	24·09	24·13	0·09
Sulphanilic acid	8·09	8·08	0·12

* Mean of 10 determinations; samples each 3–10 mg.
† s = standard deviation.

Table 2. Determination of nitrogen in fertilizers with the Rapid-N apparatus

Fertilizer	Official method*	Rapid-N†
Nitrophoska, blue	12·01	12·01
Nitrophoska, red	12·89	12·96
Nitrophoska 15 : 15 : 15	14·84	14·80
Nitrophoska 20 : 20 : 0	19·54	19·58
Nitrophoska 15 : 15 : 6 : 4	14·78	14·71
Ammonium sulphate/nitrate	26·12	26·12
Calcium cyanamide	18·63	18·64
Blended fertilizer CDH	20·21	20·26
Grass fertilizer 20 : 5 : 8 : 2	20·14	20·21
Floranid	28·36	28·40
Potassium/ammonium nitrate	22·66	22·59

* From the Deutsche Methodenbuch.
† Mean of 10 determinations; samples each 5–30 mg.

contents, and independent of the type of nitrogen group, and the standard deviation did not exceed 0·15%. Quantitative oxidation was achieved by the quasi-explosive combustion in pure oxygen, even with substances such as pigments and plastics that burn with great difficulty. Volatile pyrolysis products were also completely decomposed.

Because the method is both rapid and universally applicable,[3] its use has not been confined to industrial and university microanalytical laboratories. In many branches of industry it has been welcomed as a substitute for inconvenient, time-consuming, and messy Kjeldahl determinations. Apart from the pollution aspects of acid digestion—which have been proposed as grounds for its prohibition—the Kjeldahl method gives good results only with compounds containing nitrogen groups that are readily converted into ammonia. Thus our method has been adopted for the analysis of foodstuffs, cattle feed, and above all fertilizers.[5,6] Table 2 shows a number of fertilizers that are analysed on a routine basis with the Rapid N, which gives results fully as reliable as those officially prescribed in the "Deutsche Methodenbuch". BASF's Nitrophoska fertilizers give just as little difficulty as Floranid, calcium ammonium nitrate, or calcium cyanamide. The last is already widely analysed by our rapid method; for instance, the Süddeutschen Kalkstickstoffwerke at Trostberg has entirely abandoned Kjeldahl determinations and now uses only Rapid N equipment. One of the advantages of the rapid nitrogen determination is that it can be used for production control, and allows better matching of product shipments to specified nitrogen limits.

An interesting application of the method is the determination of traces of nitrogen in solids and aqueous solutions. An additional oxidation stage in the horizontal furnace before the copper gauze ensures that volatile pyrolysis products do not enter the nitrometer even when larger samples are examined. For aqueous solutions, such as effluent water, deproteinated fluids, or immunization serums, the sample-entry stop-cock is replaced by an injection block with self-sealing rubber septa. The modified combustion unit is shown in Fig. 4. The size of the sample depends on the concentration of organic substances it contains, up to a limit of 1 ml; the minimum amount of nitrogen that can be determined is 0·005%.

CARBON AND HYDROGEN

The success of the nitrogen method confirmed our belief that nitrogen, carbon and hydrogen should be determined separately by appropriate rapid methods. Since full

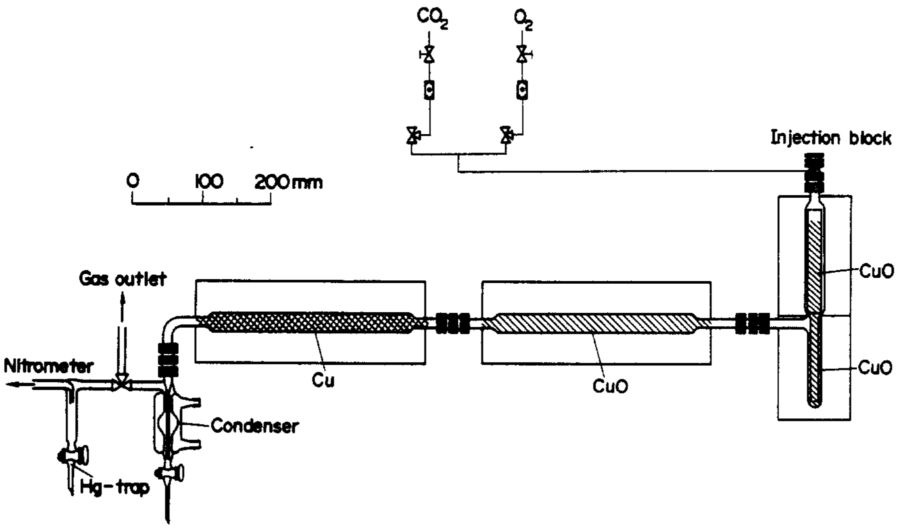


Fig. 4. Combustion section.

automation must include automatic sample introduction, which causes no difficulty when a vertical combustion tube is used, it was decided to adapt the very successful combustion technique of the nitrogen determination to the determination of carbon and hydrogen. It was immediately obvious that in this case principle would have to yield to expedience, since separate equipment for carbon determinations and hydrogen determinations would be unjustifiably expensive. The problem that remained was the choice of the end-determinations.

Complete oxidation yields carbon dioxide and water. The carbon dioxide can be determined by several methods, but only two appeared suitable for automation: conductivity measurement and titration in a non-aqueous medium. However, after many preliminary experiments, the former was found to be less reproducible and we decided to use non-aqueous titration.

Water is first separated by freezing, revaporized, and passed through 1,1-carbonyldiimidazole[7] to release the equivalent amount of carbon dioxide; the latter is then titrated just as in the carbon determination. The titrations were carried out automatically with colorimetric end-point determination. The entire procedure could be automated, and the end-determination was not dependent on non-linear physical calibration, thus the method satisfied the condition of strict proportionality we had imposed at the outset.

Principle

The sample is weighed in tinfoil boats and burned, as described for the nitrogen determination, in a stream of pure oxygen in a vertical combustion tube. The water formed is collected in a freezing-trap and the carbon dioxide is flushed out in a stream of oxygen and absorbed in a titration cell containing 2-aminoethanol in dimethylformamide. The carbon dioxide is titrated as the carbamic acid salt with tetrabutylammonium hydroxide, with thymolphthalein as indicator; the end-point is determined colorimetrically, the titre being automatically printed out or fed to the calculator. The trapped water is vaporized in a stream of oxygen and carried over 1,1-carbonyldiimidazole at 50°. The carbon dioxide formed is absorbed and titrated.

By using two traps in parallel and duplicate titration cells, water from a previous combustion can be determined at the same time as carbon dioxide, so that effectively carbon and hydrogen are determined simultaneously. The analysis time for both carbon and hydrogen is then 8 min, including an allowance for substances difficult to combust and the time required for preparing the titration cells for the next determination.

Apparatus

The automatic equipment we developed for this determination consists of the combustion unit, the separation and conversion unit for isolating water and converting it into carbon dioxide, two titration stands with piston burettes and reservoirs for absorption solution and titrant, the control unit for the titrimeters and for programming the analysis, and a printer or a calculator.

The combustion unit is essentially the same as for the nitrogen determination, and in fact the same basic module can be used for either determination.

The separation system for carbon dioxide and water has two spiral silver traps, which are successively cooled and heated in turn. Four magnetic valves direct the gas stream emerging from the combustion unit at about 60 ml/min through whichever of the traps is being cooled; at the same time a separate stream of oxygen flushes water vapour from the heated trap into the conversion system, where an equivalent amount of carbon dioxide is generated.

The colorimetric titrimeters are simplified versions of the apparatus described by Brodkorb and Scherer,[8] whose method of determining the end-point is considerably more sensitive than any other. Diffuse light falls on two pairs of photoresistors after passing through the entire solution and two pairs of interference filters that transmit either light of the same colour as the indicator or its complementary colour. Control of the burette is achieved *via* the resistors, which are connected in a Wheatstone bridge; the filters are arranged so that dissimilar filters are disposed asymmetrically on either side of the bridge.

When the solution has the required colour the bridge is balanced by a potentiometer that is preset to a certain position: the input signal controlling the burette motor is zero and the titration stops. Before this point is reached a signal initiates the change from continuous to stepwise addition of titrant, whereby the rate of addition is controlled by the error signal from the bridge; this eliminates the risk of overshooting the end-point

The titration stands were specially developed for the titration of carbon dioxide. A magnetic stirrer keeps the solution well mixed during absorption and titration of carbon dioxide. The burettes are fitted with impulse-actuated valves, to avoid heating effects that would affect the temperature and hence the factor of the titrant The titrant can be standardized with carbon dioxide from a receiver of known volume alternatively it can be standardized against salicylic acid in isobutyl alcohol.

The entire analysis, including the end-titrations, proceeds automatically. The titres can be printed out or fed direct to a calculator; one gives the carbon content of the sample last introduced into the combustion unit, while the other gives the hydrogen content of the previous sample.

The weighing, introduction, and combustion of the samples proceed as described for the nitrogen determination Before a sample is introduced into the combustion chamber, the titration cells (Fig. 5) are filled with absorption solution (20 ml), which is then pretitrated to a colour determined by the setting of the potentiometer in the detector circuit. After returning to the zero position the burettes start to titrate the carbon dioxide as it is absorbed (Fig. 6); the control circuits are so arranged that the burettes can resume continuous addition of titrant if the flow of carbon dioxide restarts after the end-point has already been approached and stepwise addition of titrant has started. Both burettes are switched off after a predetermined time Finally the titration vessels are emptied by suction, ready for the next analysis cycle.

Results and discussion

Table 3 gives results illustrating the accuracy and precision of determinations carried out by our method. The values given are means of ten determinations, and in no case does the absolute standard deviation exceed 0·25%, either for carbon or for hydrogen. The greatest advantage of the method is however the working time it saves: the automatic Rapid CH apparatus requires no supervision, and samples can be introduced automatically from a magazine loaded with 30–50 weighed samples. The central control unit governs both the normal sequence of the analysis and the introduction of successive samples; a new cycle begins every time the titration vessels are emptied.

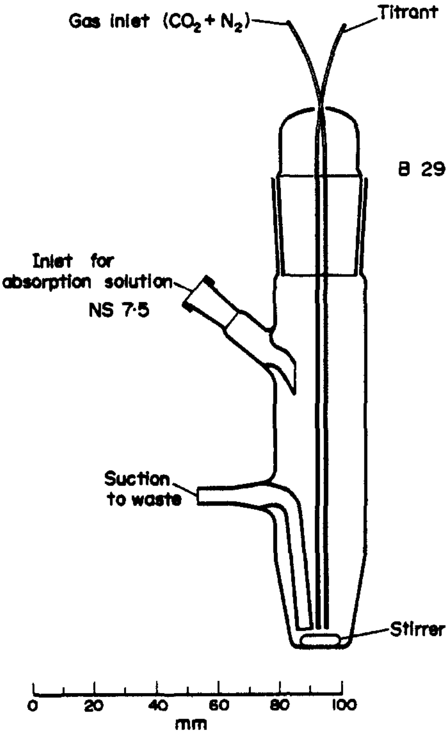


Fig. 5. Titration vessel.

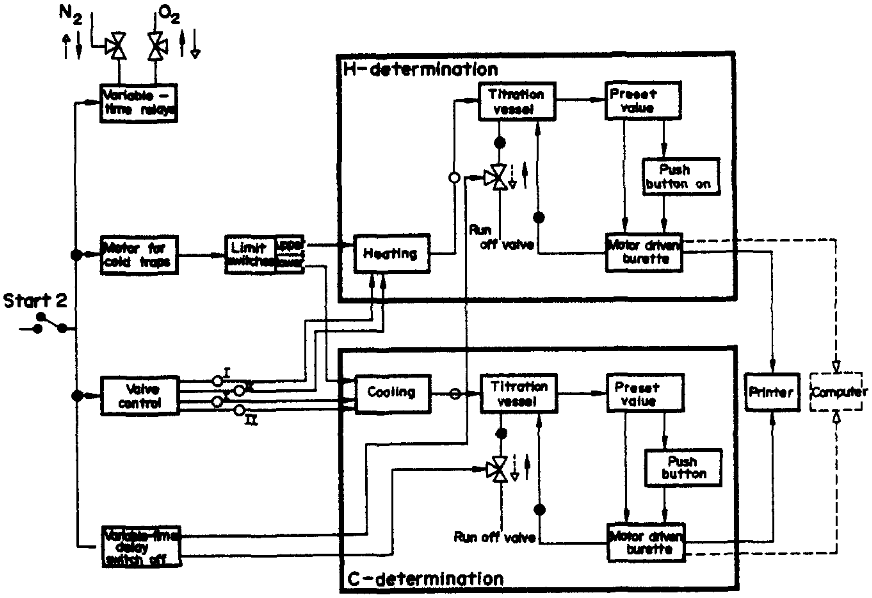


Fig. 6. Analysis programme for carbon and hydrogen.

Table 3. Results obtained for standards with the Rapid CH Analyser

Substance	Carbon, % Theory	Carbon, % Found*	s†	Hydrogen, % Theory	Hydrogen, % Found*	s†
Iodobenzoic acid	33·89	33·98	0·13	2·03	2·04	0·10
Potassium hydrogen phthalate	47·05	47·07	0·15	2·47	2·57	0·15
Sulphamic acid	0·0	0·11	0·15	3·11	3·13	0·16
Stearic acid	76·00	76·02	0·15	12·76	12·60	0·21
Melamine	28·57	28·66	0·15	4·80	4·93	0·21
Urea	20·00	20·12	0·20	6·71	6·63	0·18
Acetanilide	71·09	71·18	0·18	6·71	6·74	0·18
Copper phthalocyanine	66·72	66·62	0·20	2·80	2·85	0·17
Picric acid	31·45	31·54	0·15	1·32	1·44	0·14
2-Chloro-4-nitro-6-bromoanaline	28·66	28·63	0·19	1·60	1·79	0·21
p-Fluorobenzoic acid	60·02	59·99	0·12	3·57	3·61	0·13

* Mean of 10 determinations.
† *s* = standard deviation.

Like the apparatus for nitrogen determination, the Rapid CH can be left to carry out determinations overnight.

The modules of the Rapid series—built under licence from our designs—can be used to assemble an apparatus exclusively for carbon determinations. This is often done by laboratories where the primary concern is not organic elemental analysis, for instance, for the routine determination of carbon in waste water and waste gases. In practice it has also proved to be faster and simpler than any other commercial apparatus for carbon determinations. By injecting water samples of 1–2 ml it is possible to determine carbon mass concentration as low as 10 mg/l.

If the Rapid CH is operated with automatic sample introduction and direct transmission of weighings from an electronic balance to a calculator, one laboratory assistant can carry out on average 60 determinations of carbon and hydrogen in a working day. With the Rapid N he can carry out 80 determinations of nitrogen in a day, so that the average number of carbon, hydrogen, and nitrogen determinations carried out by one man in 1 day is at least 30 each. This figure is scarcely attainable with any of the current commercial units for determining carbon, hydrogen, and nitrogen simultaneously. In addition, the equipment of the Rapid series is more reliable, since it requires no calibration, giving results strictly proportional to amounts, and the sample size corresponds to what is usually regarded as microanalysis rather than ultramicroanalysis; indeed for nitrogen determinations it is possible to use macro-samples and to determine trace amounts.

OXYGEN

For the automatic determination of oxygen a method based on conversion into carbon dioxide appeared the most appropriate, since a unit for automatically titrating carbon dioxide was already available. However, the first stage of such a method, namely pyrolysis of the sample and formation of carbon monoxide in a bed of carbon, is not amenable to speeding up in the way that combustion in oxygen is. First, pyrolysis in a vertical tube leads to contamination of the carbon by interfering elements, causing inevitable errors. Secondly, the relative retention time of carbon monoxide is lengthened by comparatively slow adsorption and desorption processes, and the absolute retention time cannot be reduced by increasing the flow because the carbon offers too much resistance.

We abandoned attempts to depart from the conventional horizontal tube for pyrolysing the sample, and reduced the average analysis time by operating a pair of units in parallel, each with its own titrimeter; a single control unit, an electronic balance, and a calculator completed the assembly.[9,10] The analytical cycle proceeds fully automatically, each titre being coupled with the sample number and the appropriate weight, which is entered from the balance when released by the operation of a switch.

The way in which the calculator is used in fully automatic operation is given here as an illustration of the principles involved; in the determination of nitrogen or carbon and hydrogen there are only differences of detail.

Apparatus

Figure 7 shows the block diagram of the complete assembly for the automatic determination of oxygen. The assembly includes two pyrolysis units, two photometric titrimeters with central reservoirs for absorption solution and titrant, the control unit, a gating unit, the calculator, the electronic balance, and an interface to convert the parallel binary-coded decimal data into the serial machine code of the calculator.

Each pyrolysis unit has a silica tube with sample inlet, one short and one long furnace, a copper section and a source of prepurified nitrogen. The carbon filling is maintained at 1120°.

The motor-driven piston burettes of the titrimeters are fitted with inductive pulse units, the output from which is received by counters built into the gating unit. The blank correction is made in the gating unit by suppressing the equivalent number of pulses (up to 1 decade); in principle the correction could be made in the calculator, but the limited storage of the Diehl Combitron S calculator makes this impossible.

The gating unit receives the signals representing the net and gross weights from the electronic balance, and couples them with the appropriate titres.

Automatic operation of the titrimeters proceeds just as in the determination of carbon and hydrogen. The central control unit governs the overall cycle, with the gating unit to eliminate mutual interference of the two determinations running in parallel. Pyrolysis and purging times can be preset to values suitable for the samples being analysed.

Programme

The programme for the calculation is shown in Fig. 8. The computer programme is entered manually or by means of punched tape in digital coded form. The date, code for the operator, and factor of the titration solution are added and stored. At any one time four sample-weights are held in store, of which the first is already printed out together with the identifying data. The titres are entered automatically and

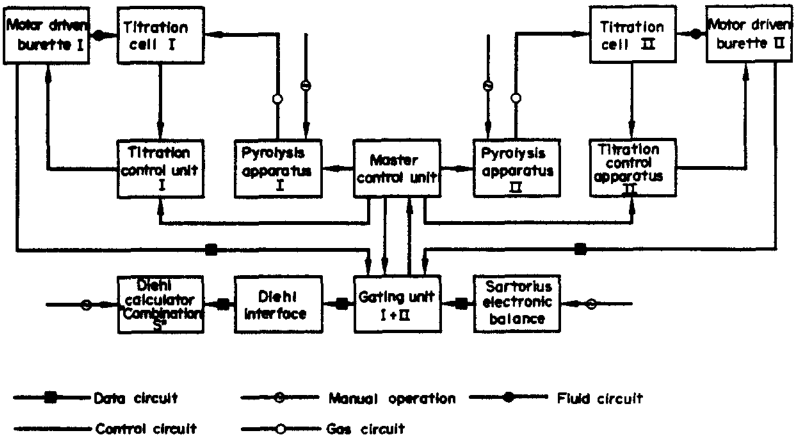


Fig. 7. Block diagram of automated oxygen analyser.

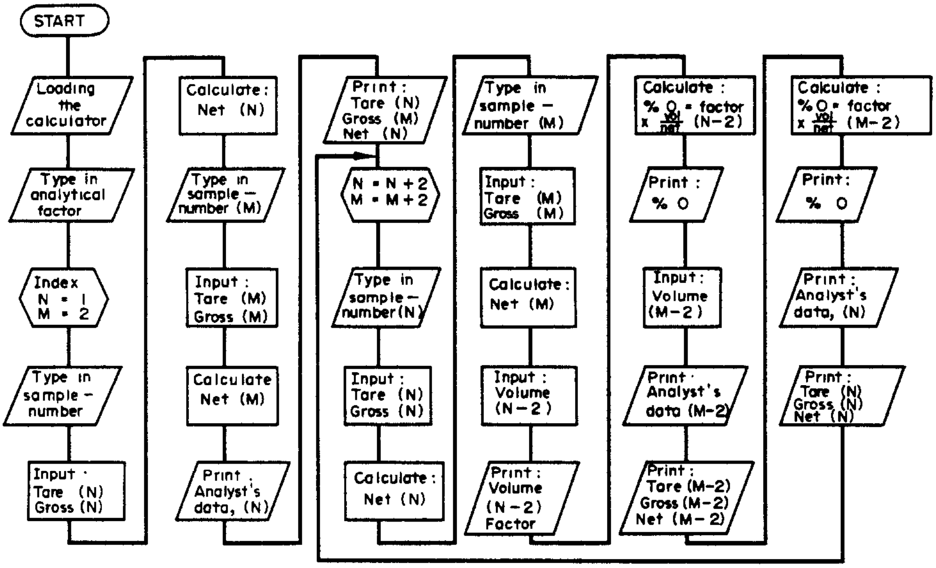


Fig 8. Flow diagram for calculation of oxygen content.

coupled with the appropriate weights, and the oxygen contents are printed out. As soon as the results for the first two samples and the weight of the third sample have been printed out the programme returns to the start of the loop: the next two sample weights are then entered.

The analysis programme, which is controlled on a time basis, starts with the short furnace being switched on; 30 sec later the furnace starts to move forward. After 2 min (or whatever time is preset) the furnace pauses for 30 sec at a position before the sample boat, so that pyrolysis proceeds slowly enough to avoid sudden expansion of vapour against the direction of gas flow. The furnace then moves under the sample and remains there for a suitable time up to 2 min (which is long enough for even the most difficult sample). In the following 2 min the short furnace reaches the long furnace, pushes it forward 2-3 cm, and stops; 30 sec later, after the zone previously covered by the end of the long furnace has been heated, the short furnace is switched off. After a purging time of up to 8 min the control unit gives the "interrogate volume" signal to the calculator, which then receives the reading of the first burette *via* the gating unit. The oxygen content of the sample is printed out, and after a pause the reading of the second burette is entered and the corresponding result is printed out.

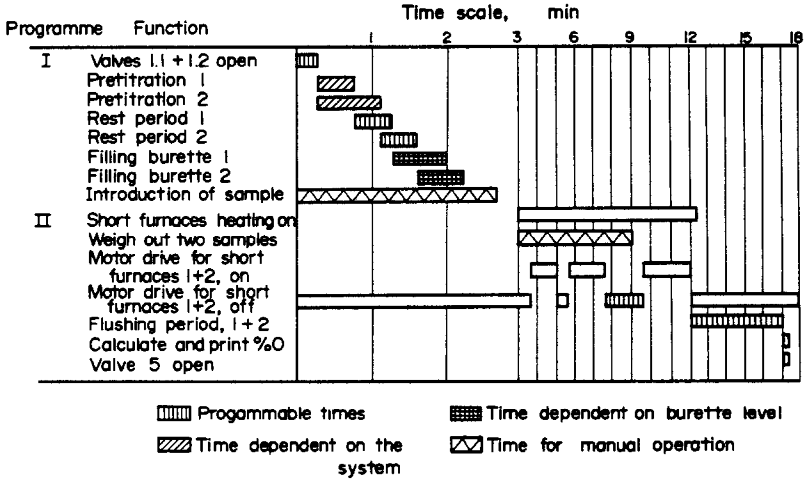


Fig. 9. Analysis programme for oxygen analyser.

The total time required for each pair of determinations is 14–18 min, depending on the length of the variable pyrolysis and purging times. The exact times for each stage, including the operations carried out manually, are shown in Fig. 9. One operator can carry out twice as many determinations in a day as with the classic Zimmermann-Unterzaucher method, even with the longest analysis programme. With easily pyrolysable samples the ratio is even more favourable for our method. For routine analysis 50 determinations per day is reasonable for each set of equipment. The highest rate of throughput can be achieved by matching the analysis programme to the properties of the substances being analysed; this also virtually eliminates faulty pyrolysis and allows the operation of the equipment by less well-qualified staff.

RECORDING AND PROCESSING DATA

The use of calculators with very limited storage capacity—desk-top computers—is really only suitable for smaller laboratories with few sets of equipment for the determination of individual elements, although it has been the preferred arrangement in the U.S.A. It has the advantages that programming is simple and that results are immediately at hand. Desk-top computers are quite cheap nowadays, but they are too slow and too restricted for use with a number of sets of automatic equipment operated simultaneously. While we were developing our methods, such a computer (the Diehl Combitron S) was suited to our requirements, but as soon as the methods for carbon and hydrogen and for nitrogen had proved suitable for routine use, and we had developed the method for oxygen, it became clear that a more efficient system would have to be found. However many calculators we acquired, they could not sufficiently reduce the paperwork involved in recording requests for analysis, noting results, and making reports. Without such a reduction we could not reorganize our laboratory procedures radically enough to make substantial savings in labour.

A degree of automation going beyond logging data involves control of the equipment providing the data and presenting of results in a satisfactory form of report. For this the only economical way of providing the necessary data-storage and data-processing capacities is to acquire a share in the use of a large computer,[11] such as the IBM 1800 Process Computer or one of the IBM 360 series computers with a teleprocessing terminal.

We have approached the problem of automation of elemental analysis in two phases. First, the reorganization of internal procedures such as registering incoming samples and allocating tasks; second, on-line connection of automatic analytical equipment to the computer system. The first phase has already been realized with an IBM 2741 Data Communications Terminal connected to the BASF computer centre. This is a terminal equipped with a typewriter keyboard, with tabulator, and connected to the computer system by telephone line. The data are processed in accordance with our own programme, which allows great flexibility by keeping to bare essentials, by the remote batch-entry system.

To facilitate processing of the data, a number of procedures had to be modified. These included registration, identification and distribution of samples, and allocation of priorities. Figure 10 shows the flow of paperwork: procedures affected by Phase 1 automation concern the areas marked with a single black dot. Incoming samples and requests for analysis are given numbers that identify them in all three departments of our Analytical Laboratory. If determinations are to be carried out in more than one department or in several places in the same department the sample is divided accordingly. The information on the request for analysis is registered *via* the terminal connected with the IBM 360/50 intermediate computer, which is situated 1 km away in the

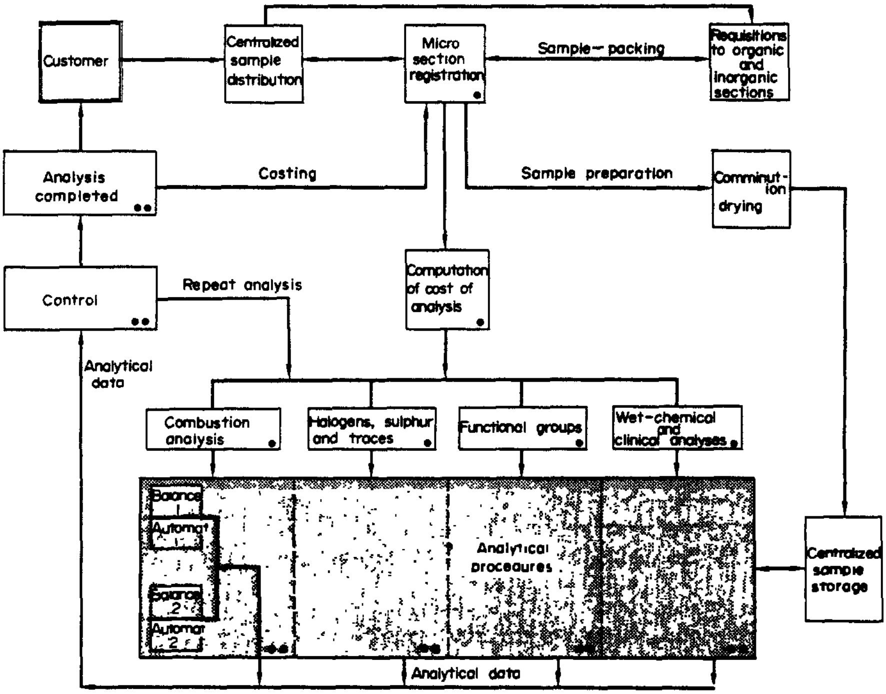


Fig. 10. Block diagram of organization of analysis.

computer centre. The data are transferred to the queue of the IBM 360/65 working computer, to await evaluation, by giving the command signal (EXEC) at the terminal; the programme is stored on magnetic disc. When the IBM 360/65 has completed its task the results are stored in the IBM 360/50 and can be called forward from the terminal by the appropriate signal.

Programme

Figure 11 is an example of a record of incoming analyses, divided into fields giving analysis number, amend or erase sign, priority, name and telephone number of person initiating the analysis, designation of sample, determinations required, whether single or duplicate determinations required, whether determinations are to be carried out in other departments, and abbreviated information on the properties of the sample. Information

```
10101   wohlgemuth  21809   desty frt/8 c h o n cl              o      abzug
      t prim.,sek.,tert. amine - bestimmen
10102 e mayer       7685    rueckst 35  c32h16n8cu38                   vak.80
11003   schmidt     1376    v635/3 a    c717h61n104/o118        ao
      t anorg:sulfat-asche  org:molgew.benzol loeslich
10104   #           #       #    4 b    o262/c h                ao
      t "
10105   hartmann    3885    extr.13/71  cl ab                          explosiv
10102ke #           #       #           c32h16n8cu18          1        #
10105   fischer             band 17     p                              spuren
10106   friedrich   28589   frakt.36/19 c h s
101061
10107 h froehlich   4978    10914/24    n o                   1
10104kt #                   org:molgew.dioxan
10108   wunder      22629   f12/2       4
10109   #           #       #           3
10110 e schnell     4947    vorl 33     cl                      o
```

Fig. 11. Record of incoming analyses.

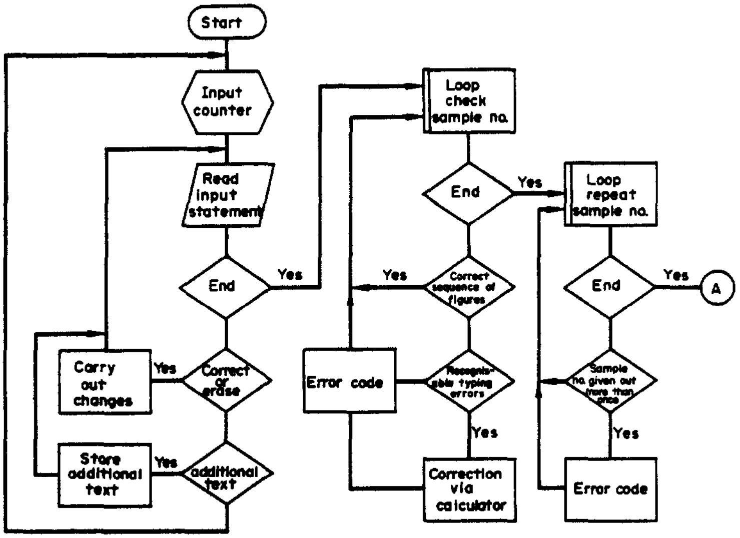


Fig. 12. Programme flow-chart, Part I, connected to Part II (Fig. 13) atⒶ.

such as solubility for molecular-weight determinations, column for gas-chromatographic separations, can be entered in an additional line; for this no attempt is made to introduce mnemonic codes, since the key for them would be far too extensive.

Figures 12 and 13 show the simplified programme flow-chart, divided into two parts; Ⓐ is the connector. The analysis number is checked to ensure that it is neither out of sequence nor a repetition; obvious typing errors are corrected automatically, and other errors are given in a coded list. Any line can be corrected or erased by adding the appropriate code sign (K or L). If an analysis has special priority it is brought to the front of the work list that is finally printed. Figures in the field showing determinations required indicate the proportions of the elements whose symbols they follow, and the addition of an ampersand indicates that the theoretical molecular formula and not mass fraction is meant and that the computer has to calculate the mass fractions; for example, C6H6& indicates the formula of benzene, and not mass fractions of 6% carbon and 6% hydrogen. Symbols following a solidus relate to the proportions of elements present in the sample but not to be determined. If the signs A or O are present in the appropriate field, requisitions are automatically made out for the department that will carry out the analysis not done in the microanalytical laboratory. The costs of all determinations are automatically added to information provided initially. Work lists are prepared for each working group, and several times a day—three times at the moment—the load of determinations is found for each element, allowing the available staff to be assigned to tasks in the most effective way.

When all the information has been processed the following are printed out:

(1) the revised sample register, which includes the theoretical mass fractions of each element (when the molecular formula is known or postulated) and the costs of the analyses, as in Fig. 14;

(2) the number of samples;

(3) work lists, as in Fig. 15;

(4) requisitions for determinations to be carried out in other laboratories, as in Fig. 16.

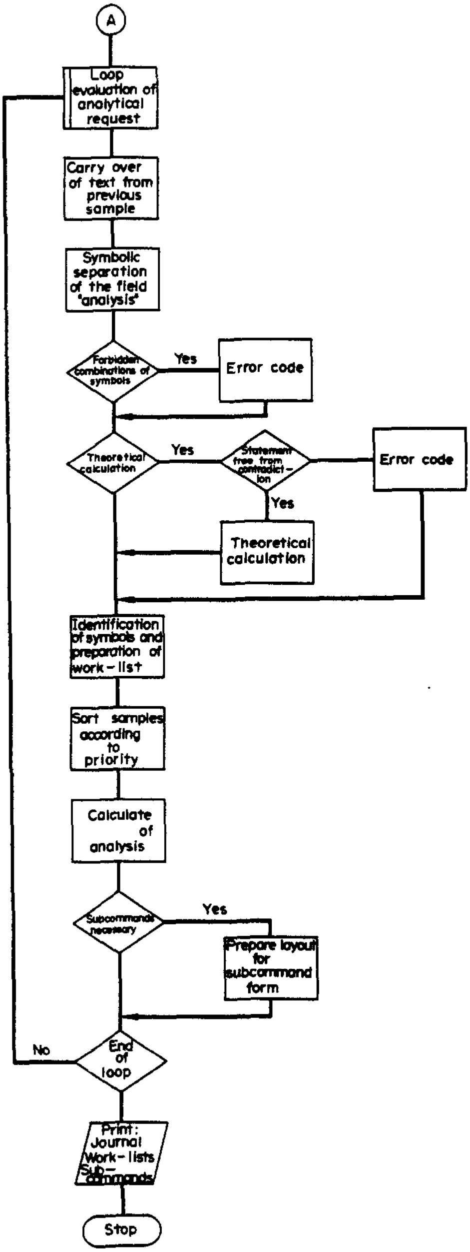
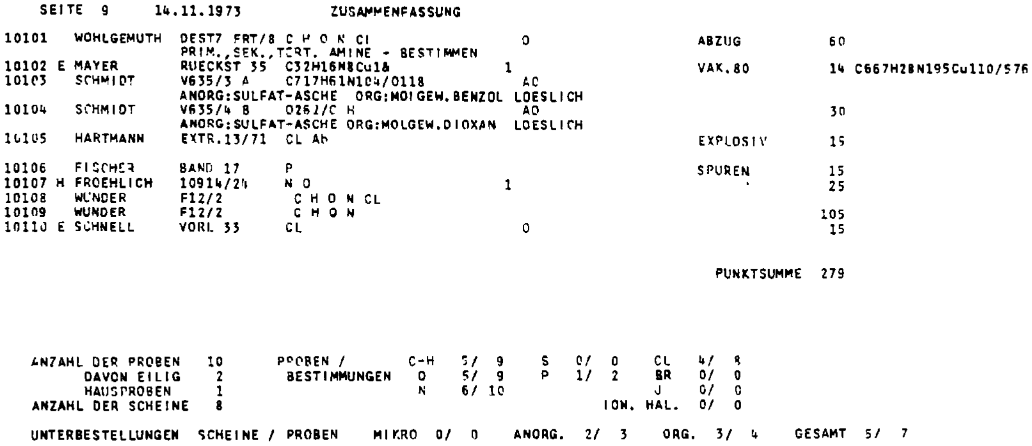


Fig. 13. Programme flow-chart, Part II, connected to Part I (Fig. 12) at Ⓐ.

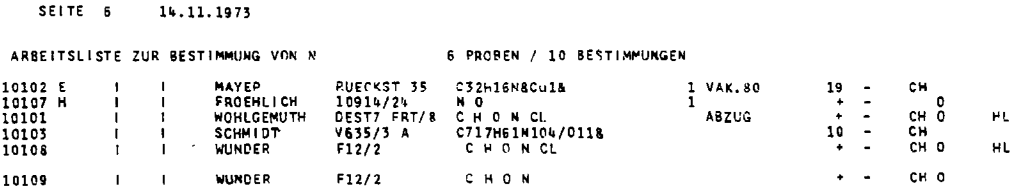
Phase 2

The operation of Phase 1 has proved satisfactory for routine work, and we intend to go ahead with the implementation of Phase 2—on-line connection of all equipment, including electronic balances, to the data-processing system. The procedures affected by Phase 2 are shown in Fig. 10; the corresponding areas are marked with two black dots.



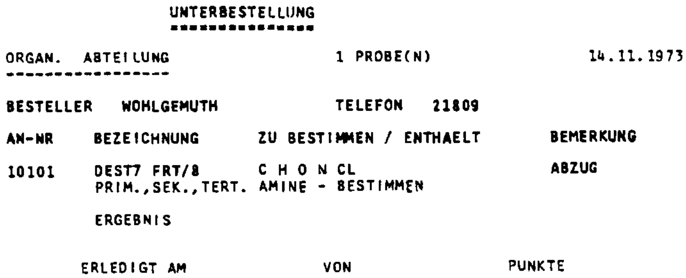
```
    SEITE  9     14.11.1973           ZUSAMMENFASSUNG

10101    WOHLGEMUTH  DEST7 FRT/8 C H O N CL             0           ABZUG         60
                     PRIM.,SEK.,TERT. AMINE - BESTIMMEN
10102 E MAYER        RUECKST 35  C32H16N8Cu18         1             VAK.80        14 C667H28N195Cu110/576
10103    SCHMIDT     V635/3 A     C717H61N104/0118      AO
                     ANORG:SULFAT-ASCHE  ORG:MOIGEW.BENZOL LOESLICH
10104    SCHMIDT     V635/4 B     0262/C H              AO                        30
                     ANORG:SULFAT-ASCHE ORG:MOLGEW.DIOXAN  LOESLICH
10105    HARTMANN    EXTR.13/71  CL AB                              EXPLOSIV      15

10106    FISCHER     BAND 17      P                                 SPUREN        15
10107 H FROEHLICH    10914/24     N O                 1                  '        25
10108    WUNDER      F12/2         C H O N CL
10109    WUNDER      F12/2         C H O N                                       105
10110 E SCHNELL      VORL 33      CL                    0                         15

                                                                      PUNKTSUMME 279



  ANZAHL DER PROBEN   10      PROBEN /         C-H    5/  9    S   0/  0    CL    4/  8
       DAVON EILIG     2       BESTIMMUNGEN     O     5/  9    P   1/  2    BR    0/  0
       HAUSPROBEN      1                        N     6/ 10                  J    0/  0
  ANZAHL DER SCHEINE   8                                           ION. HAL.  0/  0

  UNTERBESTELLUNGEN  SCHEINE / PROBEN    MIKRO  0/  0    ANORG.  2/  3    ORG.  3/  4    GESAMT  5/  7
```

Fig. 14. Print-out of sample register.



```
    SEITE  6     14.11.1973

 ARBEITSLISTE ZUR BESTIMMUNG VON N            6 PROBEN / 10 BESTIMMUNGEN

10102 E      I    I      MAYER       RUECKST 35   C32H16N8Cu18          1 VAK.80      19  -    CH
10107 H      I    I      FROEHLICH   10914/24     N O                   1              +  -      O
10101        I    I      WOHLGEMUTH  DEST7 FRT/8  C H O N CL              ABZUG        +  -    CH O     HL
10103        I    I      SCHMIDT     V635/3 A     C717H61N104/0118                    10  -    CH
10108        I    I    ' WUNDER      F12/2         C H O N CL                          +  -    CH O     HL

10109        I    I      WUNDER      F12/2         C H O N                             +  -    CH O
```

Fig. 15. Print-out of work-lists.



```
                      UNTERBESTELLUNG
                      ***************

ORGAN.  ABTEILUNG                    1 PROBE(N)                 14.11.1973
-----------------

BESTELLER   WOHLGEMUTH               TELEFON   21809

AN-NR    BEZEICHNUNG      ZU BESTIMMEN / ENTHAELT        BEMERKUNG

10101    DEST7 FRT/8      C H O N CL                     ABZUG
         PRIM.,SEK.,TERT. AMINE - BESTIMMEN

         ERGEBNIS


              ERLEDIGT AM                VON                 PUNKTE
```

Fig. 16. Print-out of requests for determination in other laboratories.

Phase 2 requires considerable capital expenditure, since all equipment has to be modified for automatic operation.

There are two possible ways of on-line operation for Phase 2. The first is shown in Fig. 17 and is based on the use of a satellite processer in the laboratory; this would collect data and transfer them to the central processer in blocks. This would however be rather inefficient, since the satellite processer would be waiting for data for much of the time. A more cost-effective solution would be to use a process computer on a time-sharing basis (Fig. 18). Since data are generated very sparsely in organic elemental

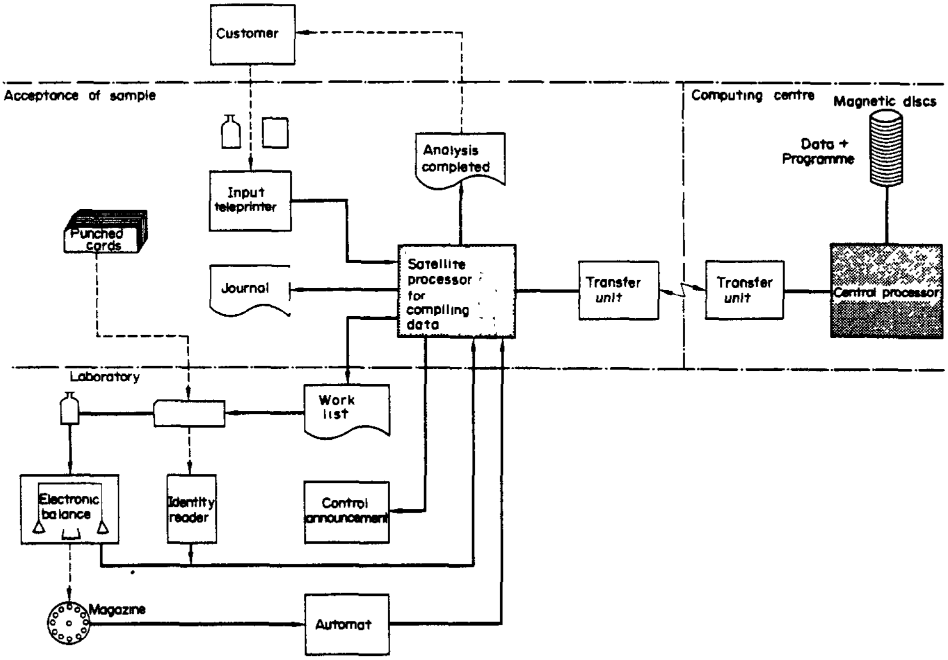


Fig. 17. On-line operation *via* a satellite processer.

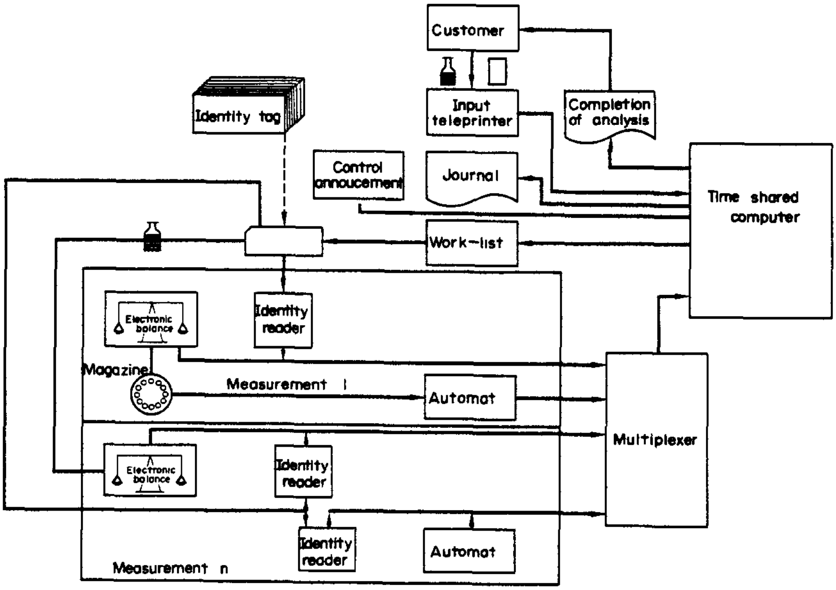


Fig. 18. On-line operation *via* a time-shared computer.

analysis (in contrast to mass-spectrometry for instance), it would in fact be possible to use a background programme.

The identification of samples presents a problem, since none of the current commercial systems is really suitable or cheap enough; the first step before implementing Phase 2 was therefore the development of a satisfactory identity reader.

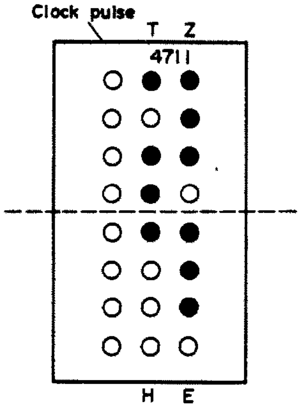


Fig. 19. An identity tag. T = thousands, H = hundreds, Z = tens, E = units.

For each sample a plastic identity tag is prepared (Fig. 19). The tag measures 25 mm × 45 mm, and bears the sample number both in figures and in BCD form as punched holes. The latter are read by a photoelectric reader developed by BASF. The tag, which has a guide to ensure correct presentation, is inserted in the reader, and falls under gravity past three sets of light beams and photodiodes. The perforations on the left provide the clock pulse, while the other two rows give signals in BCD code for thousands and hundreds and tens and units respectively. The thousands and tens and the hundreds and units are read in parallel, but the total number is read serially in the corresponding register; thus the tag illustrated carries the number 4711.

Unless the tag is grossly soiled it can be read without error, since two pairs of beams and detectors per row measure the contrast of light and dark. The detectors and the logic elements are connected so that an error at any one detector prevents the whole number from being read.

Each identity reader has storage registers in which measurements from a given set of automatic analysis equipment can be entered manually or automatically. The readers are interrogated in turn by a BASF multiplexer, which conveys the data to the central processor; the interrogate cycle can be set so that the waiting time is negligible. The information received by the central processor includes the number of the identity reader (or of the corresponding analysis equipment), the sample number, and the measured values. For the latter, storage capacity for a 2 × 16-bit word is provided. If the reader has information available when interrogated, the multiplexer gives the central processor an interrupt signal, and in turn receives a ready signal when data can be transmitted again.

When all the data pertaining to a given sample are available, they are evaluated and the analysis report is printed out. The programme, written in FORTRAN, was drawn up by us so as to ensure maximum practical utility and flexibility. The status of any analysis can be ascertained *via* a console typewriter in the laboratory. Obvious errors are reported automatically.

When large magazines of samples are used the analysis equipment can be run without supervision. The computer takes over control, preventing the start of a new analysis if the results of one of the checks carried out intermittently on a standard are outside predetermined limits.

The advantages of incorporating automatic data-processing in the laboratory system are as follows:

(1) data are recorded without error;

(2) the data are available when required;

(3) unusual situations are immediately noticeable and can be dealt with as they occur;

(4) service is improved by quicker presentation of analytical reports;

(5) productivity is increased by a reduction in the average time for sample to be dealt with;

(6) labour is saved, resulting in an overall reduction in costs after allowing for the increased capital investment.

We intend to exploit these advantages in BASF's Microanalytical Laboratory.

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Zusammenfassung—Es wurden automatische Methoden zur raschen Bestimmung von Kohlenstoff, Wasserstoff, Stickstoff und Sauerstoff zum Gebrauch in Verbindung mit einer modernen Datenverarbeitungsanlage entwickelt. Es werden Einzelheiten der Arbeitsweise, Geräte, Programmierung und Ermittlung der Ergebnisse angegeben.

Résumé—On a mis au point des méthodes automatisées pour le dosage rapide des carbone, hydrogène, azote et oxygène pour l'emploi conjointement à un équipement de traitement des données moderne. On présente des détails quant aux méthodes, appareils, programmation des techniques et évaluation des résultats.

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APPLICATIONS OF MIXED-LIGAND COMPLEXES IN ANALYTICAL CHEMISTRY (1966–1972)

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Summary—A review is given of developments in the understanding and application of mixed-ligand complexes in analytical chemistry.

The complex compounds formed by a central ion with two or more different ligands are usually termed ternary or mixed-ligand complexes. However, the first term is not generally accepted, since such complexes often contain not two but three or more different ligands.

Complex formation between one central ion and two or more different ligands leads to an increase in reaction selectivity since the probability of interaction with other central ions to form similar compounds is reduced. The absorption spectra of mixed-ligand complexes differ from those of the corresponding single-ligand complexes in both the position and height of the absorption maxima. This allows higher sensitivity of determination to be achieved. Furthermore, the formation of these complexes causes a change in properties such as solubility in water and organic solvents, extraction rate, and others which are important in analytical chemistry.

Thus, conversion of complexes with a homogeneous co-ordination sphere into compounds containing several different ligands is an effective means of solving one of the most important problems of analytical chemistry—to increase the sensitivity and selectivity of analytical reactions.

The formation of mixed-ligand complexes in solution is a rule rather than the exception it was formerly thought to be. Even if there are apparently only two components in the solution, we still cannot call it a single-ligand compound, since in most cases the complex contains solvent molecules as well as hydroxyl ions as a result of central ion hydrolysis.

The solvent effect is especially noticeable when alcohols are present. They cause an absorption-band shift of the complexes, indicating a chemical interaction of the solvent with the complex. The situation is more complicated if three or more components interact.

In practical chemical analysis two types of mixed-ligand complexes are most widely used. In the first, the complexes are formed by co-ordinating two or more different ligands to one central ion; in the other, by association of a co-ordinatively saturated charged complex with a ligand counter-ion. Nowadays, reactions based on interaction of one ligand with two different metals are also widely used.

The ever-growing interest in mixed-ligand complexes stimulated the development of new methods of analysing them and the publication of a number of reviews on analytical applications of certain types of reactions[1–9] as well as on general conditions of formation, the stability of mixed complexes and the compatibility of heterogeneous ligands in the inner sphere,[9–13,14] the mechanism of reactions,[15,16] the kinetics of ligand interchange,[16–20] structure and stereoisomerism.[17–26] Investigation of the mechanism of mixed-ligand complex formation has promoted further progress in their analytical application.

Thus in recent years there has been growing interest in the use of highly selective and sensitive gravimetric determinations with quaternary ammonium salts,[27,28] tetraphenylarsonium,[29] pyridine[30] and pyrazolone derivatives[8,31–34] as precipitants. The bases are precipitated from nitrate[28] and fluoride media[29] where they serve as outer-sphere cations as well as reagents entering the inner-sphere structure.[30,31]

The introduction of a large hydrophobic base into the precipitate reduces its solubility in water, while the greater molecular weight increases the accuracy of determination. Methods of determination of a number of metals by potentiometric titration of non-aqueous solutions of compounds $[\mathrm{MeA}_x\mathrm{R}_y]$ or $(\mathrm{AH})_x[\mathrm{MeR}_y]$ have been described,[35–38] which extend the range of application of the methods.

EXTRACTION OF MIXED-LIGAND COMPLEXES

Application of mixed-ligand complexes in extraction procedures has been highly developed. Most attention is paid to the theoretical and scientific aspects of the extraction of anionic complexes with organic cations[3–5,13,39,40] as well as of adducts (compounds with a mixed co-ordination sphere[41,42]). Of great interest are papers on the synergic effects arising from metal extraction by chelate-forming reagents and on extraction of anion and cation intracomplex compounds.[43,44]

The mechanism of extraction of ion-association compounds has been studied, especially the extraction behaviour of amine salts.[45,46] Amine salts in the form of ion-pairs $\mathrm{AH}^+\mathrm{R}^-$ are the usual form in a dilute solution with a low dielectric constant. If the solvent has both low dielectric constant and low solvating ability, an ammonium salt can associate to ion-quadrupoles and even more complex aggregates $(\mathrm{AH})_n\mathrm{R}_n$.[39,46,47] The degree of aggregation will increase with decreasing dielectric constant of the solvent and molecular weight of the amine. Such aggregate particles can solvate metal salts, thus complicating the treatment of distribution-ratio data. It was found, for example, that association complexes $[(\mathrm{AHNO}_3)_{n-1}]_2^{2+}[\mathrm{Bi}(\mathrm{NO}_3)_5]^{2-}$ are formed during bismuth extraction from nitrate media by xylene-type solvents. If the dielectric constant of the solvent is increased, the degree of association of the amine salt decreases and the Me:A relationship is expressed by simple stoichiometry.[46–48]

The solvation of amine salts non-aggregated in a solution is shown in a number of cases.[3,40,49,50] Thus, an increase in the extraction of cerium and americium thenoyltrifluoracetonates by benzene has been established as due to the formation of neutral chelate compounds with tri-n-octylammonium salts: $\mathrm{MeTTA_3R_3NHCl}$; $\mathrm{MeTTA_3R_3NH\,.\,TTA}$; $\mathrm{MeTTA_3R_3NHCl\,.\,HTTA}$.[49] Numerous studies of the extraction of multi-charged anionic complexes have allowed the optimum conditions for their formation to be established, depending on the nature of the high molecular-weight quaternary ammonium cation, in particular when steric effects in the case of ternary amines[51] are taken into account.

New highly selective methods of extracting metals with amines from nitrate,[52] perchlorate[53] and phosphate[54,55] media, as fluoride complexes,[56] have been developed. The extraction by amines of metal complexes with organic acids, oxy-acids[57–60] in particular, has received much greater attention. Although high molecular-weight amines are weakly hydrated in common solvents, an appreciable quantity of water is extracted during amine salt extraction. Infrared spectra show the water to be bonded to the ammonium salt.[39,61]

The systems involving extraction from acetate media[62] or from chlorine-substituted acids[63] are of certain interest. It is shown that water actively participates.[57]

The extraction of co-ordinatively saturated adducts formed as a result of interaction of a metal chelate or anionic complex with a neutral reagent, usually an amine, is still extensively used.[41,64–67]

Synergism in adduct formation can be of different origins. Recent studies, however, leave little doubt that synergism is connected with introduction of the neutral ligand into the inner sphere and displacement of water from the complex co-ordination sphere. The co-ordinative character of the bonding in adducts is evidenced by the dependence of synergism on steric factors, amine basicity and the relative strengths of the metal bonds to both ligands.[68–70]

The efficacy of synergism in adduct formation can be illustrated by extraction of lanthanide thenoyltrifluoracetonates with addition of heterocyclic bases (1,10-phenanthroline, 2,2′-bipyridyl). Without the base, equilibrium is reached in 6 hr; introduction of the base makes equilibrium possible in 1 min, with the distribution coefficient increasing by a factor of 10^6.[71]

Sulphur-containing reagents,[72,73] the reactivity of which is in some cases greater than that of oxygen-containing ligands, are promising.

PHOTOMETRIC AND EXTRACTION-PHOTOMETRIC METHODS

The application of mixed-ligand complexes in photometric or extraction–photometric analysis is very versatile. In this connection various types of mixed-ligand complexes may be considered. Equilibria in the system metal-ion (M), organic base (A) and electronegative ligand (R) have been thoroughly investigated. The formation of complexes with both ligands in the inner sphere $[MA_xR_y]$ as well as compounds of the ion-association type $(AH)_x[MR_y]$. $[MA_x]R_y$ is known in such systems. Many photometric methods are based on the formation of such complexes.[2,4–8]

Organic reagents, chelate-forming reagents in particular, are widely used as electronegative ligands[74] which increase the specificity and sensitivity of reactions.

Organic bases used to form stable bonds to metals include 1,10-phenanthroline, 2,2′-bipyridyl,[10,12,75] pyridine and its derivatives[76] and pyrazolone derivatives.[7,8] If the amine occupies all the co-ordination sites on the central ion a large hydrophobic cation is formed. Its combination with simple or anionic complex anions can serve as a basis for a number of photometric methods. Thus ferroin is known to be widely used for extraction–photometric determination of a number of anions such as ClO_4^-, SO_4^{2-}, I^-, NO_3^- and anions of organic acids.[77–80] The complex cation is the chromophoric centre in these compounds.

The combination of the colourless phenanthroline complexes of metals with coloured anions of acid dyes (eosin,[81,82] Bromophenol Blue,[83] Bromopyrogallol Red[74,84] and a number of others[81,84–88]) permits the development of highly sensitive extraction–photometric or extraction–fluorometric[82,87,89] methods of analysis.

In some cases the acid dye has several functional groups, in particular sulphonic acid groups which do not take part in chelate formation. Here charged chelates are formed.

For the neutralization of such compounds the use of strongly basic organic cations —quaternary ammonium salts,[90–97] diphenylguanidine[98–105] and other bases—is effective.[106–108] Addition of an organic cation shifts the pH of compound formation to a more acidic region. The acid dye under these conditions is in the molecular form.

The introduction of organic cations also increases the number of dye molecules bonded to the metal, which makes the reaction more sensitive. Thus, gallium forms a 1:2 complex with Pyrocatechol Violet, with molar absorptivity $7{\cdot}3 \times 10^4$ l.mole^{-1}.cm^{-1}. The introduction of diphenylguanidine results in the formation of an extractable complex (99% extraction), with the components in ratio 1:3:3 and molar absorptivity (ε) $1{\cdot}08 \times 10^5$ l.mole^{-1}.cm^{-1}.[109]

COMPLEXES WITH BASIC DYES

There has been intensive development of methods for determination of traces of metals as compounds of their anionic and cations of basic dyes.[4,6] The reactivity of the dye depends on its state in solution,[110–113] structure and basicity.[114,115] The results obtained are only a rough approximation since electron density was neglected in the calculations. Furthermore, some change of electron density occurs during anion interaction, *i.e.*, the anions polarize the electron shells of the dye as is shown by the changing coulomb integral of an atom to which the anion is attached. The anion will increase the energy of electrons in the atom it approaches and consequently will decrease the coulomb integral and hence increase the positive charge on the atom. The derivative $\partial q/\partial \alpha$ is the measure of the increase, q and α being the electron density and coulomb integral for the given atom.

Dyes with a greater $\partial q/\partial \alpha$ value possess greater selectivity. The polarization of molecules may also be characterized by the change in energy of π-electrons with the change in coulomb integral, *i.e.*, by the $\partial E/\partial \alpha$ value. This value is determined by the electron density on the atom $\partial E/\partial \alpha = q$.

The application of this group of reagents requires investigation of the solvent and many other factors. Rules for the prediction of interaction of a given anion with dyes have not yet been established.

Besides the simple 1:1 association complexes, compounds containing two dye shift ions may be extracted, the reaction sensitivity being thus increased. For instance, the interaction between tellurium bromide and Butyl Rhodamine S involves the formation of $[\mathrm{Dye}^+][\mathrm{TeBr}_5^-]$($\varepsilon_{max} = 7{\cdot}8 \times 10^4$ l.mole^{-1}.cm^{-1}) and $[\mathrm{Dye}^+]_2[\mathrm{TeBr}_6^{2-}]$($\varepsilon_{max} = 1{\cdot}5 \times 10^5$ l.mole^{-1}.cm^{-1}).[116]

The application of negatively-charged chelates has caused new developments in the analytical use of association complexes of basic dyes with complex anions.[117–122] Salicylic acid,[117,122] benzoic acid,[119] 8-hydroxyquinoline[121] and dibromo-8-hydroxyquinoline[118] are used as chelate-forming reagents. The chelates formed are successfully used for extraction–photometric or fluorimetric determination of a number of metals including rare-earth[117–120,122] or alkaline-earth[120,123] metals. Development of new types of basic dyes has been carried out.[124]

Oxidizing agents can be used to form dye oxidation products which in some cases are more intensely coloured. This method is more effective for determining oxidant anions.[125] The fading of the colour of the basic dye association-complexes, caused by reduction (*e.g.*, with alkaloids) is used for their extraction–photometric determination.[126]

Exchange reactions seem promising for the further application of basic dyes. To extract a metal as an anionic complex a more selective dye is used, for example Crystal Violet, and to increase the reaction sensitivity this base is substituted by another dye, *e.g.*, Rhodamine 6G.[127–129] If a colourless base is used as the displacing reagent and forms more stable complexes, differential displacement of dye occurs. This method is used for determining a number of bases, *e.g.*, diantipyrylmethane.[126] Decolourization of the ferroin–iodide complex when cyanide ions are added is used for cyanide determination,[130] and displacement of the acid dye Bromophenol Blue from its tetraphenylarsonium salt is used for photometric determination of twelve different anions.[131]

HETEROPOLY ACID EXTRACTION

Alkyl and aryl amines are used for the extraction of heteropoly acid "blues".[132] Basic dyes are used to extract unreduced heteropoly acids, and this is the basis of highly sensitive methods for determining germanium,[133] samarium,[134] phosphorus[135–137] and silicon.[138] Antipyrine dyes are also effective for the extraction of heteropoly acids.[139]

COMPLEXES WITH TWO ELECTRONEGATIVE LIGANDS

Halide or thiocyanate–halide complexes as well as mixed-ligand chelates have been the subject of numerous investigations of the general problems of the compatibility of different ligands in the inner sphere.[9,10,12,140–145] The influence of solvents on the formation of mixed-ligand complexes has been studied in detail.[146,147]

The formation of mixed-ligand complexes is of great importance in the photometry of high oxidation-state metals, in particular when these metals (niobium, titanium, tantalum) interact with metallochromic reagents. Addition to these systems of reagents such as hydrogen peroxide,[148–150] oxy-acids[151] or fluoride[152,153] and sometimes the use of two different ligand-forming acid reagents[154,155] gives quicker and more complete complex formation. This is probably due to quicker central-ion dehydration under the influence of the additional component.

Charged chelates in association with an electronegative ligand constitute a separate group of mixed-ligand complexes. Such compounds are important in the extraction–photometric determination of bismuth,[156] iron,[157] tin[158] and other metals. The uncharged complexes thus formed are easily extracted by non-aqueous solvents, *e.g.*, formation of the zinc hydroxyquinolinate perchlorate complex $[Zn_2Ox_3(HOx)_3ClO_4]$[159] increases the degree of extraction of the zinc.

Synergism is exhibited when Methyl-Orange is used as counter-ion to neutralize the charge on the complex in extraction of tin(IV) oxinate, the sensitivity being increased.[160]

EXTRACTION OF COMPLEXES WITH TWO DIFFERENT CHELATING LIGANDS

Studies of the extraction of mixed-ligand diketonates[42,161] or the combination of diketonates with other anionic ligands[162] are of some interest. There appears to be an increase of polarity in mixed-ligand complexes of the type $MR'R''$. Their extraction appears to be poorer than that of MR'_2 or MR''_2 compounds.[163]

An interesting application of mixed-ligand complexes of this type is the increase of reaction selectivity by the method of competing ligands. Here the introduction of a second ligand depresses the interaction of some ions with a chelating agent whereas another group of ions under the same conditions forms mixed-ligand compounds. Thus, introducing benzoic acid (Bz) inhibits the colour reaction between the cerium group elements and quinalizarin (Q), but the elements of the yttrium group form easily extractable mixed-ligand complexes $[M]:[Q]:[Bz] = 1:1:2$. These complexes have higher molar absorptivities, thus increasing the sensitivity and selectivity of determination.[164]

The use of complexes with two anionic ligands for determining one of them is well known. Thus, the mixed-ligand complex of cerium(III) with alizarin complexone and fluoride is used for the direct photometric determination of fluorine.[165] An analogous method is based on the formation of a zirconium complex with Calcein Blue and fluoride.[166]

TWO-METAL ONE-LIGAND COMPLEXES

The complexes least studied are compounds of two different metals and one ligand, which could reasonably be called mixed-metal compounds. Some general characteristics of the conditions for formation of such complexes have been given.[2,9,11,167]

Several publications deal with the formation of mixed-metal complexes of dioximes.[167–171] Owing to their intense colour, stability and often good extractability, compounds of the type metal–tin–dioxime find application in the determination of a number of metals.[167]

The complexes formed between platinum metals, tin and halide are also interesting. Their chemistry has not yet been fully elucidated,[9,11] though analytical methods based on formation of these complexes or extraction of platinum-metal anionic-complex ion-association compounds with organic cations are widely used to determine some platinum metals.[172–174]

The formation of mixed-metal complexes is to be expected when multidentate ligands, especially oxy-acids, are used.[175–177] Such complexes are not usually used in photometry as they are often kinetically inert and then effectively mask their component metals in whole or in part. One interesting and promising group of mixed-metal compounds involves ligands which are acid dyes, *e.g.*, dioxoazo-compounds.[178] It was shown that the formation of mixed-metal compounds in the system azo-dye–rare earth–Fe^{3+} or R–Sc–M, *etc.*, substantially increased the sensitivity of reaction and the distribution coefficient.[178,179] Physicochemical analysis and preparation of the compounds proved their existence, and the discovery of similar complexes in other systems, *e.g.*, lanthanum–nickel–Alizarin Blue,[180] erbium–calcium–Alizarin S,[181] suggests that many others exist.

QUATERNARY AND MORE COMPLEX COMPOUNDS

In some cases, especially when extraction–photometric analysis is used, complex compounds containing three or more ligands are employed for successful extraction of intensely coloured compounds of high oxidation-state metals. For convenience, some types of such complexes may be delineated.

Complex cation–complex anion $M'A_x \cdot M''R_y$

Phenanthroline or bipyridyl complex cations in combination with halide or oxalate anionic complexes are commonly used,[182] usually for the determination of the metal in the anion.[182–187] The methods for determining tin,[182] antimony,[183] thallium,[184] platinum and nickel,[185] cadmium[186] and boron[187] are well known. The association compounds formed are easily extracted by non-aqueous solvents, and their colour depends on the colour of the complex cation (usually ferroin).

Ion-association complexes of mixed-ligand complex anions[188,189]

These complexes have the composition $(AH)_xMR'R''$. The organic cation, usually alkylammonium[190–192] or tetraphenylarzonium,[193–195] forms a strong base. Halide or thiocyanate combined with oxalate,[190,191] diketonate,[195] or sulphate[192] are used as anionic ligands. Germanium gives similar complexes where the metal is bonded to three different anionic ligands, two of which constitute the inner sphere (*e.g.*, phenylfluorone and benzoylphenylhydroxylamine) while the third is in the outer sphere and neutralizes the residual positive charge.[196] Under such conditions complexes of the type $[MR'_xR''_y]R'''_z$ are formed, which considerably improve germanium determination.

A similar type of complex can be represented schematically as $[MR'_xA_y]R''_z$.[197–202] As an example we might consider the germanium complex,[200] the inner sphere of which consists of fluorone and antipyrine and the outer sphere of bromide or perchlorate. The conditions for the formation of such complexes as well as the methods of determining their nature have been described.[200–203] In a number of cases the formation of such association complexes is complicated by the influence of other metals. The formation of the complex compound of gallium with PAR, antipyrine and perchlorate, $[Ga]:[PAR]:[ANT]:[ClO_4] = 1:1:3:2$, may serve as an example. The extraction of a new compound with $[Ga]:[In]:[PAR]:[ANT]:[ClO_4] = 1:1:2:4:2$ occurs in the presence of indium. The reaction sensitivity is increased by the introduction of a second PAR anion into the compound.[204]

The group of complexes in question includes the mixed adducts obtained by the addition of two different amines to a metal chelate.[39,205] The extraction of these compounds of the type $[MRA'A'']$ is far greater than that of the normal adducts, $[MRA_2]$ $(D_{MRA'A''}/D_{MRA_2} = 1500)$,[205] which is accounted for by a more complete dehydration of the central ion.

CONCLUSIONS

The mixed-ligand and mixed-metal complexes find wide application in a number of kinetic[206] and luminescence methods,[82,87,206–208] and in chromatographic or extraction–chromatographic separation.[209,210]

The experimental material shows the essential role of the mixed-ligand complexes in redox reactions, catalysis, and reactions important in biochemistry.[13,26]

Preconcentration by extraction of mixed-ligand complexes is used in atomic-absorption determination[211] or activation analysis,[212] and makes the determination more sensitive.

It should be noted that the addition of masking agents, or buffer mixtures to decrease metal hydrolysis, often results in the formation of mixed-ligand or mixed-metal complexes which strongly affect the photometric determination. Thus complexes of niobium with PAR and EDTA were found to be formed,[74] though the EDTA was originally added as a masking reagent. It was established[213] that the interaction of germanium with lumogallion (Lg) in the presence of phosphoric acid formed the $LgGeO_2POOH$ complex.

The practical importance of mixed-ligand and mixed-metal complexes has prompted further study of mechanism and kinetics of formation, and of the structure, extraction and other properties of these complex and interesting compounds.

To classify the compounds under consideration, they should be divided into the following groups and more complicated ones.[214]

I. $(AH)_x[MR_y]$
II. $[MA_x]R_y$
III. $[MA_xR_y]$
IV. $[MR'_xR''_y]$
V. $[M'_xM''_yR_z]$
VI. $[M'A_x][M''R_y]$
VII. $(AH)_x[MR'_yR''_z]$
VIII. $[MR'_xA_y]R''_z$
IX. $[MR'_xR''_y]R'''_z$
X. $[MR_xA'_yA''_z]$
XI. $[M'M''R'_xA_y]R''_z$

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Zusammenfassung—Es wird eine Übersicht über die Entwicklung im Verständnis und in der Anwendung von Komplexen mit verschiedenen Liganden in der analytischen Chemie gegeben.

Résumé—On présente une revue des progrès dans la compréhension et l'application des complexes coordinats mixtes en chimie analytique.

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DETERMINATION OF RARE EARTHS AND THORIUM IN APATITES BY THERMAL AND EPITHERMAL NEUTRON-ACTIVATION ANALYSIS*

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Summary—A procedure is described for the non-destructive determination of Na, Mn, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu and Th in apatites by thermal and epithermal neutron-activation of independent portions of the material. The method was applied to three apatites with different contents. The precision obtained was better than ±5% for La, Ce, Sm, Eu, Gd, Tb and Dy and ±20% for Yb, Nd, Ho, Er and Lu for an apatite with a total rare-earth oxide content of the order of 1%. Determination of Ce, Tb and Yb could only be carried out with thermal neutron-activation analysis, while Gd, Ho and Er could only be determined after irradiation with epithermal neutrons.

Several analytical techniques have been used for the determination of rare-earth elements (REE) in apatites, $Ca_5(PO_4)_3(OH, F, Cl)$, *e.g.*, X-ray fluorescence spectrometry,[1,2] emission spectrometry,[2–4] neutron-activation analysis (NAA) both by radiochemical[5,6] and non-destructive[7] methods, electron microprobe[8–11] and atomic-absorption spectrophotometry.[2] As the REE content of apatites is of the order of tenths of 1% or higher, the REE can be determined non-destructively by neutron activation using a short irradiation time. Steinnes[7] has shown that La, Sm, Eu and Dy can be determined non-destructively with NaI(Tl) γ-ray spectrometry after thermal neutron irradiation of apatites for 10–30 min. Recent work is reported by Brunfelt and Steinnes[12] on determination of nine REE in silicate rocks by 1 hr epithermal neutron activation followed by a simple group separation procedure and Ge(Li) γ-ray spectrometry.

The procedure described in this work for determination of REE and Th in apatites is based on irradiation of two independent portions of the material with thermal and epithermal reactor neutrons for 2 and 15 min respectively, followed by Ge(Li) γ-ray spectrometry counting. Replicate analyses of three apatites of different REE concentration were carried out.

The present method has been developed to facilitate current studies of REE distribution in coexisting minerals from anorthosites, norites and mangerites selected from different anorthosite intrusions in the Norwegian precambrian terrain.

EXPERIMENTAL

Gamma-ray spectrometer and activity measurements

The detector used for this study was a 7229 S/N 251 Canberra coaxial Ge(Li) detector with a resolution of 2·5 keV (FWHM) and peak/Compton ratio 23/1 for 1331-keV peak of ^{60}Co; the relative efficiency was 5·7%

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[comparable to that of a 3 × 3 in. NaI(Tl) scintillation detector at 1331 keV]. The pulse-height analysis was performed with a Hewlett–Packard 200 MHz ADC interfaced to a NORD-1 digital computer (16 K, 16 bit). A pulser was applied for determination of counting time as well as for dead-time correction (as described by Anders[13]). In all measurements, the dead-time was kept below 10%. The peak-area integrations were performed according to the method of Covell.[14] Table 1 shows the photopeaks and experimental conditions selected for the determination of each of the radionuclides.

The activity measurements following the thermal neutron activation were performed twice on each sample, except for the counting of 2·582 hr ^{56}Mn and 2·36 hr ^{165}Dy which were based on only one counting for each sample.

Thermal neutron activation

Preparation of samples and reference standards. About 100 mg of finely powdered apatites were accurately weighed into 15 × 15 mm polyethylene envelopes which were then heat-sealed. Standard stock solutions of each REE were prepared by dissolving appropriate accurately weighed amounts of the 99·9% pure oxides in a few ml of nitric acid and diluting with water to 100 ml. The cerium solution was prepared from $(NH_4)_2Ce(NO_3)_6$. The standards were corrected for weight loss on ignition (950°), determined on separate oxide samples.

Reference standards were prepared by pipetting aliquots of 100 μl of the stock solutions of the individual REE onto small polyethylene sheets and carefully evaporating to dryness under an infrared lamp; the sheets were enclosed in polyethylene bags by heat-sealing. The amounts of REE in these reference samples were approximately as follows: La 50 μg; Ce 200 μg; Nd 150 μg; Sm 50 μg; Eu 10 μg; Gd 75 μg; Tb 10 μg; Dy 60 μg; Ho 10 μg; Er 30 μg; Yb 20 μg; Lu 5 μg.

Irradiation. Irradiation of the samples together with reference standards in duplicate was carried out for 2 min in the JEEP-II reactor, Institutt for Atomenergi, Kjeller (Norway), at a thermal neutron flux of about $1{\cdot}7 \times 10^{11}$ n . mm^{-2}. sec^{-1}.

Epithermal neutron activation

Preparation of samples and reference standards. Accurately weighed apatite samples of about 100 mg each were wrapped in 30 × 25 mm sheets of aluminium foil (prewashed with dilute nitric acid and rinsed with water). Aliquots (100 μl) of standard stock solutions of the individual REE were pipetted onto small sheets of aluminium foil and evaporated to dryness. The sheets of aluminium foil were afterwards carefully folded.

Irradiation. The apatite samples and a duplicate set of reference standards were packaged together in a 0·7 mm thick cylindrical cadmium box of 14 mm internal diameter and 10 mm internal height, as described previously.[15] The box was irradiated for 15 min in the JEEP-II reactor (Kjeller) in a fixed position at a thermal neutron flux of *ca.* $1{\cdot}7 \times 10^{11}$ n . mm^{-2}sec^{-1}. The cadmium ratio of ^{197}Au in this position was 2·8.

RESULTS AND DISCUSSION

In Table 2, mean values from replicate results obtained in this work for 3 apatites of different concentration range are presented for each element. The precision is indicated by the relative standard deviation of a single determination.

Thermal neutron activation

Lanthanum. La abundances can be determined accurately from both the 487·0 and 1596·6 keV photopeaks of ^{140}La. The range of precision obtained for the three apatites was 1–3%.

Cerium. The ^{141}Ce peak at 145·5 keV was used for the determination. The 142·6-keV contribution[16] of ^{59}Fe is not significant in this case owing to the low content of iron in the apatites studied in this work. The ^{175}Yb (144·7 keV) interference is also negligible if the counting is delayed until 30 days after the end of the neutron irradiation.[17] The precision obtained was in the range 1·5–3·4%.

Neodymium. The lines of ^{149}Nd were not observed after the 2 min irradiation time and the determination of Nd was based upon the 531·0 keV peak of 11·06 d ^{147}Nd, although it was very weak. The precision obtained by using this interference-free photopeak was 2·4% and 3·4% for the Ødegaarden and Hesnes apatites respectively, while for the Durango it was 14·5%. The advantage of a "low-energy-photon" Ge(Li) detector for the determination of Nd *via* the 91·1 keV peak of ^{147}Nd has recently been demonstrated by Rosenberg *et al.*[18] and Hertogen *et al.*[19]

Table 1. Half-lives, decay times, counting geometry and counting times for the radionuclides of interest

Element	Radionuclide measured	Half-life[26]	Thermal NAA			Epithermal NAA		
			Decay time	Distance from counter, *cm*	Counting time, *min*	Decay time	Distance from counter, *cm*	Counting time, *min*
Na	^{24}Na	15 hr	1 d	10	10			
Mn	^{56}Mn	2·582 hr	3 hr	20	5			
La	^{140}La	40·27 hr	1–2 d	10	10	1 d	10	5
Ce	^{141}Ce	32·5 d	10–15 d	2	50–240			
Nd	^{147}Nd	11·06 d	15–30 d	2	50–240			
	^{149}Nd	1·8 hr				3 hr	20	5
Sm	^{153}Sm	47·1 hr	1–4 d	10	10	1 d	10	5
Eu	^{152m}Eu	9·35 hr	3h–1 d	20–10	5	3 hr	20	5
	^{152}Eu	12·2 y	15–30 d	2	50–240			
Gd	^{159}Gd	18·0 hr				1 d	10	5
Tb	^{160}Tb	73·0 d	15–30 d	2	50–240			
Dy	^{165}Dy	2·36 hr	3 hr	20	5	3 hr	20	5
Ho	^{166}Ho	26·9 hr				3 hr	20	5
Er	^{171}Er	7·8 hr				3 hr	20	5
Yb	^{169}Yb	30·6 d	15–30 d	2	50–240			
	^{175}Yb	101 hr	10–15 d	2	50			
Lu	^{176m}Lu	3·71 hr				3 hr	20	5
	^{177}Lu	6·75 d	10–15 d	2	50			
Th	^{233}Pa	27 d	30 d	2	240			

Table 2. Mean values (*ppm*) and relative standard deviations (%) for 3 apatites

Radionuclide measured	γ-energy used,[25] *keV*	Ødegaarden 9/67* (3 analyses)		Hesnes 66–33† (6 analyses)		Durango‡ (4 analyses)	
		TNAA	ENAA	TNAA	ENAA	TNAA	ENAA
^{24}Na	1368·4	2331 (1·8%)		893 (1·5%)		1983 (3·6%)	
^{56}Mn	846·7			1709 (2·0%)		66 (2·9%)	
^{140}La	487·0	620 (3·0%)	723 (7·3%)	903 (1·0%)	998 (5·6%)	3146 (2·2%)	3380 (7·7%)
	1596·6	644 (2·5%)	686 (5·8%)	920 (2·6%)	981 (4·8%)	3279 (1·4%)	3385 (5·5%)
^{141}Ce	145·5	2234 (1·8%)		2649 (1·5%)		4183 (3·4%)	
^{147}Nd	531·0	1850 (2·4%)		2108 (3·4%)		1185 (9·0%)	
^{149}Nd	211·4		1894 (5·5%)		1864 (11·9%)		1441 (14·5%)
^{153}Sm	103·2	539 (1·5%)	553 (1·8%)	465 (0·9%)	467 (2·3%)	133 (2·4%)	140 (1·9%)
^{152m}Eu	121·8	45·1 (2·1%)	52·5 (4·6%)	44·1 (1·3%)	47·3 (7·6%)	14·6 (3·8%)	15·9 (6·5%)
	841·6	44·8 (2·4%)		43·7 (2·4%)		15·0 (4·1%)	
	963·3	45·9 (1·2%)		45·1 (1·5%)		15·2 (3·1%)	
^{152}Eu	121·8	44·9 (3·2%)		44·7 (1·9%)		14·8 (3·1%)	
	344·2	44·5 (2·9%)		45·1 (1·0%)			
^{159}Gd	363·3		624 (4·7%)		423 (4·6%)		85·5 (22%)
^{160}Tb	298·6	115 (3·1%)		71·1 (1·4%)			
	879·3	103 (1·5%)		64·7 (1·8%)		15·8 (3·6%)	
^{165}Dy	94·5	516 (2·5%)	572 (13·5%)	300 (1·4%)	303 (21·9%)	75·7 (5·3%)	93·5 (18·8%)
^{166}Ho	80·6		84·2 (12·8%)		49·1 (7·5%)		9·2 (31·3%)
^{171}Er	308·3		266 (8·8%)		142 (19·0%)		60·9 (24·8%)
^{169}Yb	177·0	162 (7·9%)		88·8 (2·9%)		34·7 (11·2%)	
^{175}Yb	396·1	142 (1·2%)		79·0 (5·6%)		34·7 (9·6%)	
^{177}Lu	208·3	19·5 (1·7%)		10·4 (6·7%)		3·6 (18·8%)	
^{176m}Lu	88·3		20·8 (7·8%)		12·9 (17·7%)		3·2 (65·0%)
^{233}Pa	311·9	23·1 (3·0%)		5·0 (12·8%)		192 (1·3%)	

* Chloroapatite from Ødegaarden, Bamle, Norway.
† Fluoroapatite separated from nelsonite, Hesnes, Norway.
‡ Unpurified fluoroapatite from Cerro de Mercado, Durango, Mexico.

Samarium. As expected from the good counting statistics of the 103·2 keV line from ^{153}Sm, the precision for this element was good (0·9–2·4%).

Europium. For the first count the strong peak of ^{152m}Eu at 121·8 keV was used. The second measurement was based on the 121·8 and 344·2 keV peaks from ^{152}Eu. The 344·2 keV peak cannot be used for samples with a high content of thorium, owing to the 340·5 keV peak of ^{233}Pa. The precision of the results obtained from these photopeaks was better than 4·1% and good agreement was observed between the mean values obtained.

Terbium. The agreement between the results obtained from the 298·6 and 879·3 keV peaks was good for the Ødegaarden and Hesnes apatites, but the result for the Durango apatite was higher by a factor of two for the first peak than for the second, owing to interference from ^{233}Pa (300·1 keV). The precision obtained was in the range 1·5–3·6% for the 879·3 keV photopeak.

Dysprosium. The precision obtained for the 94·5 keV peak from ^{165}Dy was 1·4–5·3%.

Ytterbium. The mean values obtained from the 396·1 keV photopeak of ^{175}Yb were about 10% higher than those from the 177·0-keV line of ^{169}Yb in the case of the apatites from Ødegaarden and Hesnes. For the Durango apatite the mean values obtained from the two peaks were, however, in good agreement. The 396·1 keV photopeak should be free from interferences.[17]

Lutetium. The Lu abundances were determined with a precision of 1·7–18·8% by means of the 208·3 keV peak from ^{177}Lu. The 113·0 keV line of ^{177}Lu was not used, because of various interferences from ^{169}Yb (110·0 keV), ^{175}Yb (113·5 keV) and ^{233}Pa (110·0 and 114·6 keV) as also pointed out by Cobb[16] and Gordon *et al.*[20]

Thorium. The Th content was determined with good precision *via* the 311·9 keV peak of ^{233}Pa, by comparison with G-2 (using the assigned value of 23·3 ppm[15]).

In addition to the REE and Th, the content of sodium and manganese can also be determined. The precision obtained for both these elements was 1·5–3·6%. The results given in Table 2 for these two elements are based on W-1 with assigned values of 2·15 and 0·17% respectively for Na_2O and MnO.[27]

Epithermal neutron activation

The theoretical considerations of epithermal neutron activation have been discussed previously.[21–24] In the recent work by Brunfelt and Steinnes[12] the feasibility of epithermal activation for the determination of REE in silicate rocks was assessed by means of calculated and observed "advantage factors", as introduced by Brune and Jirlow[21] for a given nuclide and defined as

$$F_a = \frac{(R_{Cd})_d}{(R_{Cd})_D}$$

where $(R_{Cd})_d$ and $(R_{Cd})_D$ are the cadmium ratios of an interfering nuclide and of the nuclide in question. From the observed advantage factor F_a as given in the work of Brunfelt and Steinnes[12] it appeared that Nd *via* 1·8 hr ^{149}Nd (211·4 keV; $F_a = 11$), Gd *via* 18·0 hr ^{159}Gd (363·3 keV; $F_a = 36$), Ho *via* 26·9 hr ^{166}Ho (80·6 keV; $F_a = 17$), Er *via* 7·8 hr ^{171}Er (308·3 keV; $F_a = 8{\cdot}0$) and Lu *via* 3·71 hr ^{176m}Lu (88·3 keV; $F_a = 35$) are favourable cases for determination with the epithermal technique whereas ^{165}Dy ($F_a = 0{\cdot}29$), ^{152m}Eu ($F_a = 1{\cdot}3$) and ^{140}La ($F_a = 2{\cdot}7$) are not. For Ce (33·4 hr ^{143}Ce) and Pr (19·2 hr ^{142}Pr), the conditions for determination by the epithermal technique seemed unfavourable as indicated by the calculated advantage factors given by Steinnes,[23] 3·7 and 2·7 respectively. The ^{153}Sm activity gives a strong peak in both epithermal and thermal spectra, but is more pronounced in the former ($F_a = 24$).

In Fig. 1, gamma spectra of two samples of Ødegaarden apatite recorded 2 hr after the irradiation are shown. One of the samples was irradiated inside the cadmium box, while the other was simultaneously activated outside, at a distance of 10 cm from the cadmium box, both samples being included in the same irradiation container.

The depression of the photopeaks of ^{165}Dy in the γ-spectra resulting from the epithermal neutron activation is clearly shown as well as the enhancement of γ-lines from ^{149}Nd, ^{153}Sm and ^{171}Er.

The application of epithermal activation analysis for REE in apatites is discussed below.

Neodymium. The 211·4 keV photopeak from ^{149}Nd (1·8 hr) was used. The precision for the three apatites was 5·5–14·5%, which was not as good as that obtained *via* ^{147}Nd in the thermal activation experiment. If a more restricted number of samples is to be analysed than was the case in this work, longer counting periods could be used to improve the precision.

Gadolinium. Gd was easily determined from the 363·3 keV line of ^{159}Gd after one day's cooling. The precisions obtained for Ødegaarden and Hesnes were 4·7 and 4·6% respectively; the precision obtained for the Durango was, however, only 22%, which is explained by the lower content of gadolinium (86 ppm) in this apatite compared to the other two (624 and 423 ppm).

Holmium and erbium. Previously data for these two elements have been obtained on silicate rocks by epithermal NAA combined with a group separation.[12] In the apatites these elements were determined non-destructively, with a precision in the range 7–30%.

Lutetium. The precision for lutetium obtained in the epithermal NAA *via* 3·7-hr ^{176m}Lu was worse than that obtained *via* the 6·75 d ^{177}Lu after thermal NAA. The counting periods were, however, only 5 min in the epithermal NAA. The agreement between the mean values obtained by these two methods was good.

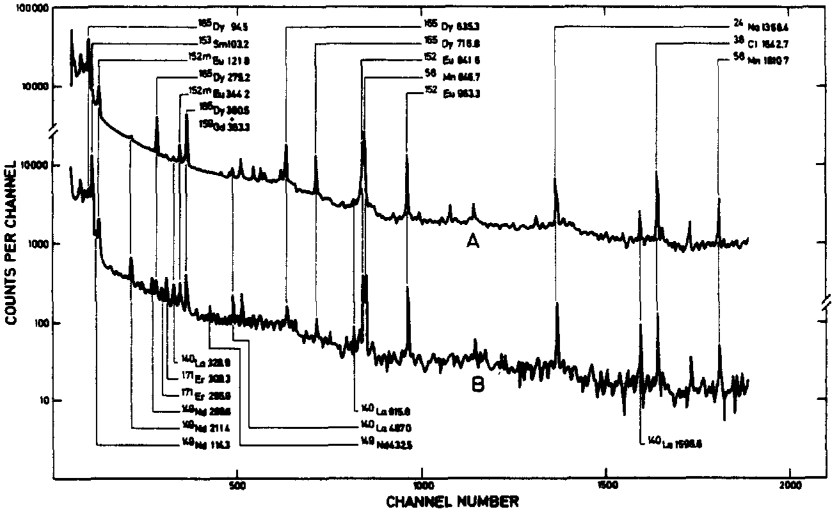

Fig. 1. Gamma-ray spectra of apatite samples from Ødegaarden (Norway) taken 2 hr after the end of irradiation. (*A*) thermal-neutron activated (weight of sample 20 mg, counting time 5 min); (*B*) epithermal-neutron activated (weight of sample 100 mg, counting time 10 min); 1 keV per channel.

Other rare-earth elements. As predicted by the "advantage factors" the precisions for La, Eu and Dy obtained by epithermal NAA were not as good as those obtained by the thermal activation method.

Cerium, terbium and ytterbium could not be determined by epithermal NAA in the apatites studied. The results obtained with thermal neutron activation are systematically lower than those obtained in the epithermal work for La, Sm, Eu, Dy and Lu. These discrepancies might be explained by a shielding effect in the thermal-neutron irradiated apatites, caused mainly by gadolinium which has an extremely high thermal-neutron absorption cross-section ($\sigma_0 = 5 \times 10^4$ b) compared with the small resonance absorption integral of this element, which is only 67 b as given in the compilation by Drake.[28] Therefore, we consider the results obtained in this work by epithermal neutron irradiation to be more accurate than those obtained by thermal neutron irradiation analysis.

The quality of REE data for rocks and minerals may be judged on the basis of comparison diagrams with chondritic meteorites[29] (*i.e.*, the ratio of each REE content in ppm to the average content of the same element in chondritic materials, plotted against atomic number or ionic radius). Owing to the nature of the partial separations within the REE group that accompany rock formation processes, such comparison diagrams are likely to exhibit smooth curves, except for Ce and Eu which may have been selectively separated from the other REE by natural processes involving changes in oxidation state. Comparison diagrams of the three apatites investigated in the present work are shown in Fig. 2. The chondritic values used are taken from Haskin *et al.*[30] For elements which can be determined both by thermal and epithermal neutron activation analysis the mean value was used. Apart from the marked negative Eu anomalies, smooth curves are obtained, except for holmium which seems to be systematically low. The apparently low results for holmium might be explained by the effect of a systematic base-line error.

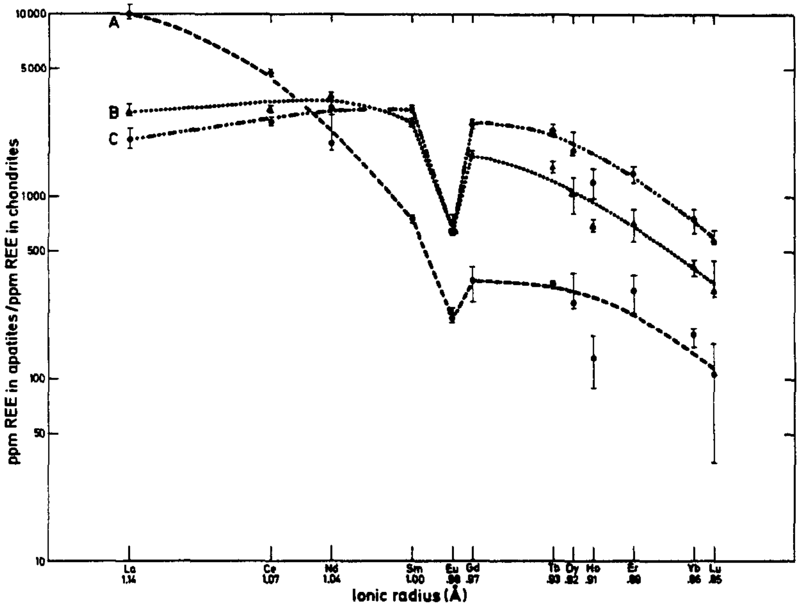

Fig. 2. Chondrite-normalized patterns for 3 apatites. Ionic radii taken from Ahrens.[31] (*A*) Fluoroapatite from Cerro de Mercado, Durango (Mexico); (*B*) fluoroapatite from Hesnes (Norway); (*C*) chloroapatite from Ødegaarden (Norway).

A non-destructive determination of REE in apatites, as demonstrated in this work, is of analytical interest because of the relative simplicity as compared to methods based on radiochemical group separations. During a group separation of the REE based on repeated precipitation steps unwanted fractionation may occur between light and heavy REE, and it may be necessary to perform a separate chemical yield determination for each of the elements involved.

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Zusammenfassung—Ein Verfahren zur zerstörungsfreien Bestimmung von Na, Mn, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu und Th in Apatiten durch Aktivierung verschiedener Teile des Materials mit thermischen und epithermischen Neutronen wird beschrieben. Die Methode wurde auf drei Apatite verschiedener Zusammensetzung angewandt. Die erhaltene Geneuigkeit war besser als ±5% bei La, Ce, Sm, Eu, Gd, Tb und Dy und ±20% bei Yb, Nd, Ho, Er und Lu in einem Apatit, dessen Gesamtgehalt an Oxiden seltener Erden bei etwa 1% lag. Die Bestimmung von Ce, Tb und Yb ließ sich nur nach Aktivierung mit thermischen Neutronen durchführen, die von Gd, Ho und Er nur mit epithermischen Neutronen.

Résumé—On décrit une technique pour la détermination non-destructive de Na, Mn, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu et Th dans les apatites par activation de neutrons thermiques et épithermiques de fractions indépendantes de la substance. La méthode a été appliquée à trois apatites avec des teneurs diférentes. La précision obtenue a été meilleure que ±5% pour La, Ce, Sm, Eu, Gd, Tb et Dy et ±20% pour Yb, Nd, Ho, Er et Lu pour une apatite avec une teneur totale en oxydes de terres rares de l'ordre de 1%. Le dosage de Ce, Tb et Yb n'a pu être effectué que par analyse par activation de neutrons thermiques, tandis que Gd, Ho et Er ont pu être seulement déterminés après irradation avec des neutrons épithermiques.

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SPECTROPHOTOMETRIC STUDY OF THE REACTIONS OF ARSENAZO III WITH ALKALINE-EARTH METALS

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Summary—Arsenazo III is used as a spectrophotometric reagent for alkaline-earth metals. The molar absorptivities of the calcium, strontium and barium complexes at 650 nm are $4{\cdot}40 \times 10^4$, $4{\cdot}00 \times 10^4$ and $3{\cdot}65 \times 10^4$ l.mole^{-1}.cm^{-1} respectively. The interference of magnesium is eliminated at pH 5–6. The use of sodium sulphate as masking agent permits the determination of small amounts of calcium, strontium and magnesium in the presence of barium. The alkaline-earth ions can be determined in the presence of each other at pH 4·2 at the 2–10 μg level. Some organic solvents such as dioxan, acetone and ethanol increase the sensitivity and selectivity in acidic medium. The stability constants have been measured and the structure of the complexes is discussed.

Savvin has shown that Arsenazo III is an excellent reagent for the spectrophotometric determination of Th, Zr, Hf, U, rare earths *etc.*[1,2] We have shown that it may also be used for the determination of metal ions with a rare-gas or d^{10} configuration such as Ca^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Mg^{2+}.[3–6] Hence it seemed of interest to study the reactions of arsenazo III with strontium and barium. A more detailed examination of the calcium–arsenazo III reaction has also been made. It was shown recently[2,7,8] that arsenazo III forms blue and violet-blue complexes with calcium, strontium and barium at pH 4–5 and the molar absorptivities of the complexes are *ca.* 10^4 l.mole^{-1}.cm^{-1}. Buděšínský has shown[9] that the reactions of arsenazo III with strontium and barium proceed mainly at pH 6·3 and 5·3 and the molar absorptivities of the complexes are $7{\cdot}25 \times 10^3$ and $5{\cdot}10 \times 10^3$ l.mole^{-1}.cm^{-1} respectively. Our study covers the pH range 3–10 and shows that complex formation is maximal at pH 9–10. The molar absorptivities are $4{\cdot}40 \times 10^4$, $4{\cdot}00 \times 10^4$ and $3{\cdot}65 \times 10^4$ l.mole^{-1}.cm^{-1} for the calcium, strontium and barium complexes respectively.

The sensitivity of the reactions in acidic media is increased by addition of organic solvents such as dioxan, ethanol and acetone. Despite their similarities the alkaline-earth ions can be determined in the presence of each other in acid media and with the addition of a masking agent. The interference of magnesium is serious but can be overcome.

EXPERIMENTAL

Reagents

Arsenazo III. A $10^{-4}M$ solution was standardized by spectrophotometric titration with thorium nitrate solution at pH 3 and 600 nm. An aqueous 0·04% w/v solution was used for analytical purpose.

Strontium and barium nitrate solutions. Stock solutions were standardized by complexometric titration[10] and diluted as required.

Calcium chloride solution, $10^{-2}M$. Standardized complexometrically.

Reagent grade dioxan, ethanol and acetone. Buffer solutions. The pH was adjusted with dilute sodium hydroxide and 0·2*M* acetate, 0·1*M* biphthalate and 0·1*M* borate buffer solutions.[11] The ionic strength was maintained at 0·1*M* with sodium nitrate.

All other reagents were analytical-reagent grade.

Recommended procedure

Place the test solution (~ 10^{-4} *M*, 0·50–6·00 ml) in a 25 ml volumetric flask, add 2·50 ml of 0·04% arsenazo III solution and 5·0 ml of pH 9 borate buffer, dilute to volume and mix thoroughly. The blue or blue-violet colour develops immediately with barium, in 15 min with calcium and in 25 min with strontium. Once formed it is stable for at least 26 hr. Read the absorbance in a 3 cm cuvette at 600 and 650 nm against a reagent blank solution.

RESULTS AND DISCUSSION

Absorption spectra

Arsenazo III [3,6-bis(2'-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid] forms blue complexes with strontium and barium. The absorption spectra for strontium presented in Fig. 1 show that the complex formation begins at pH > 3 and is greatest at pH 9–10. Two well-defined peaks occur at 600 and 650 nm for both the strontium and barium complexes. Two maxima also occur in the absorption spectrum of the calcium complex,[3] and they are observed in the spectra of arsenazo III complexes with many metals. This is explained by the inductive effect of the two conjugated systems of the reagent.[7,9,12] The absorbance of the arsenazo III must also be taken into account because of its bathochromic shift in alkaline medium. Figure 2 shows the spectra of the metal complexes compared with the spectrum of the H_3L^{5-} and H_2L^{6-} reagent forms at pH 9. The difference between complex and reagent is greatest at 650 nm.

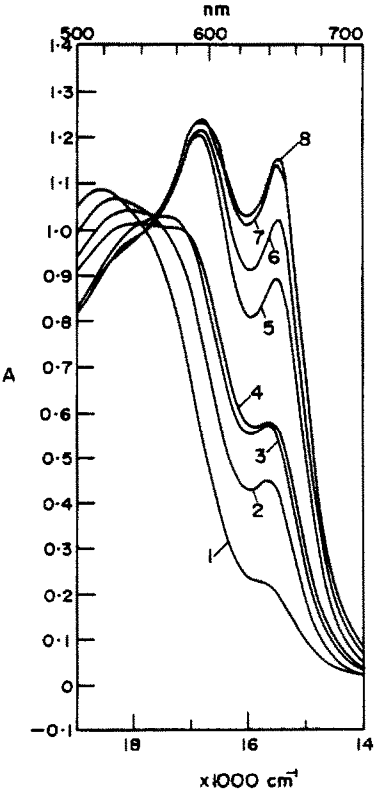


Fig. 1. Dependence of absorbance spectra on pH for strontium(II)–arsenazo III complex. $C_{Sr} = 2{\cdot}06 \times 10^{-4} M$; $C_R = 1{\cdot}72 \times 10^{-5} M$, l = 2 cm; vs. water. pH (*1*) 3·35, (*2*) 4·54, (*3*) 5·10; (*4*) 6·16; (*5*) 7·43; (*6*) 8·25; (*7*) 9·10; (*8*) 9·88.

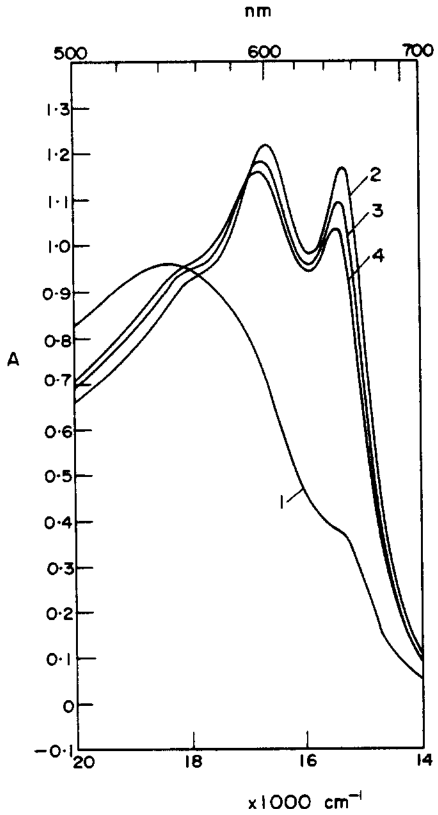


Fig. 2. Absorption spectra of arsenazo III and its complexes with calcium(II), strontium(II), barium(II) at pH 9·10. $C_M = C_R = 2{\cdot}06 \times 10^{-5}M$; $l = 2$ cm; *vs.* water. (*1*) Arsenazo III, (*2*) Ca-complex, (*3*) Sr-complex, (*4*) Ba-complex.

Composition of the complexes

A series of solutions at pH 9 with M : L varying from 1 : 10 to 20 : 1 was made and two maxima were observed in all the spectra, which became virtually identical for M : L > 1 : 1, thus confirming the composition ML. The 1 : 1 composition was checked by the molar-ratio, Asmus[13] and Bent and French[14] methods.

Sensitivity of the reactions and conformity to Beer's law

Because of the low stability of the complexes ($\log \beta \sim 8{\cdot}5$), a relatively high concentration of the reagent was used for the determination of alkaline-earth metals. The molar ratio of reagent to metal was $\geqslant 3$. The optimum pH was 9, because of completeness of complex formation and the relatively low absorbance of the reagent alone. The molar absorptivities of the complexes under the conditions above were calculated by standard statistical methods.[15] The absorbance of the solution, A_s, must be corrected for the absorbance of the free reagent, A_R. At pH 9 $A_R = (C_{R_0} - C_{M_0})\varepsilon_R$, where C_{R_0} and C_{M_0} are the total concentrations of the reagent and the metal and ε_R is the molar absorptivity of the reagent ($C_{R_0} > C_{M_0}$). The molar absorptivities are given in Table 1. The results for calcium differ from those reported earlier,[3] which were based on the differential molar absorptivity measured *vs.* reagent blank.

Table 1. Molar absorptivity ε (10^4 *l. mole*$^{-1}$. *cm*$^{-1}$) of the arsenazo III complexes with alkaline-earth metals at pH 9·10

λ, nm	Ca	Sr	Ba
600	4·15	3·78	3·30
650	4·40	4·00	3·60

Beer's law is obeyed over the final concentration ranges 0·05–1·20 μg/ml (Ca), 0·10–1·90 μg/ml (Sr) and 0·15–3·00 μg/ml (Ba).

Effect of organic solvents on the complex formation

The effect of dioxan, ethanol and acetone on the absorbance of the complexes is more pronounced in acidic media and at high concentration of organic solvent. A 60% v/v concentration of organic solvent was used without addition of buffer. Apparent final pH values (glass electrode) were 4·5, 4·2, 4·3 in the presence of dioxan, ethanol and acetone respectively. The absorption spectra are shown in Fig. 3. The organic solvents decrease the absorbance maximum at 540 nm and cause the appearance of a small maximum at 650 nm, and the reagent spectra in the non-aqueous media became similar to those in alkaline aqueous

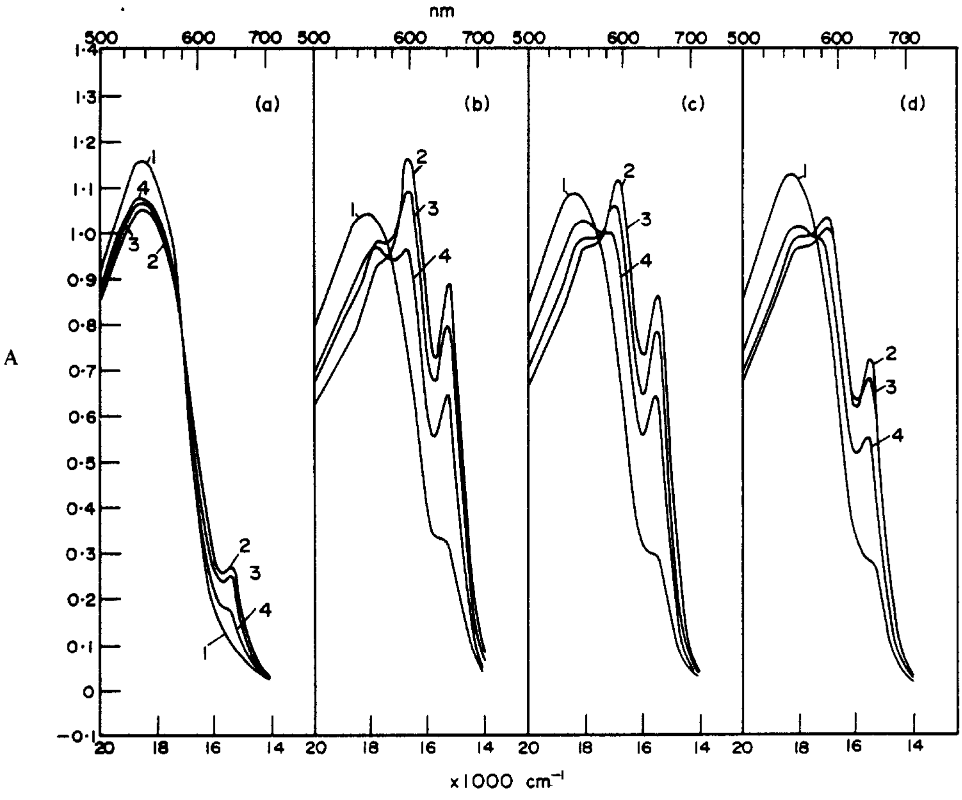


Fig. 3. Effect of organic solvents on the absorbance of arsenazo III and its complex formation with alkaline-earth metals. $C_M = C_R = 2{\cdot}06 \times 10^{-5}M$, 60% (v/v) organic solvent, pH 4·20 for aqueous solutions, apparent pH 4·2–4·5 in the presence of organic solvents; $l = 2$ cm; *vs.* water. (*a*) Arsenazo III; (*b*) Ca-complex; (*c*) Sr-complex; (*d*) Ba-complex. (*1*) aqueous solutions; (*2*) in the presence of dioxan; (*3*) in the presence of ethanol; (*4*) in the presence of acetone.

media. It is obvious that these changes are due to the shift of the tautomeric equilibrium of the reagent forms. As Savvin and Kuzin reported[16] the absorbance bands at 620–670 nm in the spectra of arsenazo III arise when both the azo and quinone–hydrazone ionized forms co-exist. Using the MOLCAO method these authors confirmed that in acidic media the reagent is in an azo form, but at the same time emphasized that in less polar solvents a maximum at 620–630 nm may arise owing to the presence of small amounts of the quinone–hydrazone form. There is agreement between these predictions and our experiments.

The spectra in Fig. 3 show that in aqueous–organic media the complex-formation processes are stabilized and cause the increase of the reaction sensitivities compared with those in aqueous media at pH 4·20 (Table 2).

Table 2. Molar absorptivity ε (10^4 *l. mole*$^{-1}$. *cm*$^{-1}$) of the arsenazo III complexes with alkaline-earth metals in the presence of 60% v/v organic solvents

Complexes	Medium				
	aqueous*	dioxan	ethanol	acetone	λ, *nm*
Ca-complex	0·78 0·65	3·82 3·40	3·50 2·82	3·00 1·83	600 650
Sr-complex	0·65 0·60	3·45 3·00	3·11 2·60	2·61 1·65	600 650
Ba-complex	0·65 0·55	2·44 1·77	2·20 1·70	2·00 1·20	600 650

* The differential molar absorptivities at pH 4·20.

The effect of organic solvents can generally be associated with decrease in the dielectric constant of the reaction medium. The dielectric constants for the pure solvents are 2·2, 21·0, 24·3 for dioxan, acetone and ethanol respectively.[17] According to these data the action of ethanol is stronger than expected.

The same two maxima are observed and therefore the composition of the complexes and the mechanism of the reactions has not changed.

Selectivity of the reactions

The selectivity of the reactions was varied by using a suitable acidity and a masking agent. Table 3 summarizes the results of the interference studies, made under the most favourable conditions.

The results for Al(III), Fe(III), Ti(IV) and Mn(II) in alkaline medium were improved by addition of 3 ml of 20% triethanolamine solution for each 25 ml of solution (Table 4), which brings the final solution to pH 10·7.

Magnesium and manganese(II) did not interfere appreciably when the reactions took place at pH 5·6–5·8. Under these conditions the differential molar absorptivities measured against a reagent blank were: Ca-complex $\Delta\varepsilon = 7{\cdot}0 \times 10^3$ l.mole^{-1}.cm^{-1} at 590 nm, $9{\cdot}0 \times 10^3$ at 600 nm; Sr-complex $\Delta\varepsilon = 6{\cdot}0 \times 10^3$ at 590 nm, $7{\cdot}0 \times 10^3$ at 600 nm; Ba-complex $\Delta\varepsilon = 6{\cdot}5 \times 10^3$ at 590 nm.

The selectivity of the calcium and strontium reactions was increased by using ethanol and acetone. In aqueous media small amounts of calcium, strontium and magnesium could be determined in the presence of barium if this was masked with 10% $Na_2SO_4 . 10H_2O$ solution. The alkaline-earth ions did not interfere with each other in acidic medium at pH

Table 3. Interference of ions

Ion tested	Amount taken, μg	Interfering ion	Amount tolerated,* μg	λ, nm	pH†
Calcium	12·4	Al(III)	270	600	9·08
		Fe(III)	28	600	9·08
		Mn(II)	3	600	9·08
			1650	590	5·80
		Ti(IV)	10	600	9·08
Strontium	27·1	Al(III)	190	600	9·08
		Fe(III)	17	600	9·08
		Mn(II)	3	600	9·08
			440	600	5·60
			3295	590	5·60
		Ti(IV)	5	600	9·08
Barium	42·4	Al(III)	270	600	9·08
		Fe(III)	6	600	9·08
		Mn(II)	6	600	9·08
			2200	600	5·60
			4400	590	5·60
		Ti(IV)	1	600	9·08

* The tolerance limit is the amount causing a change ≤0·010 in the absorbance.
† Adjusted with borate (pH 9) or acetate (pH 5·7) buffer.

4–4·3, if the interfering ion was present in amounts of 2–10 μg. In these conditions the reaction sensitivities are low and small amounts of the other ions did not appreciably affect the absorbance of the ion being determined. The differential molar absorptivities of the complexes at pH 4–4·3 are close to those at pH 5·6–5·8. All the results are given in Table 5.

Table 4. Interference of ions in the presence of 2·4% triethanolamine at pH 10·7. The solutions tested contained 12·4 μg of Ca, 27·1 μg of Sr or 42·4 μg of Ba

Ion tested	Interfering ion	Amount tolerated, μg	λ, nm
Calcium	Al(III)	1350	650
		1890	600
	Fe(III)	390	650, 600
	Mn(II)	220	650, 600
	Ti(IV)	96	650, 600
Strontium	Al(III)	810	600
		1350	590
	Fe(III)	110	600
		390	590
	Mn(II)	495	650
		550	600
	Ti(IV)	48	650, 600
Barium	Al(III)	810	600
		1350	590
	Fe(III)	56	600
	Mn(II)	110	650, 600
	Ti(IV)	25	600

Table 5. Determination of alkaline-earth ions and magnesium in the presence of each other

Ion tested	Amount taken, μg	Interfering ion	Amount tolerated, μg	λ, nm	pH
Calcium	12·4	Mg	1220	590	5·80
			12,150*	600	4·20
		Sr	6	590	4·15
		Ba	7	590	4·15
			14†	590	4·30
			137‡	600, 650	9·10
Strontium	27·1	Mg	730	590	5·80
		Ca	2	590	4·15
		Ba	10	590	4·15
			27†	590	4·30
			42†	580	4·30
			60§	590, 600	9·10
Barium	42·4	Mg	190	600	5·80
		Ca	2	590	4·15
		Sr	6	590	4·15
Magnesium	7	Ba	137‡	600, 650	9·10

* In the presence of 60% (v/v) ethanol.
† In the presence of 60% (v/v) acetone.
‡ In the presence of 0·8% $Na_2SO_4 . 10H_2O$.
§ In the presence of 2% $Na_2SO_4 . 10H_2O$.

Stability constants

Over the pH range 7–8·5, H_3L^{5-} is the form of the reagent which predominates,[18] and hence for the 1:1 complexes studied the following reaction is proposed:

$$M^{2+} + H_3L^{5-} \rightleftharpoons MH_{3-n}L^{2-(5+n)} + nH^+. \tag{1}$$

The equilibrium constant, K_{eq}, is defined as

$$K_{eq} = \frac{[MH_{3-n}L^{2-(5+n)}][H^+]^n}{[M^{2+}][H_3L^{5-}]}. \tag{2}$$

The number of protons released during the complex formation and the stability constants were determined by the method of Shimizu and Ogami,[19] modified for 1:1 complex composition. For the equimolar solutions the following expressions were used:

$$[ML] = \frac{A_s - \varepsilon_R . C_{L_0}}{\varepsilon_C - \varepsilon_R} \tag{3}$$

$$\beta_{11} = \frac{[ML]}{(C_{M_0} - [ML])^2} \tag{4}$$

where [ML] is the complex concentration, β_{11} is the conditional stability constant, A_s the absorbance of the solution, ε_C and ε_R are the molar absorptivities of the complex and the free reagent, and C_{M_0} and C_{L_0} are the total concentrations of the metal and the reagent. The values of β_{11} were calculated and plotted against pH according to the equation

$$\log \beta_{11} = \log K_{eq} + n\text{pH}. \tag{5}$$

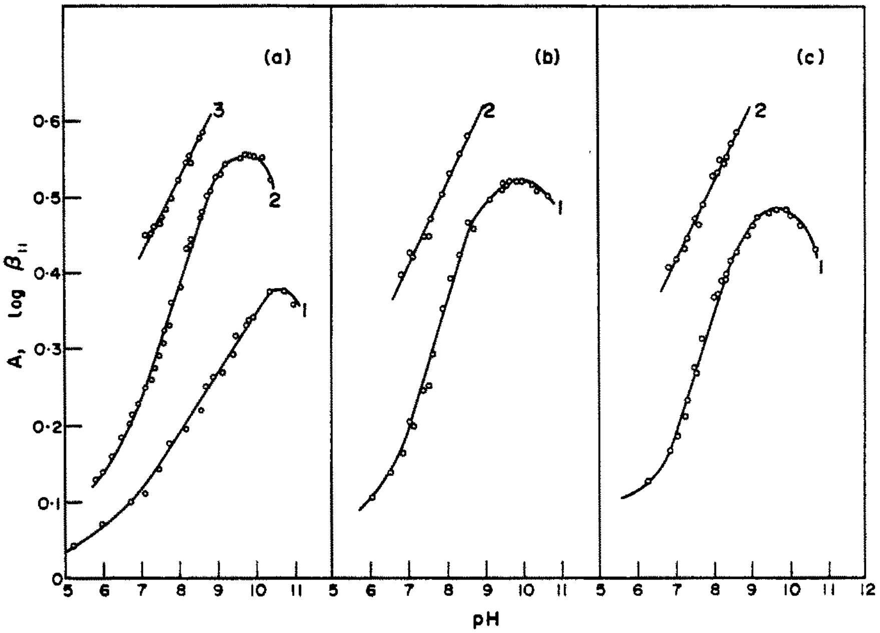
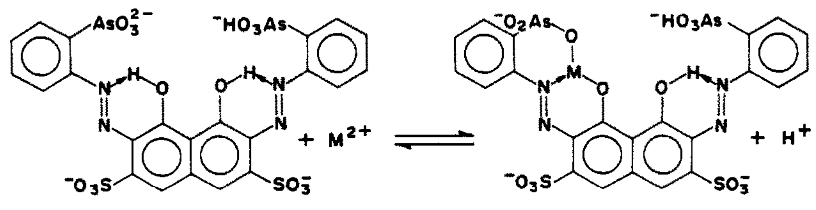


Fig. 4. pH-absorbance plots of arsenazo III and its complexes with alkaline-earth metals. Dependence of the conditional stability constants β_{11} on pH. $C_M = C_R = 2{\cdot}06 \times 10^{-5} M$, ionic strength 0·1*M*, $\lambda = 650$ nm, $l = 1$ cm, *vs.* water, pH adjusted with sodium hydroxide. (*a*) Ca-complex; (*1*) absorbance of arsenazo III; (*2*) absorbance–pH plot of the complex; (*3*) plot according to equation (5); (*b*) Sr-complex; (*c*) Ba-complex; (*1*) absorbance–pH plot; (*2*) plot according to equation (5).

The results are shown in Fig. 4. The slopes $n = 1{\cdot}02$ (Ca), 1·00 (Sr) and 1·06 (Ba) confirmed the splitting off of one proton. Therefore, the following equilibrium should be valid in the pH range studied:

$$M^{2+} + H_3L^{5-} \rightleftharpoons MH_2L^{4-} + H^+. \tag{6}$$

The information obtained in this way can contribute to establishment of the structure of the complexes. For this purpose it is important to know the structure of the reagent in the pH range studied. Savvin and Kuzin assumed that in alkaline medium there is tautomeric equilibrium between the azo (88%) and quinone–hydrazone (12%) forms of the reagent. Absorption bands at 620–670 nm arise as a result.[16] We consider the small maximum at 650 nm in the spectrum of arsenazo III at pH 9 (Fig. 2), shows the existence of tautomeric equilibrium. We suppose, however, that in the reaction studied only the azo form of the reagent takes part. Otherwise the chromogenic effect would be much bigger. By use of the latest views on the structure of bis(arylazo) derivatives of chromotropic acid[9,20] the following reaction scheme can be proposed:



Since the complex formation exhibits a bathochromic effect it is obvious that the hydroxyl group on the naphthalene ring is engaged in the reaction. The arsono group forms σ-bonds with the benzene ring only and therefore its dissociation or release of protons during the complexation causes only a very small colour effect. This confirms that the proton is split off from a naphthalene ring hydroxyl group.

According to this consideration the following complex formation reaction should be valid:

$$M^{2+} + HH^*L^{6-} \rightleftharpoons MHH^*L^{4-} \tag{7}$$

where H is the arsono group proton and H* is that of the second naphthalene ring hydroxyl group. Then the stability constant β_{121} is defined as

$$\beta_{121} = \frac{[MHH^*L^{4-}]}{[M^{2+}][HH^*L^{6-}]}. \tag{8}$$

This constant, however, could not be calculated by using the value of α_H for arsenazo III only. The values[21] of α_H for MHH^*L^{4-} and HH^*L^{6-} are also necessary but we did not have these data. Some calculations were made, using the values of the conditional stability constants of the complexes studied, which are low and very close. For instance at pH 8 the values of log β_{11} are 5·2, 5·1, 5·1 for the calcium, strontium and barium complexes respectively. The low stability of the complexes may be connected with the rare-gas electronic configuration of the alkaline-earth ions and the mainly ionic nature of the bonds formed. According to the values of the ionic potential and the electronegativity, the order of stability constants of the alkaline-earth ions should be Ca > Sr > Ba, but the larger ionic radii of strontium and barium cause more favourable contact with the ligand groups. It is probable that this fact contributes to the stabilities being very similar.

Because the complexes are charged they can be separated by ion-exchange, *e.g.*, with Dowex 1 × 8 (chloride form).

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Zusammenfassung—Arsenazo III wird als spektrophotometrisches Reagens auf Erdalkalimetalle benützt. Die molaren Extinktionskoeffizienten des Calcium-, Strontium- und Bariumkomplexes bei 650 nm betragen $4{,}40 \times 10^4$, $4{,}00 \times 10^4$ bzw. $3{,}65 \times 10^4$ $l.mol^{-1}.cm^{-1}$. Bei pH 5-6 ist die Störung durch Magnesium beseitigt. Die Verwendung von Natriumsulfat als Maskierungsmittel erlaubt die Bestimmung kleiner Mengen Calcium, Strontium und Magnesium in Gegenwart von Barium. Die Ionen der Erdalkalien können bei pH 4,2 nebeneinander in Mengen von 2–10 μg bestimmt werden. Einige organische Lösungsmittel wie Dioxan, Aceton und Äthanol steigern die Empfindlichkeit und Selektivität in saurem Medium. Die Stabilitätskonstanten wurden gemessen und die Struktur der Komplexe wird diskutiert.

Résumé—On utilise l'Arsenazo III comme réactif spectrophotométrique pour les métaux alcalino-terreux. Les coefficients d'absorption molaires pour les complexes de calcium, strontium et baryum à 650 nm sont respectivement 4.40×10^4, 4.00×10^4 et 3.65×10^4 $l.mole^{-1}.cm^{-1}$. L'interférence du magnésium est éliminée à pH 5–6. L'emploi de sulfate de sodium comme agent de dissimulation permet le dosage de petites quantités de calcium, strontium et magnésium en la présence de baryum. Les ions alcalino-terreux peuvent être dosés en la présence l'un de l'autre à pH 4,2 à la teneur de 2–10 μg. Quelques solvants organiques tels que le dioxane, l'acétone et l'éthanol accroissent la sensibilité et la sélectivité en milieu de caractère acide. Les constantes de stabilité ont été mesurées, et l'on discute de la structure des complexes.

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INFLUENCES DES ENTRAÎNEURS Ga_2O_3 ET NaF SUR LA VOLATILISATION ET L'EXCITATION DU VANADIUM DANS LA METHODE DE SCRIBNER–MULLIN

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Résumé—Etude de l'influence de NaF et de Ga_2O_3 utilisés comme entraîneurs, sur l'intensité des raies du spectre d'émission atomique du vanadium et, par suite, sur la sensibilité et la limite de détection par la méthode de Scribner-Mullin. L'influence des deux entraîneurs est différente quant à la volatilisation du vanadium. A l'aide de mesures radiométriques et en employant ^{48}V, des degrés de volatilisation de 37% avec NaF et 0,9% avec Ga_2O_3 ont été déterminés dans les conditions d'excitation adoptées. L'emploi de NaF a permis d'augmenter notablement la sensibilité, la limite de détection étant abaissée de près de cinquante fois, avec la même précision. L'influence des conditions physico-chimiques du plasma sur l'intensité d'émission n'est pas apparue différente pour l'un ou l'autre entraîneur, suivant les résultats obtenus à l'aide d'un schéma de calcul proposé.

Dans le dosage du vanadium dans U_3O_8 par la technique de distillation fractionnée, la nature chimique de l'entraîneur modifie les caractéristiques de volatilisation tandis que la concentration et le potentiel d'ionisation de son cation déterminent les conditions d'excitation dans le plasma.

Une étude a été effectuée sur l'influence de NaF et Ga_2O_3. Le choix de NaF comme entraîneur a été motivé par la formation avec le vanadium de composés volatils analogues à ceux mentionnés par Neuilly[1] pour d'autres éléments; celui de Ga_2O_3 par son action sélective sur les conditions d'excitation.[2–5]

Les concentrations adoptées ont été, pour NaF, celle précédemment décrite: 5%,[6] et, pour Ga_2O_3: 3% et non 2%,[7] afin d'utiliser les mêmes conditions opératoires.

Le mode de calcul de la valeur du rapport des facteurs dépendant des conditions d'excitation, f_{p1}/f_{p2}, a été développé ci-après, les valeurs de K_1 et K_2 ont été obtenues à partir des courbes analytiques et f_{V1} et f_{V2} calculés à l'aide des résultats des mesures radiométriques avec le traceur ^{48}V.

MODE DE CALCUL PROPOSÉ

Dans l'expression empirique de la courbe analytique:[8] $i = Kc^n$, I est l'intensité relative, K une constante, c la concentration dans l'échantillon et n le facteur d'émission.

La sensibilite S[9] et la limite de détection sont fonction des paramètres K et n. Lorsque $n = 1$

$$S = \frac{dI}{dC} = K \qquad \text{et} \qquad c = \frac{i}{K} \tag{1}$$

où c est la limite de détection, i le signal significatif minimal ($i = ts_f$), t le facteur statistique pour un niveau de confiance de 1%, et s_f l'écart type des intensités relatives du fond. Si l'on suppose que tous les atomes volatilisés de l'élément envisagé se trouvent dans la zone de décharge, la relation entre la quantité intégrée de cet élément dans le plasma et sa concentration dans l'échantillon peut être exprimée par

$$\int_0^\tau Q\,dt = \frac{f_V . N . m}{M}\cdot C \tag{2}$$

pour laquelle Q = nombre d'atomes de l'élément qui passent de l'électrode au plasma par unité de temps; τ = temps de pose; f_V = degré de volatilisation; N = nombre d'Avogrado; m = masse d'échantillon dans l'électrode et M = poids atomique de l'élément.

Dans le but d'analyser les divers facteurs de la constante de proportionnalité, c'est l'expression développée par de Galan[10] pour l'émission spectrale d'une raie dans un arc à courant continu qui a été utilisée.

Le rapport des constantes correspondant à une même raie, obtenues avec différents entraîneurs (en l'absence d'autoabsorption) est exprimé par

$$\frac{K_1}{K_2} = \frac{f_{p1}}{f_{p2}}\cdot\frac{f_{V1}}{f_{V2}} \tag{3}$$

où f_p est fonction des conditions d'excitation dans le plasma (température absolue et pression électronique).

PARTIE EXPERIMENTALE ET RESULTATS

Détermination radiométrique de la quantité de vanadium volatilisée pendant l'excitation

Réactifs

$^{48}VO_2Cl$, sans entraîneur, Amersham. V_2O_5, *p.a.* U_3O_8, Ga_2O_3 et NaF, pureté spectrographique. Electrodes en graphite, "National" SPK (anodes, taillées d'après Scribner et Mullin;[7] cathodes, diam. 3,2 mm).

Appareils

Spectromètre à scintillation, "Nuclear," Mod. S.F.P. 65502. Cristal de NaI(Tl), "Integral Line," puits axial 5 × 5 cm. Source d'excitation, "Jarrel-Ash, Custom-Varisource." Mode: arc continu à courant constante.

Mode opératoire

La volatilisation du vanadium dans U_3O_8 a été mesurée radiométriquement, en utilisant Ga_2O_3 ou NaF comme entraîneurs.

(*a*) Quatre étalons synthétiques de concentration connue en vanadium (Tableau 1), à l'aide de l'isotope ^{48}V comme traceur, ont été mélangés aux entraîneurs aux concentrations: 5% en NaF ou 3% en Ga_2O_3.

(*b*) Quantités de equivalentes à 100 mg d'étalon de ces mélanges ont été incorporées à des électrodes de Scribner et Mullin, en réalisant pour chaque mélange six et neuf électrodes avec NaF ou Ga_2O_3 respectivement.

(*c*) L'activité de chaque électrode chargée a été mesurée (pic d'annihilation) quatre fois.

(*d*) L'excitation a été réalisée par un arc de 12 A ("entrode": 4 mm), pendant 60 sec. Pour chaque concentration, les témoins sont des électrodes non excitées, deux pour l'halogénure et trois pour l'oxyde.

(*e*) Les activités des électrodes excitées et des témoins ont été de nouveau mesurées, en répétant cette opération le même nombre de fois que dans la mesure initiale.

(*f*) La quantité de vanadium volatilisé dans chaque électrode a été calculée ainsi que le degré de volatilisation % (f_V%).

(*g*) Enfin, a été calculé l'écart moyen (erreur type) pour la masse de vanadium dans chaque électrode avant et après l'excitation et également l'erreur de leur différence (S_D%). Pour déterminer si ces différences sont statistiquement significatives, le test *t* au niveau de confiance 5 et 2,5% a été appliqué.

Les résultats sont consignés dans le tableau 1.

Détermination de K, S y C pour les deux entraîneurs

Appareils

Spectrographe: "Hilger, Automatic Large Quartz" (170 cm). Mod. E. 492. Plaques spectrographiques: Kodak. SA no. 1. Microphotomètre enregistreur: "Jarrell Ash" Mod. 23101.

Tableau 1. Degré de volatilisation du vanadium avec NaF 5% et Ga_2O_3 3%

Entraîneur	Nombre d'essais	Vanadium dans l'électrode, µg	Vanadium volatilisé absolu µg	Vanadium volatilisé absolu s_D, %	Vanadium volatilisé relatif, f_V %	Vanadium volatilisé relatif, f_V % (moy.)
NaF	4	5	1,82	3,1	36,6	37,0
	4	10	3,77	3,6	37,4	
Ga_2O_3	6	160	1,53	25	0,96	0,94
	6	80	0,74	27	0,92	

Mode opératoire

Les essais ont été réalisés sur une série d'étalons synthétiques à teneurs variables de 2 à 800 ppm V/U_3O_8, avec un facteur de dilution égal à deux. Les conditions spectrographiques ont été les mêmes pour les deux entraîneurs, et les conditions d'excitation ont été comme précédemment.

Temps de pose: 60/4 sec, 75% d'atténuation avec un secteur rotatif. Calibration de l'émulsion: spectres du fer, avec un secteur rotatif à 7 échelons.

Chaque étalon a été excité au total sept fois pour l'un et l'autre entraîneurs, dans trois séries d'expériences répétées. La raie atomique V 3183,98 Å a été mesurée microphotométriquement et les valeurs d'intensité relative résultantes ont été corrigées du fond.

Avec l'expression logarithmique de l'équation $I = KC^n$, on a calculé n et l'écart-type (s_n) correspondant avec l'entraîneur NaF à des teneurs de 2 à 20 ppm et, pour Ga_2O_3, 50 à 200 ppm, la méthode des moindres carrés étant utiliseé

$$n_{Ga_2O_3} = 0{,}943 \qquad (s = 0{,}037)$$

$$n_{NaF} = 0{,}968 \qquad (s_n = 0{,}019).$$

Les valeurs de K et de ses erreurs (s_K), pour les teneurs mentionnées, ont été calculées à l'aide de l'équation $I = KC^n$, pour une valeur unitaire de n, en appliquant la même méthode.

$$K_{Ga_2O_3} = 0{,}0630 \qquad (s_K = 0{,}0037)$$

$$K_{NaF} = 3{,}01 \qquad (s_K = 0{,}15).$$

En appliquant la relation $c = i/K$ la limite de détection pour chaque cas est

$$C_{Ga_2O_3} = 20 \text{ ppm}$$

$$C_{NaF} = 0{,}4 \text{ ppm}.$$

La différence entre les valeurs expérimentales de s_r pour les deux entraîneurs n'a pas été statistiquement significative. Le s_r total, avec 14 degrés de liberté, a été 0,40 et $t^*s_r = 1{,}19$ ($t^*_{0,01} = 2{,}98$).

Pour la raie de vanadium choisie, l'écart-type relatif des valeurs d'I a été de l'ordre de 6% dans les deux cas.

Calcul du rapport $f_p(NaF)/f_p(Ga_2O_3)$

Avec les valeurs expérimentales du degré de volatilisation (f_V %) et celles de la constante de proportionnalité (K), données plus haut, on a calculé la valeur du rapport des facteurs dépendant des conditions d'excitation (f_p), en employant l'équation (3):

$$\frac{f_p(\text{NaF})}{f_p(\text{Ga}_2\text{O}_3)} = \frac{3{,}01}{0{,}0630} \cdot \frac{0{,}94}{37{,}0} = 1{,}21 \pm 0{,}34.$$

CONCLUSIONS

Les résultats du Tableau 1 font apparaître un degré de volatilisation du vanadium avec NaF trente-neuf fois plus grand qu'avec Ga_2O_3. La très faible volatilisation obtenue avec l'oxyde a été responsable de l'erreur (S_D%) assez grande dans la détermination radiométrique du vanadium volatilisé.

La différence de volatilisation du vanadium, avec les entraîneurs essayés, a été traduite dans une sensible variation de la constante de proportionnalité (K) de la courbe analytique, quarante-huit fois pour le NaF.

Par suite, la limite de détection avec Ga_2O_3 est environ quarante-huit fois plus grande que celle trouvée avec NaF et la sensibilité autant de fois plus faible.

D'ailleurs, étant donné que l'écart-type relatif des valeurs d'intensité relative de la raie a été le même pour les deux entraîneurs, on conclut que l'emploi de NaF permet de diminuer d'environ cinquante fois les concentrations, sans perdre la reproductibilité.

La contribution des conditions physico-chimiques du plasma à la valeur de la constante de proportionnalité (K) n'a pas été significativement différente pour l'un et l'autre entraîneurs, d'après les résultats obtenus sur la base du schéma de calcul proposé.

Les valeurs de n se sont montrées indépendantes de la concentration jusqu'à des teneurs de 20 et 200 ppm V/U_3O_8 pour le NaF et le Ga_2O_3 respectivement.

Du point de vue statistique, ces facteurs d'émission ne se sont pas significativement éloignés de la valeur théorique unitaire, c'est-à-dire que, suivant les expériences réalisées, on ne peut pas affirmer qu'il y ait d'autoabsorption. Ceci a permis d'employer une expression linéaire entre l'intensité relative d'émission et la concentration, l'équation $I = KC^n$ pour $n = 1$, et calculer les valeurs de K correspondantes.

Dans ces conditions, l'expression (3) permet de révéler la valeur du rapport des contributions des conditions d'excitation aux correspondants de sensibilité.

Sachant que la présence du sodium détermine dans le plasma une température inférieure à celle obtenue avec le gallium, la valeur 1,21, non significativement différente de l'unité, indiquerait que les divers facteurs responsables de l'intensité d'émission se compensent, si l'on accepte l'expression développée par de Galan.[10]

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Summary—A study has been made of the effect of NaF and Ga_2O_3 as entrainers, on the spectral line intensities of vanadium, and on the sensitivity and detection limits by the Scribner-Mullin method. The two entrainers have different effects on the volatilization of vanadium. By radiotracer methods with ^{48}V, the degree of volatilization was found to be 37% with NaF and 0·9% with Ga_2O_3. Use of NaF greatly increases the sensitivity, lowering the detection limit by a factor of about 50, without affecting the precision. The physicochemical conditions in the plasma do not seem to influence the line intensities with either entrainer.

Zusammenfassung—Der Einfluß von NaF und Ga_2O_3 als Schleppmittel auf die Intensität der Spektrallinien von Vanadium, auf Empfindlichkeit und Nachweisgrenze wurde mit der Methode von Scribner-Mullin untersucht. Die beiden Schleppmittel haben unterschiedlichen Einfluß auf die Verflüchtigung von Vanadium. Mit Radiotracer-Methoden unter Verwendung von ^{48}V wurde gefunden, daß der Verflüchtigungsgrad mit NaF 37% und mit Ga_2O_3 0,9% beträgt. Die

Verwendung von NaF steigert die Empfindlichkeit erheblich; die Nachweisgrenze wird um einen Faktor von etwa 50 herabgedrückt, ohne daß die Genauigkeit beeinflußt würde. Seitens der physikalisch-chemischen Bedingungen im Plasma scheint bei beiden Schleppmitteln kein Einfluß auf die Linienintensität zu bestehen.

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ANWENDBARKEIT DER FLAMMENLOSEN ATOMABSORPTION IN DER MESSENDEN KOMPLEXCHEMIE

VERTEILUNG VON Cu(II) ZWISCHEN CHLOROFORM UND WASSER IN GEGENWART VON 8-HYDROXYCHINOLIN

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Zusammenfassung—Es wurde die Anwendbarkeit der Atomabsorption in einer Graphitrohrküvette für das Studium von Verteilungsgleichgewichten am Beispiel des Cu-Oxinates untersucht. Die Rückextraktion von Cu(II) aus oxinhaltiger $CHCl_3$- Lösung wurde in Gegenwart von 0,1*M* Tetramethylammoniumnitrat durchgeführt und ermöglichte die Bestimmung der Stabilitätskonstanten β_1, β_2 und der Verteilungskonstanten K_N des Cu(II)-Oxinates. Die zur Auswertung benötigten Protonierungskonstanten K_1 und K_2 des Oxinations bzw. die Verteilungskonstante K_{HL} des Oxins wurden durch potentiometrische Titration bzw. Zweiphasentitration ermittelt. Die erhaltenen Stabilitätskonstanten stimmen mit Literaturdaten gut überein.

Als Standardmethode für die Untersuchung von Verteilungs-Gleichgewichten schwer wasserlöslicher Metallkomplexe dient die radiochemische Bestimmung der Metallkonzentration in beiden Phasen. Gewisse Schwierigkeiten treten bei Elementen auf, von welchen keine geeigneten Isotope erhältlich sind. Ebenfalls kann in gewissen Laboratorien das Arbeiten mit radioaktiven Lösungen sowie die Beseitigung der Abfälle unbequem werden. In solchen Fällen wäre der Einsatz einer analytischen Methode, welche die Bestimmung der Metalle in sehr kleinen Konzentrationen ermöglicht und die genannten Nachteile nicht aufweist, wünschenswert. Da die Empfindlichkeit der Atomabsorptionsspektrophotometrie in den letzten Jahren durch die Einführung der Graphitrohr-Küvetten-Technik sehr stark gesteigert werden konnte, erscheint der Einsatz dieser flammenlosen Technik für die Untersuchung von extremen Verteilungsgleichgewichten als sehr angebracht. Bei dieser Methode werden 10 bis 100 μl Lösung in einer Graphitküvette zur Trockene abgedampft, und das zurückgebliebene Metallsalz durch plötzliches Erhöhen der Temperatur zu Atomen dissoziiert. Es wird nun die Absorption der atomaren Resonanzlinie des zu bestimmenden Elementes gemessen (für Literatur siehe Zitat[1]). Diese Art der Metallbestimmung bringt es mit sich, daß folgende Faktoren bei der Bestimmung von Verteilungsverhältnissen besonders berücksichtigt werden müssen:

Wenn aus den Verteilungsmessungen die Stabilitätskonstante β_2 und die Nernst'sche Verteilungskonstante K_N des extrahierbaren, neutralen Komplexes berechnet werden sollen, muß die ionale Stärke μ konstant gehalten werden. Das Metall muß daher in Anwesenheit großer Mengen eines Inertsalzes bestimmt werden. Dieses Salz darf jedoch nicht mit dem zu bestimmenden Metall gleichzeitig verdampfen oder dissoziieren, da sonst unspezifische Absorption die Bestimmung stören kann.

Bei der radiochemischen Methode verursacht das Einschleppen von nicht radioaktivem Metall keine große Störung. Dagegen muß bei der atomabsorptiometrischen Methode nach der Probenahme jegliche Kontamination peinlichst vermieden werden.

ERMITTLUNG DER GLEICHGEWICHTSKONSTANTEN

Gewöhnlich macht man die Annahmen,[2] daß die organische Phase (Index 0) nur die ungeladenen Moleküle HL (Oxin) und CuL_2 (Kupferoxinat) enthält und sich in der wäßrigen Phase neben diesen Partikeln noch die geladenen Teilchen H_2L^+, L^-, Cu^{2+} und CuL^+ befinden. Für das Verteilungsverhältnis q_{Cu} erhält man daher:

$$q_{Cu} \equiv \frac{[Cu]_{t,0}}{[Cu]_t} = \frac{K_N . \beta_2 . [L]^2}{1 + \beta_1 . [L] + \beta_2 [L]^2}. \tag{1}$$

Hierbei bedeuten:

$[Cu]_t$ die atomabsorptiometrisch bestimmte totale Kupferkonzentration (Mole/Liter)
K_N $= [CuL_2]_0/[CuL_2]$ = Nernst'sche Verteilungskonstante des ungeladenen Komplexes CuL_2
β_n $= [CuL_n]/[Cu][L]^n$ = Bruttostabilitätskonstante ($n = 1$ bzw. 2)
$[L]$ = Molarität des freien Oxinations.

Um [L] aus der Menge Q_{HL} ($[Q]$ = mMole) des eingesetzten Oxins und aus dem pH-Wert der wäßrigen Phase einfach zu erhalten, wird Q_{HL} 50 bis 100 mal größer als die Cu-Menge Q_{Cu} gewählt. Dann gilt die folgende Beziehung:

$$Q_{HL} = (K_{HL} . K_1 . [H] . V_0 + \alpha_L . V) . [L], \tag{2}$$

wobei

$K_{HL} = [HL]_0/[HL]$ = die Nernst'sche Verteilungskonstante des Oxins
$K_1 = [HL]/[H] . [L]$ = die erste Protonierungskonstante des Oxinatliganden
$K_2 = [H_2L]/[H] . [HL]$ = die zweite Protonierungskonstante von L^-
V, V_0 = Volumen der wäßrigen bzw. der organischen Phase
$\alpha_L = 1 + K_1 . [H] + K_1 . K_2 . [H]^2$
sind.

Die logarithmierte Form (s. Zitat[3]) der Gleichung 1 hat zwei Assymptoten:

$$\log q_{Cu}([L] \rightarrow 0) = \log K_N + \log \beta_2 + 2 . \log [L]. \tag{3}$$

$$\log q_{Cu}([L] \rightarrow \infty) = \log K_N. \tag{4}$$

Der Schnittpunkt SP beider Geraden ergibt:

$$\log \beta_2 = -2 . \log [L]_{SP} \tag{5}$$

β_2 und K_N werden schließlich in Gleichung 1 eingesetzt, deren Lösung β_1 liefert.

EXPERIMENTELLER TEIL

Apparatives

Die Kupferbestimmungen wurden auf einem Perkin-Elmer Atomabsorptionsspektrometer Modell 303, welches mit einem Deuteriumuntergrundkompensator und einer Graphitrohrküvette HGA-72 ausgerüstet war, durchgeführt. Als Schutzgas wurde Stickstoff verwendet. Zur Berechnung der optischen Dichte D wurde die

Peakhöhe des Absorptionssignals (% ABS) bezogen auf die Grundlinie bei 900°C verwendet. Die Grundlinie bei der Atomisierungstemperatur von 2600°C wurde bei der verwendeten Versuchsanordnung durch Emission der glühenden Küvette verschoben und konnte nicht als Bezugslinie verwendet werden.

Die potentiometrischen Titrationen wurden bei 25°C unter Stickstoff ausgeführt, wobei eine Glaselektrode und eine Kalomelelektrode verwendet wurden, welche über die Salzbrücke 0,1*M* $[Me_4N]NO_3$/3,5*M* KCl/0,1*M* KCl verbunden waren. Als Meßgerät diente das pH-Meter Metrohm E 388, welches eine Ablesegenauigkeit von 0,1 mVolt gestattete. Der pH-Wert wurde bei den Extraktionen mit einer kombinierten Einstabmesskette ermittelt, in welcher sich zwischen der Ag/AgCl-Elektrode und der Glaselektrode 3,5*M* KCl befand.

Reagenzien

Chloroform wurde vor dem Gebrauch durch Ausschütteln mit doppelt destilliertem Wasser alkoholfrei gemacht. Cu-Oxinat CuL_2 stellte man nach einer Standardmethode der gravimetrischen Analyse her. Zur Herstellung von $[Me_4N]NO_3$ wurde eine 1*M* $[Me_4N]OH$-Lösung mit 1*M* HNO_3 neutralisiert und mit einer 0,01*M* Oxinlösung in $CHCl_3$ ausgeschüttelt. Eine Hydroxydlösung mit dem ursprünglichen Cu-Gehalt von 75 ppb ergab nach der Aufarbeitung ein festes Nitrat, dessen Cu-Gehalt unter der Nachweisgrenze von 1 ppb lag.

Versuche zur Ermittlung eines geeigneten Inertsalz

Zur Einstellung einer konstanten ionalen Stärke werden Alkali-Nitrate oder Perchlorate eingesetzt, da diese Anionen mit Metallkationen keine Komplexe bilden. Um festzustellen, ob die Anwesenheit dieser Salze die atomabsorptiometrische Cu-Bestimmung beeinflußt, wurden je 50 μl 0,1*M* Lösungen dieser Salze in 0,1*M* Salpetersäure thermisch behandelt. Das verwendete Programm ist im unteren Teil der Abb. 1 (s. Kurve *e*) angegeben.

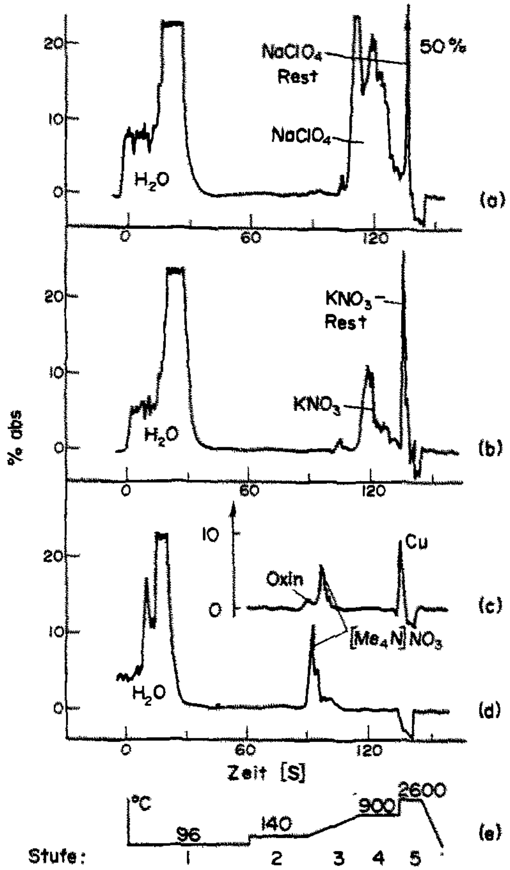

Abb. 1. Zeitlicher Verlauf des Absorptionssignals für die Resonanzlinie des Kupfers (324,8 nm) bei der thermischen Behandlung von je 50 μl Lösungen von $NaClO_4$ (*a*), KNO_3 (*b*), Tetramethylammoniumnitrat (*d*) und der wäßrigen Phase einer Extraktion (*c*). Der zeitliche Temperaturverlauf in der Graphitrohrküvette ist aus der untersten Skizze (*e*) ersichtlich.

Man verfolgte das Abdampfen bzw. das Absublimieren des Lösungsmittels und des betreffenden Inertsalzes durch den zeitlichen Verlauf der Absorption (% ABS) bei der Resonanz-Wellenlänge des Kupfers. Bei 96°C erscheint ein scheinbares Absorptionsband, welches von Lichtstreuung an Wassertröpfchen herrührt. Im Graphitrohr besteht nämlich ein kleines Temperaturgefälle, welches Anlaß zu einer Kondensation des Dampfes im Strahlengang gibt. Natriumperchlorat und Kaliumnitrat lassen sich bei 900°C während 20 Sek. aus der Küvette nicht vollständig entfernen und verursachen daher in der Atomisierungsstufe 5 eine nichtspezifische Absorption. Diese konnte durch Einschalten der Deuteriumlampe nicht kompensiert werden. Überhaupt ist die Anwendung des Deuterium-Untergrund-Kompensators wegen seiner schwachen Intensität bei 325 nm sehr beschränkt. Versuche, diese Inertsalze bei höherer Temperatur zu zersetzen, gaben unbefriedigende Resultate. Ein vollständiges Vertreiben dieser Salze aus der Küvette gelingt nämlich erst bei so hohen Temperaturen, bei welchen bereits starke Cu-Verluste auftreten. Abbildung 2 zeigt den prozentualen Anteil (% Verlust) der vorgelegten Cu-Menge, welcher in der 4. Stufe verloren ging. Die Temperatur dieser Stufe wurde zwischen 900°C und 2600°C variiert. Die maximal erlaubte Zersetzungstemperatur (kein Verlust) und die minimal benötigte Atomisierungstemperatur (100% Verlust) können aus der Abb. 2 entnommen werden. Als Zersetzungstemperatur wählten wir 900°C und als Atomisierungstemperatur 2600°C. Kupfer atomisiert bereits bei 2200°C während 10 Sek. vollständig (100% Verlust) gibt aber ein breites Signal, welches nicht genau ausgewertet werden kann. Bei Verlängerung der Sublimationsstufe 4 über eine Minute traten bereits bei 900°C Cu-Verluste auf.

Schließlich wurde Tetramethylammoniumnitrat $[Me_4N]NO_3$ als gut geeignetes Inertsalz ermittelt. Der zeitliche Verlauf des Absorptionssignals ist für die thermische Behandlung dieses Salzes in Abb. 1 ebenfalls eingezeichnet (Kurve *d*). Das Salz zersetzt sich bei *ca.* 500°C vollständig, so daß in Abwesenheit von Kupfer kein Absorptionssignal auftritt. Kurve *c* in Abb. 1 zeigt ein Cu-Signal für 50 μl $1{,}4 . 10^{-7} M$ Cu in $0{,}1 M$ $[Me_4N]NO_3$-Lösung. Diese Lösung stammte aus einem Extraktionsversuch und enthielt zusätzlich auch noch Oxin, welches etwas früher als das Inertsalz aus der Küvette entweicht.

In einer Versuchsreihe wurde festgestellt, daß die Anwesenheit dieses Salzes die Empfindlichkeit der Kupferbestimmung nicht beeinflußt. Die optischen Dichten D_1 und D_2 wurden für 7 verschiedene Mengen (10–100 μl) einer $5 . 10^{-7} M$ $Cu(NO_3)$-Lösung in 0,1 HNO_3 ohne (Serie 1, liefert D_1) und mit 0,1 M $[Me_4N]NO_3$ (Serie 2, liefert D_2) bestimmt. Man erhielt die folgende Korrelationsgerade: $D_2 = (-0{,}05 \pm 2{,}27) . 10^{-3} + (0{,}998 \pm 0{,}012) . D_1$. Damit ist bewiesen, daß für gleiche Cu-Mengen in Lösungen mit und ohne $[Me_4N]NO_3$ die gleichen Resultate erhalten werden ($D_2 = D_1$). Ein Zusatz dieses Salzes zu den Eichlösungen erübrigt sich damit.

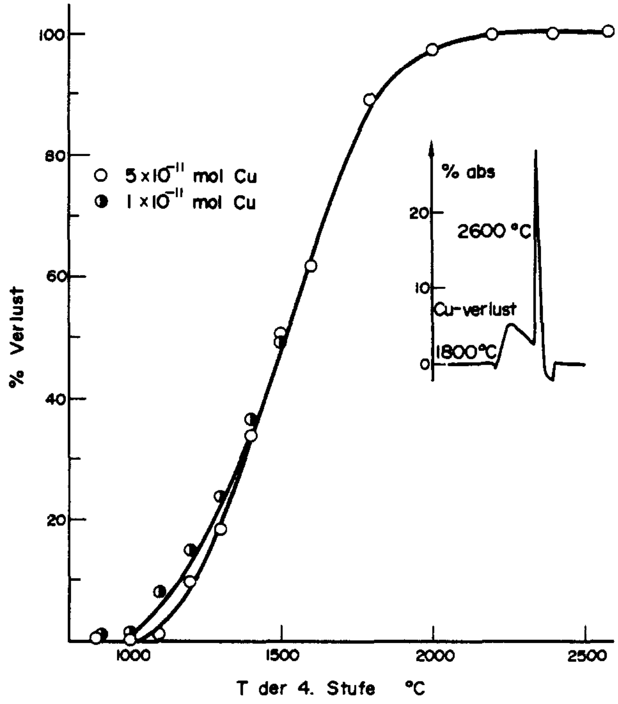

Abb. 2. Abhängigkeit des Cu-Verlustes (% Verlust während 20 Sek.) von der Temperatur der 4. Stufe. Rechts im Bild ist das Absorptionssignal für zwei verschiedene Temperaturen dargestellt.

Acidimetrische Titrationen

Für die Bestimmung der Protonierungskonstanten K_1 und K_2 wurde eine $2.10^{-3}M$ Oxinlösung, welche noch $2.10^{-3}M$ HNO_3 und $0{,}1M$ $[Me_4N]NO_3$ enthielt, mit einer $0{,}1M$ Lösung von $[Me_4N]OH$ titriert. Man erhielt (25°, $\mu = 0{,}1$): $\log K_1 = 9{,}579 \pm 0{,}009$ und $\log K_2 = 4{,}923 \pm 0{,}007$). Die Fehlerangaben bedeuten die einfache Standardabweichung, welche aus verschiedenen Titrationen ermittelt wurde.

K_{HL} wurde durch Zweiphasentitration nach Dyrssen[4] ermittelt. Die Meßkette wurde zuerst durch Titration von HNO_3 mit $[Me_4N]OH$ in Gegenwart von $CHCl_3$ und $[Me_4N]NO_3$ geeicht (Ermittlung von E^0_H, ψ_H bzw. E^0_{OH} und ψ_{OH} nach Dyrssen.[4]). Danach wurden 50 ml einer $2.10^{-2}M$ HNO_3 Lösung, welche noch $0{,}08M$ $[Me_4N]NO_3$ enthielt, mit 50 ml $2.10^{-2}M$ Oxinlösung in Chloroform versetzt und mit 0,2 bzw. $1M$ $[Me_4N]OH$-Lösung titriert Den Protonierungsgrad p_0 für das Zweiphasensystem berechnete man aus folgender Beziehung:

$$p_0 = \frac{Q_{H,geb}}{Q_{HL}} = (Q_{HNO_3} + Q_{HL} - Q_{Me_4NOH} + [OH].V - [H].V)/Q_{HL}. \qquad (6)$$

Die Protonierungsgleichung einer zweibasischen Säure H_2L, deren einfach protonierte Form HL ungeladen und daher in der organischen Phase löslich ist, lautet für das Zweiphasensystem:

$$(p_0 - 2).[H].K_2 + (p_0 - 1) + p_0/[H].K_1 + (p_0 - 1).K_{HL}.V_0/V = 0. \qquad (7)$$

Da die Protonierung des Oxinations L^- in gut getrennten Stufen erfolgt, kann K_{HL} aus folgenden Beziehungen erhalten werden:

in saurem Gebiet ($2 < p_0 > 1$),

$$\log K_{HL} = \log K_2 - pH + \log\frac{p_0 - 2}{1 - p_0} + \log(V/V_0) = \log K_2 - \log K^0_2. \qquad (8)$$

und in alkalischem Gebiet ($1 < p_0 > 0$),

$$\log K_{HL} = -\log K_1 + pH + \log\frac{p_0}{1 - p_0} + \log(V/V_0) = \log K^0_1 - \log K_1. \qquad (9)$$

Man erhielt: $\log K_{HL} = 2{,}595 \pm 0{,}025$ (25°, $\mu = 0{,}1$). (Die durch Gleichung 8 bzw. 9 definierte K^0_2 bzw. K^0_1 bedeutet die zweite bzw. die erste Protonierungskonstante des Oxinations in Gegenwart von $CHCl_3$.)

Ausführung der Extraktionen und Ermittlung von q_{Cu}

Die Extraktionen wurden in verschlossenen Zentrifugenröhrchen von *ca.* 10 ml Fassungsvermögen ausgeführt. Die Röhrchen und Glaswaren wurden vor dem Gebrauch zuerst einige Tage mit Chromschwefelsäure, und darauf mit einer Mischung von verdünnter HCl und HNO_3 (je *ca.* $2M$) ebenfalls einige Tage behandelt. Zum Spülen wurde stets doppelt-destilliertes Wasser verwendet. Zur Ausführung der Extraktionen wurden je 2 ml einer $2.10^{-4}M$ Lösung von CuL_2 in $CHCl_3$, welche noch $0{,}01M$ HL enthielt, mit je 2 ml der vorgemischten wäßrigen Phase versetzt und 3 Stunden mit einer Schüttelmaschine im thermostatisierten Raum bei 25° hin und her bewegt. Für die Zubereitung der wäßrigen Phase wurde die anfängliche [H]- bzw. [OH]-Konzentration mit HNO_3 bzw. $[Me_4N]OH$ vorgegeben, und die totale Elektrolytkonzentration mit $[Me_4N]NO_3$ auf $0{,}1M$ eingestellt. Nach dem Schütteln wurde der pH-Wert in der wäßrigen Phase gemessen. Die Einstabmeßkette wurde jedesmal mit mehreren (HNO_3 bzw. $[Me_4N]OH$)/$[Me_4N]NO_3$-Mischungen geeicht. Vor der Probenentnahme von je 1 ml aus beiden Phasen wurden die Röhrchen 20 Min bei 3600 U/Min. zentrifugiert. Die Proben aus der organischen Phase wurden gewogen, zur Trockene abgedampft, und die Rückstände in je 1 ml $0{,}1M$ HNO_3 aufgenommen. Die Proben aus der wäßrigen Phase wurden sofort mit je 10 μl konz. HNO_3 angesäuert. Nötigenfalls wurden die Proben mit $0{,}1M$ HNO_3 weiter verdünnt. Von den Proben wurden schließlich 10–100 μl nach dem beschriebenen Programm (s.Abb.1) analysiert, wobei von jeder Probe mehrmals verschiedene Mengen eingespritzt wurden. Zur Eichung wurden 10^{-7} bis $10^{-6}M$ $Cu(NO_3)_2$-Lösungen in $0{,}1M$ HNO_3 verwendet, wobei gewöhnlich 5 Cu-Mengen im Bereich von 4.10^{-12} bis 5.10^{-11} Mol atomisiert wurden. Die optische Dichte D in Funktion von der Cu-Menge Q_{Cu} ergab eine leicht gekrümmte Kurve, so daß die Auswertung durch Einsetzen von D in eine parabolische Regressionskurve durchgeführt wurde. Für die analytische Form einer typischen Eichkurve erhielt man z.B. $Q_{Cu}[\mu Mol] = 6{,}07.10^{-7} + 1{,}413.10^{-4}D + 9{,}16.10^{-5}D^2$, wobei das Quadrat des Korrelationskoeffizienten 0,9983 betrug. Da der Koeffizient von D^2 recht klein ist, weicht die Kurve wenig vom linearen Verlauf ab.

Die Berechnung von q_{Cu} erfolgte für nicht extreme Cu-Verteilungen nach der Definitionsgleichung (1). Für q_{Cu}-Werte unter 0,05 bzw. über 50 wurde Kupfer nur in der Cu-armen Phase bestimmt, und q_{Cu} nach folgenden Gleichungen berechnet:

$$q_{Cu} = \frac{(Q_{Cu} - [Cu]_t V)/V_0}{[Cu]_t} \text{ bzw. } q_{Cu} = \frac{[Cu]_{t,0}}{(Q_{Cu} - [Cu]_{t,0} V_0)/V}. \qquad (10)$$

Q_{Cu} bedeutet hier die zur Extraktion eingesetzte Cu-Menge in mMol.

RESULTATE UND DISKUSSION

Die bei verschiedenen Oxinatkonzentrationen erhaltenen Verteilungsverhältnisse sind in Abb. 3 graphisch dargestellt. Wegen besserer Übersicht wurde meistens der Mittelwert nahegelegener Meßpunkte eingezeichnet. Gewöhnlich wurden nämlich mehrere Extraktionen mit der gleichen vorgewählten [H]-Konzentration angesetzt, welche bei genügender Pufferkapazität, praktisch den gleichen Meßpunkt ergaben. Die 20 Meßpunkte, welche bei pH-werten bis 1,85 erhalten wurden, ergaben die folgende Regressionsgerade:

$$\log q_{\mathrm{Cu}} = (26{,}506 \pm 0{,}137) + (2{,}0257 \pm 0{,}0256) . \log[\mathrm{L}]. \qquad (3')$$

Da die experimentell bestimmte Neigung von 2,026 mit der theoretischen Neigung von 2 innerhalb der Standardabweichung übereinstimmt, ist das Molverhältnis 2 des Oxinations zu Cu(II) im extrahierten Komplex erneut bestätigt. Bemerkenswert ist die recht große Genauigkeit (1 % rel.), mit welcher das Molverhältnis ermittelt werden konnte.

Die 18 Meßpunkte zwischen den pH-Werten 5,49 und 10,46 streuten um die Gerade:

$$\log q_{\mathrm{Cu}} = (3{,}399 \pm 0{,}031) + (0{,}0026 \pm 0{,}0041) . \log[\mathrm{L}]. \qquad (4')$$

Da die Standardabweichung dieser Geraden klein, jedoch größer als die Neigung selbst ist, muß q_{Cu} von $[\mathrm{L}^-]$ unabhängig sein. Daher wurde $\log K_{\mathrm{N}}$ als ein Mittelwert dieser $\log q_{\mathrm{Cu}}$-Werte berechnet. $\log K_{\mathrm{N}}$ wurde nun in Gleichung (3′) eingesetzt, und aus dem erhaltenen $(\log[\mathrm{L}]_{\mathrm{SP}})$-Wert berechnete man $\log \beta_2$ gemäß Beziehung 5.

$$\log K_{\mathrm{N}} = 3{,}380 \pm 0{,}031 \quad \text{und} \quad \log \beta_2 = 22{,}83 \pm 0{,}12\,(25°, \mu = 0{,}1).$$

Die übrigen 5 Punkte in Abb. 3 (Mittelwerte aus je 4 Extraktionen) wurden zur Berechnung von β_1 aus Gleichung 1 verwendet. Die Resultate sind in der Tabelle 1 zusammengestellt.

Die Übereinstimmung der 5 $\log \beta_1$-Werte und die relativ kleine Standardabweichung von $\log \beta_2$ zeigen die Anwendbarkeit der atomabsorptiometrischen Kupferbestimmung beim Studium von Extraktionsgleichgewichten.

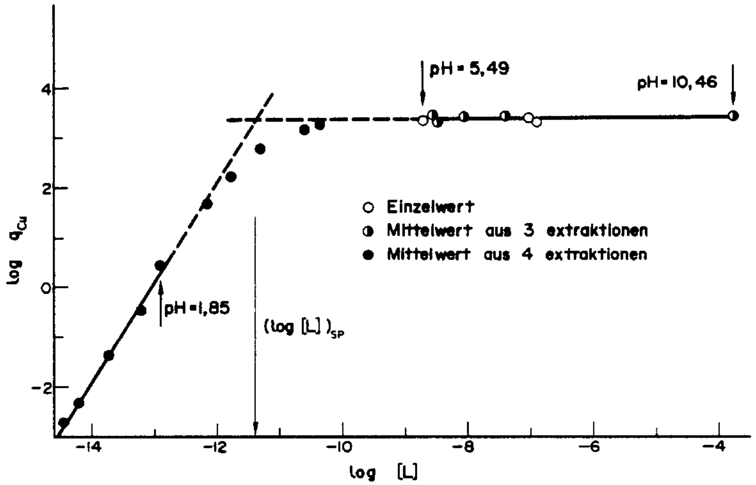

Abb. 3. Abhängigkeit des Verteilungsverhältnisses q_{Cu} von der Molarität [L] des freien Oxinations.

Tabelle 1. Berechnung der $\log \beta_1$-Werte

pH	$[Cu]_t \cdot 10^6$	$\log q_{Cu}$	$\log[L]$	$\log \beta_1$
2,33	3,74 ± 0.09	1,72	−12,14	11,89
2,57	1,21 ± 0,05	2,22	−11,80	11,92
2,95	0,331 ± 0,016	2,78	−11,32	11,88
3,52	0,142 ± 0,007	3,15	−10,68	11,97
3,83	0,110 ± 0,007	3,26	−10,47	11,84
			Mittelwert:	11,90 ± 0,05

Die Literaturwerte[2,5] betragen für $\log K_N$, $\log \beta_2$ und $\log \beta_1$ der Reihe nach 3,48, 23,00 und 12,10. Die gute Übereinstimmung zwischen den radiochemischen[5] und atomabsortiometrisch bestimmten Werten ist um so mehr bemerkenswert, als wir das Gleichgewicht ausgehend vom Cu(II)-Oxinat herbeigeführt haben. Bei dieser Methode bleibt die ganze Menge des Kupfers stets in homogener Lösung, im Gegensatz zu Versuchen, in welchen mit dem Aquokomplex begonnen wird. Die Fällung von CuL_2 verläuft nämlich schneller als seine Extraktion, da die wäßrige Phase an Oxinat wegen seiner Schwerlöslichkeit stark übersättigt ist. Die Übersättigung ist besonders groß bei höheren, freien Oxinatkonzentrationen, d.h. bei höheren pH-Werten. Vorübergehend ist daher bei der Extraktion von Cu(II) ein Niederschlag des Oxinates vorhanden, welcher sich nur sehr langsam in $CHCl_3$ vollständig löst. Die Rückextraktion von Cu(II) aus oxinhaltigem $CHCl_3$ verlief dagegen bis zu hohen pH-Werten (bis 11 getestet) ohne Auftreten einer festen Phase.

Um die Richtigkeit der Kupferbestimmung und der Ausführung der Rückextraktion zu prüfen, wurde die Mengenbilanz für 8 Extraktionen kontrolliert. Da diese dann am stärksten beeinflußt wird, wenn sich die eingesetzte Cu-Menge Q_{Cu} ungefähr gleich auf beide Phasen verteilt, hat man diese Kontrollen bei tiefen pH-Werten durchgeführt (s. Tabelle 2).

Tabelle 2. Mengenbilanz für 2 Serien mit je 4 parallelen Extraktionen (Cu-Mengen in mMol)

pH	$Q_{Cu} \cdot 10^4$	$Q_{Cu,o} \cdot 10^4$	$Q_{Cu,w} \cdot 10^4$	$Q_{Cu,t} \cdot 10^4$
1,69	4	1,27 ± 0,04	2,77 ± 0,15	4,04 ± 0,18
1,85	4	2,88 ± 0,10	1,14 ± 0,03	4,02 ± 0,13

Die total gefundene Cu-Menge $Q_{Cu,t}$ stimmt mit der eingesetzten Menge gut überein. Die Richtigkeit der Mengenbilanz ermöglicht die Berechnung des Verteilungsverhältnisses q_{Cu} aus der ermittelten Kupferkonzentration der Cu-armen Phase und aus der eingesetzten Cu-Menge gemäß Gleichung 10. Die benötigte Analysenzeit kann dadurch auf die Hälfte reduziert werden.

Das Inertsalz $[Me_4N]NO_3$ wurde aus meßtechnischen Gründen gewählt. Es besitzt aber auch die notwendige Inertheit gegenüber Bildung von Ionenpaaren vom Typ $[Me_4N]^+L^-$ und $([Me_4N]^+L^-)_0$. Das folgt aus der Tatsache, daß $\log K_1$ und $\log K_{HL}$ in verschiedenen Medien praktisch gleich sind:

	Medium	$\log K_2$	$\log K_1$	$\log K_{HL}$
Diese Arbeit	0,1*M* $Me_4N\,NO_3$	4,92	9,58	2,60
Diese Arbeit	0,1*M* KCl	4,92	9,63	2,59
Dyrssen[2,4]	0,1*M* $NaClO_4$	4,92/5,00	9,66	2,58*/2,66†

* spektrophotometrisch, † mittels Zweiphasentitration.

Für das beschriebene System erwies sich die Atomabsorption als sehr geeignet. Es müssen jedoch andere Metalle untersucht werden, bevor man von einer generellen Anwendbarkeit dieser Methode reden kann. Versuche an anderen extremen Verteilungsgleichgewichten sollen folgen.

Der Eidg. Stiftung zur Förderung Schweizerischer Volkswirtschaft durch wissenschaftliche Forschung danken wir für finanzielle Unterstützung.

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Summary—Atomic-absorption spectrophotometry with the graphite furnace atomizer has been used in a study of the extraction equilibria of copper oxinate. The amounts of copper back-extracted from chloroform solutions of oxine into aqueous solutions containing tetramethyl ammonium nitrate were determined, and the stability constants β_1 and β_2, and the distribution coefficient K_N for copper oxinate, were then calculated. The protonation constants K_1 and K_2 for the oxinate anion and the distribution coefficient K_{HL} for oxine were determined by potentiometric aqueous and two-phase titrations respectively. The values obtained are in good agreement with published data.

Résumé—La spectrophotométrie d'absorption atomique avec l'atomiseur à tige de carbone a été utilisée dans une étude des équilibres d'extraction de l'oxinate de cuivre. On a déterminé les quantités de cuivre réextrait de solutions chloroformiques d'oxine dans des solutions aqueuses contenant du nitrate de tétraméthylammonium, et l'on a alors calculé les constantes de stabilité β_1 et β_2 et le coefficient de partage K_N pour l'oxinate de cuivre. Les constantes de protonation K_1 et K_2 pour l'anion oxinate et le coefficient de partage K_{HL} pour l'oxine ont été déterminés par titrages potentiométriques aqueux et en deux phases, respectivement. Les valeurs obtenues sont en bon accord avec les données publiées.

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FLUOROMETRIC DETERMINATION OF AROMATIC ALDEHYDES WITH 1,2-DIAMINONAPHTHALENE

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Summary—A new fluorometric method for the determination of aldehydes is presented. 1,2-Diaminonaphthalene reacts with aldehyde in dilute sulphuric acid to give a compound which fluoresces intensely in alkaline medium. The fluorescences produced from aromatic aldehydes in this method are fairly characteristic of individual aldehydes and their intensities are generally higher than those of fluorescences from aliphatic aldehydes. The only interference is from 2-oxo acids. The method may be suitable for the determination of aldehyde in complex samples.

Numerous fluorometric methods have been developed for the determination of aliphatic aldehydes. These include the determination of formaldehyde with acetylacetone and ammonia,[1] J-acid[2] and dimedone,[3] of malondialdehyde with 4,4′-sulphonyldianiline, 4-aminobenzoic acid or its ethyl ester and 4 aminoacetophenone,[4] of succindialdehyde with *o*-phenylenediamine[5] and of succinsemialdehyde with 3,5-diaminobenzoic acid.[6] In the detection and identification of several aromatic aldehydes, barbituric or thiobarbituric acid,[7] salicyloylhydrazide[8] and 2-hydroxy-1-naphthylhydrazine[9] were investigated as reagents which form fluorescent compounds with the aldehydes. Acetal formation was also utilized for the characterization of substituted aromatic aldehydes.[10] Fluorometric methods for aldehydes have been reviewed by Pesez and Bartos.[11]

For the determination of aromatic aldehydes, however, the only recent method for the assay of vanillin is based on the fluorescence reaction of aromatic aldehydes with 2-aminothiophenol in an acidic medium.[12]

During the course of studies on the assay of monoamine oxidase, 1,2-diaminonaphthalene was found to react selectively with aldehyde in acidic medium to give a compound which fluoresces intensely in an alkaline medium. This fluorescence reaction can be used more advantageously for a simple and sensitive determination of aromatic aldehydes. Benzaldehyde and cinnamaldehyde were employed as model compounds to establish the reaction conditions.

EXPERIMENTAL

Reagents

All reagents used were reagent grade (Japanese Industrial Standards), unless otherwise stated.

1,2-Diaminonaphthalene monosulphate(1,2-*DNS*). 1,2-DNS is stable enough to use for the present purpose though the free amine is unstable in air and in daylight. Therefore, the crude commercial amine was purified as the sulphate as follows. Suspend 1 g of the crude amine in 150 ml of water and boil it for about 10 min. Filter the resulting solution through a glass filter while hot to remove undissolved impurity and add 10 ml of 10% sulphuric acid to the filtrate to form a crystalline precipitate of the sulphate. Collect the sulphate by filtration, wash several times with small portions of water and dry over phosphorus pentoxide *in vacuo*, to obtain colourless leaflets, m.p. 262° (decomp.), yield 0·4–0·5 g.

Aldehydes. Commercial aldehydes used in the present work (those listed in Table 1 and salicylaldehyde, 4-hydroxybenzaldehyde, 2,4- and 3,4-dihydroxybenzaldehydes, vanillin, 4-aminobenzaldehyde and 4-nitrobenzaldehyde) were purified just before use by distillation or recrystallization in the usual manner, except 4-sulphamoylbenzaldehyde, which was prepared from 4-toluenesulphonylamide.[13]

Water. Redistilled water was used throughout the work.

Reagent solutions

1,2-DNS solution (45 $\mu g/ml$). Dissolve 45 mg of 1,2-DNS in 15 ml of concentrated sulphuric acid (>95%) and add approximately 900 ml of water, the solution being water-cooled to room temperature, and dilute with water to 1000 ml. The solution is about 0·25*M* in sulphuric acid and keeps for 2 days at room temperature.

Sodium hydroxide solution, 2·5M

Aldehyde solutions. Prepare aqueous solutions unless otherwise noted. Water should be degassed by boiling for several min to prevent oxidation of aldehyde by dissolved oxygen.

Apparatus

Spectrofluorometer. Fluorescence spectra and intensities were measured with a Hitachi 203 Spectrofluorometer equipped with a xenon arc-lamp and a quartz cell of 1 × 1 cm optical path lengths. In this instrument, the slit-widths in terms of wavelength were fixed at 10 nm in both the exciter and the analyser.

A daily check of sensitivity of the instrument was made by measuring the fluorescence intensity of a 1 $\mu g/ml$ solution of quinine sulphate dihydrate in 0·05*M* sulphuric acid at an emission wavelength of 450 nm with excitation at 350 nm, or the intensity of the Raman line at 416 nm with irradiation at 365 nm.

The fluorescence spectra, and excitation and emission maxima described in this paper are uncorrected.

Procedure

To 2·0 ml of 1,2-DNS solution placed in a glass-stoppered test-tube, add 1·0 ml of the test solution and heat in a boiling water-bath for 20 min. Cool in ice-water, and add 2·0 ml of sodium hydroxide solution. At the same time, prepare a reagent blank by treating 1·0 ml of water in the same manner. Measure the fluorescence intensities of the test and blank at the emission maximum with irradiation at the excitation maximum (see Table 1). Read the concentration of aldehyde from a calibration curve prepared in the usual manner.

RESULTS AND DISCUSSION

Determination of benzaldehyde

The excitation and emission spectra obtained when the procedure is applied to benzaldehyde are shown in Fig. 1, and compared with those of the reagent blank.

The emission spectrum has a maximum at 385 nm and is similar to that of the blank in shape and maximum. On the other hand, the excitation spectrum has a maximum at 353 nm and is partly overlapped by that of the blank.

The spectra of the blank were considered to be due to environmental aliphatic aldehydes in the laboratory (see Table 1), the fact that the intensities changed slightly each time the procedure was performed suggesting that the concentration of these aldehydes varied with time. Therefore, the reagent blank should be prepared fairly strictly at the same time as the sample solution.

Effect of sulphuric acid. 1,2-DNS is hardly soluble in water, but sparingly in dilute sulphuric acid. Therefore, a sulphuric acid solution of the reagent was used in the procedure. The concentration of sulphuric acid affects the fluorescence development as shown in Fig. 2, giving a maximum and constant intensity at a sulphuric acid concentration ranging from 0·065 to 0·5*M*, and the prescribed concentration, approximately 0·25*M*, was selected for convenience. The fluorescence reaction was observed to occur even in a neutral medium (in water or aqueous ethanol) when the aldehyde was treated as in the procedure with a suspension of 1,2-DNS in water or ethanol, but the measured fluorescence intensity varied considerably.

Effect of 1,2-DNS concentration. The concentration of 1,2-DNS in the reaction mixture does not affect the fluorescence development over the concentration range 30–60 $\mu g/ml$ in the reagent solution, with a lower concentration of the aldehyde (1×10^{-7}–$1 \times 10^{-6}M$).

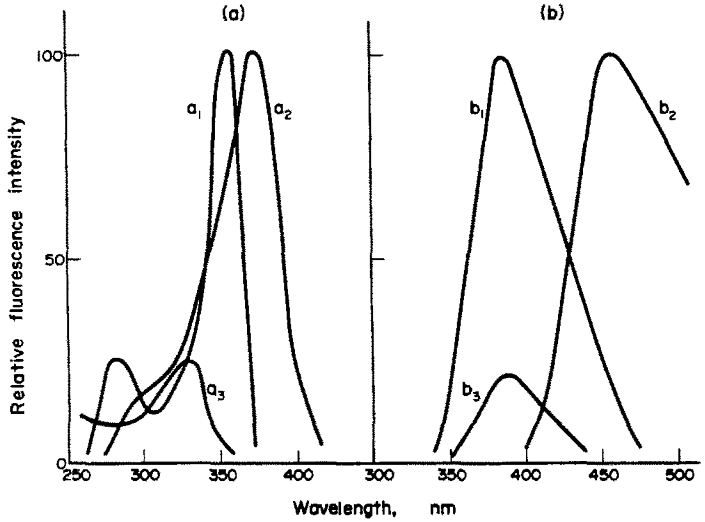

Fig. 1. Excitation and emission spectra of the reaction mixtures of benzaldehyde and cinnamaldehyde, and the reagent blank.
a, Excitation spectra *b*, Emission spectra
1·0-ml portions of 1 × $10^{-5}M$ aldehyde solutions were treated according to the procedure. a_1 and b_1, benzaldehyde; a_2 and b_2 cinnamaldehyde; a_3 and b_3, the reagent blank.
Excitation wavelength (nm): b_1, 353; b_2, 370; b_3, 330.
Emission wavelength (nm): a_1, 385; a_2, 460; a_3, 390.

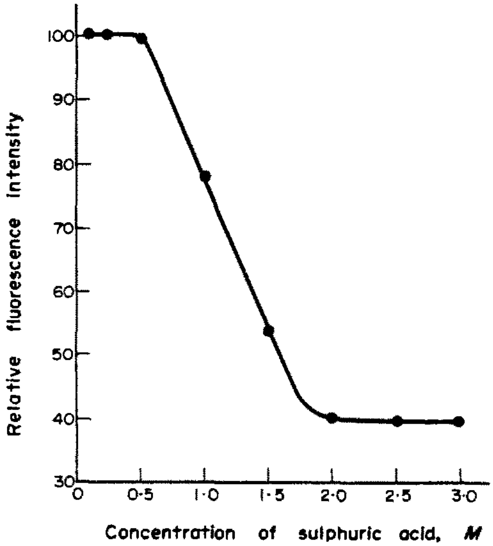

Fig. 2. Effect of the concentration of sulphuric acid used to dissolve 1,2-DNS, on the fluorescence development.
1·0 ml portions of 1 × $10^{-5}M$ benzaldehyde solutions were treated as in the procedure with 1,2-DNS dissolved in various concentrations of sulphuric acid. Each plot was the mean value of triplicate determinations.

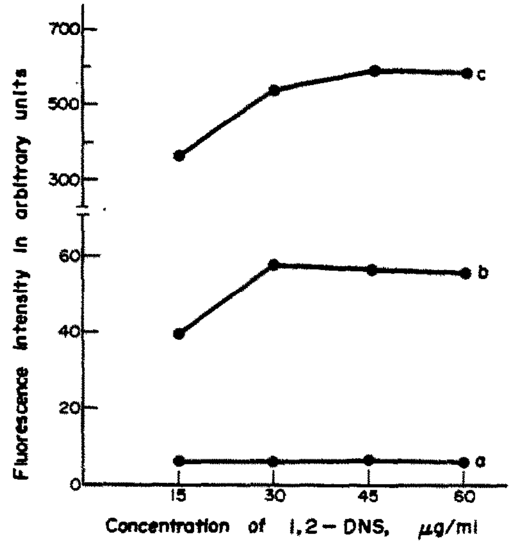

Fig. 3. Effect of the concentration of 1,2-DNS on the fluorescence development. 1·0-ml portions of benzaldehyde solutions (*a*, $1 \times 10^{-7}M$; *b*, $1 \times 10^{-6}M$; *c*, $1 \times 10^{-5}M$) were treated as in the procedure with various concentrations of 1,2-DNS. Each plot was the mean value of triplicate determinations.

With a more concentrated aldehyde solution, however, a 45 µg/ml solution gives the maximum intensity, and hence this concentration was selected as optimum (Fig. 3).

Effect of heating. The heating time influences the fluorescence development. The intensity reaches the maximum after the reaction mixture has been heated at 100° for 15 min. This maximum is reached for heating periods of 15–60 min; 20 min was selected as a convenient time for heating.

Effect of sodium hydroxide. The reaction mixture fluoresces only in a strongly alkaline medium and a maximum and constant value of the intensity is obtained when the mixture is made more than about 0·4*M* in sodium hydroxide, which can be done by addition of the 2·0 ml of 2·5*M* solution employed in the procedure.

Stability of complex and precision of procedure. The fluorescence developed under the prescribed conditions does not change on irradiation for 5 min at the excitation maximum of 353 nm and is stable for at least 6 days in daylight. The calibration curve is a straight line for concentrations of the aldehyde ranging from 1×10^{-7} to $1 \times 10^{-5}M$.

The precision of the procedure was established by performing 17 analyses on a $1 \times 10^{-6}M$ benzaldehyde solution at the same time. The coefficient of variation was 2·8%.

Determination of cinnamaldehyde

The fluorescence of the reaction mixture obtained when the procedure is applied to cinnamaldehyde has the excitation and emission maxima at 370 and 460 nm, respectively. Thus, the fluorescence from cinnamaldehyde is not affected by the blank (Fig. 1).

The conditions for maximum fluorescence intensity are identical with those for the determination of benzaldehyde. The fluorescence is also stable for several days even on standing in daylight and resistant to exposure to the excitation light.

The calibration curve is a straight line over a concentration range of 1×10^{-7}–$1 \times 10^{-5}M$. The coefficient of variation was 2·3% (17 analyses of $1 \times 10^{-6}M$ solution).

Fluorescence from other aldehydes

Some aldehydes tested fluoresce when treated under the conditions of procedure. The determinable limits of concentration, and the excitation and emission maxima for these aldehydes are shown in Table 1. For aliphatic aldehydes the excitation and emission maxima are at 330–333 and 385–395 nm, respectively, indicating that the fluorescences are not characteristic of the individual aldehydes. The intensities are generally less than those for aromatic aldehydes.

Aromatic aldehydes generally show fluorescences with excitation and emission maxima at longer wavelength regions than those for aliphatic aldehydes, and their spectra seem to be characteristic of the individual aldehydes (Table 1). However, aromatic aldehydes having a hydroxyl, amino or nitro group hardly fluoresce when treated under the conditions of the procedure. Those examined were salicylaldehyde, 4-hydroxybenzaldehyde, 2,4- and 3,4-dihydroxybenzaldehydes, vanillin, 4-aminobenzaldehyde and 4-nitrobenzaldehyde.

Table 1. Excitation and emission maxima of the fluorescences from aldehydes and their determinable limits of concentration

Aldehyde	Excitation maximum,* *nm*	Emission maximum,* *nm*	Determinable limit, *M*,† *μg/ml*‡
Formaldehyde	330	385	2×10^{-6} (0·06)
Acetaldehyde	333	395	2×10^{-6} (0·09)
Propionaldehyde	333	395	2×10^{-6} (0·12)
Crotonaldehyde	333	395	2×10^{-6} (0·14)
Benzaldehyde	353	385	1×10^{-7} (0·01)
Cinnamaldehyde	370	460	1×10^{-7} (0·01)
4-Dimethylamino-benzaldehyde	360	465	1×10^{-6} (0·15)
4-Sulphamoyl-benzaldehyde	360	435	1×10^{-7} (0·02)
4-Methylsulphonyl-benzaldehyde§	390	475	1×10^{-7} (0·02)
Furfural	350	405	1×10^{-6} (0·10)
Pyridine-2-aldehyde¶	330	400	1×10^{-6} (0·11)

* 1·0 ml portions of $1 \times 10^{-5}M$ aldehyde solutions were treated according to the procedure.

† Expressed as a concentration which gives a fluorescence intensity more than 1·5 times that of the blank.

‡ Actual amount of aldehyde in 1·0 ml of the sample solution.

§ This compound is hardly soluble in water, and so the aqueous solution was prepared after dissolving it in a small amount of dimethylformamide.

¶ The reaction mixture also showed fluorescence in dilute sulphuric acid (excitation maximum, 340 nm; emission maximum, 420 nm).

Reaction of substances other than aldehydes

No fluorescence was observed from acetone, acetophenone, benzophenone, cyclohexanone and acetoacetic acid at a concentration of $2 \times 10^{-5}M$, amino-acids (L-alanine, L-glycine, L-tyrosine, L-tryptophan and L-phenylalanine) $1 \times 10^{-4}M$ and creatinine and benzoic acid at $2 \times 10^{-5}M$ and $1 \times 10^{-4}M$ respectively.

Diketones such as acetylacetone, benzil and diacetyl, sugars such as D-glucose, D-xylose, D-fructose, L-ascorbic acid and D-glucuronolactone, and uric acid show very weak fluorescence at a concentration of $2 \times 10^{-5}M$. A very weak fluorescence is also observed with a 7·5 mg/ml solution of bovine serum albumin (fraction V).

2-Oxo acids show almost identical fluorescence spectra at a concentration of $1 \times 10^{-4}M$: the spectra from pyruvic, oxalacetic, 2-oxobutyric, 2-oxoglutaric and 2-oxocaproic acids have their excitation and emission maxima at 330 and 395, respectively, and those of phenylpyruvic and *p*-hydroxyphenylpyruvic acids have the same excitation maxima at 340 nm and slightly different emission maxima at 385 and 370 nm respectively. The detection limits of the acids (defined as a concentration which gives a fluorescence intensity approximately 1·5 times that given by the blank) are higher than approximately $1 \times 10^{-5}M$.

The proposed method is very sensitive for benzaldehydes, and may be applicable to the assay of serum monoamine oxidase which catalyses the oxidative deamination of benzylamines to benzaldehydes. Studies on the mechanism of the fluorescence reaction are in progress.

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Zusammenfassung—Eine neue fluorimetrische Methode zur Bestimmung von Aldehyden wird angegeben. 1,2-Diaminonaphthalin reagiert mit Aldehyd in verdünnter Schwefelsäure zu einer Verbindung, die in alkalischem Medium intensiv fluoresziert. Die an aromatischen Aldehyden auf diese Weise hervorgerufenen Fluoreszenzen sind für einzelne Aldehyde recht charakteristisch; ihre Intensität ist im allgemeinen höher als die der Fluoreszenzen von aliphatischen Aldehyden. Nur 2-Oxosäuren stören. Vielleicht ist die Methode zur Bestimmung von Aldehyden in kompliziert zusammengesetzten Proben nützlich.

Résumé—On présente une nouvelle méthode fluorimétrique pour le dosage d'aldéhydes. Le 1,2-diaminonaphtalène réagit avec l'aldéhyde en acide sulfurique dilué pour donner un composé qui offre une fluorescence intense en milieu alcalin. Les fluorescences produites à partir des aldéhydes aromatiques dans cette méthode sont assez caractéristiques des aldéhydes déterminés et leurs intensités sont généralement plus élevées que celles des fluorescences obtenues à partir des aldéhydes aliphatiques. La seule interférence provient des 2-oxoacides. La méthode peut convenir pour le dosage d'aldéhyde dans des échantillons complexes.

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COMPARISON BETWEEN AMPEROMETRIC AND TRUE POTENTIOMETRIC END-POINT DETECTION IN THE DETERMINATION OF WATER BY THE KARL FISCHER METHOD

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Summary—A rapid and sensitive method using true potentiometric end-point detection has been developed and compared with the conventional amperometric method for Karl Fischer determination of water. The effect of the sulphur dioxide concentration on the shape of the titration curve is shown. By using kinetic data it was possible to calculate the course of titrations and make comparisons with those found experimentally. The results prove that the main reaction is the slow step, both in the amperometric and the potentiometric method. Results obtained in the standardization of the Karl Fischer reagent showed that the potentiometric method, including titration to a preselected potential, gave a standard deviation of $0{\cdot}001_1$ mg of water per ml, the amperometric method using extrapolation $0{\cdot}002_4$ mg of water per ml and the amperometric titration to a preselected diffusion current $0{\cdot}004_7$ mg of water per ml. Theories and results dealing with dilution effects are presented. The time of analysis was 1–1·5 min for the potentiometric and 4–5 min for the amperometric method using extrapolation.

INTRODUCTION

Several procedures have been proposed for the determination of water by the Karl Fischer method. In the methods described by ASTM[1] and by British Standards[2] both a direct titration and a back- or "residual" titration are used. The direct titration method is considered to be more convenient and easier to automate but the removal of water from some sample components may be too slow for practical use. An abundance of end-point detection techniques has been proposed, *e.g.*, visual,[3] amperometric,[4] spectrophotometric,[5] bimetallic[6] (potentiometric), and true potentiometric.[7] The most common are the amperometric methods using either constant voltage or constant current. Recently Beasley *et al.*[8] published a paper which deals with the amperometric methods. They recommend the use of 0·5 cm^2 platinum flag electrodes polarized with 250 mV to obtain maximum sensitivity and stability. However, no correlation between the reaction rate of the main reaction and the electrode behaviour was made. As stated by Lingane[9] the accuracy and precision of most detecting techniques are usually governed by the chemical and thermodynamic characteristics of the titration system rather than by limitations of the measuring technique itself. Earlier studies in our institute[7,10] have made it possible to determine the order of the reaction between water and the Karl Fischer reagent and to estimate the rate constant ($k = 1{\cdot}2 \pm 0{\cdot}2 \times 10^3\ l^2 . mole^{-2} . sec^{-1}$ for a methanolic reagent with excess of pyridine). As some very important information about the titration system itself has been gained by these kinetic studies, attention can now be turned to the indicating system. The first step of the work described in this paper has been to develop manual titration methods. The end-point techniques were studied simultaneously in the same titration cell.

EXPERIMENTAL

Reagents

The Karl Fischer reagent was a methanolic solution 0·1*M* in iodine (Merck p.a.), 0·6*M* in sulphur dioxide (Fluka AG, >99·97% sulphur dioxide in steel cans), 1*M* in pyridine (Mallinckrodt A.R.). The methanol was Merck p.a. (max. water 0·03%). The titre of the reagent was normally 0·7–1·2 mg of water per ml depending on the age. The reagent was allowed to stabilize for at least one day after the preparation as the change in titre is most rapid in a fresh solution.

Apparatus

A special cell was made in which both potentiometric and amperometric measurements could be made simultaneously. The cell (see Fig. 1) consisted of a 75 ml sample compartment in contact with an auxiliary reference compartment of about 5 ml. The contact consisted of an asbestos (Hopkin–Williams Ltd.) liquid junction. The cap of the sample compartment was made from solid Teflon with an O-ring seal. The feed-through for the electrodes and glass capillary consisted of O-rings inserted into holes bored in the Teflon cap A silicone-rubber septum for sample introduction was fitted into the Teflon cap. In the sample compartment there were three 0·5-cm^2 square platinum electrodes and in the auxiliary compartment two reference electrodes, one a platinum spiral of approximately 0·5 cm^2 and the other a calomel electrode (Radiometer K 901) consisting of a salt bridge containing a saturated aqueous solution of lithium chloride. The auxiliary compartment was filled with Karl Fischer reagent containing a slight excess of iodine complex. This solution was renewed when the colour disappeared, normally twice a week. The potentiometric measurements were made by a Solartron 7040 digital voltage meter and the amperometric measurements were carried out with a current-to-voltage converter. The voltage representing diffusion current was registered on a Servogor recorder. The stirrer was a d.c. motor. The Karl Fischer reagent was added from a 10 ml burette through a very fine capillary. Samples were added with calibrated syringes: 25 μl Hamilton (rel. std. devn. 0·17%, 10 determinations), 500 μl Agla micrometer syringe (rel. std. devn. 0·07%), 5 ml all-glass syringe (rel. std. devn. 0·06%).

Procedure

Potentiometric titration. About 25 ml of the Karl Fischer reagent were transferred into the sample compartment. Distilled water was then added with a 25 μl syringe until only a slight excess of iodine complex remained as determined from the colour. The potential between a platinum electrode in the sample compartment and the calomel reference electrode was noted. Then, for example, 25 μl of 8% v/v solution of water in methanol (= 2 mg of water) were added and titrated back to the potential noted, which normally was done with an accuracy of better than 0·1 mV. The aim with this first procedure was to get a rapid approximate value of the titre of the Karl Fischer reagent. Then reagent was added up to a 30 ml volume mark on the sample compartment, and distilled water then carefully added with a 25 μl Hamilton syringe until the colour changed from red to yellow. On the basis of the approximate reagent titre, titration was done stepwise until the titration curve response was 0·8–1 mV per 5 μg of water. The potential at this slope corresponds to a 0·12–0·15m*M* excess of iodine complex. The cell was

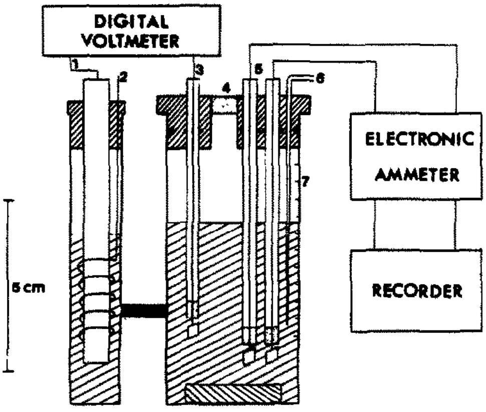

Fig. 1. Titration cell. (*1*) calomel reference electrode, (*2*) platinum wire reference electrode, (*3*) platinum foil indicating electrode, (*4*) silicone-rubber septum, (*5*) platinum electrodes (amperometric system), (*6*) from burette, (*7*) volume mark.

now ready for sample introduction. Provided that the calomel reference electrode was used, this potential was checked only once a week. The variation of this value is due to changes in the liquid junction potential. The calomel electrode can be replaced by a platinum electrode (redox potential) at the cost of more frequent checking of the selected end-point potential, because of changes in the iodine complex concentration with time. The platinum electrode had a better short-term stability because there is no liquid junction.

Amperometric titration. Two of the platinum electrodes were polarized[8] with 250 mV and the resulting diffusion current was read on the recorder. Increments of 0·05 ml of reagent were added to a solution containing very little water. The mean value of the diffusion current after each addition was plotted against the reagent volume and the equivalence point was found by extrapolation (3 or 4 points) to zero current. Amperometric titration to a preselected value of the diffusion current was also investigated, the current being read on the recorder.

THEORY

Reactions

The main Karl Fischer reaction according to Mitchell[4] is

$$C_5H_5N.I_2 + C_5H_5N.SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5NH^+.I^- + C_5H_5N.SO_3 \quad (1)$$

which in the presence of methanol proceeds further:

$$C_5H_5N.SO_3 + CH_3OH \rightarrow C_5H_5NH^+.SO_4CH_3^-. \quad (2)$$

If the activity coefficients as well as the pyridine and the pyridinium ion concentrations are assumed to be constant, the potential of a platinum electrode *vs.* a reference electrode can be written

$$E = E' + \frac{RT}{2F}\ln\frac{[C_5H_5N.I_2]}{[C_5H_5NH^+.I^-]^2}. \quad (3)$$

Cedergren[7] showed that a plot of $-\log[C_5H_5N.I_2]$ *vs.* the electrode potential became a straight line down to at least $10^{-4·5}M$ iodine complex concentration.

In the biamperometric case

$$i_d = k[C_5H_5N.I_2] \quad (4)$$

where i_d is the diffusion current and k the diffusion constant as defined by Stock.[11] The value of k is critically dependent on stirring conditions and also on factors such as temperature, electrode area, reversibility of the system, polarization voltage.

Kinetics

Cedergren[10] found that his data could be fitted to equation (4) for a methanolic reagent provided there was an excess of pyridine over that stoichiometrically required.

$$-\frac{d[C_5H_5N.I_2]}{dt} = k[C_5H_5N.I_2][C_5H_5N.SO_2][H_2O]. \quad (5)$$

The rate constant k was found to be $(1·2 \pm 0·2)10^{-3}\ l^2.\text{mole}^{-2}.\text{sec}^{-1}$. If t is derived from equation (5), then

$$t = \frac{1}{k}\cdot\frac{1}{(A_0 - B_0)}\cdot\frac{1}{(B_0 - C_0)}\cdot\frac{1}{(C_0 - A_0)}\ln\left(\frac{A_t}{A_0}\right)^{B_0-C_0}\left(\frac{B_t}{B_0}\right)^{C_0-A_0}\left(\frac{C_t}{C_0}\right)^{A_0-B_0}. \quad (6)$$

where $A_t = [C_5H_5N.I_2]$, $B_t = [H_2O]$, and $C_t = [C_5H_5N.SO_2]$, all at time t sec, all concentrations being expressed in mole/l., and A_0 *etc.* being the concentrations at time zero.

Dilution effects

The use of a correction for the dilution has not been described earlier in the literature on Karl Fischer titration, although it should be quite large in some cases.

Amperometric titration to a preselected diffusion current. Let v_0 be the initial volume and the preselected diffusion current correspond to an iodine complex concentration C_A. Assume that titration of v_s ml of sample requires v ml of K.F. reagent to bring the system back to the preselected current. Then the titration error is

$$[(v_0 + v_s + v)C_A - v_0 . C_A] \text{ mmole of } C_5H_5N . I_2 \equiv (v_s + v) . C_A . 18 \text{ mg of } H_2O. \quad (7)$$

For $v_s \ll v$, as for example in the standardization of the K.F. reagent, the error in the titre value is $18 . C_A$ mg/ml (0·002 mg/ml for $C_A = 0{\cdot}1mM$).

Amperometric titration with extrapolation to zero current. There will be no systematic titration error due to dilution as $C_A = 0$ at zero diffusion current.

Potentiometric titration to a preselected potential. The preselected end-point potential corresponds to an iodine-complex concentration C_A. Let v_0 be the initial volume, v_s the volume of sample added and v the volume of K.F. reagent required to bring the potential back to the original value. Assume further that the concentration of the pyridinium iodide before sample addition is C_y and the iodine complex concentration after dilution and titration is C_x. Assuming the activity coefficients to be constant, equation (3) gives

$$\frac{C_A}{C_y^2} = \frac{C_x}{\left[\dfrac{(v + v_0)C_y}{v + v_0 + v_s}\right]^2}; \qquad C_x = \frac{C_A(v + v_0)^2}{(v + v_0 + v_s)^2}. \quad (8)$$

The difference in the number of mmoles of water before and after titration is thus

$$\left[\frac{C_A(v + v_0)^2}{v + v_0 + v_s} - C_A . v_0\right] \text{mmole of } H_2O \equiv \frac{-18 . C_A(v_0 . v_s - v . v_0 - v^2)}{v + v_0 + v_s} \text{mg of } H_2O. \quad (9)$$

If $v_0 = 40$ ml, $v_s = 3$ ml, $v = 2$ ml, $C_A = 0{\cdot}1mM$, the error is $-0{\cdot}002$ mg or $<0{\cdot}0001\%$ v/v of water.

If $v_s \ll v$, as for example in the standardization procedure, the titre error expressed by equation (9) is

$$18C_A \text{ mg/ml}. \quad (10)$$

RESULTS

Reaction rates

Figure 2 shows the influence of the sulphur dioxide concentration on the shape of an amperometric titration curve. The two curves represent titration of 0·12 mg of water in media that are respectively 0·02 and 0·5*M* in sulphur dioxide. The Karl Fischer reagent (titre 0·82 mg/ml) was added stepwise at a rate of 0·05 ml/30 sec. The plotted values of the diffusion current are those obtained 30 sec after each addition. As is evident from the diagram the curve representing the high concentration of sulphur dioxide is linear above 70 μA, compared to 160 μA for the low concentration. This is an important difference, since the uncertainty of the current measurement increases with increasing current, which also can be seen in Fig. 2. Consequently, if a low concentration of sulphur dioxide is present only very uncertain and high values of the diffusion current can be used to determine the

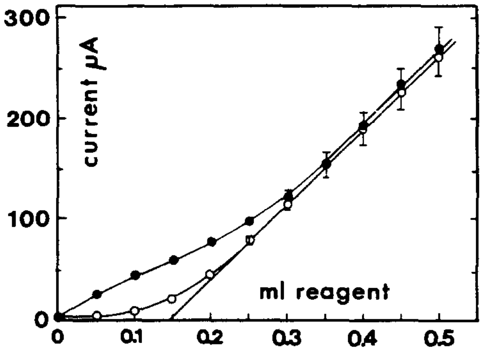

Fig. 2. The influence of the concentration of sulphur dioxide on the amperometric titration curve. v_0 = 40 ml. The titre of the Karl Fischer reagent was 0·82 mg/ml. The reagent was added stepwise at 0·05 ml/30 sec. Plotted diffusion current values were read after every 30 sec. (●) 0·02*M* sulphur dioxide, (○) 0·5*M* sulphur dioxide. Bars denote the uncertainty of the current measurement.

end-point of the titration. This will of course result in poorer accuracy and precision.

In order to examine the diffusion current behaviour in more detail, a theoretical titration curve was calculated and compared with one experimentally found. The result is shown in Fig. 3. In this example 100 μg of water were added to 50 ml of spent Karl Fischer reagent (titre 0·660 mg/ml), containing no water and a negligible excess of iodine complex. The concentration of sulphur dioxide was kept constant at 0·5*M*. The solution was titrated stepwise with 0·05 ml of reagent per min and the diffusion current recorded as a function of time. By use of equations (1) and (6) along with a value of the rate constant *k* equal to 1·3 × 10^3 $l^2 . mole^{-2} . sec^{-1}$, the iodine complex concentration was calculated as a function of time. Thanks to the linear relationship between diffusion current and iodine complex concentration the recorded current values were easily converted into concentrations. This made it

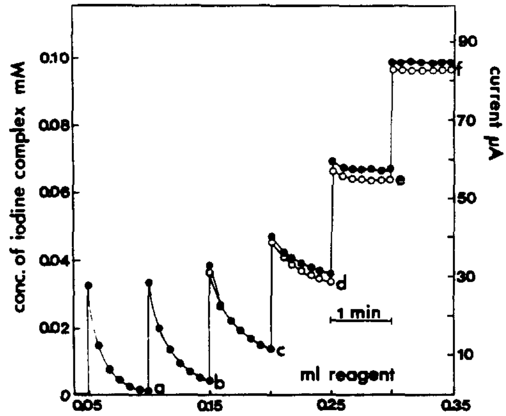

Fig. 3. (○) A theoretically evaluated titration curve compared with (●) one amperometrically indicated. 100 μg of H_2O were added to 50 ml of a solution approx. zero in water and iodine complex concentrations. This solution was titrated stepwise with 0·05 ml of Karl Fischer reagent (titre 0·660 mg/ml). The concentration of sulphur dioxide complex was 0·5*M* during the titration. Calculated unreacted amounts of water at the points (*a*)–(*f*) were (*a*) 68 μg, (*b*) 38·5 μg, (*c*) 15 μg, (*d*) 2·8 μg, (*e*) 0·2 μg, (*f*) 0·0 μg.

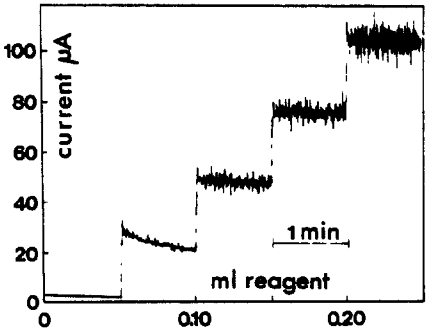

Fig. 4. Recorded amperometric titration of water. The Karl Fischer reagent (0·83 mg/ml) was added in steps of 0·05 ml at intervals of 1 min v_0 = 50 ml.

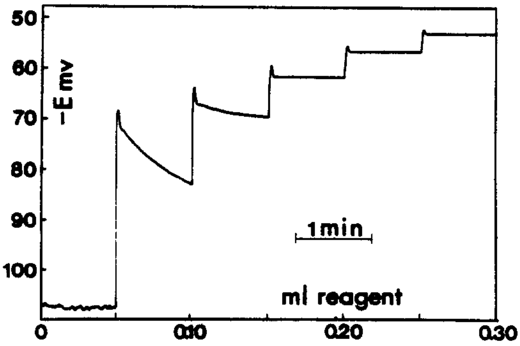

Fig. 5. Recorded potentiometric titration of water. Conditions as for Fig. 4.

possible to compare the theoretical curve with that found experimentally. As can be seen from Fig. 3 the curves are practically identical. This proves that the main reaction is slow while the electrode response is rapid. Consequently, by using equation (6) it is possible to optimize the performance of either a direct or a back-titration.

Stability and sensitivity of the amperometric and the potentiometric end-point systems

A comparison between the amperometric and the potentiometric indicating systems can be made by using the titration curves represented in Figs. 4 and 5. The slope of the amperometric curve was 0·66 µA per µg of water. The uncertainty of the current at 50 µA was ±2 µA which corresponded to 0·1m*M* iodine complex for this experiment. This is equal to ±3 µg of water. In the potentiometric case with the same iodine complex concentration at the end-point, the slope was about 0·2 mV per µg of water. However, the precision of the potential reading was better than 0·1 mV. This uncertainty corresponded to ±0·5 µg of water. Thus the precision of the potentiometric method was significantly better than that of the amperometric.

Standardization of the Karl Fischer reagent

A test of the expressions for dilution effects described in equations (7) and (9) was performed. The results in Tables 1 and 2 show that a correction for the dilution effect caused by the Karl Fischer reagent is justified and worthwhile. The uncertainty was somewhat larger in the amperometric case. In an ordinary titration to a preselected concentration of iodine complex of about 0·1m*M* with a titre larger than 2 mg/ml this correction was less than 0·1% of the titre value.

In Table 3 the true potentiometric end-point technique is compared with the amperometric methods using either a preselected diffusion current or extrapolation. These experiments were carried out with an effective concentration of sulphur dioxide of 0·5*M*. As suggested above, the reaction between water and the reagent then goes to completion with a relatively small excess of iodine complex. The reaction is then sufficiently fast, even for a comparatively small excess of the iodine complex, resulting in a more accurate extrapolation. This will, of course, increase the precision of end-point location. If the concentration of sulphur dioxide had been in the range normally reported in the literature the extrapolation would have resulted in much larger errors, for the reason shown in Fig. 2.

Table 3 shows that the precision of the potentiometric method is somewhat better than that of the amperometric method using extrapolation. Moreover, the analysis time was about 1·5 min for the potentiometric compared to 4–5 min for the amperometric titration. The commonly used amperometric method employs preselected current. Compared to this method the analysis time of the potentiometric method is the same but the precision is significantly better.

Determination of water in some organic solvents

The influence of large sample volumes was studied and the results are presented in Table 4. The results show that the potentiometric method and the amperometric method using extrapolation give equal precision. The increased uncertainty of the potentiometric method

Table 1. Potentiometric standardization of the Karl Fischer reagent, using various end-point concentrations of iodine complex

End-point conc. of $C_3H_5N.I_2$, *mM*	Found, *ml*	Titre, *mg/ml*	Correction, *mg/ml*	Corrected titre, *mg/ml*
0·065	30·06	$0{\cdot}665_3$	$0{\cdot}001_1$	0·666
0·322	30·29	$0{\cdot}660_2$	$0{\cdot}005_8$	0·666
0·780	30·72	$0{\cdot}651_0$	$0{\cdot}014_1$	0·665

Table 2. Amperometric standardization of the Karl Fischer reagent,* using various preselected diffusion currents

End-point conc. of $C_5H_5N.I_2$, *mM*	Found, *ml*	Titre, *mg/ml*	Correction, *mg/ml*	Corrected titre, *mg/ml*
0·16	24·12	0·829	0·003	0·832
0·98	24·65	0·811	0·018	0·829

* The same original reagent composition was used for these experiments and those in Table 1, but the titres differed.

Table 3. Comparison between the amperometric and the potentiometric method in the standardization of the Karl Fischer reagent. (1·682 mg of H_2O in methanol was added. All preselected values correspond to an excess of 0·1m*M* iodine complex)

Method		Found, mean value, *mg/ml*	Correction for dilution, *mg/ml*	Corrected mean value, *mg/ml*	Standard deviation, *mg/ml*	No. of detns.	Time/detns., *min*
Amperometric	To preselected diffusion current	0·649	$0{\cdot}001_8$	$0{\cdot}650_8$	$0{\cdot}004_7$	5	1·5
	Extrapolation 3 or 4 points	$0{\cdot}649_4$	—	$0{\cdot}649_4$	$0{\cdot}002_4$	8	5
Potentiometric	To preselected potential	$0{\cdot}649_6$	$0{\cdot}001_8$	$0{\cdot}651_4$	$0{\cdot}001_1$	5	1·5

Table 4. Determination of water in various solvents. (5·00 ml of solvent taken. The iodine complex concentration at the end-point of the potentiometric method was about 0·1m*M*. v_0 = 40 ml. Karl Fischer reagent titre = 0·920 mg/ml),

Solvent	Amperometric (with extrapolation) Found, mg H_2O	% v/v	Potentiometric (preselected potential) Found, mg H_2O	% v/v
Trichloroethylene	0·534	0·0107	0·543	0·0108
	0·541	0·0108	0·534	0·0107
Isopropyl alcohol	0·895	0·0180	0·942	0·0188
	0·909	0·0182	0·942	0·0188
n-Heptane	0·086	0·0017	0·068	0·0014
	0·067	0·0013	0·083	0·0016
Methanol	1·201	0·0240	1·200	0·0240
	1·208	0·0242	1·202	0·0240

compared to the results shown in Tables 1 and 2 is probably due to dilution. In determination of even smaller concentrations of water, *e.g.*, less than 1 mg/l., this dilution effect must be compensated for either by the use of equation (9) or with a method previously described.[7] In the latter method the titration curve both before and after addition of the sample must be known. Then the dilution effect is graphically evaluated.

A comparison between the methods when small amounts of water are determined can be found in Table 4. The results show that the precision of the potentiometric method is significantly better than that of the amperometric. In judging the values of the standard deviations given in the table the standard deviation of the reagent addition, corresponding to 0·5 μg of water, should be taken into account.

DISCUSSION

As mentioned in the introduction to this paper most procedures and end-point detection systems have been described without taking the kinetics of the main reaction into consideration. Besides that, information about the effective concentration of the sulphur dioxide is usually lacking. Furthermore the concentration of this component varies considerably not only during a determination but also according to the method used. From kinetic data and ideas developed in this paper the following conclusions can be drawn. If there is too low a concentration of sulphur dioxide present the most important parameter is the time required to complete the main reaction. Assuming that the titration is carried out to a low iodine complex excess, the question of choice of indicating system is of secondary interest, as the result of the determination is mainly affected by the incomplete main reaction. At a low concentration of the iodine complex it is difficult to differentiate between the behaviour of the current and the degree of completeness of the main reaction. At a high concentration of sulphur dioxide the main reaction is rapid and the situation is different. Under such conditions a discussion of indicating systems is more adequate because the main error of the determination can be attributed to the end-point technique used. In this paper all results presented have been obtained by the use of a high concentration of sulphur dioxide and therefore a high precision of the results has been obtained.

Table 5. Comparison of the various methods when small amounts of water are determined. (v_0 = 40 ml)

Method		Found (mean value), μg	Std. devn., μg	No. of detns.
Amperometric	Preselected diffusion current*	12·5	2·3	5
	Extrapolation (2 points)	13·2	1·6	5
Potentiometric	Preselected* potential	12·5	0·7	5

* 0·13 mM excess of iodine complex.

Some curious results have been reported by Beasley *et al.*[8] in a critical study of the Karl Fischer end-point system. They stated that the amperometric titration curve is non-linear below an iodine complex concentration of about 0·26mM. The slope of the titration curve in an interval corresponding to $0{\cdot}01_3$–$0{\cdot}06_5$mM iodine complex concentration was only 41% of the slope at above 0·26mM. This was supposed to depend on the presence of a large iodine–sulphur dioxide complex with a lower diffusion coefficient than that of the iodine complex. However, the reagent used was diluted approximately fifty times, giving a sulphur dioxide concentration of at most 0·01M after reaction. The kinetic data presented in the present paper show that the time required for 99% reaction with 0·01M sulphur dioxide present should be several hours at low concentrations of iodine complex. The time for the current to decrease from 5 to 2·5 μA should also be a few hours, for example, if 5μM water had been present under the conditions used by Beasley. This example shows that water may be present even if the current is apparently stable and different from zero.

The results presented in this paper show that the Karl Fischer titration can be very accurate even for small amounts of water if suitable reactant concentrations are used. Under these conditions a comparison could be made between various modes of end-point detection. Titration to a preselected diffusion current value is usually employed in commercial titrators. Potentiometric methods should be capable of giving somewhat better results, especially for small amounts of water. A potentiometric method combined with coulometry has been described by the author,[7] and it had a detection limit of 0·05 μg of water.

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Zusammenfassung—Eine rasche und empfindliche Methode zur Karl Fischer-Bestimmung von Wasser mit wahrer potentiometrischer Endpunktsanzeige wurde entwickelt und mit der üblichen amperometrischen Methode verglichen. Der Einfluß der Schwefeldioxidkonzentration auf die Form der Titrationskurve wird gezeigt. Mit Hilfe kinetischer Daten war es möglich, den Titrationsverlauf vorauszuberechnen und mit dem experimentell gefundenen zu vergleichen. Die Ergebnisse beweisen, daß die Hauptreaktion sowohl bei der amperometrischen als auch bei der potentiometrischen Methode der langsame Schritt ist, sofern eine hohe Schwefeldioxidkonzentration vorliegt. Bei der Standardisierung des Karl Fischer-Reagens erhaltene Ergebnisse zeigen, daß die potentiometrische Methode mit Titration bis zu einem vorgewählten Potential eine Standardabweichung von $0{,}01_1$ mg Wasser pro ml ergab, die amperometrische Methode mit Extrapolation $0{,}002_4$ mg Wasser pro ml und die amperometrische Titration bis zu einem vorgewählten Diffusionsstrom $0{,}004_7$ mg Wasser pro ml. Theorien und Ergebnisse, die sich mit Verdünnungseffekten befassen, werden mitgeteilt. Die Analysenzeit betrug 1–1,5 min für die potentiometrische und 4–5 min für die amperometrische Methode mit Extrapolation.

Résumé—On a élaboré une méthode rapide et sensible utilisant la détection du point de fin de dosage potentiométrique vrai et on l'a comparée à la méthode ampérométrique classique pour le dosage de l'eau selon Karl Fisher. On montre l'influence de la concentration en anhydride sulfureux sur l'allure de la courbe de titrage. En utilisant les données cinétiques, il a été possible de calculer le développement des titrages et de faire des comparaisons avec ceux trouvés expérimentalement. Les résultats prouvent que la réaction principale est le stade lent, tant dans la méthode ampérométrique que potentiométrique, en admettant qu'il existe une concontration élevée en anhydre sulfureux. Les résultats obtenus dans la normalisation du réactif de Karl Fisher ont montré que la méthode potentiométrique, y compris le titrage à un potentiel présélectionné, donne un écart type de $0{,}001_1$ mg d'eau par ml, la méthode ampérométrique utilisant l'extrapolation $0{,}002_4$ mg d'eau par ml et le titrage ampérométrique à un courant de diffusion présélectionné $0{,}004_7$ mg d'eau par ml. On présente les théories et résultats ayant trait aux effets de dilution. Le temps d'analyse est de 1–1,5 mn pour la méthode potentiométrique et de 4–5 mn pour la méthode ampérométrique utilisant l'extrapolation.

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RAPID DETERMINATION OF ANTIMONY IN STEEL BY FLAMELESS ATOMIC-ABSORPTION

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Summary—A method for the determination of 1–30 ppm or more of Sb in steel by using flameless atomic absorption has been developed. The sample was dissolved in *aqua regia* and 10 μl were pipetted into the Massmann-type furnace. It was shown that interferences from HCl, HNO_3, Ni and Fe could be eliminated if oxygen was excluded and the heating rate was sufficiently high. Chromium was added to the samples and standards to compensate for its influence. Cu, Co, Mn, Ti and Sn did not interfere. An intercomparison with other laboratories showed that this method gives the same result as extraction with TOPO in MIBK. The time for a complete analysis including dissolution was 15 min.

Antimony, lead, bismuth and some other elements have a deleterious effect on the quality of steels even in very small amounts. If more than about 20 mg/kg is present, cold-rolling may be impossible. It is therefore important to analyse the raw materials and the melted ingots for these elements. Mixing of different raw materials should be performed so that the melted ingots contain less than the set limits. There is thus a need for a rapid method for analysing the steel for these elements in the range 1–25 ppm. The results should, if possible, be reported within 30 min after the sample has been taken, in order to control further processing of the melt.

Byrne *et al.*[1] have summarized the methods for analysis of trace elements in steel. The inherently rapid methods such as emission spectroscopy and X-ray fluorescence have too low a sensitivity whereas other methods such as polarography and colorimetry are too time-consuming. During the last few years several papers have appeared describing the determination of antimony by atomic-absorption techniques. Direct analysis of a dissolved sample by aspiration into a flame has too low a sensitivity; a detection limit of 35 ppm has been reported.[2]

To increase the sensitivity, concentrated hydrochloric acid solutions of the dissolved sample have been extracted with methyl isobutyl ketone (MIBK)[3–5] or di-isopropyl ether[6] from trioctylphosphine oxide (TOPO) has been added to the MIBK to increase the extraction efficiency.[7] All these authors analysed the organic phase by atomic-absorption spectroscopy; Yanagisawa[5] and Schreiber[6] used flameless AAS. The sensitivity is sufficiently high and most of the interfering elements can be removed, but the time required before the result is available amounts to several hours, *i.e.*, the time is of the same order as for colorimetric methods.[8]

Antimony has also been determined by AAS after conversion into SbH_3.[9,10] The sensitivity is high but no work has been done showing the usefulness of the method for analysis of a matrix. Moreover, this special approach can only be used for antimony and bismuth, and separate procedures must then be employed for lead.

This work describes a method for the determination of antimony by direct analysis of the dissolved steel sample without extraction procedures. Interferences can be controlled by proper design of the equipment so that separation by extraction becomes unnecessary.

EXPERIMENTAL

Spectrometer

The atomic-absorption spectrometer was described earlier.[11] It has provision for a hydrogen-background corrector but this was not used in the work described here. The furnace is of the Massmann-type. The furnace was gas-tight and could be flushed with an inert gas such as argon. It was also described earlier.[12] The temperature of the graphite tube is monitored by an infrared-sensitive diode and the furnace can be heated very rapidly to a preset temperature and then operated isothermally.[11] The important differences between this equipment and commercial instruments such as the Perkin–Elmer 303 with HGA 72, are that temperature-controlled operation is possible and that the furnace is gas-tight.

Procedure

A 0·5 g sample is weighed and dissolved in 5 ml of conc. hydrochloric acid and 2·5 ml of conc. nitric acid in a 50 ml Erlenmeyer flask. The flask is slightly heated on a sand-bath. The dissolved sample is transferred to a 500 ml standard flask and diluted to the mark with water containing 200 ppm of chromium, added as chromium chloride. After mixing, 10 μl of this solution are transferred into the graphite tube with an Oxford microsampler pipette. The sample is dried during 30 sec at about 80°, ashed for 60 sec at a final temperature of 850° and analysed at an atomization temperature of 1940°, using the line at 217·6 nm and a slit-width of 65 μm. After each cycle the furnace is heated at high temperature (2600°) for 10 sec in order to remove matrix elements which otherwise would accumulate in the graphite cuvette. The total time required for the procedure described is 15 min.

A standard is prepared by dissolving 1 g of antimony metal in 10 ml of hydrochloric acid and 20 ml of nitric acid. The solution is transferred to a 1 litre measuring flask and diluted with 180 ml of nitric acid, 90 ml of hydrochloric acid and water to the mark. Dilutions to 10 ppm of Sb are made weekly from this stock solution. Further dilutions are made daily (with water containing 200 ppm of chromium). The pH of the test solutions should be less than 1·5.[13] These standard solutions are analysed in the same way as described for the sample.

RESULTS AND DISCUSSION

The antimony halides are very volatile and losses in the dissolution step might occur. In order to check the procedure, a steel sample (BCS 330) certified to contain 180 ppm of Sb was dissolved in a flask, by using the apparatus and procedure described by Gorsuch.[14] A few ml were distilled and analysed for antimony. Less than 0·7 μg of Sb/l. (the detection limit) in a water solution was found and it was therefore concluded that no losses occurred during the dissolution stage.

Samples containing 1 ng of Sb were analysed after ashing for 1 min at various temperatures. The result is shown in Fig. 1 and it is seen that ashing could be performed at 850°C without loss. During ashing a constant voltage is applied to the graphite tube, which results in a

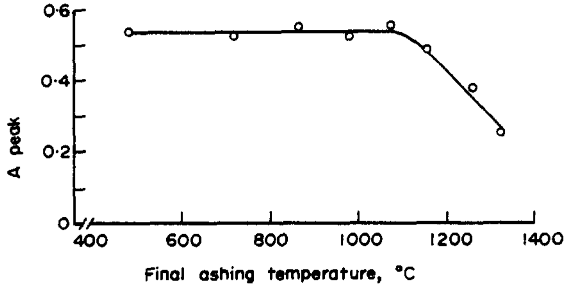

Fig. 1. Variation of absorbance peak with final ashing temperature.

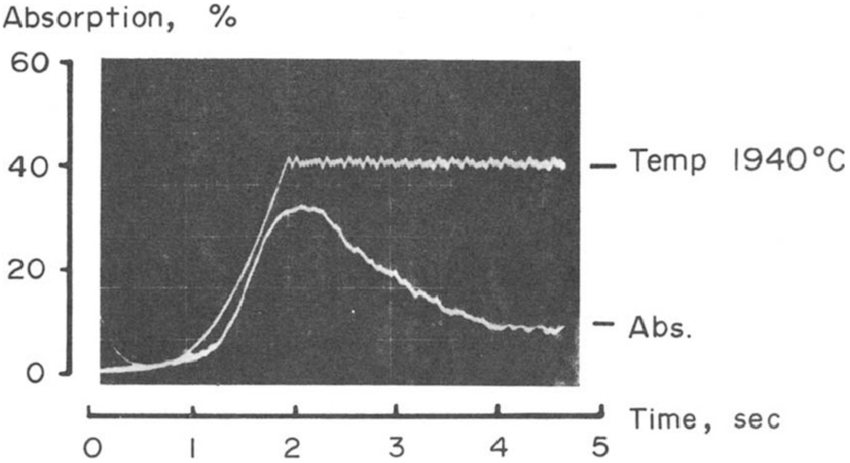

Fig. 2. Absorption (%) for antimony (lower trace) and temperature of the furnace (upper trace) as a function of time.

ballistic temperature rise with time. The main losses occur of course at the end of the period and therefore the final temperatures are given.

The peak-height of the antimony absorption was found to depend on three parameters: rate of heating, final temperature and matrix. By making the atomization rate very high compared to rate of diffusional loss a concentrated atomic vapour cloud can be built up during a short time. The highest possible rate of atomization is desired but the temperature should not be increased more than necessary to accomplish this, as there then will be additional losses due to diffusion. Too high a temperature may also cause vaporization of other elements from the matrix.

Full power was applied to the graphite tube until an infrared sensor signalled that a preset value was reached. A "triac" then reduced the power to keep the graphite-tube temperature constant. By using different tappings on the power transformer the heating rate could be selected to be about 220, 450 or 900°C/sec. The time required to reach the preset temperature, 1940°C, was thus much shorter with a heating rate of 900°C/sec than for a lower heating rate and the atomization thus occurred more rapidly. Especially at somewhat lower temperature the rate of vaporization of an element may depend on the matrix. It was found that the peak-height for antimony differed between a steel sample and a water solution when a lower heating rate was used but not for the maximum heating rate.

The optimum final atomization temperature was determined from an oscilloscope photo, see Fig. 2, as described by Lundgren.[15] One trace shows the temperature and the other the % absorption as a function of time when the temperature setting was 1940°. The output from the infrared temperature sensor was not linear and therefore the trace is curved at the beginning. The course of the % absorption with time illustrates the building up and losses of antimony vapour. Too low a temperature setting results in a delayed atomization, which gives a lower sensitivity. During atomization the gas-flow was stopped without adverse effects since the furnace was gas-tight.

Interferences

Schreiber and Frei[6] found that the absorption signal decreased when the amount of

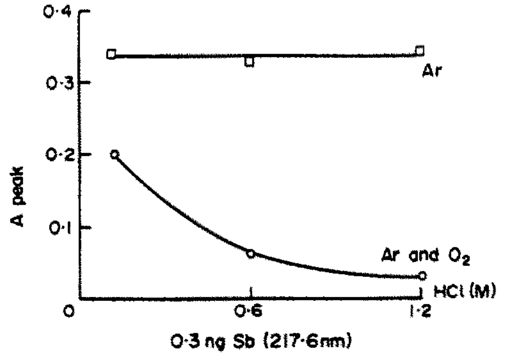

Fig. 3. Dependence of absorption peak on hydrochloric acid concentration in the presence of Ar only (□) and a mixture of Ar and O_2 (○).

hydrochloric, nitric and to some extent sulphuric acid in the sample increased. Figure 3 shows that in the presence of pure argon the absorbance is independent of the amount of hydrochloric acid, but if the furnace is filled with a mixture of argon and air the absorbance decreases with the amount of hydrochloric acid, as found by Schreiber and Frei. These authors used a Perkin-Elmer HGA 70, which is open so that air can enter into the graphite tube. We also found that the signal was independent of the amount of nitric acid when the furnace was filled with argon but varied with it when oxygen was present. These results indicate that when both oxygen and acid are present the antimony signal will decrease, possibly because only a fraction of the antimony will be reduced to metal. The salt may evaporate as volatile $SbCl_3$ during ashing. It is therefore important to exclude oxygen from the graphite tube in order to eliminate the interference from hydrochloric and nitric acid.

Yanagisawa *et al.*[5] and Schreiber[6] have reported interference from several metals in determining antimony by flameless methods. Cr, Ni, Fe and Mo are potential interfering elements in the steels studied in this work. Ag, V and Cu among others might also interfere when present. Figure 4 shows the absorbance of 0·3 ng of antimony when various amounts of chromium are present. For more than 200 ppm of chromium a constant absorption signal was observed. Therefore chromium was added to the standards and if necessary to the samples so that measurements were always made on the plateau where small variations of

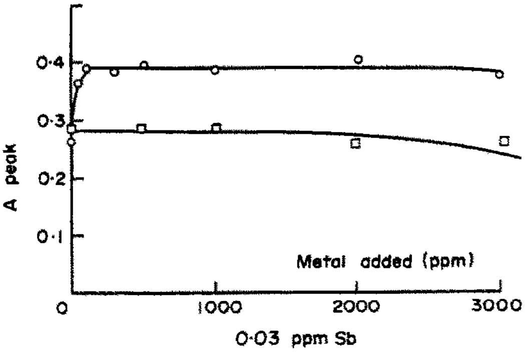

Fig. 4. Variation of absorbance peak with chromium (○) and iron (□) concentrations.

the chromium content did not change the signal. Figure 4 also shows a similar study of the influence of iron. In order to limit the excess of iron to 1000 ppm the dissolved sample was diluted as described in the procedure.

Maruta and Takeuchi[16] observed that the interference from Ni and some other elements varied with the temperature setting of their instrument, a Nippon Jarrel–Ash AA-EE, modified tantalum-filament atomizer. The temperature setting changed simultaneously both the rate of heating and the final temperature. Table 1 shows that different results were obtained for two different heating rates both for Ni and for Fe. At the higher heating rate the interference from both nickel and iron disappeared (for the quoted concentrations). This again demonstrates the advantages of using very rapid initial heating. No experimentally supported explanation can be given at present.

Table 1. Variation of the absorbance as a function of the atomization rate in the presence of Ni or Fe. The preset atomization temperature was 1940°C in the presence of Ni and 1300°C in the presence of Fe

Heating rate	450°C/*sec*		900°C/*sec*	
Ni added to 0·25 ng of Sb, μg	0	10	0	10
A (peak)	0·265	0·365	0·379	0·377
Fe added to 0·27 ng of Sb, μg	1·1	11	1·1	11
A (peak)	0·258	0·195	0·273	0·273

Table 2 shows that no interference was encountered from Cu, Co and Mn under the operating conditions described. Large amounts of Ti seemed to produce a slightly positive error. Sn produced interference from molecular absorption when present in 3000-fold amounts but not at in 1000-fold amounts. For all other determinations in this work no non-specific absorption was observed. This was confirmed by measurements made with a hydrogen lamp at the antimony resonance line, 2176 Å, with a slit-width of 110 μm. As there are lines at 2170 and 2179 Å, which are close to the resonance line at 2176 Å,[17] for antimony determinations a slit-width of 65 μm was used. The dispersion of the monochromator was 22 Å/mm. Especially with samples containing larger amounts of antimony, it is important to reduce the spectroscopic interference by using a narrow slit-width. The hydrogen-background corrector was not used, because the signal from the hydrogen lamp was too low at 2176 Å if the slit-width was kept narrow.

Table 2. Peak absorbance of 0·3 ng of Sb in the presence of various amounts of other elements. Heating rate 900°C/sec, atomization temperature 1940°C

Ratio of foreign elements to antimony added, w/w	0	1000	3000	10,000
Cu	0·495	0·520	0·525	0·500
Co	0·498	0·495	0·507	0·498
Ti	0·482	0·517	0·530	0·550
Mn	0·521	0·522	0·538	0·527
Sn	0·515	0·523	—	—

Analysis of steel

A number of steel samples were analysed by the procedure described. Some of the samples had certificates of analysis and for some others this work was part of an investigation leading to certification. Results for non-certified samples were: BCS 277 (mild steel) 10 ppm; BCS 334 (austenitic stainless steel) 18 ppm; BCS 335 (austenitic stainless steel) 27 ppm. Some of the samples were also analysed by extraction with TOPO into MIBK and determination in an air–acetylene flame according to Burke.[7] The extraction method was also used by six other laboratories in analysing these samples for antimony. The intercomparison is shown in Table 3. It is seen that the method described here compares well with the other results. This also indicates that interference from elements not studied separately is probably small.

Table 3. Intercomparison of results (ppm) obtained for determination of antimony with TOPO/MIBK extraction[7] and comparison with described procedure. Most of the values represent the mean of 10 determinations

		Laboratory*							This work	
Designation	Matrix	1	2	3	4	5	6	Extraction†	Described procedure	Certificate value
BCS 330	mild steel	170	179	179	178	181	180	150	174	180
BCS 336	austenitic stainless steel	30	—	20	26	33	19	29	28	—
JK 1C	ultrapure mild steel	3	—	2	2	2	1	1	2	2
JK 2C	low-alloy steel	35	30	30	30	34	28	27	29	30
JK 8C	austenitic stainless steel type 316	22	—	13	17	22	14	21	20	19
JK 16A	ferromolybdenum	10	—	9	8	—	7	13	10	—

* 1—Fagersta AB, Fagersta; 2—Asea, Västerås; 3—Domnarvet. Steel factory; 4—Nyby, Steel factory; 5—Ovako Oy, Imatra Steel factory; 6—Avesta, Steel factory.

† Ref. 7 obtained 169 ppm Sb for BCS 330.

The calibration curves obtained by analysing standard solutions containing chromium, and by standard additions to a dissolved steel sample, JK 1C, were linear up to 120 ppm of Sb. The standard deviation of the absorption measurements increased as the amount of Sb decreased. It was found to be 18% for JK 1C containing 2 ppm of Sb. The standard deviation of the complete procedure was determined by dissolving 6 samples each of JK 8C, BCS 334 and BCS 335 and making the 18 analyses. The relative standard deviation found was 2·8% at 20–30 ppm Sb. The detection limit for Sb in steel by this method was estimated to be 0·7 ppm.

Acknowledgement—The author thanks the steel works participating in the committee on determination of trace metals in steels for financial support and for valuable discussions and permission to publish the results of the intercomparison. Also many thanks to Professor Gillis Johansson and to Dr. Gillis Lundgren for valuable discussions and to Dr. Michael Sharp for linguistic revision of the manuscript.

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Zusammenfassung—Ein Verfahren zur Bestimmung von 1–30 ppm oder mehr Sb in Stahl mit Hilfe der flammenlosen Atomabsorption wurde entwickelt. Die Probe wurde in Königswasser gelöst und 10 μl in den Ofen vom Massmann-Typ pipettiert. Bei Ausschluß von Sauerstoff und ausreichend hoher Aufheizgeschwindigkeit störten HCl, HNO_3, Ni und Fe nicht. Chrom wurde Standards und Proben zugesetzt, um seinen Einfluß zu kompensieren. Cu, Co, Mn, Ti und Sn störten nicht. Ein Vergleich mit den Ergebnissen anderer Laboratorien zeigte, daß diese Methode dasselbe Ergebnis liefert wie Extraktion mit TOPO in MIBK. Der Zeitbedarf für eine ganze Analyse einschließlich Aufschluß betrug 15 min.

Résumé—On a élaboré une méthode pour le dosage de 1–30 ppm ou plus de Sb dans l'acier en utilisant l'absorption atomique sans flamme. L'échantillon est dissous dans l'eau régale et l'on pipette 10 μl dans le four de type Massmann. On a montré que les interférences de HCl, HNO_3, Ni et Fe peuvent être éliminées si l'oxygène est exclu et si la vitesse de chauffage est suffisamment élevée. On ajoute du chrome aux échantillons et aux étalons pour compenser son influence. Cu, Co, Mn, Ti et Sn ne gênent pas. Une intercomparaison avec d'autres laboratoires a montré que cette méthode donne les mêmes résultats que l'extraction par le TOPO en méthylisobutylcétone. Le temps our une analyse complète y compris la dissolution est de 15 mn.

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DIRECT DETERMINATION OF NANOGRAM AMOUNTS OF IODINE BY ATOMIC-ABSORPTION SPECTROSCOPY USING A GRAPHITE-TUBE ATOMIZER

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Summary—The direct determination of iodine by AAS at its 183·0 and 178·2 nm resonance lines by using a small graphite-tube atomizer, electrodeless discharge-lamp source and vacuum monochromator is described. Optimum conditions for the determination of iodine have been established; similar sensitivity is obtained when iodide or iodate samples are examined. With 10 μl aqueous samples sensitivities (for 1% absorption) of 4×10^{-10} g and 2×10^{-10} g of I were obtained at 183·0 and 178·2 nm respectively; a detection limit of 2×10^{-9} g was observed at both lines. Non-specific molecular absorption from common inorganic salts causes interference with the determination; the iodine non-resonance line at 184·4 nm may be employed to correct for this interference when moderate amounts of common salts are present.

Recent work in our laboratory has been concerned with the development of direct methods for the determination of non-metallic elements by the techniques of atomic absorption and emission spectrometry. As a number of these elements, notably sulphur, phosphorus and iodine, exhibit their useful ground-state atomic lines at wavelengths shorter than 200 nm it is necessary that the optical path through the atom cell and the instrumental assembly should be transparent at these wavelengths. We have described the direct determination of sulphur,[1] phosphorus[2] and iodine[3] by atomic-absorption spectrometry utilizing the fuel-rich nitrogen–separated nitrous oxide–acetylene flame and by atomic-emission spectrometry with a high-frequency induction-coupled plasma source.[4,5] In both techniques sample solutions are nebulized into the flame or plasma cell, a relatively large volume being required, and the sensitivity is limited by the difficulty of achieving high sample concentrations in the cell owing to dilution by the support gases. Both limitations of flame cells can be overcome by use of non-flame atomizers such as the graphite tube or graphite filament. The nature of flames and plasmas also imposes limitations at short wavelengths where atmospheric absorption is appreciable, as it is difficult to avoid degradation of the observed signal:noise ratio caused by fluctuating absorption at the interface between the flame or plasma and the atmosphere. For these reasons, the direct atomic-absorption spectrometry of elements such as iodine, sulphur and phosphorus by using non-flame atomization should give high sensitivity. L'vov and Khartsyzov[6] have reported sensitivities for the determination of sulphur, phosphorus and iodine by atomic-absorption spectrometry (AAS) using pulse vaporization in a graphite cuvette. This paper describes the direct determination of iodine by AAS at its ground-state atomic lines at 178·3 ($6s^2P_{3/2}$–$5p^5\,{}^2P_{3/2}$) and 183·0 nm ($6s^4P_{5/2}$–$5p^5\,{}^2P_{3/2}$), by using a vacuum monochromator, a nitrogen-purged optical system, an iodine microwave-excited electrodeless discharge-lamp source and a small heated graphite-tube atomization cell.

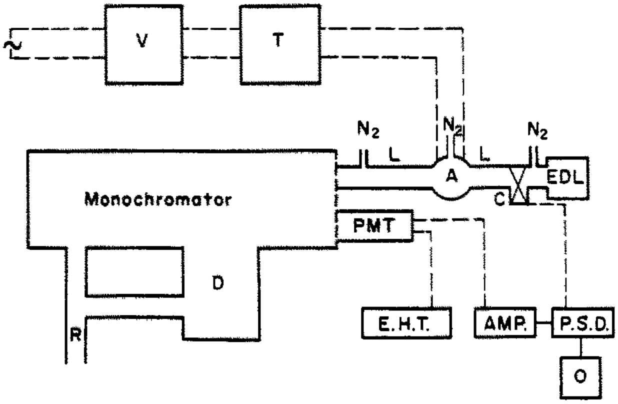

Fig. 1. Schematic diagram of instrumentation employed.

EXPERIMENTAL

Apparatus

The instrumental arrangement is shown schematically in Fig. 1. An iodine electrodeless discharge-lamp (EDL) was used as the source. This was made from silica tubing (i.d. 8 mm, 1 mm wall thickness) to form a bulb 200 mm in length, and containing a few mg of iodine. The EDL was supported in a 3/4-wave resonant cavity (Model 210L, Electromedical Supplies Ltd., Wantage, U.K.) by means of a metal holder which allowed reproducible positioning of the lamp. The source was powered by a 2450 MHz Microtron Mk. III microwave generator (EMS Ltd., Wantage), using a reflected-power meter (EDT Ltd., London S.W.6) connected in series between the generator and cavity to allow the lamp/cavity assembly to be tuned to minimum reflected power. Radiation from the source was focused into the graphite-tube atomizer by a biconvex calcium fluoride lens (25 mm diameter, 50 mm focal length). The radiation emerging from the atomizer was then brought to a focus on the entrance slit of a 1-metre vacuum grating monochromator (Rank Precision Instruments, Margate, U.K.) by a similar calcium fluoride lens. The optical path was formed from glass tubing (25 mm i.d.) placed between the source and graphite atomizer and between atomizer and monochromator entrance slit; this path was maintained under a slightly positive pressure of oxygen-free nitrogen. The 1-metre vacuum monochromator had a reciprocal linear dispersion of 1·6 nm/mm and was operated in conjunction with a rotary roughing/backing pump and an oil diffusion pump. While pressures of less than 10^{-5} mm Hg are possible with this arrangement the operating pressure employed in this work was *ca.* 0·1 mm Hg; this is sufficient to provide good transmission of radiation at the wavelengths employed. An EMI 6256B end-window photomultiplier tube with a 50 mm diameter silica window was attached to the monochromator at the exit slit by a rubber O-ring seal so that a vacuum-tight seal was obtained at the slit. The photomultiplier tube was operated with a Brandenburg model 475R EHT unit at the voltage which gave the best signal: noise ratio with the light levels available (1620 V). The photomultiplier output was led to a low-noise amplifier (Brookdeal type 450, Brookdeal Electronics Ltd., Berks., England) and phase-sensitive detector (Brookdeal type 411) and a model DM64 oscilloscope (Telequipment Ltd., U.K.).

Modulation of the radiation from the EDL source was achieved by means of a rotating sector placed between the 3/4-wave cavity and the lens. The rotating sector chopped the light beam at 285 Hz; the sector also provided a reference voltage for operation of the phase-sensitive detector. The rotating sector was also purged with nitrogen.

The graphite-tube atom cell employed is shown in Fig. 2 and is similar to that described by Dagnall, Johnson and West.[7] A graphite tube (high-purity grade) of 6 mm o.d., and 4 mm i.d. and 20 mm in length was machined from graphite rod (Ringsdorf Company Ltd.). A sample introduction port was provided by a 2 mm hole drilled through the wall of the tube. The graphite tube was supported by a graphite split-ring at each end and the assembly was then retained by two stainless-steel L-shaped holders. One holder was secured to a stainless-steel support column and the second rested on a second column and was earthed *via* a length of copper braiding attached to the base of the unit. One holder was thus allowed to "float" to simplify the alignment procedure and prevent fractures in the graphite tube owing to its expansion on heating. Both support columns were water-cooled.

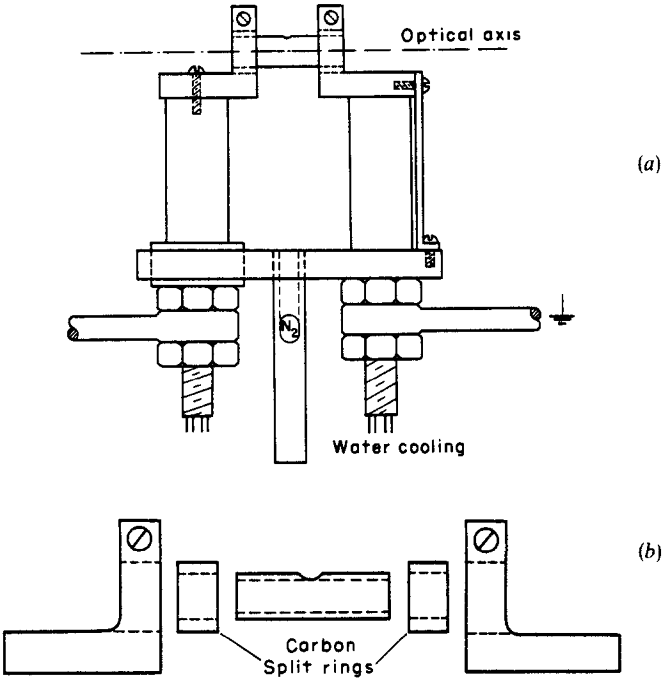

Fig. 2. (*a*) Graphite-tube furnace assembly.
(*b*) Detail of construction of graphite tube and holders.

The graphite tube was heated electrically; power was supplied *via* a Variac transformer (20-A, Claude Lyons Ltd., Liverpool, U.K.) and a large power transformer (rating 10 kW, Foster Transformers Ltd., London S.W.19) to provide 10 V and up to 450 A across the furnace. The entire cell unit was maintained under a constant flow of oxygen free nitrogen by means of a glass housing fitted with a removable cover to allow the sample to be transferred to the tube, and calcium fluoride windows to permit transmission of the source radiation. The atom-cell was nitrogen-purged by a supply separate from that used for the optical system, so that the flow-rate could be adjusted without affecting the transmission of the optical path. Sample solutions (10 μl) were transferred to the graphite tube by Eppendorf micropipette.

RESULTS AND DISCUSSION

Operation of iodine EDL source

The relationship between emission intensity and applied microwave power for the iodine electrodeless discharge-lamp source was studied at both the 183·0 and 178·2 nm iodine resonance lines. The variation in line emission intensity at 183·0 nm with microwave power is shown in Fig. 3; the curve obtained at 178·2 nm was similar. The decrease in intensity with increasing applied power reflects the increasing temperature attained in the resonant cavity with increasing applied power and subsequent condensation of the iodine onto the cooler wall of the EDL, not contained in the cavity. The discharge was difficult to sustain at less than 10 W. At between 10 and 15 W the emission intensity remained relatively constant. The absence of a well-defined region at low power in which the discharge can be maintained and where the emission intensity changes rapidly with variation of applied microwave power (*i.e.*, the power curve has a steep positive slope) results in inability to modulate the radiation electronically. As shown in Fig. 3, if modulation is applied

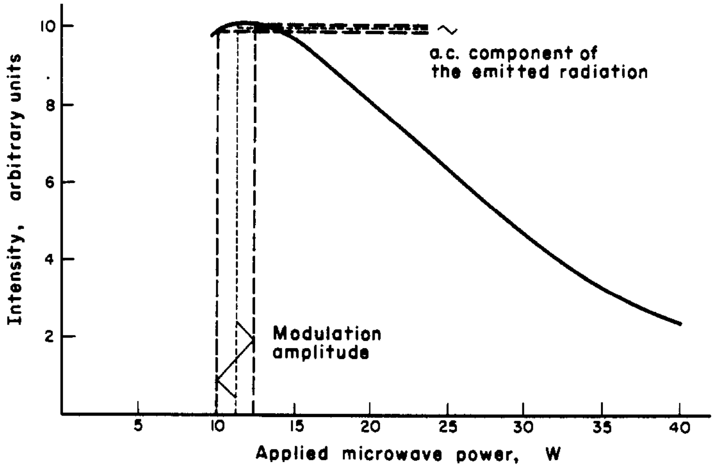

Fig. 3. Variation of emission intensity at 183·0 nm from iodine EDL source with applied microwave power.

at the 10–15 W applied-power level the resulting radiation exhibits only a small a.c. component. Mechanical modulation of the source intensity at 285 Hz with a rotating sector as described above was therefore employed. For the determination of iodine by AAS the power to the EDL source was maintained at 10–12 W; this power was found to give the best signal:noise intensity ratio at both resonance lines.

Operation of graphite-tube furnace for the determination of iodine

The optimum operating conditions for the determination of iodine with the graphite-tube furnace and instrumental assembly described, were established *via* atomization and measurement of the peak absorbance obtained at 183·0 nm with 10 μl aliquots of aqueous potassium ammonium iodide solution. Figure 4*a* shows the variation in absorbance at 183·0 nm for 2 ppm of iodine with variation in voltage applied across the graphite-tube furnace. All measurements were made with an applied voltage of 8·5 V. Figure 4*b* shows the variation in absorbance at 183·0 nm with flow-rate of nitrogen in the furnace chamber. A nitrogen flow-rate as high as 1·5 l./min may be used before any decrease in absorbance is detected in the atomization of 10 μl of a 2-ppm iodine solution (potassium iodide). Above this flow-rate, cooling and dilution effects are observed and the peak absorbance decreases and becomes less reproducible. When a nitrogen flow-rate of less than 0·5 l./min is used the purging time required between samples and between the drying and atomization steps is lengthened considerably. A flow rate of 1 l./min was maintained in all further work.

The exit and entrance slits of the monochromator were set at 30 μm (spectral band pass 0·05 nm) and a photomultiplier EHT voltage of 1620 V was employed. These settings were found to give optimum signal:noise and signal:background intensity ratios. The photomultiplier output was led to the amplifier, which was adjusted to produce a signal for the phase-sensitive detector such that its d.c. output voltage was 10 V at 100% transmission. The variable time-constant of the phase-sensitive detector was optimized to produce the best signal:noise ratio without distortion of the analytical signal by overdamping. The value of the time-constant used was 100 msec (bandwidth 3 Hz).

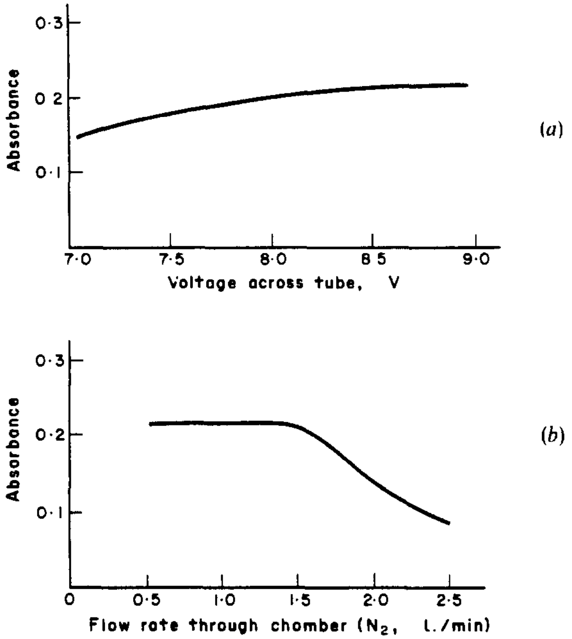

Fig. 4. (*a*) Variation of absorbance at 183·0 nm for 10 μl of 2 ppm iodide solution with voltage applied across graphite tube.
(*b*) Variation of absorbance at 183·0 nm for 10 μl of 2 ppm iodide solution with flow-rate of nitrogen in atomizer chamber.

AAS characteristics of iodine in the graphite-tube furnace

With the optimum operating conditions established, calibration graphs for iodine atomic absorption at 183·0 nm were constructed, the samples being introduced as aqueous solutions of potassium iodide, ammonium iodide and potassium iodate. Calibration graphs of identical slope and linear range were obtained in each case; 10 μl samples produced calibration graphs linear up to 6 ppm and the sensitivity (for 1% absorption) was 0·04 ppm, *i.e.*, 4×10^{-10} g. For the 178·2 nm iodine resonance line the sensitivity (for 1% absorption) was found to be better by a factor of two, *i.e.*, 0·02 ppm in a 10 μl sample. This corresponds to an absolute detection limit of 2×10^{-10} g. Although higher sensitivity is obtained at 178·2 nm the recorded emission intensity from the source is lower at this line than at 183·0 nm, so the precision of measurement is lower and a similar practical detection limit of 2×10^{-9} g is observed. The absorption signals recorded were wholly atomic in nature; no non-specific absorption from aqueous samples solutions was observed at the 179·9, 184·4 and 187·6-nm iodine non-resonance lines from the source when 10 μl aliquots of 20 ppm iodide solutions were atomized.

Effect of foreign ions

In many sample types in which the determination of traces of iodide is of interest the predominating inorganic species present from the matrix are salts of the alkali metal and alkaline earth ions. Thus, for example, in biological and botanical samples, foodstuffs and water, large excesses of sodium and potassium (and frequently calcium and magnesium) are present. After sample pretreatment to destroy organic matter by wet oxidation, these

Table 1. Effect of common inorganic salts on iodine absorption

Salt studied MX	Concentration ratio, MX:iodide	183·0 *nm*		Absorbance 184·4 *nm*
		Change in absorbance, %	Increase in absorbance	
NaCl	1:1	0	0	0
	10:1	+25	0·05	0·05
	100:1	+100	0·22	0·22
	1000:1	100% absorption of radiation at each line		
KCl	1:1	0	0	0
	10:1	0	0	0
	100:1	+40	0·10	0·10
	1000:1	100% absorption of radiation at each line		
Na_2SO_4	1:1	0	0	0
	10:1	0	0	0
	100:1	+40	0·10	0·10
	1000:1	100% absorption of radiation at each line		
$NaNO_3$	1:1	0	0	0
	10:1	0	0	0
	100:1	+15	0·03	0·03
	1000:1	+200	0·40	0·40
Na_2HPO_4	1:1	0	0	0
	10:1	+25	0·05	0·05
	100:1	+75	0·15	0·15
	1000:1	100% absorption of radiation at each line		

ions may be present in conjunction with one or more common anions such as chloride, sulphate, nitrate or phosphate. The effect on the iodine determination of different weights of several common inorganic salts likely to be present after sample pretreatment, has been investigated. The effect of these salts on the absorbance recorded for 10 μl aliquots of 2-ppm potassium iodide solution (20 ng of iodide) at 183·0 nm is shown in Table 1. The interferences recorded were all positive. This effect may be attributed wholly to non-specific absorption at the 183·0 nm line by molecular species such as NaCl. This was demonstrated by measurement of the absorption at the nearby iodine 184·4 nm non-resonance line for similar sample solutions. In each case the same absorbance was obtained at this line as that at the 183·0 nm resonance line for blank solutions containing only the salt investigated, and this was the same as the increase in absorbance recorded at this wavelength for iodide solutions when the foreign salt was added. It is therefore possible to correct for the non-specific absorption interference observed in the presence of moderate concentrations of the salts investigated, by subtraction of the absorbance obtained at 184·4 nm from that at 183·0 nm. In the presence of 1000-fold w/w quantities of most of the salts studied, however, virtually complete absorption of incident radiation at both wavelengths is obtained and such a correction cannot be made. In the presence of a 1000-fold amount of sodium nitrate, however, it was possible to record absorption signals at both wavelengths, and correct for non-specific background absorption. This relative transparency obtained with nitrate is possibly due to more complete atomization of this salt under the conditions employed. Conversion of alkali metal salts into the nitrates before atomization would thus be preferable in methods developed for examination of biological and botanical samples. As nitrate may be employed in many sample pretreatment procedures for the oxidative degradation of organic material, this conversion might be accomplished without complication.

Conclusion

The graphite-tube atomizer reported here can provide an efficient atom-cell for the direct determination of nanogram amounts of iodine by atomic-absorption spectroscopy at 183·0 nm. Though non-specific absorption interference is encountered from moderate amounts of simple inorganic salts, the iodine 184·4 nm non-resonance line may be employed for its correction.

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Zusammenfassung—Die direkte Bestimmung von Jod durch AAS an seinen Resonanzlinien bei 183,0 und 178,2 nm wird beschrieben. Es wird eine Atomquelle aus einem kleinen Graphitrohr, eine elektrodenlose Entladungslichtquelle und ein Vakuum-Monochromator verwendet. Die besten Bedingungen zur Bestimmung von Jod wurden ermittelt; eine ähnliche Empfindlichkeit wird erhalten, wenn man Jodid- oder Jodatproben untersucht. Mit 10 μl wäßriger Lösung wurden Empfindlichkeiten (für 1% Absorption) von 4×10^{-10} und 2×10^{-10} g J bei 183,0 bzw. 178,2 nm erzielt; bei beiden Linien betrug die Nachweisgrenze 2×10^{-9} g. Unspezifische Molekülabsorption häufig vorkommender anorganischer Ionen stört bei der Bestimmung; sind mäßige Mengen gewöhnlicher Salze anwesend, dann kann man mit der Jodlinie bei 184,4 nm ohne Resonanzcharakter dafür korrigieren.

Résumé—On décrit le dosage direct de l'iode par spectrométrie d'absorption atomique avec ses raies de résonance 183,0 et 178,2 nm en utilisant un petit atomiseur à tube de graphite, une lampe à décharge sans électrode comme source et un monochromateur sous vide. On a établi les conditions optimales pour le dosage de l'iode; une sensibilité similaire est obtenue quand on examine des échantillons d'iodure ou d'iodate. Avec des échantillons de 10 μl, on a obtenu des sensibilités (pour 1% d'absorption) de 4×10^{-10} g et 2×10^{-10} g de I à 183,0 et 178,2 nm respectivement; on a observé une limite de détection de 2×10^{-9} g pour les deux raies. L'absorption moléculaire non spécifique des sels minéraux communs provoque une interférence dans le dosage: la raie de non-résonance à 184,4 nm peut être employée pour tenir compte de cette interférence quand des quantités modérées de sels communs sont présentes.

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KATALYTISCHE BESTIMMUNG VON SILBERSPUREN IN WAßRIGER LÖSUNG UND NACH EXTRAKTION

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(*Eingegangen am* 5 *November* 1973. *Angenommen am* 11 *Januar* 1974)

Zusammenfassung—Die Anwendung der katalysierten Oxydation von Brompyrogallolrot durch Peroxodisulfat zur Bestimmung von Silber wird diskutiert. In wäßriger Lösung kann man 0,5 bis 10 μg/ml, bei Anwendung von 1,10-Phenanthrolin als Aktivator 1 bis 13 ng/ml bestimmen. Durch Kombination einer Solventextraktion mit anschließender katalytischer Bestimmung des in die organische Phase extrahierten Silbers läßt sich die Bestimmung auch in Gegenwart von 200 μg Fe(III), Co(II) und Pb(II) durchführen. Mit Hilfe einer mechanisierten Variante der Simultankomparationsmethode kann die Bestimmung noch empfindlicher (0,2–20 ng/ml) gestaltet werden.

Die Anwendung katalytischer Reaktionen zur quantitativen Spurenanalyse wird gegenwärtig intensiv untersucht.[1,2] Bis jetzt sind mehr als 250 analytisch genutzte Reaktionen zur Bestimmung von etwa 45 Elementen bekannt. Bisher wurden vor allem katalytische Redoxreaktionen studiert. Sie sind sehr empfindlich, die Nachweisgrenzen liegen gewöhnlich zwischen 10^{-1} und 10^{-4} ppm.

Der allgemeine katalytische Zyklus, der bei solchen Redoxreaktionen häufig beobachtet wird, kann durch folgende Gleichungen wiedergegeben werden:

$$\begin{array}{lllr} \mathrm{Red} + \mathrm{M}^{(n+1)} & \rightarrow \mathrm{P} & + \mathrm{M}^{n+} & (1a) \\ \mathrm{M}^{n+} + \mathrm{Ox} & \rightarrow \mathrm{M}^{(n+1)} & + \mathrm{Q} & (1b) \\ \hline \mathrm{Red} + \mathrm{Ox} & \rightarrow \mathrm{P} & + \mathrm{Q} & (1c) \end{array}$$

(Red, Ox = Reagenzien der Redoxreaktion; P, Q = Reaktionsprodukte)

Silberionen können dann als Katalysatoren für Redoxreaktionen in Lösung wirken, wenn ein Oxydationsmittel gefunden wird, das Ag(I) zu Ag(II) oxydieren kann (Gl. 1*b*), und mit dem Substrat nach Gl. 1*c* dagegen praktisch nicht reagiert. Persulfat ist ein typischer Oxydant dieser Art, wie bereits beim Vergleich der Standardoxydationspotentiale der Redoxpaare $S_2O_8^{2-}/SO_4^{2-}$ (2,05 V) und Ag(II)/Ag(I) (1,98 V) zu sehen ist. Die Ag(II)-Ionen reagieren in einer schnellen Reaktion (Gl. 1*a*) mit dem Substrat. Die reduzierte Form des Katalysators tritt dann wieder in den Reaktionszyklus ein. Als Substrate für solche Umsetzungen sind aromatische Amine, Phenole sowie organische Farbstoffe geeignet.

Wir untersuchten systematisch eine Reihe metallochromer Indikatoren (Eriochromschwarz T, Brompyrogallolrot, Xylenolorange und Murexid) auf ihre Eignung als Substrate für katalytische Redoxreaktionen. Dabei erwies sich das Brompyrogallolrot (BPR) für eine katalytische Silberbestimmung mit Persulfat als Oxydationsmittel als besonders geeignet. Brompyrogallolrot gehört zur Reihe der Oxytriphenylmethanfarbstoffe, die bisher in der Katalymetrie nur wenig untersucht wurden.

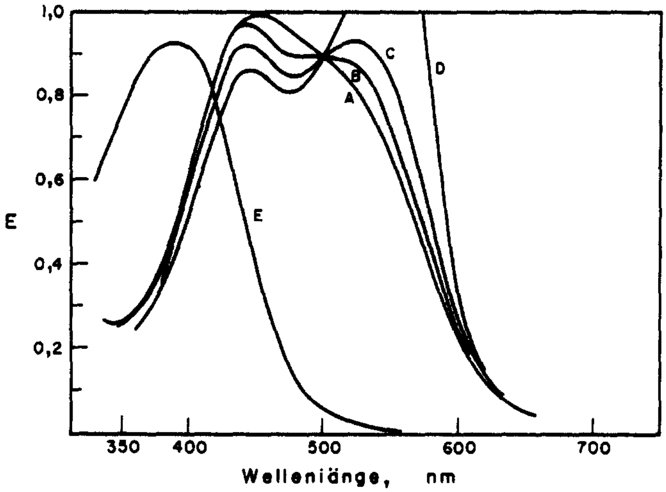

Abb. 1. Absorptionsspektren von $10^{-4}M$ BPR bei verschiedenen pH-Werten und das Absorptionsspektrum des Oxydationsproduktes.
A: pH = 1,65; *B*: pH = 2,45; *C*: pH = 3,25; *D*: pH = 4,10; *E*: Oxydationsprodukt.

BPR wird im Verlaufe der Oxydation entfärbt, so daß der Reaktionsverlauf photometrisch verfolgt werden kann. Die Absorptionsspektren von BPR bei verschiedenen pH-Werten und das Absorptionsspektrum des Oxydationsproduktes sind in Abb. 1 dargestellt.

Der allgemeine katalytische Zyklus (1*a* und 1*b*) kann im untersuchten konkreten Fall wiedergegeben werden durch:

$$\mathrm{BPR} + S_2O_8^{2-} \rightarrow \mathrm{P} + 2SO_4^{2-} \qquad (2)$$

Diese Reaktion ist thermodynamisch möglich, aber kinetisch stark gehemmt. Für die katalysierte Reaktion gilt:

$$\mathrm{BPR} + Ag^{2+} \rightarrow \mathrm{P} + Ag^{+} \text{ (schnell)} \qquad (3)$$

$$2Ag^{+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Ag^{2+} \text{ (schnell)} \qquad (4)$$

Die unkatalysierte Reaktion (Gl. 2) kann jedoch mit meßbarer Geschwindigkeit ablaufen (hohe Blindwerte), wenn durch Dissoziation Sulfatradikale entstehen.

$$S_2O_8^{2-} \rightarrow 2\,{}^{\cdot}SO_4^{-} \qquad (5)$$

Ein Mechanismus unter Beteiligung von Ag^{3+}-Species ist nach Angaben der Literatur wenig wahrscheinlich.[3,4]

Im allgemeinen ist die Erhöhung der Reaktionsgeschwindigkeit bei redox-katalysierten Reaktionen durch Silber nicht sehr groß, so daß Analysen im Nanogrammbereich nicht möglich sind. Die Nachweisgrenzen dieser Reaktionen liegen bei 10^{-4} bis 10^{-7} g/ml. Man kann jedoch die Empfindlichkeit von katalytischen Bestimmungsmethoden durch Aktivatoren steigern, wodurch die Geschwindigkeit einer katalysierten Reaktion weiter erhöht wird.[5]

Besonders geeignet als Aktivatoren für katalytische Silberbestimmungen nach einem Redox-Mechanismus sind stickstoffhaltige Chelatbildner, die durch Komplexbildung die Oxydationsstufe II des Silbers stabilisieren und das Standardoxydationspotential des Systems Ag(II)/Ag(I) erniedrigen. So fanden Scrocco *et al.*,[6] daß das Standardoxydationspotential des Systems Ag(II)/Ag(I) durch Anwesenheit von 2,2'-Dipyridyl auf 1,453 V im Vergleich zu 1,914 V in 2*M* Salpetersäure bzw. 2,00 V in 4*M* Perchlorsäure herabgesetzt wird. Von verschiedenen Autoren[7–10] wurden bereits Vorschläge zur Anwendung stickstoffhaltiger Liganden als Aktivatoren angegeben.

Der Verlauf katalytischer Reaktionen wird durch Fremdionen oft empfindlich gestört. Dieser Störioneneinfluß hat bisher die praktischen Einsatzmöglichkeiten von katalytischen Bestimmungsmethoden beschränkt. Aktivatoren erhöhen zwar die Empfindlichkeit eines analytischen Verfahrens, verbessern aber in der Regel die Selektivität des Verfahrens nicht. Es besteht aber die Möglichkeit, die Silberionen durch eine Solventextraktion von den Störionen abzutrennen und dann als Katalysator einzusetzen. Um die Empfindlichkeit des Verfahrens weiter zu erhöhen und um eine Rationalisierung (Mechanisierung) der Bestimmung vornehmen zu können, kann eine mechanisierte Variante der von Bognar[11] vorgeschlagenen Simultankomparationsmethode angewendet werden.

EXPERIMENTELLER TEIL

Geräte

Alle Glasgeräte wurden durch konzentrierte Salpetersäure und mehrfaches Spülen mit destilliertem bzw. bidestilliertem Wasser gereinigt.

Als Gerätekombination zur Registrierung der Extinktions- (bzw. Durchlässigkeits-) Zeit-Kurven wurde ein Spektralphotometer "Spekol" (VEB Carl Zeiss Jena, DDR) mit Meßansatz "EK 5" in Verbindung mit einem Kompensationslinienschreiber "EZ 31" (Laboratorni Přistroje N.P., Praha, Petřiny) aufgebaut. Der Küvettenansatz ist thermostatierbar und kann Küvetten der Schichtdicken 0,1 bis 5 cm aufnehmen. Der Lampenstrom für das Spektralphotometer wird über eine Wechselspannungsregler "Statron 220/0,45" (PGH Statron Fürstenwalde, DDR) stabilisiert.

Zur Mechanisierung der Silberbestimmung wurde eine Gerätekombination (Blockschaltbild siehe Abb. 2) verwendet. Kernstück der Apparatur ist der Meßansatz "EK 5–Aut" zum "Spekol" (VEB Carl Zeiss Jena, DDR), dessen Kurvenscheibe über eine Getriebewelle vom Standard-Kompensationsschreiber "G 1 B 1" (VEB Carl Zeiss Jena, DDR) angetrieben wird und so den automatischen Küvettenwechsel in einem wählbaren Zyklus (in unserem Fall aller 30 Sekunden) vornimmt. Der Photostrom wird im Standardkompensationsschreiber verstärkt und registriert.

Als Reaktionsgefäße wurden entweder dreischenklige Glasgefäße mit Schliffstopfen oder hydrophobierte Reagenzgläser verwendet. Bei der mechanisierten Variante kam eine Startpipette zum Einsatz.

Reagenzien zur Silberbestimmung in wäßriger Lösung

Falls nicht anders angegeben, wurden alle Lösungen mit bidestilliertem Wasser aus Chemikalien der Reinheit p.A. angesetzt.

Brompyrogallolrot, $10^{-3}M$ wäßrige Lösung. (Die Lösung ist *ca.* 2 Wochen beständig.)

$K_2S_2O_8$, $10^{-1}M$ wäßrige Lösung. (Diese Lösung ist täglich frisch herzustellen.)

Acetatpuffer (pH = 4,62).

1,10-Phenanthrolin, 10^{-1} *M* (Zur Herstellung der Lösung wird das Monohydrat in Wasser suspendiert und bis zur vollständigen Auflösung mit Salpetersäure versetzt und dann mit Wasser aufgefüllt.)

Salpetersäure, 0,1*M*.

Silbernitrat-Lösung. Aus einer Stammlösung (1 mg/ml) wurden kurz vor jeder Bestimmung salpetersaure Untersuchungslösungen geringerer Konzentration hergestellt.

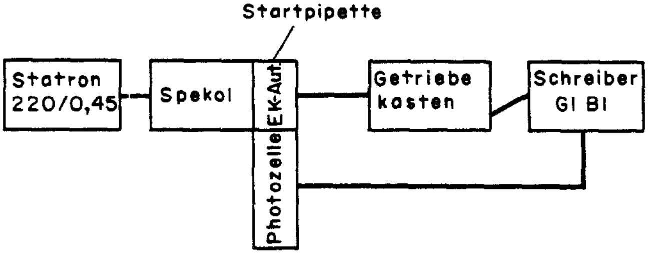

Abb. 2. Blockschaltbild der Gerätekombination zur Simultankomparationsmethode.

Zur Ermittlung des Störioneneinflusses wurden Stammlösungen (Metall-Gehalt 1 mg/ml) verschiedener Metalle in Form ihrer Chloride oder Nitrate hergestellt.

Reagenzien zur Silberbestimmung nach Extraktion

Extraktionsreagenzien

Brompyrogallolrot, $10^{-4}M$, in 1%iger, wäßriger Ammoniumacetatlösung. (Die Lösung ist 5 Tage haltbar.)
1,10-Phenanthrolin, $10^{-3}M$.
ÄDTA, $0{,}1M$, (Die Lösung wird in einer Polyäthylenflasche aufbewahrt.)
Ammoniumacetat, 20%ige, wäßrige Lösung.
Kaliumnitrat, 10%ige, wäßrige Lösung.
Nitrobenzol, reinst, im Vakuum fraktioniert destilliert.

Bestimmungsreagenzien

Brompyrogallolrot, $5 \times 10^{-4}M$, in Dioxan–Wasser-Gemisch (1:1 v/v).
$K_2S_2O_8$, $0{,}1M$, in Dioxan–Wasser-Gemisch (1:1 v/v).
1,10-Phenanthrolin, $0{,}1M$.
Salpetersäure, $0{,}1M$.
Dioxan, rein, mit Ätzkali am Rückfluß gekocht und fraktioniert destilliert.

Bestimmung der Katalysatorkonzentration

Von den experimentell möglichen Methoden zur Bestimmung der Katalysatorkonzentration[12,13] wählten wir die Einpunktmethode der "fixierten Konzentration", bei der die Zeit t gemessen wird, die für eine bestimmte Konzentrationsänderung (Δx) des Indikatorstoffes erforderlich ist.

Die Katalysatorkonzentration ([C]) kann in diesem Fall nach der Beziehung

$$[C] \sim 1/\Delta t \text{ für } \Delta x = \text{const.}$$

ermittelt werden. Aus den registrierten Extinktions–Zeit-Kurven wurden durch Extrapolation für $t = 0$ die Ausgangsextinktionen ermittelt und dann die Zeit bestimmt, die erforderlich war, um zur Hälfte der Ausgangsextinktion zu gelangen.

Silberbestimmung in wäßriger Lösung ohne Aktivator

Man gibt 0,2 ml BPR-Lösung, 3 ml $K_2S_2O_8$-Lösung, die Silberprobenlösung und 5 ml Acetatpuffer in ein dreischenkliges Reaktionsgefäß mit Schliffstopfen, ergänzt mit Wasser auf 10 ml und thermostatisiert 20 Minuten bei 25,0 ± 0,1°. Nach dieser Zeit wird gemischt und die Stoppuhr gedrückt. Einen Teil der Reaktionsmischung füllt man in eine 5-cm Küvette und beginnt mit der Registrierung bei $\lambda = 500$ nm. Die Nullinie wurde vorher gegen eine Lösung, die alle Reagenzien außer BPR enthält, eingestellt.

Silberbestimmung in wäßriger Lösung mit 1,10-Phenanthrolin als Aktivator

Es wird 1 ml $K_2S_2O_8$-Lösung in den einen, 1 ml BPR-Lösung in den zweiten und 1 ml 1,10-Phenanthrolinlösung, die Analysenlösung (1–5 ml) sowie 1 ml HNO_3 in den dritten Schenkel des Reaktionsgefäßes gegeben. Die Salpetersäure dient zum Einstellen des pH-Wertes auf 2,0. Mit Wasser wird das Reaktionsvolumen auf 10 ml ergänzt. Das Reaktionsgefäß wird nun 20 Minuten bei 25,0 ± 0,1° thermostatisiert und dann 30 Sekunden kräftig geschüttelt. Die Reaktionsmischung kommt anschließend sofort in eine 1-cm Küvette und wird bei $\lambda = 500$ nm vermessen. Als Abgleich dient ein Reaktantengemisch ohne Farbstoff. Zur Ermittlung des Blindwertes verfährt man ebenso.

Extraktionsverfahren

Die Extraktion wurde nach Angaben der Literatur[14] durchgeführt (zur Maskierung der Störelement verwendeten wir 2 ml ÄDTA-Lösung). Die organische Phase wird in einen 10-ml Meßkolben abgelassen, die wäßrige Phase mit wenig Nitrobenzol nachgespült und mit Nitrobenzol bis zur Eichmarke aufgefüllt. Diese Lösungen behalten ihre volle katalytsiche Aktivität mehrere Stunden.

Silberbestimmung nach Extraktion

Es wird 1 ml $K_2S_2O_8$-Lösung in den einen, 1 ml BPR-Lösung, 7 ml Dioxan und 1 ml Analysenlösung (Nitrobenzolphase) in den zweiten und 1 ml 1,10-Phenanthrolinlösung sowie 1 ml HNO_3 in den dritten Schenkel des Reaktionsgefäßes gegeben. Nach 30-minütigen Thermostatieven bei 25,0 ± 0,1° wird geschüttelt und die Stoppuhr gedrückt. Das Reaktionsgemisch wird in einer 1-cm Küvette mit Deckel (sonst Schlierenbildung durch Verdunsten des Lösungsmittels) bei $\lambda = 540$ nm photometriert.

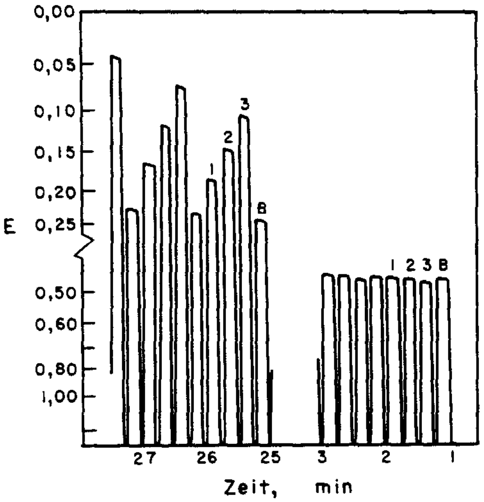

Abb. 3. Beispiel einer Silberbestimmung mit der Simultankomparationsmethode. BPR $5{,}10^{-5}M$; $K_2S_2O_8$ $0{,}01M$; 1,10-phen $0{,}01M$; pH = 2,0. [Ag]: 1: 0,5 ng/ml; Silber 2: 1.0 ng/ml; 3: 1.5 ng/ml; *B*: Blindwert.

Mechanisierte Variante der Simultankomparationsmethode

Bei der von Bognar entwickelten Simultankomparationsmethode wird die der unbekannten Katalysatorkonzentration entsprechende unbekannte Reaktionsgeschwindigkeit verglichen mit den Geschwindigkeiten einer Reihe von "Standardreaktionen" mit bekannten Katalysatorgehalten unter gleichen Bedingungen. Bei Anwendung dieser Methode sind aber wegen der visuellen Verfolgung der Reaktion große Änderungen der Farbintensitäten und mehrere Ansätze zur Bestimmung der Katalysatorkonzentration erforderlich. Man kann jedoch die Reaktion photometrisch verfolgen und mit einem gesteuerten Küvettenwechsel intermittierend mehrere Proben messen und die analoge Registrierung des Extinktionsverlaufes über der Zeit auswerten.

Eine Gerätekombination nach dem in Abb. 2. gezeigten Blockschaltbild ermöglicht eine Mechanisierung der Simultankomparationsmethode und durch die Registrierung der Extinktions-Zeit-Kurven auch eine Objektivierung der Auswertung. Da gleichzeitig 4 Bestimmungen gestartet werden und dann unter gleichen Bedingungen ablaufen, erübrigt sich ein Thermostatisieren während des Reaktionsverlaufes, wenn nicht erhöhte Temperaturen zur Reaktionsdurchführung notwendig sind. Wählt man nun 3 Standardreaktionen (Proben mit bekannten Silbergehalten) und als vierte Probe die Analysenlösung, kann man durch einen einzigen Versuch die unbekannte Katalysatorkonzentration ermitteln.

Ein weiterer Vorteil liegt darin, daß man die Reaktion über einen längeren Zeitraum (bis zu 30 Minuten und länger) unbeobachtet ablaufen und durch die Registrierung der Extinktion über die Zeit eine Trendverfolgung vornehmen kann (siehe Abb. 3.). Die Blindreaktion läuft in allen vier Ansätzen unter den gleichen Bedingungen ab und läßt sich so weitestgehend eliminieren, was auf die Steigerung der Empfindlichkeit von Nutzen ist.

ERGEBNISSE UND DISKUSSION

In wäßriger Lösung lassen sich ohne Aktivator nach der oben beschriebenen Methode Silberspuren von 0,5 bis 10 μg/ml mit einer relativen Standardabweichung von maximal 11,5% bestimmen. Da die damit erreichte Empfindlichkeit noch unbefriedigend war, untersuchten wir zur Erhöhung der Empfindlichkeit die Aktivatorwirkung von folgenden 12 Komplexbildnern auf die katalytische Silberbestimmung: Triäthanolamin, Triäthylamin, α-Aminopropionsäure, Iminodiessigsäure, Nitrilotriessigsäure, Äthylendiamintetraessigsäure, Pyridin, Pyridin-2-carbonsäure, Pyridin-3-carbonsäure, Äthylendiamin, 2,2'-Dipyridyl und 1,10-Phenanthrolin.

Dabei erwiesen sich besonders Äthylendiamin, 2,2'-Dipyridyl und 1,10-Phenanthrolin als geeignet. Zwischen der Wirksamkeit der Aktivatoren und ihrer Stellung in der spektrochemischen Reihe[15] gibt es einen direkten Zusammenhang.

Diese Ergebnisse stehen in voller Übereinstimmung mit Untersuchungen anderer Autoren über die Aktivatorwirkung stickstoffhaltiger Liganden bei redox-katalytischen Silberbestimmungen.[7–10] Die weiteren Untersuchungen wurden mit 1,10-Phenanthrolin als Aktivator durchgeführt.

Die Abhängigkeit der Reaktionsgeschwindigkeit von der Aktivatorkonzentration wird in Abb. 4. gezeigt. Ersichtlich ist ein starker Anstieg der Reaktionsgeschwindigkeit der katalysierten Reaktion bis zu einer Konzentration von $5 \times 10^{-3} M$ 1,10-Phenanthrolin, bei höheren Aktivatorkonzentrationen wächst auch die Geschwindigkeit der unkatalysierten Reaktion. Die Differenz zwischen katalysierter und unkatalysierter Reaktion ist jedoch im untersuchten Bereich bei einer Konzentration von $10^{-2} M$ am größten. Diese Konzentration wurde auch für die Silberbestimmung gewählt.

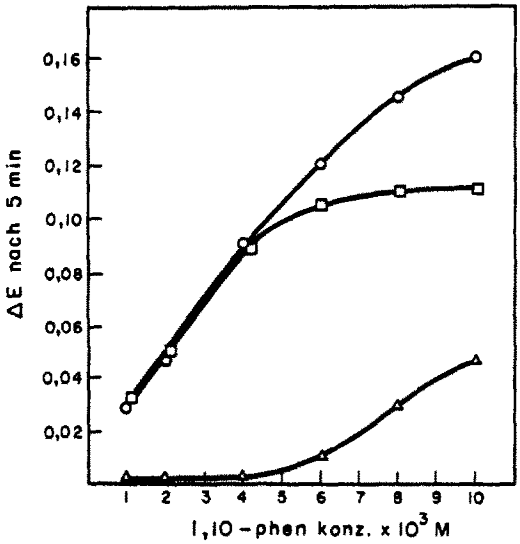

Abb. 4. Abhängigkeit der Reaktionsgeschwindigkeit von der Aktivatorkonzentration. BPR $1 \times 10^{-4} M$; $K_2S_2O_8$ 0,01M; pH = 2,0. —○——○— = katalysierte Reaktion (Ag 43 ng/ml); —△——△— = unkatalysierte Reaktion; —□——□— = Differenz zwischen katalysierter und unkatalysierter Reaktion.

Als geeignetste Wellenlänge zur Verfolgung der Konzentration des Indikatorstoffes (BPR) wurden 500 nm eingestellt. Bei dieser Wellenlänge ist die Absorption der gelblichgrünen Oxydationsprodukte (P) unbedeutend, und das BPR hat bei dieser Wellenlänge einen isosbestischen Punkt, so daß sich geringe Schwankungen im pH-Wert auf die Anfangsextinktion ($t = 0$) nicht wesentlich bemerkbar machen (siehe Abb. 1.). Als optimaler Arbeitsbereich wurde ein pH-Wert zwischen 1,9 und 2,2 ermittelt, der durch Zugabe von Salpetersäure bei jeder Bestimmung eingestellt wurde. Die Eichkurve verläuft unter den angegebenen Bedingungen in einem Ag-Konzentrationsbereich von 1 bis 13 ng/ml linear (Tabelle 1.).

Die statistische Auswertung aller Daten nach der Methode der linearen Regression auf dem Kleinrechner "Cellatron 82-05" ergab:

Geradengleichung für die Eichkurve: $y = 0{,}0152x + 0{,}0388$ (y in Min^{-1}, x in ng/ml)

Korrelationskoeffizient: 0,986

Gesamtstandardabweichung: $s = 0{,}0118\ \text{Min}^{-1}$

Tabelle 1. Abhängigkeit der reziproken Zeit von der Katalysatorkonzentration in Gegenwart von 1,10-Phenanthrolin

Silber, *ng/ml*	Reziproke Zeit, *Min*$^{-1}$*
0,00	0,0403
1,07	0,0536
2,15	0,0702
4,30	0,1060
6,45	0,1344
8,63	0,1724
10,80	0,2069
12,90	0,2319

* Mittelwerte aus 10 Messungen.

Die relativen Standardabweichungen liegen zwischen 21% (Ag 1,07 ng/ml) und 5% (Ag 12,9 ng/ml). Eingegeben wurden die reziproken Zeiten von 80 Bestimmungen im Ag-Konzentrationsbereich von 0 ng/ml (unkatalysierte Reaktion) bis 12,9 ng/ml.

Der Störeinfluß von Fremdionen wurde bei Anwesenheit des Aktivators sowohl für die katalysierte wie für die unkatalysierte Reaktion untersucht. Die Silbergehalte der katalysierten Reaktionen betrugen bei den Messungen 8,6 ng/ml. Der Reaktionsverlauf zeigte dann im Vergleich zu Reaktionen ohne Fremdionen, ob eine Beeinflussung vorhanden war und ab welcher Konzentration die Störung auftritt.

Aus Tabelle 2 ist zu entnehmen, daß insbesondere Fe(III), Co(II) und Pd(II) die Bestimmung stören. Um diesen Störeinfluß zu verringern, wurde eine Kombination von Solventextraktion mit einer anschließenden katalytischen Bestimmung des in die organischen Phase extrahierten Silbers getestet.

Tabelle 2. Auftritt von Störeffekten verschiedener Fremdionen bei der katalytischen Silberbestimmung (8,6 ng/ml) mit 1,10-Phenanthrolin als Aktivator

Störion	Maximale Konzentration, *µg/ml*
Ni(II)	15
Cu(II)	10
Co(II)	0,1
Fe(III)	0,07
Au(III)	0,5
Pd(II)	0,2
Cd(II)	200
Rh(III)	6
Pt(IV)	30
Mg(II)	300
VO^{2+}	1
Pb(II)	100
Zn(II)	50
Hg(I)	0,8

Die unkatalysierte Reaktion wird von denselben Konzentrationen gestört, mit Ausnahme von Blei, wo Störungen schon bei 25 µg/ml auftreten.

Wie von Dagnall *et al.*[16,17] angegeben, läßt sich Silber in Form des Komplexes $(1{,}10\text{-phen-Ag-}1{,}10\text{-phen})_2^+\mathrm{BPR}^{2-}$ mit Nitrobenzol in Gegenwart von ÄDTA als Maskierungsmittel extrahieren und dabei u.a. von Fe(III), Co (II) und Pd(II) abtrennen. Diese Extraktionsmethode sollte deshalb recht güngstig sein, weil als Reagenzien zur Komplexbildung gerade die Substanzen eingesetzt werden (1,10-Phenanthrolin, BPR), die auch bei der eigentlichen katalytischen Bestimmung Verwendung finden. Da Nitrobenzol mit Wasser nicht mischbar ist, mußte ein Lösungsvermittler eingesetzt werden. Als günstigste Gemische erwiesen sich Dioxan–Wasser-Mischungen.

Ein Trocknen der Nitrobenzolphase nach der Extraktion mit Ätznatron führte zum Verlust der katalytischen Aktivität des Silbers schon nach wenigen Minuten und wurde deshalb nicht angewendet.

Ein Vergleich der mit Hilfe eines Rechenprogrammes statistisch behandelten Daten im Ag-Bereich von 0 bis 1 μg/ml zeigt, daß es möglich ist, Silber in Anwesenheit von ÄDTA als Maskierungsmittel von den angeführten Störionen mit Nitrobenzol abzutrennen und Silber dann direkt in der organischen Phase katalytisch zu bestimmen.

Die Ausgleichsrechnung mit einem linearen Ansatz liefert in Abwesenheit von Störionen folgende Geradengleichung:

$$y = 0{,}000370x + 0{,}038 \ (y \text{ in Min}^{-1},\ x \text{ in ng/ml})$$

Gesamtstandardabweichung: $s = 0{,}023\ \mathrm{Min}^{-1}$

Korrelationskoeffizient: 0,986

in Anwesenheit von je 200 μg Fe(III), Co(II) und Pd(II):

Geradengleichung: $y = 0{,}000385x + 0{,}018$

Gesamtstandardabweichung: $s = 0{,}026\ \mathrm{Min}^{-1}$

Korrelationskoeffizient: 0,984

Eingegeben wurden die Dreifachbestimmungen bei sieben verschiedenen Konzentrationen.

Die katalytische Bestimmung von Silber in Dioxan–Wasser-Mischungen ist mit einem Verlust an katalytischer Aktivität gegenüber Bestimmungen in wäßriger Lösung verbunden.

Mit Hilfe der von uns als "mechanisierte Variante der Simultankomparationsmethode" bezeichneten Technik können Silberionen im Bereich von 0,2 bis 20 ng/ml bestimmt werden. Durch Anwendung dieser Technik ist es auch möglich, die katalytische Bestimmung nach Extraktion des Silbers mit Nitrobenzol empfindlicher zu gestalten.

Diese von uns angegebene Variante katalytischer Bestimmungen sollte sich überall dort als recht günstig erweisen, wo sich durch schwankende Zusammensetzung der zu untersuchenden Proben der Blindwert der Reaktion ändert. Durch Kombination der vorgeschlagenen Technik mit der Additionsmethode können recht optimale Bedingungen katalytischer Bestimmungsverfahren auch zum Einsatz in der industriellen Analytik geschaffen werden.

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Summary—The application of the catalysed oxidation of Bromopyrogallol Red by potassium persulphate for silver determination is discussed. In aqueous solution silver concentrations of 0·5–1 μg/ml can be determined and 1–13 ng/ml in the presence of 1,10-phenanthroline as activator. In combination with solvent extraction, catalytic determination of the extracted silver is possible even in presence of 200 μg of iron(III), cobalt(II) and palladium(II). By means of an automatic variant of the simultaneous comparison method a more sensitive determination (0·2–20 ng/ml) was achieved.

Résumé—On discute de l'application de l'oxydation catalysée du Rouge de Bromopyrogallol par le persulfate de potassium pour le dosage de l'argent. En solution aqueuse, on peut déterminer des concentrations en argent de 0,5–1 μg/ml, et 1–13 μg/ml en la présence de 1,10-phénanthroline comme activeur. En combinaison avec l'extraction par solvent, le dosage catalytique de l'argent extrait est possible même en présence de 200 μg de fer(III), cobalt(II) et palladium(II). Au moyen d'une variante automatique de la méthode de comparaison simultanée, un dosage plus sensible (0,2–20 ng/ml) a été réalisé.

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INSTRUMENTAL ADVANTAGES OBTAINED WITH SHORT CONTROLLED DROP-TIME a.c. POLAROGRAPHY

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Summary—The performance of short drop-time a.c. polarography has been examined in detail, and found to be better than that for natural drop-times in almost every respect. Uncompensated resistance terms are smaller and potentiostat stability is improved. In addition, faster potential scan-rates and more rapid data acquisition are possible. A variation of the drop-time over at least three orders of magnitude is possible and this, coupled with excellent instrumental performance, should offer considerable scope in studies of electrode kinetics.

Alternating current polarography generally consists of superimposing an alternating potential at a given frequency onto the d.c. potential. After electronic filtration of the d.c. current, the recording of the alternating current, or a quantity related to this, as a function of d.c. potential, provides the polarogram used in analytical and kinetic investigations.

The importance of both the a.c. and the d.c. components has been recognized, but to date the drive towards improving instrumentation and other aspects of the a.c. technique has concentrated largely on the a.c. component.[1-5] On the other hand the deliberate use of the equivalent d.c. function, the drop-time, has been relatively neglected.

Brown *et al.*[6,7] showed that polarographic instrumental ideality can be realized over a wide range of frequencies. They demonstrated that the a.c. frequency can profitably be varied over three or more orders of magnitude. The time scale and performance of a.c. polarography are of course governed independently by both the d.c. term (the drop-time) and the a.c. term (the frequency). However, to a large extent the drop-time has remained in the same range in the a.c. experiment as in d.c. polarography (2–8 sec) and has not yet been subjected to large and deliberate variations aimed at improving the scope of a.c. methods.

Recently, Bond and O'Halloran[8] showed that the use of short drop-times does not invalidate existing d.c. or a.c. theory, provided the drops are dislodged mechanically at controlled time intervals. For these conditions the theory applicable to the short drop-time is approximately that applicable to the natural drop-time, from which it is derived.

The use of short, controlled, drop-times in a.c. polarography has received some attention, mainly in analytical applications,[9] where the feature of interest has been the fast d.c. potential scan-rate. This work has mainly been done at low frequencies with measurements based on total alternating currents. However, certain other advantages became apparent recently,[10] when phase-sensitive detection at variable frequency was introduced. This work suggested that short drop-time polarography should be further investigated.

With the short controlled drop-time technique, drop-times can now be varied over three or four orders of magnitude from tens of seconds to milliseconds.[11,12] Variation of both drop-time and frequency, should give new scope to a.c. polarography, as exemplified in this paper for both analytical and kinetic investigations. Improvements in instrumentation are also discussed.

EXPERIMENTAL

All chemicals used were of reagent grade purity.

All solutions were temperature-controlled at 25 ± 0·1° and degassed with argon for 15 min before the polarograms were recorded.

All phase-selective a.c. polarograms were recorded with the PAR Electrochemistry System Model 170 (Princeton Applied Research Corporation, New Jersey).

Controlled drop-times of 5, 2, 1 and 0·5 sec were achieved with PAR Drop Timer Model 172. The circuitry is readily modified to give controlled drop-times down to 50 msec. Controlled drop-times of 0·32, 0·28, 0·24, 0·20 and 0·16 sec were obtained with the Metrohm Polarographic Stand E354.

In aqueous media a silver–silver chloride (in 5*M* sodium chloride) reference electrode and a tungsten wire auxiliary electrode were used. In acetone, two identical silver–silver chloride (0·1*M* lithium chloride; acetone) reference electrodes connected to the test solution *via* a salt bridge filled with 0·1*M* tetraethylammonium perchlorate, served as the reference and auxiliary electrodes.

The positive-feedback circuit, used in conjunction with the potentiostat, was installed and used as recommended by the manufacturer, Princeton Applied Research Corporation.

All phase-selective measurements were made either in phase with the applied alternating potential or 90° out of phase. The applied alternating potential and frequency used in the a.c. measurements are given in the text and figures.

Total alternating current polarograms were recorded with the Metrohm AC Modulator E393 used in conjunction with the Metrohm Polarecord E261. This system was converted into a 3-electrode system as described elsewhere.[13]

RESULTS AND DISCUSSION

Minimization of effects attributable to ohmic losses

The general importance of resistance effects in a.c. polarography has been recognized for a long time[1–3] and considerable research directed towards their elimination or minimization.

Resistance effects in any polarographic technique are mainly manifested as an ohmic potential loss (iR-drop). In a.c. polarography, the iR-drop problem introduces many insidious effects which restrict the nature and scope of kinetic and analytical applications. Apart from being the source of the inability of normal phase-sensitive a.c. polarography to discriminate completely against the charging current, it is also responsible for the non-linearity of analytical calibration curves and considerable distortion of wave shapes.

The first endeavours to decrease iR-drop effects in a.c. polarography were logically directed towards decreasing the effective cell resistance (impedance). Thus, reference electrodes with a low effective resistance, specially constructed dropping-mercury electrodes of low resistance, and the incorporation of Luggin probes have been suggested for use in a.c. polarography.[3]

Recently, numerous schemes, mostly based on electronic methods, have been put forward for reducing the sources of ohmic potential loss in many voltammetric and polarographic procedures. Among the most successful has undoubtedly been the application of the three-electrode potentiostat[3–7,14–36] which removes many of the sources of iR-drop in the common polarographic methods, but not all.[3,5,18,19–22,32,36] Additional electronic circuitry to eliminate the remaining uncompensated resistance in phase-sensitive a.c. polarography has been presented by Hayes and Reilley.[21] A method of general applicability has been suggested by Booman and Holbrook in which an additional positive-feedback loop is incorporated into the three-electrode potentiostat.[19]

Whatever the operating conditions, however, uncompensated resistance terms are present, and may place limitations or restrictions on a.c. polarography. Previous work[10] suggested that under one particular set of conditions ohmic losses were less important with short controlled drop-times than with the natural drop-time. The present study confirms this.

General theory

The net uncompensated ohmic losses in any electrochemical equipment are a product of current and resistance terms. That is, the product of the current and resistance terms as the drop-time decreases will determine the magnitude of the iR-loss.

A useful approximation arises from the nature of the rapid polarographic method. The short drop-time is achieved by mechanically tapping the capillary at a selected time early in the growth period of the mercury drop. The resulting flow-rate of mercury is close to that for the natural drop-time. The current–time curve recorded in the manner for the entire short drop-time, is then equivalent to the first portion of the curve for the natural drop-time.

In a.c. polarography, a small a.c. potential is superimposed on the d.c. potential and both a.c. and d.c. currents flow through the polarographic cell. Hence in considering ohmic iR-drop effects both the a.c. and d.c. components must be considered.

The magnitude of the alternating current, $I(\omega t)$, depends on several variables, including the nature of the electrode process, the applied alternating potential ΔE, the frequency ω, the concentration of depolarizer C, and the area of the electrode A.

A general result, however, is that

$$I(\omega t) \propto AC\,\Delta E f(\omega) f(\theta) \tag{1}$$

where $f(\omega)$ is a function of frequency and $f(\theta)$ is a function of the phase angle.[3]

Assuming the mercury drop to be spherical, which will be a good approximation with capillaries of internal radius between 0·017 and 0·2 mm,[37] allows calculation of the area of the drop for any instant during its growth.[38] The expression to be used is

$$A = 0{\cdot}85 m^{2/3} t^{2/3} \tag{2}$$

where m is the mercury flow-rate (g/sec), t the time of mercury drop-growth (sec) and A the instantaneous area of the drop at time t (cm^2). From equations (1) and (2) it follows that $I(\omega t)$ increases with the growth of the mercury drop, showing a dependence on $t^{2/3}$. Much of the theory for a.c. polarography has been derived for measurements made at the end of the drop-life[3] and maximum currents are normally used. This procedure will be adopted in this discussion and t will be taken as the drop-time. From equations (1) and (2) it follows that the ratio of the faradaic current for natural drop-time, $I(\omega t)_{\text{nat.}}$ to that for rapid drop-time $I(\omega t)_{\text{rap.}}$, under a chosen set of conditions and the same flow-rate of mercury for both experiments, is given by

$$[I(\omega t)_{\text{nat.}}]/[I(\omega t)_{\text{rap.}}] = [t_{\text{nat.}}]/[t_{\text{rap.}}]^{2/3} \tag{3}$$

This relationship was verified for the peak current (I_p) of several electrode processes and the considerable decrease in $I(\omega t)$ or I_p with increasing drop-time was confirmed.

The total alternating current is given by the vectorial sum of both faradaic and charging currents. At high frequencies the charging-current contribution, I_c, can become significant and may need to be considered in a discussion of iR effects. The charging current is given by the expression

$$I_c = \Delta E\,\omega \mathrm{C}_{\mathrm{dl}} \cos(\omega t) \tag{4}$$

where C_{dl} is the capacitance of the double layer. Since

$$C_{dl} \propto A \propto t^{2/3} \tag{5}$$

the charging current shows the same drop-time dependence as the faradaic current and the total alternating current will therefore also show a dependence on $t^{2/3}$.

An extremely important result from equations (1)–(5) is that the ratio of a.c. faradaic to a.c. charging current is independent of drop-time. This is an important feature of short drop-time a.c. polarography, because it implies that the use of short drop-times is not affected by unfavourable ratios of charging to faradaic current. This was confirmed by experiment over the drop-time range 5–0·05 sec. In contrast, the charging to faradaic current ratio becomes less favourable with shorter drop-time in d.c. polarography[2,10] and this is a limiting factor in the use of short drop-time d.c. polarography.

The uncompensated resistance of the electrochemical cell needs to be considered. The dependence of this term on drop-time will depend on the experimental arrangement.[36,39,40] If a simple two-electrode system is used, the total resistance, including that of the reference electrode, solution, and DME, *etc.* will be uncompensated. Under these conditions contribution of resistance terms varying with drop-time will depend on the exact nature of the experiment. However, with a three-electrode potentiostat system with or without positive-feedback circuitry, the uncompensated resistance terms are derived mainly from the solution resistance between the DME and the auxiliary electrode and the resistance of the DME itself. The uncompensated resistance is then expected to be dependent on drop-time. In the limiting case, assuming the appropriate equations to be valid for very short drop-times, it can be shown that the uncompensated resistance R varies inversely with the radius of the DME, r:[20]

$$R \propto 1/r \tag{6}$$

and since,

$$r \propto t^{1/3} \tag{7}$$

$$R \propto t^{-1/3} \tag{8}$$

in this limiting case.

The uncompensated resistance was measured over the drop-time range of 5–0·05 sec with a three-electrode system, and the predicted increase of resistance with decreasing drop-time was confirmed.

Since the alternating current shows dependence on $t^{2/3}$, the ohmic iR-drop should be dependent on drop-time raised to a power between the limits 1/3 and 2/3, and it follows that though the uncompensated resistance increases with decreasing drop-time, the iR-drop decreases. That is, when uncompensated resistance is significant, the rapid a.c. method should be less affected by this parameter.

The absolute magnitude of $I(\omega t)$ is also important in a discussion of ohmic losses. At high frequencies $I(\omega t)$ obviously increases and iR-losses must then be more important. Indeed it is well known[3] that the upper limit of usable a.c. frequency is governed by the magnitude of the iR-drop. Thus short drop-times should extend the accessible frequency range of a.c. polarography.

The d.c. current

The d.c. current, although not measured because it is filtered out, also needs to be considered. Its magnitude can be considered to be the same as in the absence of the superimposed alternating potential, and hence the diffusion current, i_d, is related to d.c. polarographic parameters by the Ilkovič equation,

$$i_d = k^* nCD^{1/2}m^{2/3}t^{1/6} \tag{9}$$

where k^* is a constant.

Thus i_d decreases only as $t^{1/6}$ and the d.c. iR-drop is therefore expected to depend on the drop-time raised to a power between 1/6 and $-1/6$ depending on the instrumentation used. The variation of the iR-drop with drop-time is therefore not particularly marked. Thus resistance effects are far more severe on the a.c. component than the d.c., and particularly with a three-electrode potentiostat d.c. ohmic loss can in general be considered negligible.

PRACTICAL ASPECTS

Three-electrode, phase-selective a.c. polarography at high frequency

Because ohmic losses are more severe at higher frequencies, the upper frequency limit is governed by the ability of the apparatus to minimize iR-losses. One important consequence of iR-drop is that it invalidates the use of simple theoretical phase-angle relationships between the faradaic and charging current components, both to each other and to the applied alternating potential.

Ideally, the charging current should be 90° out of phase from the input alternating potential, and measurement of the in-phase component should provide faradaic currents unencumbered by charging-current contributions. Ohmic losses however, cause departure from this relationship.

Figure 1 shows a series of in-phase a.c. polarograms of Cd(II) in 1*M* hydrochloric acid at 1000 Hz, recorded at natural drop-time and at controlled drop-times of 5, 2, 1, and 0·5 sec, under the same conditions.

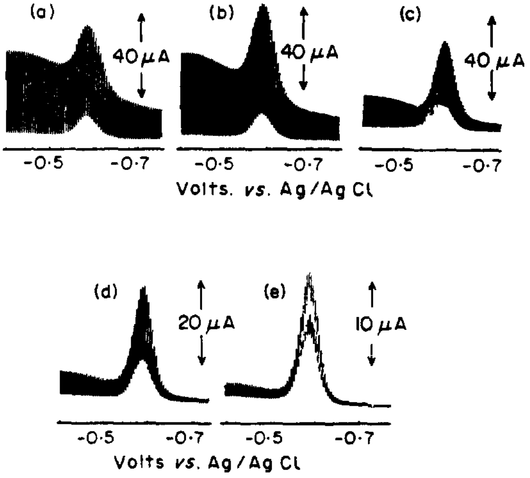

Fig. 1. Minimization of resistance effects in a.c. polarography by decreasing the drop-time. PAR Model 172 Drop Timer. [Cd] $3 \times 10^{-4}M$ in 1*M* hydrochloric acid. Three-electrode potentiostat system used without positive-feedback circuitry, ΔE = 10 mV, frequency 1 kHz.

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
Drop Time, *sec*	Natural	5	2	1	0·5
Scan-rate, *mV/sec*	1	1	2	5	10

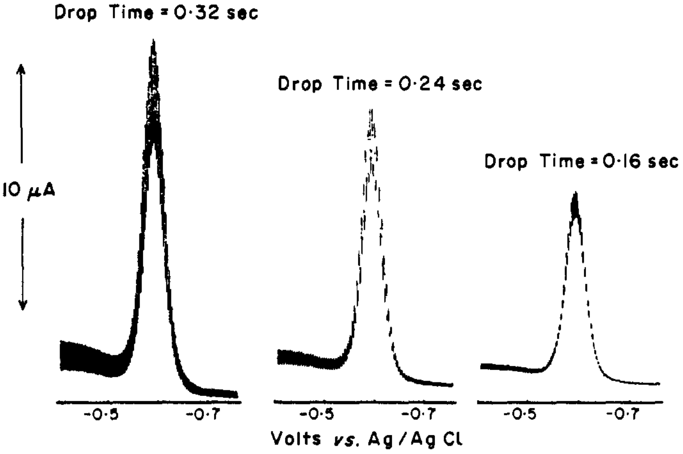

Fig. 2. Minimization of resistance effects in a.c. polarography by using short controlled drop-times. Metrohm Drop Timer. [Cd] $3 \times 10^{-4}M$ in $1M$ hydrochloric acid. Three-electrode potentiostat system used without positive-feedback circuitry. $\Delta E = 10$ mV, frequency 1 kHz.

The natural drop-time polarogram clearly has a considerable charging-current contribution to the in-phase component. The controlled drop-time polarograms clearly show the decreasing ratio of charging to faradaic current as the drop-time is shortened.

Figure 2 shows a.c. polarograms of the same Cd(II) solution at even shorter drop-times. At 0·16-sec drop-time, the contribution of the charging current is negligible and the behaviour is close to ideality, in agreement with theory.

Figure 3 shows that the positive-feedback circuit can be used to eliminate most of the charging current and achieve similar ideality to that in the short drop-time experiment and this verifies that the charging current in the experiments shown in Figs. 1 and 2 arises from uncompensated resistance effects present even with a three-electrode a.c. polarograph.

From these observations it is apparent that the operative capacity of any phase-sensitive, three-electrode a.c. polarograph can be improved considerably by using short controlled drop-times, especially the upper frequency limit. Indeed any form of a.c. polarography operated without 100% iR-compensation can be substantially improved by using

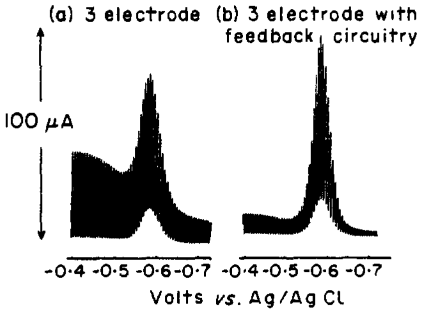

Fig. 3. Application of positive-feedback circuitry to eliminate resistance effects with natural drop-time a.c. polarography.
Metrohm Capillary. [Cd] $3 \times 10^{-4}M$ in $1M$ hydrochloric acid. $\Delta E = 10$ mV, scan-rate 2 mV/sec, frequency 1 kHz.

shorter drop-times. For the analyst this is an additional bonus to the use of considerably faster scan-rates.

Three-electrode a.c. polarography, positive-feedback circuitry, and high-resistance non-aqueous solvents

Figure 4 shows that the positive-feedback circuitry is as applicable to controlled drop-time a.c. polarography of the Cd(II) system as it is to the natural drop-time polarography. However, with any positive-feedback circuit there is always a limit to the magnitude of ohmic *iR*-drop effects than can be compensated.[18]

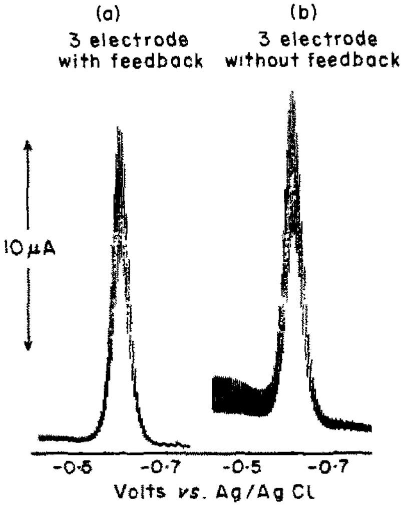

Fig. 4. Application of positive-feedback circuitry to controlled drop-time a.c. polarography. PAR Drop Timer. [Cd] $3 \times 10^{-4}M$ in $1M$ hydrochloric acid. $\Delta E = 10$ mV, scan-rate 10 mV/sec, frequency 1 kHz, drop-time 0·5 sec.

Figure 5 shows a.c. polarograms recorded at natural drop-time with a three-electrode system, both with and without positive-feedback circuitry for the electrode process

$$Na^+ + e \rightleftharpoons Na(amalgam) \qquad (10)$$

in the high-resistance solvent 0·01*M* tetraethylammonium perchlorate in acetone. This is a quasi-reversible a.c. electrode process with reversible d.c. charge-transfer. In a high-resis-

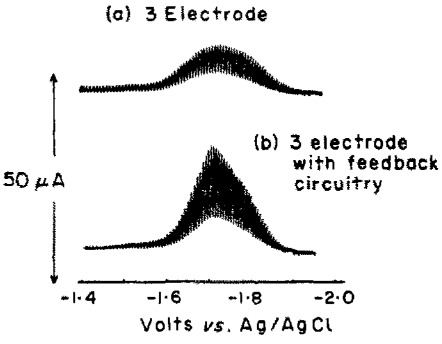

Fig. 5. Natural drop-time a.c. polarography in high-resistance non-aqueous solvents. Metrohm Capillary. Reduction of sodium in acetone. Frequency 500 Hz. $\Delta E = 10$ mV.

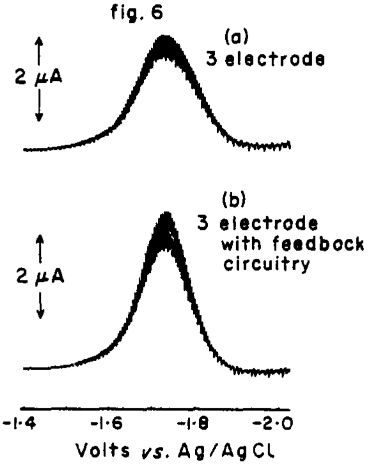

Fig. 6. Short controlled drop-time a.c. polarography in high-resistance non-aqueous solvents. Metrohm Drop Timer. Reduction of sodium in acetone. Controlled drop-time = 0·24 sec., other conditions identical with those for Fig. 5.

tance non-aqueous solvent uncompensated resistance effects are naturally extremely severe. The polarogram obtained at natural drop-time is highly distorted. Even with the positive-feedback circuitry being used to its maximum compensating capacity, 100% *iR*-compensation is not achieved, as shown in Fig. 5. Figure 6 shows the equivalent a.c. polarograms obtained at a drop-time of 0·24 sec. Without the positive-feedback circuitry, the distortion due to ohmic losses is not nearly as severe as before. With positive-feedback circuitry and short drop-times, the distortion is removed.

Two-electrode a.c. polarography

Many a.c. polarographs used for analysis are of the two-electrode variety, where no *iR*-compensation is provided, and could benefit from the short drop-time technique. The PAR Electrochemistry System used in this work is readily adapted to the two-electrode mode. Figure 7 shows that two-electrode high-frequency polarography at short controlled drop-times is easily interpreted, which is certainly not the case under the usual operating conditions.

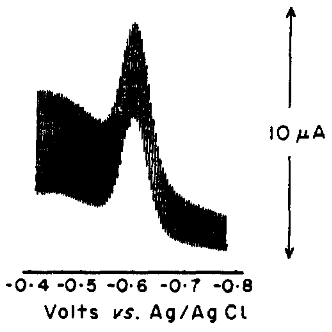

Fig. 7. High-frequency two-electrode a.c. polarography at short controlled drop-time. Conditions as for Fig. 4.

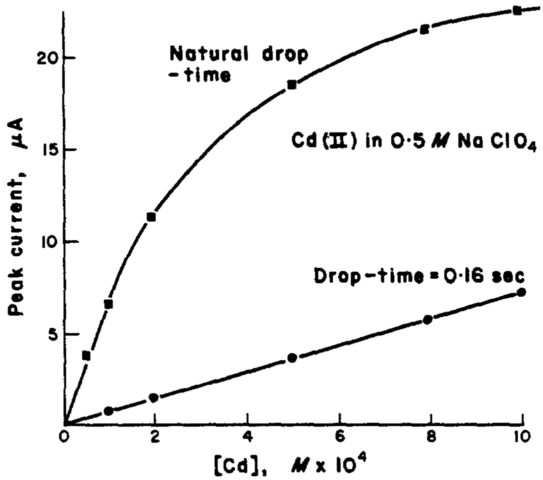

Fig. 8. Improved linearity of calibration curves obtained in a.c. polarography by using short drop-times.
Metrohm polarographic system. Frequency = 50 Hz. Applied alternating potential = 50 mV, r.m.s.

Considerable curvature in calibration curves commonly occurs in two-electrode a.c. polarography. Figure 8 shows a comparison of an analytical calibration curve under natural and controlled drop-time conditions; the difference is a direct consequence of differences in ohmic losses. The same considerations apply to three-electrode systems, particularly in non-aqueous solvents, and linear calibration curves are to be expected over wider concentration ranges with short drop-time a.c. experiments.

Potentiostat and DME stability

One further possible problem with high-frequency a.c. polarography is that it can induce difficulties associated with potentiostat instability. Examination of the theory[29] predicts that the shorter drop-time, with its associated low double-layer capacity, should in fact lead to an increase in stability. This has also been observed experimentally.

Similarly, examination of current–time curves shows that under many operating conditions the noise level is lowest early on in the drop-life and maximal late in the drop-life. Thus rapid polarographic measurements are frequently made at a point in the drop-life where noise is at a minimum. In general it would appear that rapid polarographic measurements are made under the most favourable conditions of both potentiostat and DME stability as well as with minimum ohmic losses.

Conclusions

The present work has shown that with the use of short drop-times in a.c. polarography every aspect studied is either improved or is at least as good as with natural drop-times. Previous work[8,10] has established that standard theory can be used with the technique.

In addition to its obvious advantages in analytical applications, the wide variation of the drop-time (the d.c. term) will undoubtedly assist in kinetic studies, especially on systems perturbed by subsequent chemical reactions, inhibition by adsorption, or maxima. Preliminary measurements of the second harmonic of the a.c. polarogram have shown that this technique will also benefit from the use of short controlled drop-times.

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Zusammenfassung—Die Leistungsfähigkeit der Wechselstrompolarographie mit kurzer Tropfzeit wurde im einzelnen untersucht und in fast jeder Hinsicht der mit natürlicher Tropfzeit überlegen gefunden. Die unkompensierten Widerstandsanteile sind kleiner und die Stabilität des Potentiostaten wird verbessert. Ferner ist ein schnellerer Potentialvorschub und schnellere Datenerfassung möglich. Eine Änderung der Tropfzeit über wenigstens vier Größenordnungen ist möglich; dies, zusammen mit einer hervorragenden Leistung des Geräts, sollte bei elektrodenkinetischen Untersuchungen erheblichen Spielraum bieten.

Résumé—On a examiné en détail la performance de la polarographie en courant alternatif à court temps de goutte, et on l'a trouvée être meilleure que celle pour les temps de goutte naturels à presque tous les points de vue. Les termes de résistance non compensés sont plus petits et la stabilité du potentiostat est améliorée. De plus, des vitesses d'exploration de potentiel plus rapides et une acquisition plus rapide des données sont possibles. Une variation du temps de goutte sur au moins quatre ordres de grandeur est possible et ceci, combiné à l'excellente performance instrumentale, devrait offrir une portée considérable dans les études de cinétique d'électrode.

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SHORT COMMUNICATIONS

DETERMINATION OF LEAD IN STAINLESS STEEL BY ATOMIC-ABSORPTION SPECTROSCOPY

(*Received* 7 *September* 1973. *Accepted* 29 *December* 1973)

The methods of determination of traces of lead in carbon and stainless steels are mainly based on polarographic[1–4] or colorimetric techniques.[5–7] The methods are time-consuming and difficult to carry out as a result of the complicated separations necessary for the elimination of interfering elements. Atomic-absorption spectrometry, owing to its selectivity and rapidity, eliminates most of these difficulties.

Atomic absorption has already been applied for the determination of lead in different grades of carbon steels,[8,9] but the method has been found tedious in the case of stainless steels,[10,11] because the large quantities of alloying elements make it necessary to separate the lead, either by solvent extraction[10] or ion-exchange.[11] The laboriousness of these operations reduces the inherent advantages of the atomic-absorption technique.

In this work, an atomic-absorption method for traces of lead is described, which is shorter although it still requires solvent extraction of the iron.

EXPERIMENTAL

Apparatus

A Perkin–Elmer atomic-absorption spectrophotometer model 403 was used with a lead hollow-cathode lamp run at 30 mA. A wavelength of 283·3 nm and a bandpass of 0·7 nm were used. A standard Perkin–Elmer premix burner was used with the air–acetylene ratios recommended by Perkin–Elmer, rotameter readings 60 and 40, respectively. A 6 × scale-expansion was used.

Reagents

Standard solution of lead (100 *ppm*). Dissolve 0·1598 g of $Pb(NO_3)_2$ in water and dilute to 1000 ml.

Standard solution of lead (10 *ppm*). Dilute the 100 ppm standard tenfold.

All the reagents were analytical-reagent grade.

Method

The sample is placed in a 250 ml beaker (1 or 2 g according to whether the lead content is greater or less than 25 ppm), and 30 ml of *aqua regia* are added. The beaker is heated with care, and when the reaction is complete, the solution is cooled and filtered, after which the filtrate is evaporated to dryness. The residue is taken up with 50 ml of 6·7 *M* hydrochloric acid, transferred to a separating funnel and extracted with 50 ml of methyl isobutyl ketone. (In the case of a 2 g sample, the extraction is repeated.) The aqueous phase is transferred to a 250 ml beaker which is then placed on a hot-plate and 15 ml of nitric acid are added. When the reaction is over, 25 ml of perchloric acid are added, and heating is continued until white fumes of perchloric acid are given off; the solution becomes red. Hydrochloric acid is added dropwise, until the red fumes of chromyl chloride cease to be given off. The solution becomes green. Heating is continued until white perchloric fumes are given off, and the treatment with hydrochloric acid is repeated. This operation must be repeated until the formation of the red colour on heating to fuming and the giving off of red fumes on the addition of a drop of hydrochloric acid are no longer noted.

The residue is allowed to cool, the salts are taken up with 25 ml of hydrochloric acid (1 + 4), the solution is filtered into a standard flask (50 ml) and made up to volume with hydrochloric acid (1 + 4) before atomic-absorption measurement.

Calibration curve

The calibration curve is determined by adding different quantities (0–20 ml) of the dilute solution of lead to 1 or 2 g of lead-free stainless steel (according to the lead content to be determined) and proceeding according to the method.

Interferences

The determination of lead at the 5–10 ppm level in stainless steels by atomic absorption with an air–acetylene flame is not subject to interferences of a chemical nature.[12] There are, however, interferences of a physical nature,

Table 1. Typical composition of the samples analysed

Sample	Composition, %												
	C	Si	Mn	P	S	Cu	Cr	Ni	V	Mo	Co	Ta	Nb
BCS 334	0·079	0·45	0·85	0·012	0·022	0·10	25·60	20·60	0·04	—	0·052	—	—
BCS 335	0·093	0·67	0·94	0·018	0·023	0·11	18·45	9·47	0·04	—	0·034	0·0017	—
BCS 336	0·083	0·51	0·81	0·020	0·023	0·11	17·60	9·48	0·03	2·43	0·063	—	—
BCS 337	0·081	0·50	0·87	0·016	0·018	0·10	17·80	9·52	0·02	—	0·034	0·048	1·02
CSM 4	0·560	0·51	1·45	0·030	0·014	—	18·45	8·60	—	0·22	—	—	<0·01
CSM 5	0·560	0·52	1·45	0·030	0·014	—	18·45	8·60	—	0·22	—	—	<0·01
CSM 8	0·560	0·52	1·45	0·030	0·014	—	18·45	8·60	—	0·22	—	—	<0·01

due to the presence in the solution to be examined by large quantities of dissolved salts. In this context, the interferences due to iron, chromium, nickel and molybdenum have been taken into consideration for the analysis of stainless steels.

As the solution drawn into the flame must not contain more than 1–2 g of sample per 100 ml of solution, since higher concentrations cause disturbance of the measurements, it is necessary to separate the iron. Among the methods tried for the extraction of iron, the most promising was that using methyl isobutyl ketone, but it did not allow the separation of nickel and chromium. The presence of these two elements still made a precise determination of lead impossible, and in addition, the interference effect could not be correlated with the concentration of these elements in the solution. Chromium was therefore eliminated by means of volatilization as chromyl chloride,[13] and the interference due to nickel was found to be practically independent of the nickel concentration within the range encountered in stainless steels. To control this interference, it is thus sufficient to construct the calibration curve by use of a stainless steel free from lead.

Up to 2·5% of molybdenum in the steel does not interfere.

DISCUSSION AND CONCLUSIONS

The method proposed was checked on a series of standard BCS stainless-steel samples, and on a synthetic sample prepared in the laboratory by adding quantities of nickel and chromium (corresponding to their average

Table 2. Results obtained for lead

Sample	Value certified, %	Value found, %	Deviation %
BCS 334	0·0011	0·0010	−9
BCS 335	0·0015	0·0014	−6·7
BCS 336	0·0007	0·0006	−14
BCS 337	0·0012	0·0010	−16
BCS 326 + 20% Cr +	0·014	0·0147	+5
+ 10% Ni		0·0149	+6·4
		0·0149	+6·4
		0·0150	+7·1
CSM 4	(0·0020)	0·0019	−5
		0·0022	+10
		0·0021	+5
		0·0021	+5
		0·0018	−10
CSM 5	(0·0125)	0·0132	+5·6
		0·0120	−4·0
		0·0127	+1·6
		0·0122	−2·4
		0·0119	−4·8
CSM 8	(0·0050)	0·0057	+14
		0·0054	+8
		0·0055	+10
		0·0052	+4

contents in stainless steels) to BCS 326 (carbon steel). The analysis was also extended to some samples produced at the CSN for the calibration of the "Quantometer",[14] and standardized by means of a polarographic method.[1]

The composition of the samples is shown in Table 1, and the results in Table 2. The experimental results are in satisfactory agreement with the certified values. The estimated standard deviations are ± 1·6 ppm at the 20 ppm level and ± 5·4 ppm at the 125 ppm level.

The method may be considered quite rapid (it takes about 3 hr) compared with the methods already given in the literature. In addition, in contrast to the methods based on solvent extraction of the lead and subsequent determination by atomic absorption, it has the advantage of having the lead in aqueous medium when the measurements are made. The disturbances often encountered when working with organic solvents such as aliphatic ketones are thus avoided.

The removal of the chromium, which considerably reduces the amount of solids dissolved in the solution, allows reduction of the final volume, and a consequent lowering of the detection limit.

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Summary—A method has been developed for the determination of lead in stainless steels by atomic-absorption spectrometry after removal of iron by solvent extraction and volatilization of chromium as chromyl chloride. The method proposed is suitable for the determination of lead in the range from 5 to 100 ppm.

Zusammenfassung—Ein Verfahren zur Bestimmung von Blei in rostfreiem Stahl wurde entwickelt. Es beruht auf Atomabsorptionsspektrometrie nach Entfernung des Eisens durch flüssigflüssig-Extraktion und Verflüchtigung von Chrom als Chromylchlorid. Das vorgeschlagene Verfahren eignet sich zur Bestimmung von Blei im Bereich 5–100 ppm.

Résumé—On a élaboré une méthode pour le dosage du plomb dans les aciers inoxydables par spectrométrie d'absorption atomique après élimination du fer par extraction par solvant et volatilisation du chrome à l'état de chlorure de chromyle. La méthode proposée convient pour le dosage du plomb dans le domaine de 5 à 100 ppm.

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PHASE-TITRATION ANALYSIS OF TERNARY MIXTURES CONTAINING MUTUALLY MISCIBLE COMPONENTS

(*Received* 25 *July* 1973. *Revised* 28 *November* 1973. *Accepted* 21 *January* 1974)

Phase titrations have been used for many years to analyse a variety of binary liquid mixtures composed of organic solvents.[1–3] Although the methods have had only sporadic use in the past, detailed studies of the technique in general have been made by Rogers and Özsoğomoyan,[4] who have applied the technique to over 100 binary systems. Siggia and Hanna[5] were the first to use the technique for the analysis of single-phase ternary mixtures containing two mutually immiscible components. In their method, one of the components was determined independently. A separate sample was then titrated with one of the mutually immiscible components until a turbidity appeared. The composition of the sample was then computed from the ternary phase diagram for the particular system. Recently, Suri[6,7] developed procedures for the analysis of single-phase ternary mixtures containing two mutually immiscible or partially miscible components, entirely by phase titrations.

In the present communication, a method for the analysis of ternary mixtures of mutually miscible components is described. It involves the determination of one of the components by an independent chemical or physical means, followed by adjustment of its concentration to a fixed value by addition of a calculated amount of one of the components. The resultant mixture is then titrated to a turbidimetric end-point with a titrant that is immiscible with at least one of the components of the ternary mixture, and the composition of the sample is computed from a calibration curve.

THEORY

Consider a mixture of A, B, and C, which are completely miscible with each other over the entire composition range. A titrant, T, is selected such that it is immiscible (or partially miscible) with one component, *e.g.*, A, but miscible with both the others. The binodal curves for the ternary mixtures A–B–T and A–C–T will look like Fig. 1. Binary mixtures made up of A and B or of A and C can thus be analysed by phase titration with T.[8] For the analysis of these mixtures, the titration value as a function of binary composition yields calibration curves of the type shown in Fig. 2.

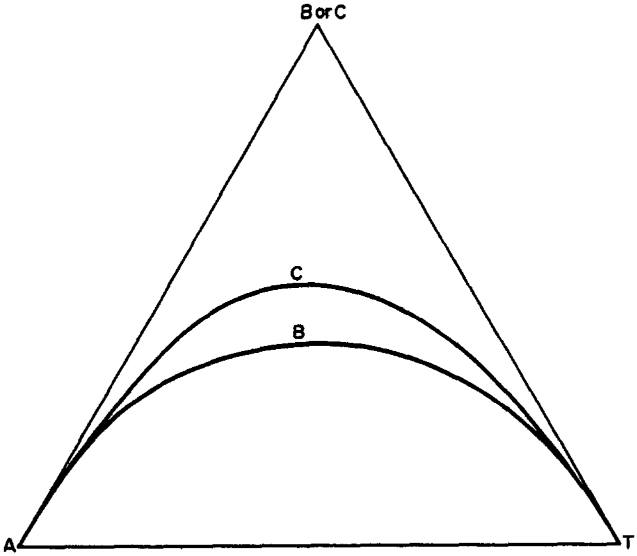

Fig. 1. Ternary liquid–liquid miscibility diagram for the systems A–B–T and A–C–T.

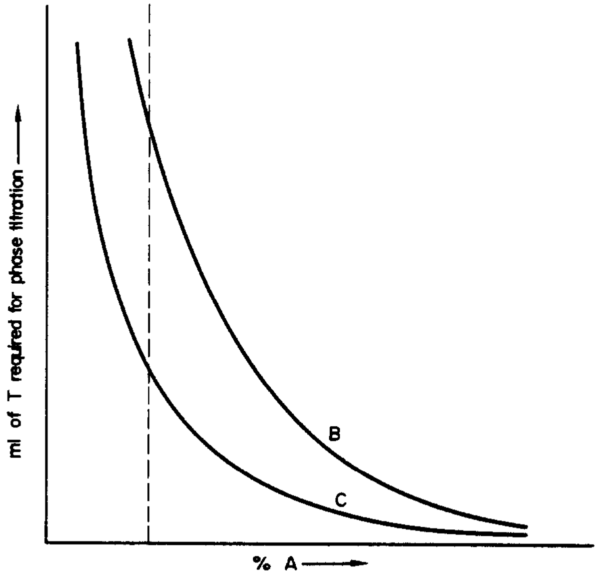

Fig. 2. Calibration curves for the analysis of binary mixtures of A and B, and A and C titrated with T to a turbidimetric end-point.

The two curves (Fig. 2) have a tendency to converge as the binary composition approaches pure A. If instead of titrating binary mixtures of A and B or A and C with T, we titrate a ternary mixture of A, B, and C with T, the titration value will fall in the area between the two calibration curves and is a function of the composition of the ternary mixture, *i.e.*,

$$[T] = f\{[A],[B],[C]\}. \qquad (1)$$

Since the summation of the three components must be 100% at the beginning of the titration, [T] is a function of only two of the variables on the right-hand side of equation (1) and hence the locus of the amount of T required

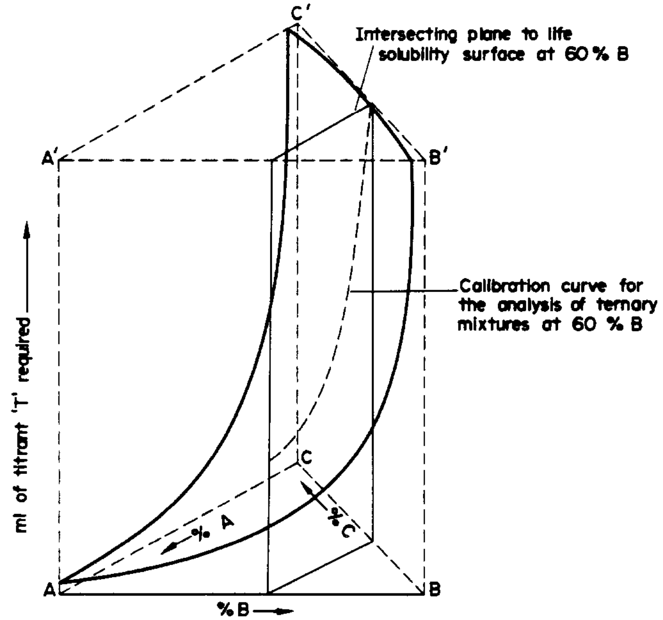

Fig. 3. The solubility surface for the ternary mixture A–B–C titrated with T.

to produce a turbidimetric end-point, as a function of the composition of the ternary mixture being titrated, is a three-dimensional surface of the type shown in Fig. 3, where the two calibration curves of Fig. 2 lie on the $AA'C'C$ and $AA'B'B$ planes respectively. The Z-axis represents the amount of titrant, T, required to cause turbidity. Since both B and C are completely miscible with T only a part of the solubility surface is shown. The two calibration curves on the $AA'C'C$ and $AA'B'B$ planes and hence the solubility surface for the system A,B,C,T meet the plane $BCC'B'$ at infinity. The intersection of the solubility surface with a plane perpendicular to the triangle ABC and parallel to any of the planes $BB'C'C$, $AA'C'C$ or $AA'B'B$ (corresponding to some fixed fraction of the component A, B, or C respectively) gives the titre value as a function of the relative amounts of the other two components in the ternary mixture at that particular fixed fraction of third component. Figure 3 shows the calibration curve for mixtures of A and C with 60% of B.

To analyse a homogeneous mixture of A, B, and C, of which one component, say A, is being determined by an independent physical or chemical procedure, a set of synthetic binary mixtures of B and C covering the entire composition range is prepared. A is then added to these binary mixtures so that its concentration (% w/w) in all the resultant ternary mixtures is the same (x%). These solutions are titrated with T to the turbidimetric end-point and a calibration curve for ml of titrant required per unit weight of the ternary is obtained as a function of %B (or %C). The unknown sample is analyzed for A. To a separate sample enough of one of the components is added to make the content of A x% w/w. A known weight of this mixture is titrated with T to the turbidimetric end-point and %B (or %C) in it obtained from the calibration curve. The composition of the original unknown can then be computed if the component immiscible with the titrant is the component determined by independent means, or if the two components other than the one being determined by independent means are immiscible with the titrant. The concentration of this component used for calibration purposes should be the value at which there is greatest separation between the two curves of Fig. 2 (represented by the dashed vertical line). For other systems it should be the value which covers the widest range of the titration values: this is found by drawing calibration curves at 3 or 4 different values for this component and comparing the ranges of titration value.

Table 1. Experimental data for calibration curve at 30°C
Solutions of benzene–methyl alcohol–acetic acid titrated with water

55% w/w acetic acid		65% w/w acetic acid		75% w/w acetic acid	
Benzene, % w/w	T*	Benzene, % w/w	T*	Benzene, % w/w	T*
9·46	0·641	3·70	1·458	5·12	0·943
14·11	0·423	7·37	0·805	7·66	0·676
18·74	0·307	11·02	0·529	10·19	0·498
23·31	0·237	14·63	0·380	12·70	0·409
27·84	0·193	18·23	0·306	15·22	0·328
32·33	0·155	21·80	0·247	17·71	0·280
36·77	0·129	25·34	0·211	20·18	0·238
41·18	0·105	28·85	0·180	22·66	0·205
44·62	0·093	32·34	0·151	25·00	0·178
—	—	34·81	0·132	—	—

Solutions of benzene–toluene–acetic acid titrated with water

55% w/w acetic acid		75% w/w acetic acid	
Benzene, % w/w	T*	Benzene, % w/w	T*
0·00	0·063	0·00	0·131
4·58	0·065	2·56	0·1355
9·15	0·0665	5·03	0·141
13·72	0·0685	7·55	0·145
18·28	0·0705	10·06	0·151
22·84	0·0715	12·50	0·156
27·39	0·0735	15·08	0·161
32·02	0·076	17·59	0·1665
36·50	0·079	20·10	0·172
41·03	0·084	24·40	0·182

T* = ml of water required to produce turbidity in 1 g of ternary mixture.

EXPERIMENTAL

The method described is illustrated for the analysis of ternary mixtures composed of benzene–methanol–acetic acid and benzene–toluene–acetic acid, with water as titrant.

The solvents were purified according to standard procedures.[9] Their densities and refractive indices showed good agreement with the values reported in the literature.[9,10] The water used as titrant was distilled immediately before use. The experimental details of the phase titrations and the apparatus have already been described.[6]

Sets of each of the two ternary mixtures were prepared, both having fixed acetic acid concentration. A known weight (corresponding to $\sim$100 ml) of each of these mixtures was titrated with water to the turbidimetric end-point and the calibration curves were drawn for titrant volume as a function of benzene concentration (Table 1).

Then two sets of synthetic ternary mixtures were prepared, and the acetic acid in them was determined independently by titration with sodium hydroxide solution. The acetic acid concentration was then adjusted to 65% w/w for the methanol set and to 75% w/w for the toluene set. A known weight (corresponding to $\sim$100 ml) of each resultant mixture was then titrated with water to the turbidimetric end-point and its composition computed from the calibration curve. The composition of the original ternary mixture was then calculated.

Table 2. Comparison of the actual and estimated composition of the ternary mixtures

Sample no.	Acetic acid, %		Benzene, %	
	Present	Estimated	Present	Estimated
Solutions of benzene–methyl alcohol–acetic acid				
1	11·84	11·8	79·25	79·5
2	17·84	17·7	59·74	60·4
3*	20·77	20·8	28·63	27·5
4*	41·29	41·9	9·87	9·2
5	45·61	45·8	28·58	29·0
6	49·94	50·1	41·76	41·6
7*	69·56	69·3	22·39	22·4
8*	87·66	87·7	6·90	7·4
Solutions of benzene–toluene–acetic acid				
1	11·73	11·6	78·56	74·9
2	17·47	17·7	58·46	59·0
3	19·79	19·9	27·29	25·2
4	39·41	39·2	9·42	10·2
5	44·81	44·3	27·87	29·1
6	49·50	49·4	41·42	40·7
7	69·02	68·9	22·21	21·0
8*	87·20	87·0	6·87	6·9

* Samples diluted with benzene before titrating with water to turbidimetric end-point.

RESULTS AND DISCUSSION

The results obtained are compared with the actual values in Table 2. Although a new assistant did the phase titrations, the agreement between the actual and the determined values was excellent for the methanol system, the maximum error being less than 1%. The agreement for the toluene system was not so good, but still tolerable for many purposes, the difference being less than 3% in most cases.

Although the method described is fairly precise for routine analysis, not requiring elaborate instrumentation, it is less time-consuming only when one of the components of the ternary mixture can be independently and rapidly determined. The method has, however, the same limitations and errors as other phase titrations.[6]

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Zusammenfassung—Ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische zus gegenseitig mischbaren Komponenten wird beschrieben. Eine der Komponenten wird unabhängig auf chemischem oder physikalischem Wege bestimmt und dann seine Konzentration im ursprünglichen Gemisch durch Zugabe einer berechneten Menge einer der drei Komponenten auf einen festgelegten Wert gebracht. Das resultierende Gemisch wird dann mit einem Titranten, der mit einer der Komponenten nicht mischbar ist, bis zum turbidimetrischen Endpunkt titriert und die Zusammensetzung der Probe mit Hilfe einer Eichkurve berechnet. Das Verfahren wird an der Analyse von Benzol-Methanol–Essigsäure- und Benzol–Toluol–Essigsäure–Gemischen veranschaulicht.

Résumé—On décrit une méthode, basée sur le titrage de phase, pour l'analyse de mélanges ternaires composés de constituants mutuellement miscibles. L'un des composants est déterminé par un moyen chimique ou physique indépendant et sa concentration dans le mélange initial est alors amenée à une valeur fixée par addition d'une quantité calculée de l'un des trois constituants. Le mélange résultant est alors titré au point de fin de dosage turbidimétrique avec un agent de titrage qui n'est pas miscible avec l'un des constituants et la composition de l'échantillon est calculée à partir d'une courbe d'étalonnage. La méthode est illustrée par son application à des mélanges benzène–méthanol-acide acétique et benzène-toluène-acid acétique.

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THE SELECTIVITY OF A MACROTETROLIDE ELECTRODE TOWARDS ORGANIC ONIUM IONS

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An attempt to detect organic onium ions with an NH_4^+-electrode has led to the present work. The need for a fast and accurate direct determination of the organic derivatives of ammonium is significant in several applications such as clinical research, water monitoring, fertilizers and ion-exchange processes.

In order to extend the scope of the recently developed NH_4^+-electrode in analytical and organic analysis, the response of the electrode towards the ions NH_4^+, Me_1^+, Et_1^+, Pr_1^+, Bu_1^+, Me_2^+, Me_3^+, Me_4^+, Et_4^+, Bu_4^+, CyH^+,

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Zusammenfassung—Ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische zus gegenseitig mischbaren Komponenten wird beschrieben. Eine der Komponenten wird unabhängig auf chemischem oder physikalischem Wege bestimmt und dann seine Konzentration im ursprünglichen Gemisch durch Zugabe einer berechneten Menge einer der drei Komponenten auf einen festgelegten Wert gebracht. Das resultierende Gemisch wird dann mit einem Titranten, der mit einer der Komponenten nicht mischbar ist, bis zum turbidimetrischen Endpunkt titriert und die Zusammensetzung der Probe mit Hilfe einer Eichkurve berechnet. Das Verfahren wird an der Analyse von Benzol-Methanol–Essigsäure- und Benzol–Toluol–Essigsäure–Gemischen veranschaulicht.

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(*Received* 18 *December* 1973. *Accepted* 30 *December* 1973)

An attempt to detect organic onium ions with an NH_4^+-electrode has led to the present work. The need for a fast and accurate direct determination of the organic derivatives of ammonium is significant in several applications such as clinical research, water monitoring, fertilizers and ion-exchange processes.

In order to extend the scope of the recently developed NH_4^+-electrode in analytical and organic analysis, the response of the electrode towards the ions NH_4^+, Me_1^+, Et_1^+, Pr_1^+, Bu_1^+, Me_2^+, Me_3^+, Me_4^+, Et_4^+, Bu_4^+, CyH^+, PipH$^+$, Na$^+$, K$^+$ and Cs$^+$ was studied, the symbols Me$^+$, Et$^+$, Pr$^+$, Bu$^+$, CyH$^+$ and PipH$^+$ referring to methyl-, ethyl-, propyl-, cyclohexylammonium and piperidinium ions, and the subscripts 1, 2, 3 and 4 denoting the mono-, di-, tri- and tetra-derivatives.

EXPERIMENTAL

The potentiometric determinations of these cations were made with a Philips IS 560-NH$_4^+$ electrode and a Philips R44-2 SD/1 double-junction reference electrode, and an Orion digital pH meter (Model 801). All these measurements were carried out over a 10^{-1} to 10^{-5} *M* concentration range and at a pH of 5·5 ± 0·5.

The response curves at 23° for the different organic cations, obtained by plotting the electrode potential (*E*) *vs.* concentration, are shown in Fig. 1. The slopes of these curves, which represent the electrode sensitivity for the particular cations, reveal in the linear portion that the sensitivity is almost constant for all the organic cations used in this work.

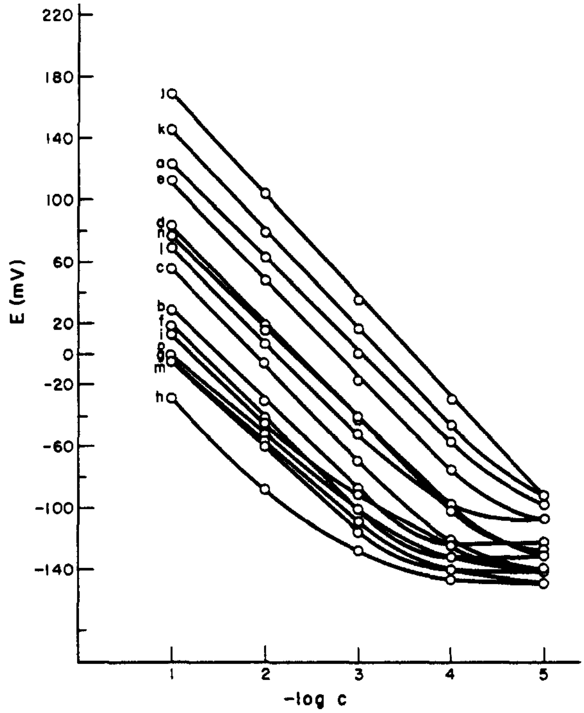

Fig. 1. Response curves at 23°C for aqueous solutions in a concentration range of 10^{-1}–10^{-5}*M*. (a) NH_4Cl; (b) CH_3NH_3Cl; (c) $C_2H_5NH_3Cl$; (d) $C_3H_7NH_3Cl$; (e) $C_4H_9NH_3Cl$; (f) $(CH_3)_2NH_2Cl$; (g) $(CH_3)_3NHCl$; (h) $(CH_3)_4NCl$; (i) $(C_2H_5)_4NCl$; (j) $(C_4H_9)_4NCl$; (k) cyclohexylammonium hydrochloride; (l) piperidinium hydrochloride.

In practice, the knowledge of the selectivity constant K_{ij} is a more useful quantitative tool to predict whether a given ion-selective electrode may be used in the presence of known interferences. Generally, the influence of any interfering ion can be checked by the Nicolsky equation:[1]

$$E = E_0' + \frac{2.3\,RT}{z_i F}\log\left[a_i + \sum_{j=1}^{N} K_{ij}(a_j)^{z_i/z_j}\right] \qquad (1)$$

where *E* is the measured potential of the electrode (mV), E_0' is the zero-potential of the system, *R* is the gas constant, *T* is the absolute temperature, *F* is the Faraday, and a_i, a_j and z_i, z_j are the sample activity levels and valencies of the ions of interest (*i*) and of the interfering ions (*j*), respectively.

Approximate E_0' values for the different organic cations, obtained from the *E* values at a concentration of 10^{-1}*M*, are plotted in Fig. 2. These E_0' values reflect also the affinity of the cations for the electrode membrane.

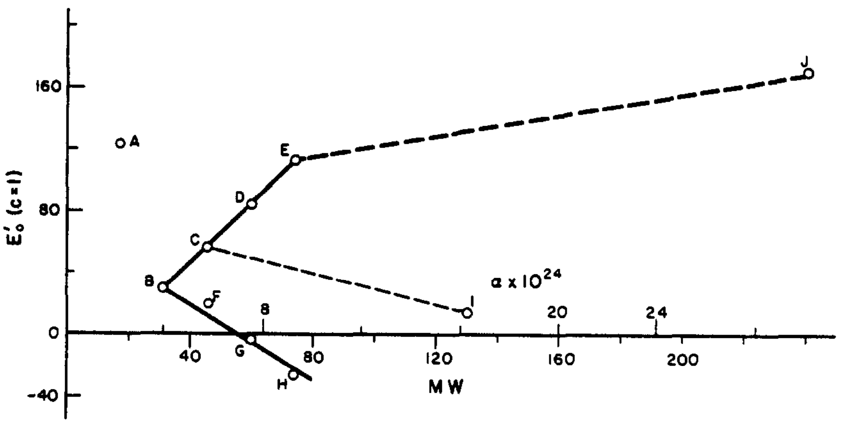

Fig. 2. The zero potential (E'_0) for the different organic cations as a function of the molecular weight (MW) and polarizability (α). (A) NH_4^+; (B) $CH_3NH_3^+$; (C) $C_2H_5NH_3^+$; (D) $C_3H_7NH_3^+$; (E) $C_4H_9NH_3^+$; (F) $(CH_3)_2NH_2^+$; (G) $(CH_3)_3NH^+$; (H) $(CH_3)_4N^+$; (I) $(C_2H_5)_4N^+$; (J) $(C_4H_9)_4N^+$.

This figure shows a linear relationship between E'_0 and the molecular weight or polarizability of the cations within a homologous series. Probably, the complexation of the ions in the electrode membrane is influenced by inductive effects, created by the alkyl chain of the organic cations. We are studying this problem in more detail.

The selectivity of the electrode is a measure of the extent to which the macrocyclic molecules in the electrode membrane sequester cations in competition with solvent molecules. The atomic factors involved in the origin of the equilibrium specificity are described by Eisenman.[2]

The selectivity coefficients for the organic cations used in this work were determined by two methods.

A. The method proposed by Eisenman, Rudin and Casby.[3] They defined the coefficient as the difference between the ion-selective potentials at identical concentrations of two ions in solution, which can be expressed as:

$$\log K_{ij} = \frac{(E_2 - E_1) z_i F}{2.3 RT} \tag{2}$$

B. The selectivity coefficient can also be defined as the ratio of the activities which give rise to identical potentials in their respective separate solutions (method of Rechnitz):[4]

$$\log K_{ij} = \left(\frac{a_j}{a_i}\right)^* \tag{3}$$

where the asterisk serves as a reminder that the activity generates the same response. The selectivity coefficients determined by those two methods are summarized in Table 1.

The values of the selectivity constants are roughly parallel with the E'_0 potentials for the different alkylammonium ions. However, these constants pronounce more the influence of the interfering cations in mixed solutions. Where the K_{ij} is large, the potential cannot be expected to be sensitive to small activities of interfering ions. The selectivity sequence with respect to interfering ions, observed in this work, is $Bu_4^+ > CyH^+ > NH_4^+ > Bu_1^+ > Pr_1^+ > K^+ > PipH^+ > Et_1^+ > Me_1^+ > Me_2^+ > Et_4^+ > Cs^+ > Na^+ > Me_3^+ > Me_4^+$.

Furthermore, a comparison between the selectivity constants obtained with a Philips IS 560 electrode and that used by Scholer *et al.*,[5] reveals that the electrode used in this work is more suitable for a selective determination of the organic cations in mixed solutions (Table 1). Both electrodes have an extremely high affinity for tetrabutylammonium ions. Therefore, the electrode potentials were measured in tetrabutylammonium solutions over a pH range from 4 to 10 (Fig. 3). These potentials varied by only 5 mV in this pH range.

Table 1 The selectivity constants obtained with a Philips IS 560 NH_4^+-electrode

Ion (j)	$K^R_{NH_4^+-j}$	log $K^R_{Cs^+-j}$	$K^E_{NH_4^+-j}$
NH_4^+	1	2	1
Bu_4^+	7·03	3.50 (7·2)[5]	4·824
CyH^+	1·66	2·27	1·88
Bu_1^+	0·54	1·78	0·56
Pr_1^+	0·186	1·32	0·18
K^+	0·186	1·32 (−1·4)[5]	0·18
$PipH^+$	0·12	1·12	0·113
Et_1^+	0·07	0·90	0·07
Me_1^+	0·03	0·53	0·028
Me_2^+	0·018	0·30	0·019
Et_4^+	0·015	0·23 (3·5)[5]	0·016
Na^+	0·008	0·05 (−2·9)[5]	0·0089
Me_3^+	0·008	0·05 (1·7)[5]	0·010
Me_4^+	0·00445	0·30	0·0031

K^R and K^E denote the selectivity constants obtained by the methods of Rechnitz and Eisenman ($C = 10^{-2}M$), respectively.

This study indicates that the recently developed NH_4^+-electrode can be used, not only to determine selectively NH_4^+ in aqueous solutions but also large organic onium ions. A preliminary study showed that even nucleosides such as solutions of cytosine could be determined. This behaviour of the electrode is very important for biological, clinical and pollution researches and might in many cases replace the distillation and titration steps in the Kjeldahl method.

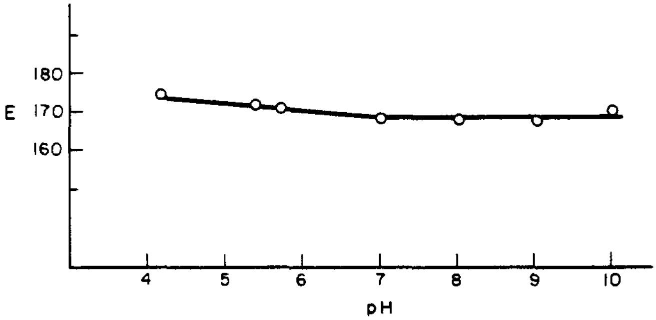

Fig. 3. The experimental potential (E) as a function of the pH for a $10^{-1}M$ aqueous solution of $(C_4H_9)_4NCl$.

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Summary—The selectivity for ammonium and some of its alkyl derivatives has been experimentally determined for a liquid-membrane ammonium electrode.

Zusammenfassung—An einer Ammoniumelektrode mit flüssiger Membran wurde die Selektivität für Ammonium und einige seiner Alkylderivate experimentell ermittelt.

Résumé—On a déterminé expérimentalement la sélectivité pour l'ammonium et quelques-uns de ses dérivés alkylés d'une électrode à ammonium à membrane liquide.

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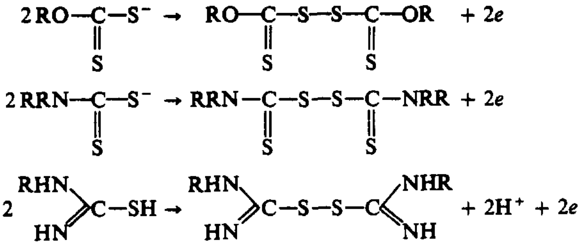
OXIDIMETRIC DETERMINATION OF THIOUREA–XANTHATE AND THIOUREA–DITHIOCARBAMATE MIXTURES

(*Received* 5 *December* 1973. *Accepted* 5 *January* 1974)

Xanthates, dithiocarbamates and thioureas have considerable industrial, medicinal and analytical importance. The determination of these compounds is therefore of interest. Oxidation of xanthates, dithiocarbamates and thioureas, mostly to the corresponding dixanthogens, thiuram disulphides and formamidine disulphides, have been extensively used for their determination.



$$2\,\mathrm{RO{-}\underset{\underset{S}{\|}}{C}{-}S^-} \rightarrow \mathrm{RO{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}OR} + 2e$$

$$2\,\mathrm{RRN{-}\underset{\underset{S}{\|}}{C}{-}S^-} \rightarrow \mathrm{RRN{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}NRR} + 2e$$

$$2\,\mathrm{\genfrac{}{}{0pt}{}{RHN}{HN}{\!\!>\!}C{-}SH} \rightarrow \mathrm{\genfrac{}{}{0pt}{}{RHN}{HN}{\!\!>\!}C{-}S{-}S{-}C{<\!\!}\genfrac{}{}{0pt}{}{NHR}{NH}} + 2H^+ + 2e$$

Though efforts have been made to develop methods which are applicable to the analysis of pure samples of each compound, little attention appears to have been directed towards analysing mixtures.

In the course of our investigations on the oxidimetric determination of organosulphur compounds in non-aqueous media, we found that xanthates and dithiocarbamates could be smoothly, rapidly and quantitatively titrated in acetonitrile medium with iodine monobromide[1] solution in acetonitrile, at room temperature. Thioureas failed to react with the oxidant in this medium but can be quantitatively oxidized with iodine monobromide in aqueous acidic medium.[2] These observations have been exploited to develop simple and accurate methods for the analysis, in the same sample solution, of thiourea–xanthate and thiourea–dithiocarbamate mixtures. The mixture-solution in acetonitrile is first titrated with iodine monobromide solution in acetonitrile. The titrated solution is then acidified with aqueous acid and titrated again with the oxidant. No indicator is required in either titration; the end-point is signalled by the production of iodine (yellow colour) by the first drop of oxidant in excess. Both titrations can also be followed potentiometrically. The non-aqueous titration corresponds to the amount of xanthate (or dithiocarbamate) and the aqueous titration gives the amount of thiourea present.

EXPERIMENTAL

Reagents

Acetonitrile. Distilled twice from phosphorus pentoxide (5 g/l).

Iodine monobromide, 0·05N *in acetonitrile.* The solid compound was prepared by the method of Popov and Skelly.[3] The standard solution was prepared by dissolving a little more than the calculated amount in acetonitrile. The solution was standardized iodometrically in aqueous medium and stored in the dark.

Summary—The selectivity for ammonium and some of its alkyl derivatives has been experimentally determined for a liquid-membrane ammonium electrode.

Zusammenfassung—An einer Ammoniumelektrode mit flüssiger Membran wurde die Selektivität für Ammonium und einige seiner Alkylderivate experimentell ermittelt.

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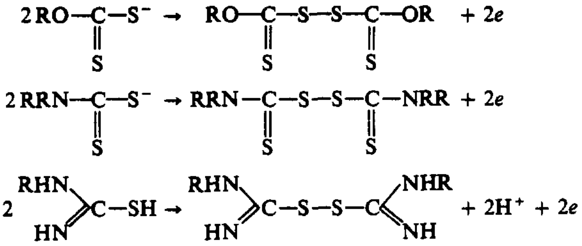

$$2\,\mathrm{RO{-}\underset{\underset{S}{\|}}{C}{-}S^-} \rightarrow \mathrm{RO{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}OR} + 2e$$

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In the course of our investigations on the oxidimetric determination of organosulphur compounds in non-aqueous media, we found that xanthates and dithiocarbamates could be smoothly, rapidly and quantitatively titrated in acetonitrile medium with iodine monobromide[1] solution in acetonitrile, at room temperature. Thioureas failed to react with the oxidant in this medium but can be quantitatively oxidized with iodine monobromide in aqueous acidic medium.[2] These observations have been exploited to develop simple and accurate methods for the analysis, in the same sample solution, of thiourea–xanthate and thiourea–dithiocarbamate mixtures. The mixture-solution in acetonitrile is first titrated with iodine monobromide solution in acetonitrile. The titrated solution is then acidified with aqueous acid and titrated again with the oxidant. No indicator is required in either titration; the end-point is signalled by the production of iodine (yellow colour) by the first drop of oxidant in excess. Both titrations can also be followed potentiometrically. The non-aqueous titration corresponds to the amount of xanthate (or dithiocarbamate) and the aqueous titration gives the amount of thiourea present.

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Table 1. Determination of ethyl thiourea and potassium ethyl xanthate in admixture

Amount of ethyl thiourea in mixture, *mg*	Amount found, *mg**		Amount of potassium-ethylxanthate in mixture, *mg*	Amount found, *mg**		Ratio of ethyl thiourea to potassium ethyl xanthate
	Visual method	Potentiometric method		Visual method	Potentiometric method	
10·00	10·02, 0·076	9·96, 0·048	10·00	10·04, 0·043	10·03, 0·041	1:1
10·00	10·06, 0·055	10·01, 0·049	20·00	20·12, 0·078	20·08, 0·063	1:2
10·00	9·97, 0·044	9·98, 0·036	30·00	29·93, 0·055	29·95, 0·047	1:3
10·00	10·03, 0·067	10·00, 0·022	40·00	40·18, 0·086	29·92, 0·068	1:4
20·00	19·96, 0·088	20·00, 0·069	10·00	10·03, 0·071	10·00, 0·045	2:1
30·00	30·25, 0·072	30·12, 0·038	10·00	10·06, 0·058	9·99, 0·044	3:1
40·00	39·80, 0·078	39·90, 0·026	10·00	10·02, 0·077	9·97, 0·056	4:1

* Mean of five determinations, and standard deviation.

Table 2. Determination of ethyl thiourea and sodium diethyldithiocarbamate in admixture

Amount of ethyl thiourea in mixture, *mg*	Amount found, *mg**		Amount of sodium diethyldithiocarbamate in mixture, *mg*	Amount found, *mg**		Ratio of ethyl thiourea to sodium diethyldithiocarbamate
	Visual method	Potentiometric method		Visual method	Potentiometric method	
10·00	9·95, 0·066	9·96, 0·048	10·00	9·93, 0·052	9·95, 0·047	1:1
10·00	10·03, 0·067	10·02, 0·036	20·00	19·92, 0·092	19·94, 0·064	1:2
10·00	10·02, 0·075	9·99, 0·028	30·00	29·88, 0·068	30·08, 0·043	1:3
10·00	9·92, 0·065	9·96, 0·043	40·00	40·32, 0·081	40·21, 0·051	1:4
20·00	20·15, 0·058	19·88, 0·036	10·00	10·06, 0·084	10·02, 0·041	2:1
30·00	30·25, 0·076	30·16, 0·024	10·00	10·03, 0·076	9·98, 0·057	3:1
40·00	39·80, 0·078	39·90, 0·026	10·00	10·04, 0·065	9·99, 0·048	4:1

* Mean of five determinations, and standard deviation.

Xanthates. Prepared by mixing equimolar quantities of the corresponding alcohols, potassium hydroxide (dissolved in minimum quantity of water) and carbon disulphide, at a temperature below 10°C. The compounds were recrystallized twice by dissolving in acetone and precipitating with petroleum ether (60–80°C).

Diethyldithiocarbamates. Commercial products or prepared by reported methods.[4,5]

The purity of xanthates and dithiocarbamates was checked by known methods.

Thioureas. Recrystallized thiourea was used. The derivatives of thiourea were prepared from their corresponding isothiocyanates by condensation with ammonia.[6]

All other reagents were of guaranteed quality.

Procedure

Aliquots of solutions (in acetonitrile) of synthetic mixtures with different ratios of thiourea and xanthate (or dithiocarbamate) were taken in titration flasks and diluted to 20–25 ml with the solvent. The solutions were titrated at room temperature (20°C) with standard (0·05N) iodine monobromide (in acetonitrile) added from a microburette provided with a guard-tube for protection from atmospheric moisture. The end-point was signalled by the yellow tint imparted to the solution by the first drop of oxidant in excess. The titrated solutions were mixed with 75 ml of 1M sulphuric acid. The acidified thiourea–dithiocarbamate solutions were heated at 70–75°C for about 10 min, then cooled to room temperature before titration. The acidified solutions were titrated again with the same iodine monobromide solution to the appearance of a yellow tint. The end-point could also be detected by using amylose (0·2 ml of 1% aqueous solution), the solution turning blue at the end-point.

Both the non-aqueous and aqueous titrations were also performed potentiometrically. In non-aqueous titrations, a bright platinum wire was used as indicator electrode and a modified calomel electrode (saturated methanolic solution of potassium chloride instead of saturated aqueous solution) as reference electrode. The titrations in aqueous medium were performed with a platinum electrode and a saturated aqueous calomel electrode.

RESULTS AND DISCUSSION

The results recorded in Table 1 show that synthetic mixtures of ethyl thiourea and potassium ethyl xanthate with ratios in the range from 1:4 to 4:1 can be analysed by visual and potentiometric titration with a relative standard deviation of 0·4%. The method has also been extended to other mixtures such as thiourea/potassium ethyl xanthate, n-propyl thiourea/potassium n-propyl xanthate, isopropyl thiourea/potassium isopropyl xanthate, n-butyl thiourea/potassium n-butyl xanthate, isobutyl thiourea/potassium isobutyl xanthate, n-amyl thiourea/potassium n-amyl xanthate, which have been analysed with the same accuracy. Synthetic mixtures of ethyl thiourea and sodium diethyldithiocarbamate over the same ratio range can be titrated visually and potentiometrically with a relative standard deviation of 0·3% (for ethyl thiourea) and 0·4% (for sodium diethyldithiocarbamate) (Table 2). The method has also been applied to the analysis of thiourea/sodium diethyldithiocarbamate, n-propyl thiourea/sodium n-propyldithiocarbamate, isobutyl thiourea/sodium isobutyldithiocarbamate, methyl thiourea/sodium dimethyldithiocarbamate mixtures, with similar accuracy.

The proposed methods, besides being simple, accurate and reliable have the added advantage that analysis can be conducted on the same sample solution, resulting in saving in time and effort. Iodine monochloride solution in acetonitrile can be equally satisfactorily used in place of iodine monobromide but the latter is preferred as it is more stable.[1] Use of a saturated aqueous calomel electrode gave fluctuations in potential when used in acetonitrile medium. The modified calomel electrode has already been found to be a suitable reference electrode in oxidimetric titrations in acetonitrile medium.[1,7]

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Summary—A convenient and accurate method has been developed for the analysis of thiourea-xanthate and thiourea-dithiocarbamate mixtures by oxidimetric titration of the mixture with iodine monobromide first in acetonitrile medium and then in acidic aqueous acetonitrile medium. The end-points can be detected both visually and potentiometrically. The methods are rapid and have wide applications.

Zusammenfassung—Eine bequeme und genaue Methode zur Analyse von Gemischen aus Thioharnstoff und Xanthat sowie aus Thioharnstoff und Dithiocarbamat wurde entwickelt. Dabei wird das Gemisch zuerst in Acetonitril und dann in saurem wäßrigem Acetonitril oxidimetrisch mit Jodmonobromid titriert. Die Endpunkte können visuell oder potentiometrisch bestimmt werden. Die Methoden gehen schnell und sind vielseitig verwendbar.

Résumé—On a élaboré une méthode commode et précise pour l'analyse de mélanges thiourée-xanthate et thiourée-dithiocarbamate par titrage oxydimétrique du mélange avec le monobromure d'iode d'abord en milieu acétonitrile puis en milieu acétonitrile aqueux acide. Les points de fin de dosage peuvent être détectés tant visuellement que potentiométriquement. Les méthodes sont rapides et ont de larges applications.

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EXTRACTIONS WITH LONG-CHAIN AMINES—VIII

COLORIMETRIC DETERMINATION OF CHROMIUM(VI) WITH DIPHENYLCARBAZIDE

(*Received* 20 *November* 1973. *Accepted* 6 *January* 1974)

In an earlier work,[1] we described the highly selective extraction of chromium(VI) with a chloroform solution of trioctylmethylammonium chloride (Aliquat 336-S) from sulphuric acid medium, by which chromate can be quantitatively separated from all the common elements with the exception of molybdenum(VI), uranium, vanadium(V), gold and the platinum metals. The yellow chloroform extract is measured spectrophotometrically at 445–450 nm. The sensitivity of the method is quite low and allows the determination of chromium in the range 26–200 μg/ml; thus it is not suitable for small traces of chromium, *e.g.*, in waters *etc.* The sensitivity of the determination can be considerably increased if we employ a sufficiently sensitive reaction for the isolated chromate. In this work we have chosen the reaction with diphenylcarbazide.

In preliminary experiments we found that the reaction with diphenylcarbazide can be carried out directly in the chloroform extract, which has the advantage that only part of the extract need be used. Under optimal conditions, described below, the determination is highly selective for the determination of chromium in the presence of other elements (M) in ratios of 1:40,000 (Cr:M).

EXPERIMENTAL

Reagents

A 5% solution of methyltrioctylammonium chloride (Aliquat 336-S) (General Mills Chemicals, Inc., Kankakee, Illinois, U.S.A.) was prepared by dissolving 50 g of the material in 1000 ml of chloroform.

A $1 \times 10^{-2}M$ Cr(VI) solution was prepared by dissolving 1·9419 g of p.a. K_2CrO_4 in 1000 ml of water. A $10^{-4}M$ solution was prepared by dilution of the stock solution.

A saturated solution of sodium sulphate and $1M$ solution of sulphuric acid were prepared from p.a. chemicals, as were $5 \times 10^{-2}M$ solutions of the accompanying cations as the sulphates.

Summary—A convenient and accurate method has been developed for the analysis of thiourea–xanthate and thiourea–dithiocarbamate mixtures by oxidimetric titration of the mixture with iodine monobromide first in acetonitrile medium and then in acidic aqueous acetonitrile medium. The end-points can be detected both visually and potentiometrically. The methods are rapid and have wide applications.

Zusammenfassung—Eine bequeme und genaue Methode zur Analyse von Gemischen aus Thioharnstoff und Xanthat sowie aus Thioharnstoff und Dithiocarbamat wurde entwickelt. Dabei wird das Gemisch zuerst in Acetonitril und dann in saurem wäßrigem Acetonitril oxidimetrisch mit Jodmonobromid titriert. Die Endpunkte können visuell oder potentiometrisch bestimmt werden. Die Methoden gehen schnell und sind vielseitig verwendbar.

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COLORIMETRIC DETERMINATION OF CHROMIUM(VI) WITH DIPHENYLCARBAZIDE

(*Received* 20 *November* 1973. *Accepted* 6 *January* 1974)

In an earlier work,[1] we described the highly selective extraction of chromium(VI) with a chloroform solution of trioctylmethylammonium chloride (Aliquat 336-S) from sulphuric acid medium, by which chromate can be quantitatively separated from all the common elements with the exception of molybdenum(VI), uranium, vanadium(V), gold and the platinum metals. The yellow chloroform extract is measured spectrophotometrically at 445–450 nm. The sensitivity of the method is quite low and allows the determination of chromium in the range 26–200 μg/ml; thus it is not suitable for small traces of chromium, *e.g.*, in waters *etc.* The sensitivity of the determination can be considerably increased if we employ a sufficiently sensitive reaction for the isolated chromate. In this work we have chosen the reaction with diphenylcarbazide.

In preliminary experiments we found that the reaction with diphenylcarbazide can be carried out directly in the chloroform extract, which has the advantage that only part of the extract need be used. Under optimal conditions, described below, the determination is highly selective for the determination of chromium in the presence of other elements (M) in ratios of 1:40,000 (Cr:M).

EXPERIMENTAL

Reagents

A 5% solution of methyltrioctylammonium chloride (Aliquat 336-S) (General Mills Chemicals, Inc., Kankakee, Illinois, U.S.A.) was prepared by dissolving 50 g of the material in 1000 ml of chloroform.

A $1 \times 10^{-2}M$ Cr(VI) solution was prepared by dissolving 1·9419 g of p.a. K_2CrO_4 in 1000 ml of water. A $10^{-4}M$ solution was prepared by dilution of the stock solution.

A saturated solution of sodium sulphate and $1M$ solution of sulphuric acid were prepared from p.a. chemicals, as were $5 \times 10^{-2}M$ solutions of the accompanying cations as the sulphates.

Extraction of chromate

Since the above-described reaction of chromate with diphenylcarbazide was studied in solution in the presence of Aliquat 336-S, it is necessary to mention the conditions for the extraction of chromate into a chloroform solution of this amine. The extraction from sulphuric acid medium with a 5% Aliquat solution in chloroform is quantitative. The efficiency of the extraction is not demonstrably affected by changes in the sulphuric acid concentration from 0·02 to 0·5*M*.

Reaction of chromate with diphenylcarbazide

As already noted, a chromate–Aliquat solution reacts directly with solid diphenylcarbazide (DPC) in the presence of dilute sulphuric acid. An intense red colour, deepening with time, appears either immediately or after a short time, depending on the chromium concentration. This qualitative observation was studied quantitatively and all factors affecting formation of the colour were determined.

Dependence on the amounts of DPC and sulphuric acid. Into 100 ml separating funnels were pipetted 2 ml of $1 \times 10^{-4}M$ chromate (10·4 μg of Cr) and this was diluted with water to 50 ml, and 5 ml of saturated sodium sulphate solution and 10 ml of 1*M* sulphuric acid were added. The solution was extracted by shaking for 2 min with 5 ml of a 5% chloroform solution of Aliquat. The chloroform phase was transferred to another separating funnel to which were added 4·5 ml of water and 0·5 ml of 1*M* sulphuric acid, followed by 25, 50 or 100 mg of diphenylcarbazide. After being shaken for 1 min the organic phase was filtered into cuvettes and the spectrum was measured in the visible region (the maximum was at 550 nm). Simultaneously, the time-dependence of the colour intensity was studied; the colour became more intense faster in the presence of large amounts of DPC. With 100 mg of DPC, the maximum absorbance was attained after 20 min. The colour then decreased very slowly (about 10% in 40 min) ($A_{20} = 0{\cdot}550$; $A_{60} = 0{\cdot}500$).

In the second series of experiments, 100 mg of DPC were used and the concentration of sulphuric acid was changed so that progressively 0, 1, 2, 3 and 5 ml of 1*M* sulphuric acid, diluted to 5 ml with water, were added to the chloroform extract. It was found that the concentration of sulphuric acid in the range given is without effect on the colour intensity, which again reaches a maximum value after 20 min. However, the absorbance was lower in the absence of sulphuric acid.

From these experiments followed the basic conditions for the photometric determination of chromate after its extraction with Aliquat. The chloroform extract containing chromate must be shaken for 2 min with an equal volume of 0·1–0·2*M* sulphuric acid in the presence of 100 mg of diphenylcarbazide, filtered through dry filter paper into a 1-cm cuvette, and measured at 550 nm after 20 min with an Aliquat solution as reference. Beer's law is obeyed over the range up to 13 μg of chromium. The molar absorptivity was calculated to be $2{\cdot}2 \times 10^4$ $\mathrm{l.mole^{-1}.cm^{-1}}$ and the Sandell sensitivity to be 0·0022 $\mu g/cm^2$.

The effect of anions

Interference from anions is important only during the chromate extraction and was studied in detail in the previous communication.[1] The extraction is not affected by high concentrations of chloride (10% NaCl) or medium concentrations of phosphate (2% K_2HPO_4). Sulphate improves the separation of the phases. Oxalate interferes. The presence of nitrate (3% KNO_3) renders the extraction impossible. Since the colour reaction is carried out after separation of the organic phase, the effect of anions on it was not studied.

The effect of cations

In the colorimetric determination of chromate,[1] interference from common cations was not observed. In spite of this, a number of determinations of chromium(VI) in the presence of these elements were carried out, concentrating mainly on those which, if extracted, could interfere, even in traces, through their reaction with diphenylcarbazide (Fe, Cu, *etc.*). It was found that even high concentrations of a large number of elements do not interfere in the determination. Solutions in which the ratio of chromium to the accompanying element was as

Table 1. The determination of chromium in the presence of other metals

Content of various metals, *mg*	Chromium taken, μg	Cr, %	Chromium found, μg
25 Fe, 15 Ni, 15 Co 13 Al, 16 Zn, 14 Mn, 16 Cu Total: 114 mg	2·6	0·0023	2·5
	2·6		2·3
	5·2	0·0046	4·5
	5·2		5·0
	7·8	0·0069	7·7
	7·8		7·7
100 Fe, 60 Ni, 60 Co, 52 Al, 64 Zn, 56 Mn, 64 Cu Total: 456 mg	2·6	0·00057	2·4
	5·2	0·00114	4·8

low as 1:40,000 (0·0025% Cr), were analysed. The following elements were without affect: iron, nickel, cobalt, manganese, zinc, aluminium and chromium(III) (see Table 1). Up to 10 mg of titanium and 50 mg of molybdenum do not interfere in the determination.

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1. J. Adam and R. Přibil, *Talanta*, 1971, **18**, 91.

Summary—Traces of chromium(VI) are extracted from sulphuric acid solution into a chloroform solution of trioctylmethylammonium chloride. After the addition of solid diphenylcarbazide to the separated organic phase, a red colour is developed and is measured spectrophotometrically at 550 nm. A great number of common metals, including iron and copper, do not interfere when present in ratios up to at least 1:40,000 (chromium:metal).

Zusammenfassung—Spuren von Chrom(VI) werden aus schwefelsaurer Lösung in eine Lösung von Trioctylmethylammoniumchlorid in Chloroform extrahiert. Nach Zugabe von festem Diphenylcarbazid zu der abgetrennten organischen Phase entwickelt sich eine rote Farbe, die spektrophotometrisch bei 550 nm gemessen wird. Eine große Anzahl häufig vorkommender Metalle, darunter Eisen und Kupfer, stören im Verhältnis bis zu mindestens 1 : 40.000 (Chrom : Metall) nicht.

Résumé—On extrait des traces de chrome (VI) d'une solution en acide sulfurique dans une solution chloroformique de chlorure de trioctylméthylammonium. Après addition de diphénylcarbazide solide dans la phase organique séparée, il se développe une coloration rouge qui est mesurée spectrophotométriquement à 550 nm. A grand nombre de métaux communs, y compris le TOPO en méthylisobutylcétone. Le temps pour une analyse complète y compris la dissolution moins jusqu'à 1 : 40.000 (chrome : métal).

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APPLICATION OF THE GRAPHITE FURNACE TO THE DETERMINATION OF TRACE IRON IN GOLD AND SILVER

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There is a growing interest in the influence of rare-earth metals on transport phenomena in metallic gold and silver. Several transition metals interfere, and iron does so most strongly. The iron content of the metals should be less than 1 ppm and preferably be known within 0·1 ppm. At this level the iron atoms are inhomogeneously distributed and so the samples of which the transport properties have been measured, must be analysed. These samples weigh about 50–100 mg, and spectrographic analysis is not sufficiently accurate. The substoichiometric isotope-dilution technique requires at least 100 mg of sample, and does not allow replicate analysis or the determination of a second element in the same solution.

Atomic-absorption spectroscopy using a flame as the absorption cell requires at least 2 ml of solution for nebulization. As a result, from a sample of 50 mg of silver or gold containing 1 ppm of iron, a solution can be obtained containing at most 0·03 ppm of iron, which is below the detection limit. On the other hand, atomic-low as 1:40,000 (0·0025% Cr), were analysed. The following elements were without affect: iron, nickel, cobalt, manganese, zinc, aluminium and chromium(III) (see Table 1). Up to 10 mg of titanium and 50 mg of molybdenum do not interfere in the determination.

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Atomic-absorption spectroscopy using a flame as the absorption cell requires at least 2 ml of solution for nebulization. As a result, from a sample of 50 mg of silver or gold containing 1 ppm of iron, a solution can be obtained containing at most 0·03 ppm of iron, which is below the detection limit. On the other hand, atomic-absorption analysis using a graphite furnace as absorption cell is satisfactory, having the advantages of a higher sensitivity, small sample size allowing replicate analyses, and a simple pretreatment. Samples can be treated *in situ* by heating them in the furnace before atomization. This can be extended to quite high temperatures, thus avoiding the production of fumes during the measurement. In inorganic analysis the pretreatment mainly serves for the removal of excess of acid and the decomposition of the metal salts into oxides or metal. This procedure is followed for nearly all metals, which implies that no special preparation procedure is necessary for a solution in which several elements have to be determined. In most cases the use of a deuterium background correction is superfluous with a well-selected temperature programme.

Under normal conditions the detection limit for iron can be assumed to be 10 pg (for a signal to noise ratio of unity), corresponding to a concentration limit of 5 ng in 10 ml, when 20 μl aliquots are injected into the furnace. If the required accuracy is $\pm 0{\cdot}1$ ppm of iron in the noble metal, it follows that 50 mg of the noble metal are required for every 10 ml of sample solution. In practice the standard-addition method is applied in order to eliminate interferences. Three solutions are sufficient as the curvature of the calibration curve is small. In practice 20–30 mg per 10 ml is satisfactory, and the 50–100 mg samples available in the research programme were sufficiently large. It is possible to decrease the volume of the solution, from which the 20 μl aliquots are withdrawn, to 2 ml, but the gain in sensitivity is usually more than offset by a loss in accuracy and reliability, as the manipulations become more complicated. Amounts smaller than 50 mg cannot be analysed with an error smaller than 0·1 ppm.

EXPERIMENTAL

The analytical work was done with a Perkin–Elmer Model 303 atomic-absorption spectrophotometer equipped with an HGA72 graphite furnace and a deuterium background corrector. The optimum operating conditions for drying, ashing and atomization were established so as to give the best reproducibility. The wavelength setting varied slightly with time and had to be checked frequently. Argon was used as the purge gas for the furnace and nitrogen as the purge gas for the monochromator. In order to protect the apparatus against corrosion from the evaporating acids hollow rings were mounted on both sides of the furnace through which the fumes were extracted by means of a water-pump. All injections were 20 μl in volume, and made with Eppendorf micropipettes. It was found that 50 μl quantities, when compared with 20 μl quantities containing the same amount of iron, systematically show a lower recorder response. The explanation is that a 50 μl volume spreads out in the tube during the drying stage; it renders possible a loss of mass through the open tube ends, before the measurements of the light absorption is completed.

The micropipettes had disposable tips, but could be used repeatedly. Their precision was better than 2%. The sample solutions were usually injected four times. In a few cases significant deviations occurred. These measurements were repeated, as contamination was responsible in nearly all cases. No memory effects were encountered with the temperature programme used. The graphite tube was replaced when the slope of the calibration graph decreased by more than 10% (after about 200 injections).

Measurement

Two basic procedures can be used: the calibration-curve and the standard-addition methods. The calibration method was used to obtain rapid approximate results and was nearly always used before the standard-addition analysis. Generally the latter method is necessary if matrix interference, co-precipitation and adsorption are expected. At least three solutions were prepared for each sample. The sample content was found in the normal way from the intersection of the extrapolated curve and the line through the blank values.

Temperature programme

Iron shows the largest sensitivity and the best signal-to-noise ratio in a sulphuric acid medium. Other acids present need not be removed in advance. If a sufficient amount of sulphuric acid is present these acids can be expelled with a temperature programme properly adapted to the amount of sulphuric acid present in the tube. Throughout our experiments the following programme was used for 20 μl portions of 0·2*M* sulphuric acid (*a*) 30 sec at 80°, (*b*) 30 sec at 150°, (*c*) from 150 to 600° in 12 sec, (*d*) 30 sec at 1200° and (*e*) 10 sec at 2540°. [For 20 μl of sulphuric acid (1:1) the programme (*a*) 30 sec, (*b*) 60 sec, (*c*) 30 min, (*d*) 5 min and (*e*) 10 sec with the same temperatures as above, should be used.] The peak heights are independent of the sulphuric acid content.

The sensitivity for iron decreases when too much silver or gold is present in the solution. The peak area remains approximately constant, which suggests that the larger amounts of salt in the matrix reduce the escape of iron atoms from the tube wall; the iron atoms are confined to a layer and because of its thickness too much time is required for evaporation. The limit is about 10 μg of gold and silver (20 μl of a 500 ppm solution). This problem cannot be solved by changing the temperature programme. Consequently at least 99·9% of these metals must be removed when a 50 mg sample containing 1 ppm of iron has to be analysed. The separation procedure is described below: gold is reduced to the metal with sulphur dioxide and silver is precipitated as silver chloride.

Contamination

Iron is one of the most severely contaminating elements in a laboratory. It is necessary to carry out all the sample manipulations with the object of preventing iron contamination. As a rule it is more effective to reduce the number of manipulations and consequently to work somewhat less precisely, than to take extensive precautions. For a determination with the graphite furnace the overall error generally lies between 5 and 10%. Other manipulations with a precision of 2% or better will not appreciably affect the overall accuracy of the determinations. For instance, a centrifuge-tube marked at 10 ml can be filled with a precision of 1%, so it can serve as centrifuge-tube, reaction-vessel and volumetric flask. Moreover its mouth is wide enough for contact between the presumably contaminated upper part and the tips of the pipettes to be avoided during sampling and addition of reagents. Another simplification is achieved as follows. The samples need to be etched in order to remove the surface iron-contamination and then weighed. This can all be done in one preweighed beaker. After etching, which additionally cleans the internal surface of the beaker, the liquid is removed by repeatedly adding ultrapure water and decanting. The beaker with the sample is then dried with an electric heater, cooled, and weighed with an error of less than 0·5 mg. Finally the sample is dissolved in the same beaker. Thus the weight is known with an error of about 1% and the sample did not leave the beaker during the etching, weighing and dissolving stage, thus minimizing the risk of contamination.

The glassware is initially cleaned in a dichromate and sulphuric acid mixture, rinsed with water and stored in 5*M* hydrochloric acid. The disposable tips of the micropipettes are clean from the manufacturer. As sometimes the time between injections is several minutes, contamination from airborne particulate matter may occur. Therefore cleaning by filling three times with 1*M* hydrochloric acid before the injections is advisable.

Reagents

The acids used were of Suprapur grade (Merck, Germany). The stock solutions all satisfied the manufacturer's tolerances with regard to iron (Table 1). The water was purified by sub-boiling distillation of demineralized water in a quartz distillation apparatus.[1] The gold and silver samples were Johnson–Matthey "Specpure" and Cominco Electronic Materials (Montreal), high-purity grade. The sulphur dioxide was laboratory grade from Matheson Gas Products.

Table 1.

Material	Fe found, *ng/ml*	Tolerance, *ng/ml*
HCl	19	25
H_2SO_4	<5	35
HNO_3	10	50
Water	2	—

Separation procedure for gold

The etched sample, weighing about 80 mg, is dissolved in 200 μl of concentrated nitric acid and a few drops of concentrated hydrochloric acid. The solution is evaporated till syrupy. Then 5 drops of concentrated sulphuric acid are added and the solution is heated till fuming. The volume is then negligible in comparison with the 20·0 ml of water which is then added. A small part of the gold may be precipitated but it does not interfere.

Three calibrated centrifuge tubes are filled with 6·0 ml of the gold solution, and 20 and 40 μl of a 12·5 ppm iron solution are added to two of them. Two extra tubes are taken for the blanks and filled with equivalent amounts of the acids. Then all the solutions are made up to 10·0 ml. Finally sulphur dioxide is passed into the solutions for 3 min. In the "zero-addition" tube the gold precipitates colloidally; in the other two sample-tubes the precipitate is coarser and darker. The gold is centrifuged to the bottom of the tube and 20 μl samples are withdrawn from the upper part of the solutions.

Separation procedure for silver

The etched sample, weighing about 80 mg, is dissolved in about 120 μl of concentrated nitric acid. The solution is evaporated to dryness and 20·0 ml of water are added.

Three calibrated centrifuge tubes are filled with 6·0 ml of this silver solution, and 20 and 40 μl portions of a 12·5 ppm iron solution are added to two of them and the solutions are thoroughly mixed by repeated drawing into and ejection from a pipette. Two extra tubes are taken for the blanks and filled with equivalent amounts of acid. To all solutions 0·5 ml of concentrated hydrochloric acid and 1 drop of concentrated sulphuric acid are added. Then all solutions are made up to 10·0 ml and mixed. To coagulate the silver chloride the tubes are heated on a water-bath for 1·5 hr. After cooling, the tubes are centrifuged to collect the suspended particles at the bottom of the tube. The 20 μl samples are withdrawn from the upper part of the solutions.

RESULTS AND DISCUSSION

In these procedures the standard amounts of iron are added before the bulk of the gold or silver is removed from solution. It was found that the curve giving the relation between absorbance and the weight of iron did not deviate significantly from a normal standard calibration curve, which shows that iron is not being co-precipitated. This has been proved with the aid of an iron tracer, the precipitates being found to show no radioactivity. The blank values agreed within the standard deviation with the values calculated from the iron contents of the acids and the water used (Table 1).

The results are given in Table 2 and agree with the manufacturer's specifications based on spectrographic estimations. An independent check with an alternative technique is not yet possible. Measurements at low temperatures of the electrical resistance of noble metals are anomalous, but this cannot be shown to be due to the presence of iron. The results are not proportional to iron concentration, because only homogeneously distributed iron is measured and iron clusters are not detected.

The relation between light absorbance and weight of iron (m) is almost linear and can be approximated by the first three terms in the series $A = a_0 + a_1m + a_2m^2$. A least-squares fit was performed with the aid of a computer, and the results did not deviate significantly from those obtained graphically. The precision obtained from the spread in the individual points was 7%, if each tube was sampled four times. This agreed with the value from a test procedure in which 2·5 g of silver were dissolved in 100 ml of acid and the iron content determined six times. The constants a_1 and a_2 do not alter very much from curve to curve and when only very small samples are available, a_1 and a_2 can be taken from a standard calibration curve.

Table 2.

Metal	Origin	Fe content given, *ppm*	Fe content found, *ppm*
Ag	Johnson–Matthey	2 ± 1*	4·8 ± 0·3†
	Johnson–Matthey	2 ± 1	4·5 ± 0·3
	Cominco	0·1 ± 0·1	0·2 ± 0·1
Au	Johnson–Matthey	1 ± 1	1·2 ± 0·1
	Cominco	0·1 ± 0·1	0·1 ± 0·1

* Uncertainty quoted on certificate.
† Standard deviation.

An attempt was made to determine other elements in one of the Cominco gold samples. Mn, Mg, Cu and Pb were not found: their contents all lay below their respective detection limits (Table 3). Silver was present at the level of 2 ppm. These results agreed with the specifications guaranteed by the manufacturers.

The method takes at most 3 hr to apply.

Table 3.

Metal	Estimated detection limits, *ppm*
Mn	0·1
Mg	0·5
Cu	0·3
Pb	0·5

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REFERENCE

1. E. C. Kühner, R. Alvarez, P. J. Paulsen and T. J. Murphy, *Anal. Chem.*, 1972, **44**, 2050.

Summary—Atomic-absorption analysis using a graphite furnace is a powerful technique for the determination of nanogram amounts of iron. It can be applied to the determination of traces of iron in gold and silver. These metals may be removed from solution by reduction to metallic gold and precipitation as silver chloride respectively. Iron is not co-precipitated. The iron content can be determined in 50–100 mg of the noble metals with an error of about 7% (or 0·1 ppm).

Zusammenfassung—Atomabsorptionsanalyse mit einem Graphitofen ist sehr nützlich bei der Bestimmung von Nanogrammengen Eisen. Sie kann auf die Bestimmung von Eisenspuren in Gold und Silber angewandt werden. Diese Metalle können durch Reduktion zu metallischem Gold bzw. durch Ausfällung als Silberchlorid aus der Lösung entfernt werden. Eisen wird nicht mitgefällt. Der Eisengehalt kann in 50–100 mg der Edelmetalle mit einem Fehler von etwa 7% (oder 0,1 ppm) bestimmt werden.

Résumé—L'analyse par absorption atomique utilisant un four en graphite est une technique puissante pour le dosage de quantités de fer de l'ordre du nanogramme. Elle peut être appliquée au dosage de traces de fer dans l'or et l'argent. Ces métaux peuvent être éliminés de la solution par réduction en or métallique et précipitation à l'état de chlorure d'argent respectivement. Le fer n'est pas coprécipité. La teneur en fer peut être déterminée dans 50–100 mg des métaux nobles avec une erreur d'environ 7% (ou 0.1 ppm).

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COULOMETRIC TITRATION OF POTASSIUM HYDROGEN PHTHALATE IN A NON-AQUEOUS SOLUTION, WITH A VITREOUS CARBON ANODE

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Previous work has shown that a vitreous carbon cathode may be used for the coulometric titration at a current density of 5 mA/cm^2 of potassium hydrogen phthalate in aqueous solution.[1] The electrode surface was not attacked but a carbon anode is corroded by electrochemically generated oxygen if current densities of 20 mA/cm^2 are used.

Potassium hydrogen phthalate behaves as a base in acetic acid–acetic anhydride medium and can be titrated coulometrically. This paper describes the use of a vitreous carbon anode for this purpose.

Preliminary work showed that when sodium perchlorate was added as supporting electrolyte the current efficiencies were low (about 85%). Presumably the electrochemical reaction for generation of protons required too high a potential. It was decided to generate the hydrogen ions by electrochemical oxidation of quinol by a method similar to that described by Vajgand and Mihajlovic.[3]

EXPERIMENTAL

Reagents

Standard potassium hydrogen phthalate solution, 0·02M. Analytical-grade reagent dried at 110°C for 1 hr and cooled in a desiccator was accurately weighed and dissolved in analytical-grade glacial acetic acid and made up at 20°C to a volume of 100 ml in a Grade-A volumetric flask and stored at 20°C in a thermostat.

Electrolyte solution. This was 0·1*M* sodium perchlorate (general-purpose reagent grade) in a mixture of analytical-grade glacial acetic acid and acetic anhydride (1:6 v/v); 25 ml, in which 0·1 g of solid analytical-grade quinol had been dissolved, were used for each titration.

Indicator solution. Malachite Green, 0·1% w/v solution in analytical-grade glacial acetic acid: 3 drops (about 0·1 ml) were used per titration. The end-point was taken as the first appearance of a green colour (corresponding to an absorbance of 0·262 at 625 nm, in a 1 cm cell).

Summary—Atomic-absorption analysis using a graphite furnace is a powerful technique for the determination of nanogram amounts of iron. It can be applied to the determination of traces of iron in gold and silver. These metals may be removed from solution by reduction to metallic gold and precipitation as silver chloride respectively. Iron is not co-precipitated. The iron content can be determined in 50–100 mg of the noble metals with an error of about 7% (or 0·1 ppm).

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Standard potassium hydrogen phthalate solution, 0·02M. Analytical-grade reagent dried at 110°C for 1 hr and cooled in a desiccator was accurately weighed and dissolved in analytical-grade glacial acetic acid and made up at 20°C to a volume of 100 ml in a Grade-A volumetric flask and stored at 20°C in a thermostat.

Electrolyte solution. This was 0·1*M* sodium perchlorate (general-purpose reagent grade) in a mixture of analytical-grade glacial acetic acid and acetic anhydride (1:6 v/v); 25 ml, in which 0·1 g of solid analytical-grade quinol had been dissolved, were used for each titration.

Indicator solution. Malachite Green, 0·1% w/v solution in analytical-grade glacial acetic acid: 3 drops (about 0·1 ml) were used per titration. The end-point was taken as the first appearance of a green colour (corresponding to an absorbance of 0·262 at 625 nm, in a 1 cm cell).

Apparatus

The titration cell has been described previously.[1] A Thorn coulometric titrator TE 110 was used to supply a constant current of 2·010 mA to the cell electrodes. The area of the vitreous carbon electrode exposed to the electrolyte solution was 1·6 cm^2, giving a current density of 1·3 mA/cm^2. This current was found to be constant during titrations to better than 0·05%. The use of higher current densities resulted in larger variations possibly because the non-aqueous solvent caused a relatively high ohmic resistance in the electrochemical cell.

Procedure and results

The main anolyte compartment of the cell was filled with 25 ml of the electrolyte solution, containing 0·1 g of quinol. About 1·5 ml of the same solution was used to cover the platinum cathode in the catholyte compartment. The solution in the anolyte compartment was stirred magnetically. Indicator was added and sufficient hydrogen ions were generated to produce the colour change. Then 1 ml of 0·02*M* potassium hydrogen phthalate was added from a calibrated Grade-A 1-ml pipette (relative standard deviation 0·1%). The current was started and stopped when the colour changed. Titration times were about 1000 sec but the end-point could not be located more precisely than within 1 sec so the random relative reading error is about 0·1%. Mean values of 4·060 and 4·069 mg of potassium hydrogen phthalate were obtained in two sets of 6 titrations of 4·054-mg samples. The relative standard deviations for each set were 0·1% and 0·2% respectively. The pretitrations were rather variable, for reasons unknown, but this is immaterial since the pretitration end-point can be located precisely.

DISCUSSION AND CONCLUSIONS

The results show that good precision and accuracy may be obtained with a vitreous carbon working electrode and they compare favourably with those for a platinum working electrode.[3] The relative standard deviation is about half that found for the titration in aqueous solution by coulometrically generated hydroxyl ions.[1] This difference may be due to the indicator end-point being sharper.

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Summary—A vitreous carbon anode has been used as working electrode in the coulometric titration of potassium hydrogen phthalate in glacial acetic acid–acetic anhydride medium with protous generated electrochemical oxidation of quinol.

Zusammenfassung—Eine Anode aus glasigem Kohlenstoff wurde als Arbeitselektrode bei der coulometrischen Titration von Kaliumhydrogenphthalat in einem Eisessig-Acetanhydrid-Medium mit Protonen verwendet, die durch elektrochemische Oxidation von Hydrochinon erzeugt wurden.

Résumé—On a utilisé une anode en carbone vitreux comme électrode de travail dans le titrage coulométrique du phtalate acide de potassium en milieu acide acétique glacial—anhydride aceétique avec oxydation électrochimique d'hydroquinone par production de protons.

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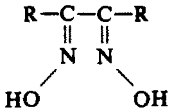
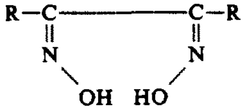
POLYSTYRENE IMPREGNATED WITH β-DIPHENYLGLYOXIME, A SELECTIVE REAGENT FOR PALLADIUM

(*Received* 5 *October* 1973. *Accepted* 12 *January* 1974)

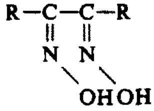
It is well known that glyoximes form complexes with several transition metals, including platinum and palladium. However, of the three possible isomer forms (*anti*, *syn*, *amphi*) only the *anti* (or α-form) is capable of forming complexes easily, whereas the *syn* (β-form) and *amphi* (γ-form) isomers form few or no complexes. This is explained by the fact that the *syn* and *amphi* isomers form strong intramolecular hydrogen bonds, in addition to possible steric hindrance.



Anti
α-form



Syn
β-form



Amphi
γ-form

In spite of this general behaviour of the β- and γ-isomers of dioximes, it was found by Dwyer and Nellar[1] that β-diphenylglyoxime ($R=C_6H_5$) forms complexes with palladium, and by Banks[2] that some γ-isomers can form 1:1 complexes. In the work described in the present paper, resins were impregnated with α- and β-isomers of diphenylglyoxime, in that way overcoming the difficulties caused by the notorious aqueous insolubility of the oximes, and the effectiveness of the impregnated resins in extracting platinum, palladium and nickel was tested.

EXPERIMENTAL

Reagents

α-Diphenylglyoxime was prepared according to Brady.[3] To a cooled solution of sodium hydroxide (80 g) in water (500 ml), there was added a solution of hydroxylamine hydrochloride (40 g in 100 ml of water), followed by finely powdered benzil (50 g) and alcohol (25 ml). After 3 days, the small amount of unchanged benzil was filtered off and the oxime was precipitated by neutralizing with solid carbon dioxide, and purified by extracting with hot alcohol. Recrystallization from methanol gave the pure product, m.p. 238–240°.

β-Diphenylglyoxime was also prepared according to Brady;[3] α-diphenylglyoxime was dissolved in boiling, freshly distilled aniline and cooled. The precipitated crystals were sucked as dry as possible, and after being washed with dilute hydrochloric acid, and then with water, were recrystallized from alcohol; m.p. 205–206°.

Impregnation of the resin. To a known amount of macroreticular polymeric absorbant XAD-2 (a polystyrene of high surface area produced by Rohm and Hass Company, U.S.A., was added a calculated amount of oxime dissolved in alcohol or acetone, and the mixture was left to stand for 2 hr, after which the solvent was evaporated and the freely flowing beads were ready for use. In this way, impregnated resins containing 8·0% (0·33 mmole/g) of α-diphenylglyoxime and 12·8% (0·53 mmole/g) of β-diphenylglyoxime were prepared.

Adsorption of palladium, platinum, and nickel

The adsorption of the metal ions from solutions of tetrachloropalladate(II), hexachloroplatinate(IV), and hexaaquonickel in hydrochloric acid solutions of various strengths was tested, followed by experiments in which all three metals were present together. The concentration of the metals varied between 1 and 10 g/l., and the molar ratio between palladium and platinum was kept at 1:1. In all the experiments the resins were shaken for 15–18 hr with excess of solution in 1:50 ratio of solid to liquid. However as the adsorption proceeds rapidly, for all practical reasons the time of shaking could be limited to 15 min. In all cases blank experiments were done with untreated XAD-2, and results were corrected accordingly.

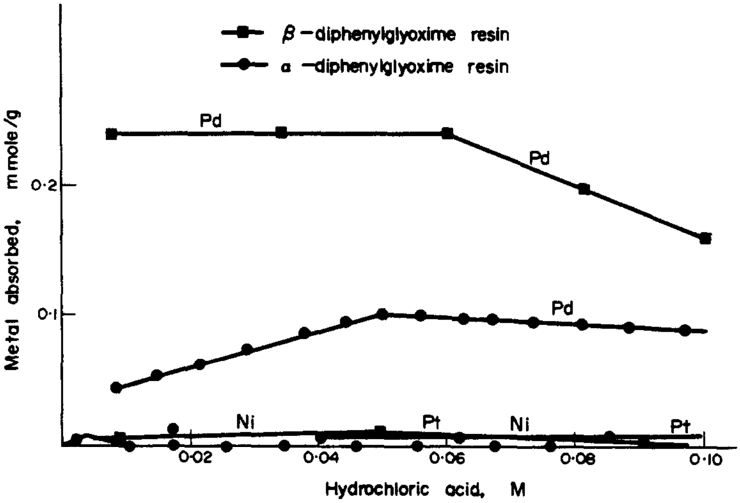


Fig. 1. Adsorption of palladium, platinum and nickel from hydrochloric acid media.

DISCUSSION

As can be seen from Fig. 1, the reagents behave satisfactorily. Their selectivity for palladium relative to platinum is about 20, and for palladium relative to nickel it is higher than 100. The reagents can easily be prepared by simple impregnation of a polymeric carrier. The oximes are retained by the resin by simple physical adsorption, and both the metal ion and the impregnating oxime can be stripped by a simple wash with a suitable organic solvent.

It is interesting to note the influence of the change in acidity on the palladium uptake by both reagents (see Fig. 1); this could probably be attributed to differences between the reagents in their tendencies at various acidities to form hydrogen bonds.

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Summary—α- and β-diphenylglyoximes impregnated on macroreticular polystyrene (XAD-2) were tested as adsorptive reagents and one of them (the β-isomer) was found to adsorb palladium in preference to platinum (selectivity factor 20) and nickel (factor >100).

Zusammenfassung—Mit α- und β-Diphenylglyoxim getränktes grob vernetztes Polystyrol (XAD-2) wurde als Adsorptionsreagens geprüft; das β-Isomere adsorbiert Palladium besser als Platin (Selektivitätsfaktor 20) und Nickel (Faktor > 100).

Résumé—On a essayé les α- et β-diphénylglyoximes imprégnées sur un polystyrène macroréticulaire (XAD-2) comme réactifs d'adsorption et l'on a trouvé que l'un d'eux (l'isomère β) adsorbe le palladium de préférence au platine (facteur de sélectivité 20) et au nickel (facteur > 100).

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PREPARATION, PROPERTIES AND ANALYTICAL APPLICATION OF THORIUM *N*-PHENYL-*o*-NITROBENZOHYDROXAMATE

(*Received* 6 *September* 1973. *Accepted* 6 *January* 1974)

The physicochemical properties [1–2] of *N*-phenyl-*o*-nitrobenzohydroxamic acid (PNHA) indicate that it is a potentially useful reagent for inorganic analysis. It forms strong and stable complexes with metal ions. In the present investigation the synthesis and properties of a new solid complex Th–PNHA are described.

EXPERIMENTAL

Reagents

The *N*-phenyl-*o*-nitrobenzohydroxamic acid was synthesized by the method described earlier;[3] m.p. 148°C (reported[4] m.p. 148°C).

The aqueous stock solution of thorium was prepared by dissolving 1·3805 g of thorium nitrate in 250 ml of doubly distilled water and standardized volumetrically.[5]

A 1:0% solution of masking agent was used.

Procedure

In a 1-litre beaker, 10 ml of 0·001*M* thorium nitrate and about 500 ml of water were heated at 60°C on a water-bath. Then 20 ml of 0·1*M* PNHA in ethanol was added dropwise with constant stirring followed by 0·1*N* ammonia solution until precipitation was complete. The pH was adjusted to 4–4·5 with 0·1*M* ammonium chloride. The granular precipitate thus formed was digested for 2–3 hr on a steam-bath, filtered off on a sintered glass crucible of porosity G4 and washed thoroughly first with hot water and finally with five 10 ml portions of 50% aqueous ethanol. The complex was purified by recrystallization from 95% ethanol, and dried at 110°C. The same procedure (except the purification) was used for gravimetric determination of thorium, the complex being weighed.

Separation of thorium from foreign ions

Thorium was precipitated with PNHA from a hot solution containing Ag(I), Cu(II), Zn(II), Cd(II), Hg(II) or Pd(II) at pH 4–4·5 in presence of excess of cyanide. The precipitate was washed with hot water before drying and weighing. In order to separate thorium from Mn(II), Ni(II), and Ga(III) cyanide and tartrate were added to the solution before its pH was adjusted to 4–4·5. Oxalate and tartrate were added in the separation of thorium from Be(II), Pb(II), Al(III), Sn(III), Sb(III), La(III), Mo(IV), Ti(IV) and Zr(IV).

Examination of the precipitate

Thermal analysis. Simultaneous TG and DTA plots were obtained at a constant heating rate of 8°C/min on a Mettler thermal analyser fitted with a 12-channel recorder. Al_2O_3 was used as a reference material for the DTA.

Chemical analysis. The thorium content of the complex was determined by EDTA titration (Xylenol-Orange indicator) after decomposition of sample with a mixture of perchloric, sulphuric and nitric acids.

Spectra. The infrared spectra of the reagent and thorium complex in KBr pellets were recorded on a Perkin–Elmer Model 237 spectrophotometer (with sodium chloride optics).

Résumé—On a essayé les α- et β-diphénylglyoximes imprégnées sur un polystyrène macroréticulaire (XAD-2) comme réactifs d'adsorption et l'on a trouvé que l'un d'eux (l'isomère β) adsorbe le palladium de préférence au platine (facteur de sélectivité 20) et au nickel (facteur > 100).

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Spectra. The infrared spectra of the reagent and thorium complex in KBr pellets were recorded on a Perkin–Elmer Model 237 spectrophotometer (with sodium chloride optics).

DISCUSSION

The physical properties of the complex are given in Table 1. Results for gravimetric determination of thorium(IV) in presence of various foreign ions are given in Tables 2 and 3. The DTA and TGA curves of the complex are reproduced in Fig. 1.

PNHA, I, is a very weak acid[6] (p*K* 8·11 at 25°) and reacts with aqueous solutions of thorium(IV) to form the complex II.

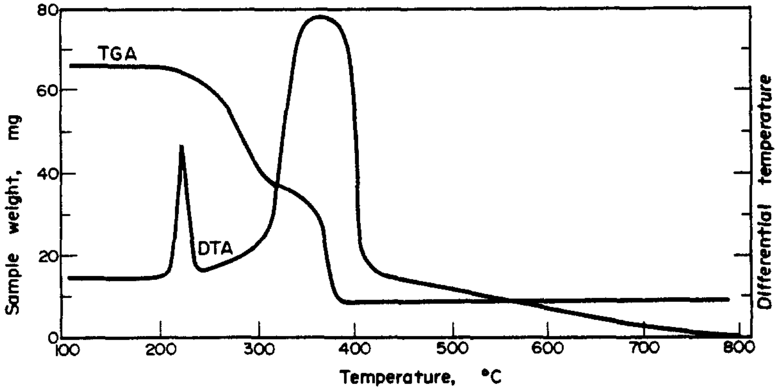

Fig. 1. DTA and TGA of thorium(IV)-*N*-phenyl-*o*-nitrobenzohydroxamic acid complex.

Table 1. Physical properties of the thorium-*N*-phenyl-*o*-nitrobenzohydroxamic acid complex

Colour	yellowish			
m.p., °C	225, decomp.			
pH of precipitation	4–4·5			
Analysis	C	H	N	Th
Calculated, %	49·53	2·88	8·88	18·40
Found, %	49·50	2·90	8·90	18·30
DTA				
Ist exotherm	225°C			
2nd exotherm	380°C			
Residue	ThO_2			
TGA				
Weight loss				
Calculated	79·47 %			
Found	79·00%			

Table 2. Gravimetric determination of thorium with *N*-phenyl-*o*-nitrobenzohydroxamic acid

Th taken, *mg*	Th found, *mg*	Th taken, *mg*	Th found, *mg*
5·00	5·01	10·00	9·98
5·00	5·00	15·00	15·02
7·50	7·48	15·00	15·01

Table 3. Separation of thorium from other metals

Thorium taken, *mg*	Foreign ions, *mg*	Masking agent	Thorium found, *mg*
5·00	Ag^{+} 60	Cyanide	5·00
5·00	Be^{2+} 80	Oxalate + tartrate	5·00
5·00	Pb^{2+} 80	Oxalate + tartrate	5·01
5·00	Mn^{2+} 80	Cyanide + tartrate	4·99
10·00	Ni^{2+} 80	Cyanide + tartrate	9·98
10·00	Cu^{2+} 80	Cyanide	10·01
10·00	Zn^{2+} 80	Cyanide	10·00
5·00	Cd^{2+} 80	Cyanide	5·00
5·00	Hg^{2+} 70	Cyanide	5·00
5·00	Pd^{2+} 100	Cyanide	5·02
5·00	Ga^{3+} 100	Cyanide + tartrate	5·03
5·00	Al^{3+} 100	Oxalate + tartrate	4·99
5·00	Sn^{3+} 70	Oxalate + tartrate	5·01
5·00	Sb^{3+} 80	Oxalate + tartrate	5·00
5·00	La^{3+} 80	Oxalate + tartrate	5·00
5·00	Ti^{4+} 100	Oxalate + tartrate	5·01
5·00	Zr^{4+} 100	Oxalate + tartrate	4·99
5·00	Mo^{6+} 80	Oxalate + tartrate	5·01
5·00	U^{6+} 60	Oxalate + tartrate	5·00

The infrared spectrum of I has characteristic peaks at 3150, 1625 and 916 cm^{-1} due to stretching vibrations of hydrogen-bonded O—H, C=O and N—O respectively. On complex formation the peak at 3150 cm^{-1} disappears owing to replacement of H^{+} by thorium and the oxygen atom is co-ordinated to the thorium. If the hydroxyl group were bonded to the metal through a lone electron pair and still retained the hydrogen atom, the O—H stretching frequency would be altered. The spectrum of II showed no appearance of such a new peak, thus confirming the co-ordination of Th^{4+} to the oxygen atom.

The carbonyl stretching vibration shifts to lower frequency (1575 cm^{-1}) owing to bonding of the carbonyl oxygen atom to thorium. The N—O stretching vibration at 916 cm^{-1} is unaltered except for its intensity, which is increased.

The thermogram for the complex heated in flowing air shows no change in weight up to around 150–180°C, indicating the absence of constitutional water. The DTA curve shows two exotherms, a very sharp one at 225°C, along with loss in weight, and a broad one around 380° with a further weight loss, presumably due to burning of organic matter. No evidence of melting is observed.

The major products of the thermal decomposition of the chelate were found by ultraviolet, infrared and X-ray analysis to be thorium benzoate, benzanilide, and finally metal oxide and tars. At about 220–300°C (first exotherm) the vaporization of benzanilide with gradual weight loss, and at about 300–380°C (second exotherm) the decomposition of metal benzoate and formation of thorium oxide are expected. The chemical and thermal analyses suggest that PNHA forms an anhydrous stoichiometric precipitate with thorium and is suitable as an analytical reagent for gravimetric estimation.

Thorium is precipitated quantitatively with PNHA from a solution containing 5–15 mg of thorium nitrate at pH 4–4·5. The yellowish precipitate is weighed directly after drying at 110–120°C. The complex is fairly soluble in ethanol and chloroform but only sparingly soluble in ether, benzene, carbon tetrachloride, acetone and glacial acetic acid. It is decomposed when treated with concentrated sulphuric, nitric, hydrochloric and perchloric acid. The analytical results indicate the composition of complex as $(C_{13}H_{9}N_{2}O_{4})_{4}Th$.

Acknowledgement—The authors are indebted to Professor A. B. Biswas, I.I.T., Bombay, for his inspiring guidance. They are thankful to Dr. S. Sampath, B.A.R.C., Bombay, for thermal analysis of the samples, and to C.S.I.R., New Delhi, for financial assistance.

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5. F. J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic Acid.* Van Nostrand, Princeton, 1961.

Summary—A new complex of thorium(IV) with *N*-phenyl-*o*-nitrobenzohydroxamic acid (PNHA) has been prepared by reacting an aqueous solution of thorium with an alcoholic solution of PNHA at 60°C and adjusting the pH to 4–4·5. The infrared spectra and thermal analysis of the complex are discussed. The use of PNHA for gravimetric determination of thorium is described.

Zusammenfassung—Das neu Komplex von Thorium(IV) mit *N*-Phenyl-*o*-nitrobenzhydroxamsäure (PNHA) wurde durch Reaktion einer wäßrigen Lösung von Thorium mit einer alkoholischen Lösung von PNHA bei 60° und Einstellung des pH auf 4–4,5 hergestellt. Die Infrarotspektren und die Thermoanalyse des Komplexes werden diskutiert. Es wird beschrieben, wie PNHA zur gravimetrischen Bestimmung von Thorium eingesetzt werden kann.

Résumé—On a préparé un nouveau complexe du thorium (IV) avec l'acide N-phényl *o*-nitrobenzohydroxamique (PNHA) en faisant réagir une solution aqueuse de thorium avec une solution alcoolique de PNHA à 60° et en ajustant le pH à 4–4,5. On discute des spectres infrarouges et de l'analyse thermique du complexe. On décrit l'emploi de PNHA pour le dosage gravimétrique du thorium.

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SUR LE MICRODOSAGE DU SOUFRE DANS LES COMPOSES ORGANIQUES, EN PRESENCE D'HALOGENES, PAR COMBUSTION ET TITRAGE COULOMETRIQUE AUTOMATIQUE DU DIOXYDE DE SOUFRE

(*Reçu le* 13 *novembre* 1973. *Accepté le* 28 *novembre* 1973)

La méthode de microdosage du soufre de Debal et Levy.[1,2] mise en oeuvre dans no laboratoires, comporte une combustion dans un courant d'oxygène à 1310–1320 C et un titrage coulométrique automatique du dioxyde de soufre.

Son application dans le cas de composés simultanément soufrés et halogénés (Cl, Br, I) exige l'emploi d'argent associé au réactif de Malissa[3]* pour la rétention des produits de combustion halogénés qui, autrement, fausseraient la mesure par acidimétrie coulométrique. Si l'halogène est du fluor, l'acide fluorhydrique doit être retenu par une solution de sulfate d'hydrazine dans l'eau chaude qui doit elle-même être précédée par une garniture d'argent et de réactif de Malissa lorsqu'un second halogène est présent en même temps que le fluor.

Or, la préparation du réactif de Malissa est longue et coûteuse, son activité est variable avec le lot de préparation et la durée de cette dernière est en outre diminuée lors de la présence de fluor.[2]

Dans la méthode décrite par Culmo[4] pour les microdosages automatiques simultanés du carbone, de l'azote et du soufre sur analyseur CHN Perkin-Elmer (modèle 240) modifié, l'auteur préconise l'emploi d'hydroxy-8 quinoléïne pour retenir les composés de combustion halogénés gênants. Il ne précise pas, toutefois, si les composés organiques porteurs de fluor peuvent être ainsi analysés.

Ce réactif (hydroxy-8 quinoléïne), associé à l'argent, a été utilisé avec succès dans le cadre de notre méthode, déjà citée, de microdosage du soufre dans les composés organiques simultanément porteurs de fluor, chlore, brome ou iode.

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* Le réactif de Malissa est préparé par fusion d'un mélange de sulfate d'argent et de pyrosulfate de potassium.

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Zusammenfassung—Das neu Komplex von Thorium(IV) mit *N*-Phenyl-*o*-nitrobenzhydroxamsäure (PNHA) wurde durch Reaktion einer wäßrigen Lösung von Thorium mit einer alkoholischen Lösung von PNHA bei 60° und Einstellung des pH auf 4–4,5 hergestellt. Die Infrarotspektren und die Thermoanalyse des Komplexes werden diskutiert. Es wird beschrieben, wie PNHA zur gravimetrischen Bestimmung von Thorium eingesetzt werden kann.

Résumé—On a préparé un nouveau complexe du thorium (IV) avec l'acide N-phényl *o*-nitrobenzohydroxamique (PNHA) en faisant réagir une solution aqueuse de thorium avec une solution alcoolique de PNHA à 60° et en ajustant le pH à 4–4,5. On discute des spectres infrarouges et de l'analyse thermique du complexe. On décrit l'emploi de PNHA pour le dosage gravimétrique du thorium.

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SUR LE MICRODOSAGE DU SOUFRE DANS LES COMPOSES ORGANIQUES, EN PRESENCE D'HALOGENES, PAR COMBUSTION ET TITRAGE COULOMETRIQUE AUTOMATIQUE DU DIOXYDE DE SOUFRE

(*Reçu le* 13 *novembre* 1973. *Accepté le* 28 *novembre* 1973)

La méthode de microdosage du soufre de Debal et Levy.[1,2] mise en oeuvre dans no laboratoires, comporte une combustion dans un courant d'oxygène à 1310–1320 C et un titrage coulométrique automatique du dioxyde de soufre.

Son application dans le cas de composés simultanément soufrés et halogénés (Cl, Br, I) exige l'emploi d'argent associé au réactif de Malissa[3]* pour la rétention des produits de combustion halogénés qui, autrement, fausseraient la mesure par acidimétrie coulométrique. Si l'halogène est du fluor, l'acide fluorhydrique doit être retenu par une solution de sulfate d'hydrazine dans l'eau chaude qui doit elle-même être précédée par une garniture d'argent et de réactif de Malissa lorsqu'un second halogène est présent en même temps que le fluor.

Or, la préparation du réactif de Malissa est longue et coûteuse, son activité est variable avec le lot de préparation et la durée de cette dernière est en outre diminuée lors de la présence de fluor.[2]

Dans la méthode décrite par Culmo[4] pour les microdosages automatiques simultanés du carbone, de l'azote et du soufre sur analyseur CHN Perkin-Elmer (modèle 240) modifié, l'auteur préconise l'emploi d'hydroxy-8 quinoléïne pour retenir les composés de combustion halogénés gênants. Il ne précise pas, toutefois, si les composés organiques porteurs de fluor peuvent être ainsi analysés.

Ce réactif (hydroxy-8 quinoléïne), associé à l'argent, a été utilisé avec succès dans le cadre de notre méthode, déjà citée, de microdosage du soufre dans les composés organiques simultanément porteurs de fluor, chlore, brome ou iode.

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* Le réactif de Malissa est préparé par fusion d'un mélange de sulfate d'argent et de pyrosulfate de potassium.

Par ailleurs, nous avons remplacé la cellule electrochimique du coulometre de Schoeps initialement utilisée pour le titrage coulométrique du dioxyde de soufre par une cellule perfectionnée à régulation de température.

ELIMINATION DE L'INTERFERENCE DES HALOGENES

Partie experimentale

L'appareil de dosage comprend un tube à combustion horizontal (Debal et Levy[1,2]) maintenu à 1310–1320 C raccordé par l'intermédiaire d'un tube de polyéthylène (longueur 30 mm, dia. intérieur: 4 mm) à un tube de verre "Pyrex" (longueur: 300 mm, dia. intérieur: 10 mm) contenant une garniture de laine d'argent vierge en rubans.[1] Un deuxième tube de verre "Pyrex" (dia. intérieur: 8 mm) est directement raccordé au premier par l'intermédiaire d'un joint conique rodé; il contient une garniture d'hydroxy-8 quinoléïne (longueur: 190 mm) suivie d'un tampon de laine d'argent vierge (longueur: 50 mm). Les deux tubes absorbeurs sont reliés à la cellule d'électrolyse par un tube de polyéthylène terminé par un tube en verre "Pyrex" (dia. intérieur: 1 mm) qui plonge dans l'électrolyte du compartiment cathodique de la cellule.

Reactifs absorbants: argent, hydroxy-8 quinoléïne. La laine d'argent est traitée quelques heures dans une étuve à 110 C avant son utilisation (ce qui permet l'obtention ultérieure de résultats de dosages plus reproductibles).

Les quantités de réactifs, préconisées ci-dessus, permettent la rétention d'environ 1,1 mg d'halogènes par analyse, quel que soit l'halogène présent. Les garnitures de réactifs doivent être remplacées lorsqu'elles ont absorbé 10 mg d'halogènes.

La réactivité de l'hydroxy-8 quinoléïne varie suivant l'halogène considéré; en effet, si la présence de fluor ou de chlore ne donne lieu à aucune difficulté, celle du brome peut conduire à des résultats erronés par défaut si la quantité de cet halogène est trop importante; dans ce cas, il est nécessaire soit d'augmenter la longueur de la garniture d'hydroxy-8 quinoléïne, soit de diminuer la masse du prélèvement analytique.

Outre, le fait qu'elle permet le microdosage du soufre en présence de fluor, l'hydroxy-8 quinoléïne est un réactif commercialisé peu coûteux et d'un emploi plus facile que le réactif de Malissa puisqu'il est utilisé à température ambiante.

Il est à remarquer que les analyses consécutives de produits contenant d'importantes quantités d'halogènes (0,9–1 mg) conduisent à des résultats erronés par excès. Il est donc souhaitable d'alterner les analyses de composés ne contenant pas d'halogènes et les composés fortement halogénés au cours d'une série d'analyses.

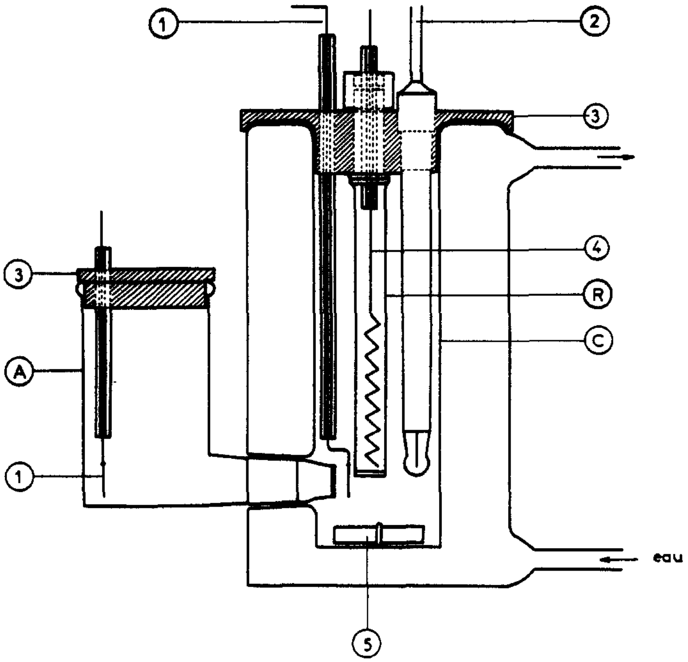

Fig. 1. Cellule de titrage en verre "Pyrex."

CELLULE ELECTROCHIMIQUE

La cellule normalement associée au coulomètre automatique à impulsions utilisé par Debal et Levy ne comporte aucun dispositif thermostatique; elle est donc sensible à toutes variations de température, ce qui se traduit par une variation du coefficient d'étalonnage du coulomètre.

En vue d'améliorer la méthode et de permettre sa mise en oeuvre, même dans des laboratoires non climatisés, nous utilisons une cellule en verre dont la double paroi permet une circulation d'eau maintenue à température constante et la régulation de la température du compartiment cathodique, où s'effectue le titrage, ainsi que du système de détection de fin de titrage (électrode de verre–électrode de référence).

Partie experimentale

Cette cellule (Fig. 1) réalisée en verre "Pyrex" comprend deux compartiments principaux. Le compartiment cathodique (*C*), où est effectué le titrage, comporte une double paroi permettant la circulation d'eau maintenue à température constante. La double paroi est traversée par un passage rodé dans lequel est logé le joint rodé mâle de raccord du compartiment anodique.

Dans le compartiment cathodique sont disposés: une électrode de platine (cathode) constituée par une feuille (10 × 10 mm) de 1 mm d'épaisseur (*1*); une électrode de verre (*2*); un compartiment de référence constitué par un tube de verre "Pyrex" dont le fond est un disque fritté (porosité n° 4); il contient l'électrolyte au sein duquel plonge l'électrode de référence (*4*) à savoir un fil d'argent ($\phi = 2$ mm), enroulé en hélice, recouvert de chlorure d'argent; un tube de verre "Pyrex" (diamètre intérieur: 1 mm) plongeant dans la solution de titrage permet l'adduction, à 1 cm du fond de la cellule, des gaz de combustion qui sont dispersés au sein de la solution par agitation magnétique; un barreau magnétique (*5*) complète le dispositif; les électrolytes identiques à ceux déjà décrits.[1,2]

La circulation d'eau permet de maintenir à température constante non seulement l'électrolyte du compartiment cathodique, mais aussi le système de détection du point final de titrage constitué par l'électrode de verre, le compartiment de référence et son électrode.

Tableau 1.

Composés soufrés	*m** *mg*	S, % Calculé	S, % Trouvé
Cystine	2,696	26,68	$26,5_8$
—	3,392	—	$26,7_7$
—	3,878	—	$26,6_0$
Sulfathiazole	2,666	25,12	$25,0_4$
—	3,161	—	$25,1_5$
—	3,828	—	$25,1_3$
Acide thiobarbiturique	4,236	22,24	$22,3_5$
—	5,152	—	$22,1_6$
—	5,341	—	$22,3_5$
Sulfanilamide	4,818	18,62	$18,6_6$
—	5,591	—	$18,5_4$
Acide p-sulfanilique	4,316	18,51	$18,4_9$
—	6,050	—	$18,5_4$
Chlorure de benzyliso-thiouronium	4,686	15,82	$15,8_4$
—	5,289	—	$15,8_2$
—	5,718	—	$15,8_0$
—	6,447	—	$15,8_2$

* *m*: Masse du prélèvement analytique.

Le compartiment cathodique est fermé par un couvercle de nylon usiné (*3*), dans lequel viennent se loger les différentes pièces énumérées ci-dessus, et pourvu d'un petit orifice destiné à l'évacuation des gaz.

Le compartiment anodique (*A*) est un récipient cylindrique pourvu d'un ajutage latéral terminé par un joint conique rodé mâle fermé par un disque de verre fritté (prosité n° 4) et d'un couvercle en nylon (*3*) pourvu d'un petit orifice destiné à l'évacuation des gaz. L'anode est une feuille de platine (10 × 10 mm) de 1 mm d'épaisseur (*1*)

Fonctionnement

L'eau utilisée pour la régulation de la température de la cellule est maintenue à température constante par l'intermédiaire d'un thermostat assurant simultanément sa circulation. Il est d'ailleurs souvent possible d'assurer une régulation suffisante de la température de la cellule, sans thermostat, par simple circulation d'eau permettant d'empêcher que la température ne subisse des variations au cours d'une journée.

Tableau 2.

Composés soufrés	m* mg	Composés d'addition	Halogènes μg	S,% Calculé	S,% Trouvé
Sulfathiazole	3,242	Trifluoroacétanilide	390 F	25,12	$24,9_7$
Cystine	3,132	—	600 F	26,68	$26,6_1$
Acide thiobarbiturique	4,264	—	750 F	22,24	$22,1_4$
Sulfanilamide	5,585	—	1050 F	18,62	$18,5_8$
Cystine	3,237	—	1110 F	26,68	$26,9_6$
Acide thiobarbiturique	3,364	Bromoacétanilide	300 Br	22,24	$22,2_1$
Cystine	3,078	—	520 Br	26,68	$26,5_0$
Sulfanilamide	5,649	—	670 Br	18,62	$18,3_6$
Sulfathiazole	3,523	—	750 Br	25,12	$25,1_5$
Cystine	3,391	—	930 Br	26,68	$26,5_3$
Acide thiobarbiturique	3,582	—	1080 Br	22,24	$22,1_4$
Sulfathiazole	3,355	Acide iodobenzoïque	150 I_2	25,12	$25,1_0$
Acide thiobarbiturique	3,452	—	459 I_2	22,24	$22,1_5$

* *m*: Masse du prélèvement analytique.

La température optimale de fonctionnement conduisant à la meilleure reproductibilité des mesures coulométriques se situe aux environs de 20°C; il convient d'éviter que le thermostat ne fournisse une eau de température supérieure à 25°C; les variations de température de l'eau doivent être comprises entre ±0,5°C.

RESULTATS

Le système des deux réactifs, argent et hydroxy-8 quinoléïne, permet le microdosage du soufre en présence de fluor, de chlore, de brome ou d'iode. Quelques résultats obtenus en présence de ces réactifs avec la cellule électrochimique décrite ci-dessus font l'objet des tableaux 1 et 2.

Pour pallier le défaut de substances de référence soufrées et halogénées, (S + F, S + Cl, S + Br, S + I), l'étude de l'influence de la présence des halogènes sur les résultats de dosage du soufre nous a conduits à effectuer nombre de déterminatins sur des mélanges de composés soufrés et de composés porteurs de ces halogènes (trifluoroacétanilide, bromoacétanilide, acide iodobenzoïque) (tableau 2).

D'autre part, l'analyse de composés de recherche soufrés contenant simultanément plusieurs halogènes (F + Cl + S, Br + I + S) a donné des résultats satisfaisants.

Les dosages ont été effectués en renouvelant systématiquement tant les réactifs, argent et hydroxy-8 quinoléine après la rétention d'environ 10 mg d'halogènes, que, journellement, les électrolytes des compartiments cathodique et de référence.

L'utilisation de la cellule à régulation de température par circulation d'eau décrite permet de travailler pendant une journée entière avec un coefficient d'étalonnage constant, quelles que soient les variations de température du laboratoire.

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Resumé—Les auteurs décrivent une amélioration de la méthode de microdosage du soufre dans les composés organiques, publiée par Debal et Levy (*Bull. Soc. Chim. France*, 1968, 426; 1971, 3374), qui comporte la combustion dans l'oxygène à 1310–1320°C, du composé organique et un titrage coulométrique automatique du dioxyde de soufre formé. Les halogènes et les composés halogénés sont retenus par une garniture d'argent en rubans, suivie d'une garniture d'hydroxy-8 quinoléïne. La précision du titrage coulométrique est améliorée par l'utilisation d'une cellule en verre à double paroi permettant la circulation d'un courant d'eau maintenue à température constante. Cette cellule permet la mise en oeuvre de la méthode, même en des laboratoires où la température ambiante varie au cours de la journée.

Summary—The method for the determination of sulphur in organic compounds (E. Debal and R. Levy, *Bull. Soc. Chim. France*, 1968, 426; 1971, 3374) by combustion in oxygen at 1310–1320°C and coulometric titration of the sulphur dioxide formed is improved. Silver and 8-hydroxyquinoline are successfully used to remove halogens (fluorine included) from combustion products. A new glass cell for the acidimetric titration of sulphur dioxide with an automatic coulometer is devised, with a water-jacket for its cathodic and reference compartments. The constant-temperature water-flow makes this determination easy to carry out with no drawbacks, even in varying ambient temperature.

Zusammenfassung—Die Methode zur Bestimmung von Schwefel in organischen Verbindungen (E. Debal und R. Levy, *Bull. Soc. Chim. France* 1968, 426; 1971, 3374) durch Verbrennung in Sauerstoff bei 1310–1320° und coulometrische Titration des gebildeten Schwefeldioxids wird verbessert. Zur Entfernung der Halogene (auch Fluor) aus den Verbrennungsprodukten werden nacheinander Silber und 8-Hydroxychinolin verwendet. Eine neue Glaszelle zur acidimetrischen Titration von Schwefeldioxid mit einem automatischen Coulometer wird entworfen; ihre Kathoden- und Referenzabteile sind mit einem Wassermantel umgeben. Die durch umlaufendes Wasser erzielte Temperaturkonstanz macht diese Bestimmung leicht und ohne Hindernisse ausführbar, selbst bei wechselnder Umgebungstemperatur.

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USE OF A LIQUID ION-EXCHANGER IN THE SOLVENT EXTRACTION AND ATOMIC-ABSORPTION DETERMINATION OF TRACE COPPER IN WATERS

(*Received* 15 *October* 1973. *Accepted* 18 *November* 1973)

The value of solvent extraction and atomic-absorption techniques for the determination of trace elements has been demonstrated in several recent papers.[1-3] Liquid ion-exchangers have not so far been employed in this kind of application, although their use has been suggested.[4] These materials often have advantages in terms of stability and extraction characteristics over other reagents used in solvent extraction and many analytical separations employing them have been reported and reviewed.[5,6] Many such systems involve the use of high concentrations of hydrochloric acid in the aqueous phase, thus increasing the risk of contamination of the sample. An alternative is described here in which copper is extracted from dilute thiocyanate solution. The method permits rapid determination with good precision in the 10–100 ppM range, by atomic-absorption spectrophotometry.

EXPERIMENTAL

Apparatus

A Pye Unicam SP90A atomic-absorption spectrophotometer fitted with an SP22 recorder was used. The working conditions were:

Wavelength 324·8 nm
Burner 10 cm acetylene
Lamp current 5 mA
Slit 0·1 mm

Resumé—Les auteurs décrivent une amélioration de la méthode de microdosage du soufre dans les composés organiques, publiée par Debal et Levy (*Bull. Soc. Chim. France*, 1968, 426; 1971, 3374), qui comporte la combustion dans l'oxygène à 1310–1320°C, du composé organique et un titrage coulométrique automatique du dioxyde de soufre formé. Les halogènes et les composés halogénés sont retenus par une garniture d'argent en rubans, suivie d'une garniture d'hydroxy-8 quinoléine. La précision du titrage coulométrique est améliorée par l'utilisation d'une cellule en verre à double paroi permettant la circulation d'un courant d'eau maintenue à température constante. Cette cellule permet la mise en oeuvre de la méthode, même en des laboratoires où la température ambiante varie au cours de la journée.

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The value of solvent extraction and atomic-absorption techniques for the determination of trace elements has been demonstrated in several recent papers.[1-3] Liquid ion-exchangers have not so far been employed in this kind of application, although their use has been suggested.[4] These materials often have advantages in terms of stability and extraction characteristics over other reagents used in solvent extraction and many analytical separations employing them have been reported and reviewed.[5,6] Many such systems involve the use of high concentrations of hydrochloric acid in the aqueous phase, thus increasing the risk of contamination of the sample. An alternative is described here in which copper is extracted from dilute thiocyanate solution. The method permits rapid determination with good precision in the 10–100 ppM range, by atomic-absorption spectrophotometry.

EXPERIMENTAL

Apparatus

A Pye Unicam SP90A atomic-absorption spectrophotometer fitted with an SP22 recorder was used. The working conditions were:

Wavelength 324·8 nm
Burner 10 cm acetylene
Lamp current 5 mA
Slit 0·1 mm

Air 2·1 kg/cm^2; 1·5 l./min
Acetylene 0·7 kg/cm^2; 1·5 l./min
Scale expansion X2

Extractant solution

Dissolve 18·7 g of Amberlite LA 2 in isobutyl methyl ketone and dilute to 500 ml. Shake the solution with equal volumes of first 2*M* hydrochloric acid and then 3*M* ammonium thiocyanate. Separation in the first step is slow and the solution should be allowed to stand overnight. The extractant solution thus prepared is stable for several months.

Procedure for copper solutions in the range 10–100 ppM

Adjust the pH of the sample solution to 1–8 with hydrochloric acid or sodium hydroxide solution. In a 100 ml separating-funnel take 50 ml of sample solution, 1 ml of 3*M* ammonium thiocyanate and 5 ml of extractant solution, shake the mixture for 2 min and allow to stand for 5 min. Discard the aqueous layer and dry the stem of the funnel with filter paper. Insert a piece of filter paper in the stem of the funnel and collect the organic layer in a 5 ml polythene cup ready for atomic-absorption analysis. Repeat the procedure with standard copper solutions and a reagent blank. Aspirate the prepared extracts into the flame, using the working conditions described above.

RESULTS AND DISCUSSION

A calibration curve gave the following absorbances for the copper concentrations given in brackets; 0·03 (0 ppM), 0·062 (20), 0·098 (40), 0·133 (60), 0·170 (80), 0·195 (100). Ten replicate determinations at the 50 ppM (parts per milliard) level gave a relative standard deviation of 3%. An absorption of 1% of full scale deflection is equivalent to approximately 3 ppM of copper. It is possible to increase the sensitivity without serious loss of precision by increasing the phase-volume ratio from 10 : 1 to 25 : 1.

Optimum extraction conditions

Atomic-absorption measurements on the aqueous phase remaining from extraction of 5 ppm of copper showed that the extraction was over 98% complete over the pH range 1–8 but fell off sharply at higher pH values. A significant drop in the extraction ratio occurred when the thiocyanate concentration in the aqueous phase was reduced below 0·005*M*, and also when the extractant concentration was reduced below 0·05*M*. It was assumed that extraction was complete at the 10–100 ppM level.

Interferences

The addition of 1 g of each of the following sodium salts to 100 ml of 5 ppm copper solution did not significantly affect the extraction: nitrite, fluoride, chloride, bromide, iodide, sulphate, nitrate, sulphite, dihydrogen phosphate. Under the conditions used, lead is not extracted, cadmium is 45% extracted, iron 83% and zinc 100% (at the 5 ppm level). Satisfactory calibration curves have been obtained for zinc.

Solvent effect

The enhancing effect obtained by the use of organic solvents in atomic-absorption spectroscopy is well known, especially that of isobutyl methyl ketone. In the present case the enhancement factor is about 8 : 1, which is multiplied by the phase-volume ratio (10 : 1) to give a large total enhancement factor.

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Summary—Copper in the 10–100 ppM range has been determined by a solvent extraction and atomic-absorption procedure involving the use of the liquid ion-exchanger Amberlite LA 2 in thiocyanate form. The procedure is rapid and gives results of good precision, and uses stable reagents and standard instrumentation.

Zusammenfassung—10–100 ppm Kupfer werden durch flüssigflüssig-Extraktion und Atomabsorption bestimmt; dabei wurde der flüssige Ionenaustauscher Amberlite LA 2 in der Thiocyanatform verwendet. Das Verfahren geht schnell und gibt genaue Ergebnisse, es werden stabile Reagentien und StandardLaborausrüstung benützt.

Résumé—On a dosé le cuivre dans le domaine 10–100 ppM par une technique d'extraction par solvant et absorption atomique comprenant l'emploi de l'échangeur d'ions liquide Amberlite LA 2 sous la forme thiocyanate. La technique est rapide et donne des résultats de bonne précision, et utilise des réactifs stables et une instrumentation normale.

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NEW QUALITATIVE COLOUR REACTION FOR THE IDENTIFICATION OF COPPER(I) COMPOUNDS AND COMPLEXES

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Numerous tests are available for the detection of copper(II), but there are few tests for copper(I). Certain organic reagents[1-7] are capable of detecting copper(I) but only when it is present in ionic form. This communication describes a new and simple qualitative colour reaction, which is useful for the detection of copper(I) in ionic form or when present in complexes with certain organic ligands. The reaction essentially consists in treating a sulphuric acid solution or suspension of copper(I) compound or complex with ferricyanide solution mixed with ammonia, whereupon a deep salmon-pink, pink-purple or purple colour or precipitate, characteristic of copper(I), is immediately formed.

EXPERIMENTAL

Reagents

Potassium ferricyanide solution. A 0·15% w/v solution in water.

Concentrated ammonia solution.

Copper(I) salts. Various copper(I) salts, *e.g.* CuCl, CuCN, CuSCN, and $Cu_2SO_3.H_2O$ were prepared by the ordinary procedures.

Copper(I)–thiourea complexes. Various copper(I)–thiourea complexes (*q.v.*) were prepared by the published procedures.[8-12]

Copper(I) complex of 1-allyl-2-tetrazoline-5-thione. This complex, hereafter referred to as CUATT-5 (HATT-5 = 1-allyl-2-tetrazoline-5-thione) was prepared as follows: A mixture of 0·05 mole of allyl isothiocyanate and 0·075 mole of sodium azide (dissolved in 100 ml of water) was stirred at room temperature for 2 hr, excess of isothiocyanate was removed by ether extraction, and the aqueous layer containing the sodium salt of the ligand (NaATT-5) was further diluted with 200 ml of water. A part of this solution on treatment with an acidic solution of cupric chloride or sulphate gave first a deep blue-green precipitate which within 30 min turned to a perfectly white complex in which copper(I) was present. This was filtered off, washed well with water, and dried. This complex is soluble in conc. sulphuric acid.

Procedure

Dissolve or suspend a few crystals (≥ 5 mg) of the test material in 0·25–0·5 ml of sulphuric acid (conc. or 3 + 1), and add a few or several drops of this solution to a test-tube containing 1 ml of 0·15% potassium ferricyanide solution and 5 or 6 drops ($\sim 0·25$ ml) of conc. ammonia solution. Immediate formation of a deep salmon-pink, red-pink, pink-purple or purple colour or precipitate indicates the presence of copper (I).

RESULTS AND DISCUSSION

Applicability of the test

The following copper(I) salts and complexes were tested, and all gave a positive colour reaction: CuCl; CuCN; CuSCN, $Cu_2SO_3.H_2O$; $[Cu(tu)_3]Cl$; $[Cu(tu)_3]_2SO_4.(H_2O)_2$; $[Cu_2(tu)_5](NO_3)_2.3H_2O$; $[Cu_2(tu)_5]SO_4.3H_2O$; $[Cu_2(tu)_6]SO_4.H_2O$; $[Cu(tu)_x]_2[Fe(CN)_5NO]$; [tu = thiourea].

Zusammenfassung—10–100 ppm Kupfer werden durch flüssigflüssig-Extraktion und Atomabsorption bestimmt; dabei wurde der flüssige Ionenaustauscher Amberlite LA 2 in der Thiocyanatform verwendet. Das Verfahren geht schnell und gibt genaue Ergebnisse, es werden stabile Reagentien und StandardLaborausrüstung benützt.

Résumé—On a dosé le cuivre dans le domaine 10–100 ppM par une technique d'extraction par solvant et absorption atomique comprenant l'emploi de l'échangeur d'ions liquide Amberlite LA 2 sous la forme thiocyanate. La technique est rapide et donne des résultats de bonne précision, et utilise des réactifs stables et une instrumentation normale.

Talanta, Vol 21, pp 635–637 Pergamon Press, 1974 Printed in Great Britain

NEW QUALITATIVE COLOUR REACTION FOR THE IDENTIFICATION OF COPPER(I) COMPOUNDS AND COMPLEXES

(*Received* 2 *October* 1973. *Accepted* 29 *November* 1973)

Numerous tests are available for the detection of copper(II), but there are few tests for copper(I). Certain organic reagents[1–7] are capable of detecting copper(I) but only when it is present in ionic form. This communication describes a new and simple qualitative colour reaction, which is useful for the detection of copper(I) in ionic form or when present in complexes with certain organic ligands. The reaction essentially consists in treating a sulphuric acid solution or suspension of copper(I) compound or complex with ferricyanide solution mixed with ammonia, whereupon a deep salmon-pink, pink-purple or purple colour or precipitate, characteristic of copper(I), is immediately formed.

EXPERIMENTAL

Reagents

Potassium ferricyanide solution. A 0·15% w/v solution in water.

Concentrated ammonia solution.

Copper(I) salts. Various copper(I) salts, *e.g.* CuCl, CuCN, CuSCN, and $Cu_2SO_3.H_2O$ were prepared by the ordinary procedures.

Copper(I)–thiourea complexes. Various copper(I)–thiourea complexes (*q.v.*) were prepared by the published procedures.[8–12]

Copper(I) complex of 1-allyl-2-tetrazoline-5-thione. This complex, hereafter referred to as CUATT-5 (HATT-5 = 1-allyl-2-tetrazoline-5-thione) was prepared as follows: A mixture of 0·05 mole of allyl isothiocyanate and 0·075 mole of sodium azide (dissolved in 100 ml of water) was stirred at room temperature for 2 hr, excess of isothiocyanate was removed by ether extraction, and the aqueous layer containing the sodium salt of the ligand (NaATT-5) was further diluted with 200 ml of water. A part of this solution on treatment with an acidic solution of cupric chloride or sulphate gave first a deep blue-green precipitate which within 30 min turned to a perfectly white complex in which copper(I) was present. This was filtered off, washed well with water, and dried. This complex is soluble in conc. sulphuric acid.

Procedure

Dissolve or suspend a few crystals (≥ 5 mg) of the test material in 0·25–0·5 ml of sulphuric acid (conc. or 3 + 1), and add a few or several drops of this solution to a test-tube containing 1 ml of 0·15% potassium ferricyanide solution and 5 or 6 drops ($\sim$0·25 ml) of conc. ammonia solution. Immediate formation of a deep salmon-pink, red-pink, pink-purple or purple colour or precipitate indicates the presence of copper (I).

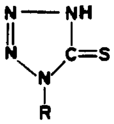
RESULTS AND DISCUSSION

Applicability of the test

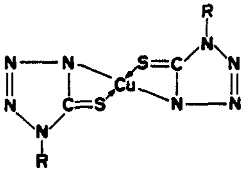
The following copper(I) salts and complexes were tested, and all gave a positive colour reaction: CuCl; CuCN; CuSCN, $Cu_2SO_3.H_2O$; $[Cu(tu)_3]Cl$; $[Cu(tu)_3]_2SO_4.(H_2O)_2$; $[Cu_2(tu)_5](NO_3)_2.3H_2O$; $[Cu_2(tu)_5]SO_4.3H_2O$; $[Cu_2(tu)_6]SO_4.H_2O$; $[Cu(tu)_x]_2[Fe(CN)_5NO]$; [tu = thiourea].

Copper(II) compounds fail to give a positive response to this test; they produce a yellow, dirty yellow, or brownish-yellow colour or precipitate under the same experimental conditions.

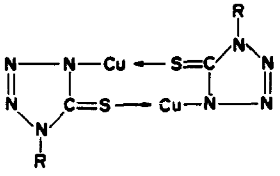
The ligand 1-allyl-2-tetrazoline-5-thione (HATT-5) (**I**) when treated with copper(II) solution, gives a deep bluish-green precipitate which is supposed to be a copper(II) complex of **I** with 1 : 2 (metal : ligand) ratio. The structure **II** for this complex is consistent with copper(II) complexes of other 1-substituted tetrazoline-5-thiones.[13,14] **II**, however, changes colour within minutes, and is converted into a perfectly white substance which may be the copper(I) complex of **I** (structure **III**). Since **I** is known to possess unusual reducing properties,[15] **III** is likely to be formed by the reducing action of **I** (present in excess) on **II**. The binuclear structure **III** for the copper(I) complex of **I** is based on similar cuprous complexes of certain other 1-substituted tetrazoline-5-thiones,[16] in which the metal is linked to the ligand molecules through both nitrogen and sulphur. The fact that **III** gives a positive response to the present colour reaction, is a direct indication that it is a copper(I) complex. Quantitative work on the action of I on copper(II) has also proved the formation of a complex with 1 : 1 (metal : ligand) ratio.



I



II



III

$(R = -CH_2-CH{=}CH_2)$

Nature of the coloured product

The exact nature of the coloured product which is formed in the test is uncertain. It may involve, *e.g.*, with cuprous chloride, the formation of a cuprous ammine chloride–ferricyanic acid complex $[Cu(NH_3)_2Cl.H_3Fe(CN)_6]$. This formula is supported by the fact that ferricyanic acid $H_3Fe(CN)_6$ tends to form addition compounds with a variety of other molecules.[17] The cuprous ammine chloride results from the action of ammonia on the cuprous compound, whereas ferricyanic acid is formed by the action of sulphuric acid on ferricyanide. At the same time, the formation of a compound of the type $[Cu(NH_3)_2]_3^{3+}[Fe(CN)_6]^{3-}$ cannot be ruled out.

Other possible applications of the reaction

The new colour reaction for copper(I) is dependent upon the presence of ammonia, and the use of alkali metal hydroxides or carbonates makes the reaction negative. This fact, therefore, can also form the basis of detecting ammonium ion *via* the release of ammonia by the action of alkali. For this purpose, a 2% w/v solution of **III** (CuATT-5) in conc. sulphuric acid is proposed as the reagent. The ammonium compound is thoroughly shaken with sodium hydroxide solution, and ferricyanide and reagent solutions are added in succession. A pink-purple colour or precipitate gives a positive indication of ammonium ion.

Ferrocyanide can also be used in place of ferricyanide in the present test, but with some reservations. The pink purple precipitate obtained with ferrocyanide turns deep blue or bluish-green on addition of a drop or two of hydrogen peroxide. This colour change is negative when ferricyanide is used. Hence, this reaction may be used for differentiating ferrocyanide from ferricyanide.

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Summary—The colour reaction of copper(I) salts and complexes, in sulphuric acid medium, with ferricyanide and ammonia, has been used for the general identification of cuprous compounds. A sulphuric acid solution of Cu(I) compound, when treated with a dilute ferricyanide solution in the presence of ammonia, gives a salmon-pink, red-pink, pink-purple or purple colour or precipitate, characteristic of copper(I). Copper(II) compounds fail to give a positive response. The reaction also forms the basis of a test for ammonium ion and differentiation between ferrocyanide and ferricyanide. The preparation of the copper(I) complex of 1-allyl-2-tetrazoline-5-thione is described.

Zusammenfassung—Die Farbreaktion von Kupfer(I)-salzen und komplexen mit Hexacyanoferrat(III) und Ammoniak in schwefelsaurem Medium wurde zur allgemeinen Identifizierung von Kupfer(I)-Verbindungen verwendet. Behandelt man eine schwefelsaure Lösung einer Kupfer(I)-Verbindung mit verdünnter Ferricyanidlösung in Gegenwart von Ammoniak, dann erhält man einen Niederschlag, die für Kupfer(I) charakteristisch sind. Kupfer(II)-Verbindungen reagieren nicht positiv. Die Reaktion liegt auch einer Probe auf Ammoniumionen und einer Unterscheidung zwischen Ferrocyanid und Ferricyanid zugrundle. Die Darstellung des Kupfer(I)-Komplexes von 1-Allyl-2-tetrazolin-5-thion wird beschrieben.

Résumé—La reaction coloree des sels et complexes du cuivre (I), en milieu acide sulfurique, avec le ferricyanure et l'ammoniaque, a été utilisée pour l'identification générale de composés cuivreux. Une solution en acide sulfurique de composé de Cu(I), quand elle est traitée par une solution diluée de ferricyanure en la présence d'ammoniaque, donne une coloration ou un précipité, rose–saumon, rose–rouge, rose–pourpre ou pourpre, caractéristique du cuivre (I). Les composés du cuivre (II) ne donnent pas de réponse positive. La réaction forme aussi la base d'un essai pour l'ion ammonium et la différenciation entre ferrocyanure et ferricyanure. On décrit la preparation du complexe du cuivre (I) de la 1-allyl 2-tétrazoline 5-thione.

Talanta, Vol. 21, pp. 638–641. Pergamon Press. 1974 Printed in Great Britain

3-NITROSO-4-HYDROXY-5,6-BENZOCOUMARIN AS A SELECTIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III)

(*Received* 2 *October* 1973. *Accepted* 8 *December* 1973)

Various reagents for the colorimetric determination of ruthenium have been reviewed.[1–4] Some of the important and recently introduced reagents are 2,3-diaminopyridine,[5] 2,4,6-tris(2′-pyridyl)-5-triazine,[6] chrome azurol S,[7] 3,4-diaminobenzoic acid,[8] acenaphthenequinone monoxime,[9] oximidobenzotetronic acid[10] and 3-nitroso-2,6-pyridinediol.[11]

3-Nitroso-4-hydroxy-5,6-benzocoumarin (NHBC) is a chelating agent which has already been used for the spectrophotometric determination of nickel[12] and as a spot-test reagent for the detection of cobalt.[13] It reacts with ruthenium(III), giving a pinkish-violet complex, which is extractable into n-butanol. Under suitable conditions, the reagent can be used for the spectrophotometric determination of ruthenium in the presence of all other platinum metals.

EXPERIMENTAL

Reagents

NHBC solution in acetone, 0·002*M*.

Ruthenium(III) stock solution, 0·01*M*. Ruthenium(III) chloride was dissolved in doubly distilled water containing sufficient hydrochloric acid to give a final acidity of 1*M* and the solution standardized by precipitating ruthenium as the hydrated oxide, igniting it carefully in air, reducing in hydrogen and cooling in an atmosphere of carbon dioxide. Working solutions were prepared by dilution of the stock solution.

All other chemicals used were of reagent grade.

Procedure

To a suitable aliquot of solution containing 11·0–63·0 μg of ruthenium(III) in a 50 ml Pyrex glass-stoppered bottle, add 1 ml of 2*M* sodium perchlorate and an excess of the reagent solution (5 ml). Adjust the pH to 5·5–8·0 and dilute to 10 ml. Heat the mixture for 40 min on a steam-bath. Cool and dilute to 10ml with doubly distilled water. Extract the pinkish-violet complex with 10 ml of n-butanol. Centrifuge the organic layer and measure its absorbance at 520 nm against a reagent blank prepared under identical conditions.

RESULTS

Absorption spectra

The absorption spectrum of the pinkish-violet complex extracted into *n*-butanol is shown in Fig. 1. The absorption maximum is at 520 nm where the absorbance of the reagent is low.

Reaction conditions

Solutions containing fixed amounts of ruthenium and reagent were prepared, of which the pH was varied from 3·5 to 10·0, and extracted as described. The absorbance at 520 nm was constant over the pH range 5·5–8·0. At lower and higher pH the absorbance decreased.

For maximum colour development, heating for at least 20 min on a steam-bath was found to be necessary. Further heating for 2 hr had no effect on the colour of the complex. Heating for 40 min is recommended to ensure complete complexation. The colour of the complex was found to be stable for at least 92 hr at room temperature.

Increasing amounts of reagent were added to 1 ml of 5×10^{-4}*M* ruthenium at pH of 6·5 (acetate buffer). After the extraction, the absorbance was measured at 520 nm against corresponding reagent blanks prepared under identical conditions. The study showed that at least a 12-fold molar excess of the reagent is required for full colour development.

The system obeys Beer's law up to 7·4 ppm of ruthenium. The optimum range for the accurate determination of ruthenium, as evaluated from a Ringbom plot, is 1·1–6·3 ppm. The molar absorptivity is $1{\cdot}04 \times 10^{4}$

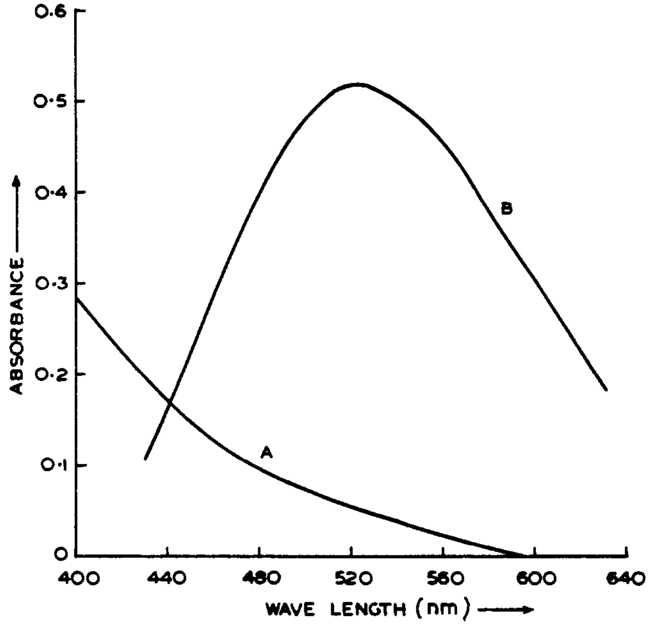

Fig. 1. Absorption spectra. (A)—Reagent blank *vs.* n-butanol (reagent $1 \times 10^{-3}M$). (B)—Ruthenium complex *vs.* reagent blank [Ru(III) $5 \times 10^{-5}M$; reagent $1 \times 10^{-3}M$).

$\text{l.mole}^{-1}.\text{cm}^{-1}$. The precision of the method was tested by measuring the absorbance of 10 samples each containing a final ruthenium concentration of 5·05 ppm. The mean absorbance was 0·520 with a standard deviation of 0·004.

Molar composition of the complex

Job's method of continuous variations and the logarithmic method of Bent and French both indicate the formation of a 1 : 2 complex (metal : ligand).

Effect of other ions

The effect of various ions was studied. With 5·05 ppm of ruthenium, the following ions present in the amounts (in ppm) shown in parentheses did not cause a deviation of more than ±2% in absorbance from that expected: chloride (3000), bromide (2000), iodide (2000), fluoride (250), citrate (200), thiocyanate (1500), oxalate (150), nitrate (3000), phosphate (50), thiosulphate (100), borate (250), sulphate (5000), sulphite (100), Hg(II) (100), Cd(II) (250), Zn(II) (25), Th(IV) (125), Cr(III) (200), Al(III) (15), Mn(II) (250), Pb(II) (150), Mo(VI) (25), Bi(III) (100), U(VI) (100), Mg(II) (200), Ca(II) (250), Ba(II) (250), Sr(II) (250), Ag(I) (50), Ce(IV) (80), As(III) (150), Sb(III) (150), In(III) (60), V(V) (5), Ni(II) (25), Pd(II) (25), Cu(II) (20), Pt(IV) (50), Os(VIII) (45), Ir(IV) (20), Rh(III) (50), Ir(III) (35), Os(IV) (45) and Au(III) (50).

EDTA, nitrite, thiourea, cobalt(II) and iron(III) were found to interfere in the determination of ruthenium. Interference due to 10 ppm of iron(III) could be removed by adding 200 ppm of fluoride. Attempts to mask cobalt(II) were unsuccessful.

Determination in ores

Synthetic mixtures containing platinum metals (*e.g.*, corresponding to osmiridium or syserkite) were prepared and the ruthenium content determined (Table 1).

Procedure. Mix the sample with sodium chloride and heat the mixture to redness in a current of chlorine. Extract with water, filter and add concentrated hydrochloric acid. The platinum metals form soluble chloro-complexes. Reflux the solution in presence of concentrated hydrochloric acid and ethanol to reduce any Ru(IV) which may be present, to Ru(III). Evaporate the solution to a small volume, cool and make it up to 50 ml with 1*M* hydrochloric acid. Determine the ruthenium content in the sample by the procedure already described in the experimental section.

Table 1. Determination of ruthenium in synthetic mixtures corresponding to osmiridium or syserkite

Ruthenium present, *ppm*	Rh, *ppm*	Ir, *ppm*	Os, *ppm*	Pd, *ppm*	Pt, *ppm*	Ruthenium found, *ppm*
2·75	—	5·24	20·57	—	0·06	2·78
4·19	—	8·00	32·97	—	0·09	4·16
5·05	—	9·64	39·66	—	0·11	4·99

CONCLUSION

Although many reagents are known for the colorimetric determination of ruthenium, comparatively few are well suited for the purpose. Thiourea[1] has proved to be satisfactory for the determination of about 2–15 ppm of ruthenium and the tolerance for iridium, rhodium, platinum and nickel offers some advantage but the sensitivity is very low and palladium interferes. 1,10-Phenanthroline and 4,7-diphenylphenanthroline[1] give sensitive colour reactions but the intensity of the colour depends upon several factors that require control to produce precise results. Considerable interference is caused by other metals and a time-consuming prior separation of ruthenium by distillation is necessary. *p*-Nitrosodimethylaniline[14] is highly sensitive (0·0028 $\mu g/cm^2$) but perhaps the most objectionable feature in this method is the narrow pH range, which is also the pH required for precipitation of ruthenium as the hydrated oxide. Osmium and nitrate interfere seriously and should be absent.

Recently 2,3-diaminopyridine,[5] 2,4,6-tris(2′-pyridyl)-5-triazine,[6] oximidobenzotetronic acid[10] and 3,4-diaminobenzoic acid[8] have been used for the determination of ruthenium. In the case of 2,3-diaminopyridine, prior separation of ruthenium from other metals is necessary. Oximidobenzotetronic acid is selective but the sensitivity is low. 3,4-Diaminobenzoic acid is a sensitive reagent but the pH range is narrow (4·0–4·5) and other platinum metals interfere.

The present procedure, involving the use of NHBC as spectrophotometric reagent for ruthenium, is fairly sensitive. None of the platinum metals interferes in the determination. Among the group VIII metals only cobalt interferes in the determination. The major advantage of this method is that the reagent can be used as such for the determination of ruthenium in presence of large quantities of other platinum metals in readily attainable oxidation states, without the use of masking agents.

Acknowledgement—The authors are thankful to the Council of Scientific and Industrial Research (India), for the award of a fellowship to one of them (N.K.).

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Summary—The pinkish-violet complex developed on interaction of ruthenium(III) with 3-nitroso-4-hydroxy-5,6-benzocoumarin (NHBC) in the pH range 5·5–8·0 can be extracted into n-butanol. The complex has an absorption maximum at 520 nm. Maximum colour development takes place

after heating for 20 min on a steam-bath and the extracted complex is stable for at least 92 hr. Beer's law is followed up to 7·4 ppm of ruthenium. The molar absorptivity is $1{\cdot}04 \times 10^4$ $l.mole^{-1}.cm^{-1}$. The composition of the complex is 1 : 2 (ruthenium : NHBC). None of the other platinum metals was found to interfere in the determination of ruthenium, even though present in large excess.

Zusammenfassung—Der rosaviolette Komplex aus Ruthenium(III) und 3-Nitroso-4-hydroxy-5,6-benzocumarin (NHBC) bei pH 5,5–8,0 kann in n-Butanol extrahiert werden. Der Komplex hat ein Absorptionsmaximum bei 520 nm. Die maximale Farbentwicklung findet nach 20 min Erhitzen auf dem Dampfbad statt; der extrahierte Komplex ist mindestens 92 h lang stabil . Das Beersche Gesetz gilt bis hochstens 7,4 ppm Ruthenium. Der molare Extinktionskoeffizient beträgt $1{,}04 \times 10^4$ $l.mol^{-1}.cm^{-1}$. Die Zusammensetzung des Komplexes ist 1 :2 (Ruthenium : NHBC). Keines der anderen Platinmetalle stört bei der Bestimmung von Ruthenium, auch nicht in großem Überschuß.

Résumé—Le complexe violet-rosâtre développé par interaction du ruthénium(III) avec la 3-nitroso 4-hydroxy 5,6-benzocoumarine (NHBC) dans le domaine de pH 5,5–8,0 peut être extrait en n-butanol. Le complexe a un maximum d'absorption à 520 nm. Le développement maximal de la couleur se fait après chauffage pendant 20 mn au bain de vapeur et le complexe extrait est stable pendant au moins 92 h. La loi de Beer est suivie jusqu'à 7,4 ppm de ruthénium. Le coefficient d'absorption molaire est $1{,}04 \times 10^4$ $l.mole^{-1}.cm^{-1}$. La composition du complexe est 1 : 2 (ruthénium : NHBC). On a trouvé qu'aucun des autres métaux du platine n'interfère dans le dosage du ruthénium, même présent en grand excès.

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ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—IV*

SELEKTIVE SORPTION DER FLIEßMITTEL AN DER SILICAGEL- UND ALUMINIUMOXIDSÄULE SOWIE AN PAPIERSTREIFEN

(*Eingegangen am* 27. *März* 1973. *Revidiert am* 12. *September* 1973. *Angenommen am* 30. *November* 1973)

Früher veröffentlichte Untersuchungen[1–3] haben gezeigt, daß es im Verlauf des chromatographischen Prozesses an der Cellulosesäule zur Entmischung der Lösungsmittel kommt und daß man die Verhältnisse an der Grenze zwischen der festen und der flüssigen Phase offensichtlich nicht nur mit der Bildung eines Cellulose-Wasser-Komplexes erklären kann. Es war nun interessant zu erfahren, ob das für Cellulose erkannte Verhalten der Fließmittel für andere Träger gilt oder ob sich der Charakter der Sorption von Fall zu Fall ändert. Darum wurde eine Versuchsreihe angesetzt, bei der einige schon früher an Cellulosesäulen durchgeführten Experimente an Silicagel- und an Aluminiumoxidsäulen sowie an Streifen von Chromatographiepapier durchgeführt wurden.

EXPERIMENTELLER TEIL

Für die Versuche wurden die früher beschriebenen Säulen[2] verwendet.

Reagenzien

Silicagel. Korngröße 0,3 bis 0,6 mm, gewaschen, bei 110 C getrocknet.
Aluminiumoxid. REANAL für chromatographische Zwecke.

Die eingesetzten Alkohole wurden durch mehrfache Destillation gereinigt. Tabelle 1 gibt die Zusammensetzung der untersuchten Alkohol–Wasser-Mischungen an.

Die Bestimmung des Wassergehalts der Lösungen erfolgte durch. Titration mit Karl-Fischer-Lösung mit biamperometrischer Endpunktsanzeige.[4] Die papierchromatographischen Untersuchungen wurden auf Streifen von Whatman Papier Nr. 3 MM durchgeführt, die entweder zwischen zwei 7 cm langen mikroskopischen Objektträgern oder zwischen zwei Glasplatten von 24 × 2 cm lagen, die durch Anritzen mit einem Diamanten in 2 cm lange Abschnitte geteilt worden waren.

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* Mitteilung III: *Talanta*, 1965, **12**, 171.

after heating for 20 min on a steam-bath and the extracted complex is stable for at least 92 hr. Beer's law is followed up to 7·4 ppm of ruthenium. The molar absorptivity is $1{\cdot}04 \times 10^4$ l.mole^{-1}.cm^{-1}. The composition of the complex is 1 : 2 (ruthenium : NHBC). None of the other platinum metals was found to interfere in the determination of ruthenium, even though present in large excess.

Zusammenfassung—Der rosaviolette Komplex aus Ruthenium(III) und 3-Nitroso-4-hydroxy-5,6-benzocumarin (NHBC) bei pH 5,5–8,0 kann in n-Butanol extrahiert werden. Der Komplex hat ein Absorptionsmaximum bei 520 nm. Die maximale Farbentwicklung findet nach 20 min Erhitzen auf dem Dampfbad statt; der extrahierte Komplex ist mindestens 92 h lang stabil. Das Beersche Gesetz gilt bis hochstens 7,4 ppm Ruthenium. Der molare Extinktionskoeffizient beträgt $1{,}04 \times 10^4$ l.mol^{-1}.cm^{-1}. Die Zusammensetzung des Komplexes ist 1 :2 (Ruthenium : NHBC). Keines der anderen Platinmetalle stört bei der Bestimmung von Ruthenium, auch nicht in großem Überschuß.

Résumé—Le complexe violet-rosâtre développé par interaction du ruthénium(III) avec la 3-nitroso 4-hydroxy 5,6-benzocoumarine (NHBC) dans le domaine de pH 5,5–8,0 peut être extrait en n-butanol. Le complexe a un maximum d'absorption à 520 nm. Le développement maximal de la couleur se fait après chauffage pendant 20 mn au bain de vapeur et le complexe extrait est stable pendant au moins 92 h. La loi de Beer est suivie jusqu'à 7,4 ppm de ruthénium. Le coefficient d'absorption molaire est $1{,}04 \times 10^4$ l.mole^{-1}.cm^{-1}. La composition du complexe est 1 : 2 (ruthénium : NHBC). On a trouvé qu'aucun des autres métaux du platine n'interfère dans le dosage du ruthénium, même présent en grand excès.

Talanta, Vol. 21, pp. 641–645. Pergamon Press, 1974 Printed in Great Britain

ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—IV*

SELEKTIVE SORPTION DER FLIEßMITTEL AN DER SILICAGEL- UND ALUMINIUMOXIDSÄULE SOWIE AN PAPIERSTREIFEN

(*Eingegangen am* 27. *März* 1973. *Revidiert am* 12. *September* 1973. *Angenommen am* 30. *November* 1973)

Früher veröffentlichte Untersuchungen[1–3] haben gezeigt, daß es im Verlauf des chromatographischen Prozesses an der Cellulosesäule zur Entmischung der Lösungsmittel kommt und daß man die Verhältnisse an der Grenze zwischen der festen und der flüssigen Phase offensichtlich nicht nur mit der Bildung eines Cellulose-Wasser-Komplexes erklären kann. Es war nun interessant zu erfahren, ob das für Cellulose erkannte Verhalten der Fließmittel für andere Träger gilt oder ob sich der Charakter der Sorption von Fall zu Fall ändert. Darum wurde eine Versuchsreihe angesetzt, bei der einige schon früher an Cellulosesäulen durchgeführten Experimente an Silicagel- und an Aluminiumoxidsäulen sowie an Streifen von Chromatographiepapier durchgeführt wurden.

EXPERIMENTELLER TEIL

Für die Versuche wurden die früher beschriebenen Säulen[2] verwendet.

Reagenzien

Silicagel. Korngröße 0,3 bis 0,6 mm, gewaschen, bei 110 C getrocknet.

Aluminiumoxid. REANAL für chromatographische Zwecke.

Die eingesetzten Alkohole wurden durch mehrfache Destillation gereinigt. Tabelle 1 gibt die Zusammensetzung der untersuchten Alkohol-Wasser-Mischungen an.

Die Bestimmung des Wassergehalts der Lösungen erfolgte durch Titration mit Karl-Fischer-Lösung mit biamperometrischer Endpunktsanzeige.[4] Die papierchromatographischen Untersuchungen wurden auf Streifen von Whatman Papier Nr. 3 MM durchgeführt, die entweder zwischen zwei 7 cm langen mikroskopischen Objektträgern oder zwischen zwei Glasplatten von 24 × 2 cm lagen, die durch Anritzen mit einem Diamanten in 2 cm lange Abschnitte geteilt worden waren.

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* Mitteilung III: *Talanta*, 1965, **12**, 171.

Tabelle 1. Wassergehalt der untersuchten Alkohol–Wasser-Mischungen

Bezeichnung der Reihen	Wassergehalt in % *w/v*			
	Methanol	Äthanol	Propanol	Butanol
1	0,09	—	0,70	0,45
2	0,44	—	0,80	0,48
3	1,19	4,93	4,48	4,09
4	3,91	5,03	5,56	5,29
5	5,43	10,45	9,59	6,80
6	17,59	21,35	9,75	9,55

ERGEBNISSE UND DISKUSSION

Entmischung der Fließmittel an der Silicagel- und an der Aluminiumoxidsäule

Als Beispiel für das Studium der Entmischung der Fließmittel an der Silicagel- und der Aluminiumoxidsäule wurden die Gemische organisches Lösungsmittel–Säure und Alkohol–Wasser gewählt.

System organisches Lösungsmittel–Säure

Als typische Beispiele wurden Gemische aus Benzylalkohol und Chlorwasserstoffsäure und Aceton und Chlorwasserstoffsäure studiert und die Abhängigkeit der Konzentration der Säure im Filtrat vom Volumen des Filtrats verfolgt.

Abbildung 1 gibt die Ergebnisse der Untersuchungen wieder.

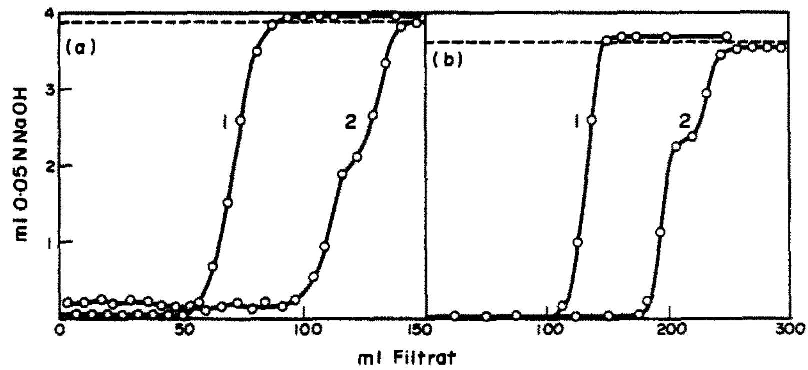

Abb. 1. Konzentrationsänderung der Salzsäure im Filtrat.
A: Silicagel, bei 110°C getrocknet. B: Aluminiumoxid, bei 110°C getrocknet. 1: Benzylalkohol-konz. HCl (98 + 2). 2: Aceton–konz. HCl (98 + 2).

Ein Vergleich der Kurven zeigt, daß der Charakter der Elutionskurven bei Silicagel und Aluminiumoxid ganz ähnlich ist. Die Lage der Säurefront ist zwar beim Aluminiumoxid zu höheren Werten verschoben, es besteht aber kein Zweifel, daß die an den beiden Trägermaterialien erhaltenen Versuchsergebnisse nur quantitativ, nicht aber qualitativ verschieden sind.

System Alkohol–Wasser

Außerdem wurde noch die selektive Sorption von Mischungen aus unterschiedlichen Alkoholen und Wasser an beiden Säulenarten getestet und die Befunde mit der bei Verwendung von Cellulose als Trägermaterial erhaltenen Ergebnissen[1] verglichen.

Abbildung 2 zeigt die Resultate an den beiden anorganischen Trägern.

Ein Vergleich der hier wiedergegebenen Befunde mit denen an Cellulosesäulen bestätigt, daß der Charakter des Entmischungsvorganges der Fließmittel bei den geprüften Trägermaterialien analog ist. Das ähnliche Verhalten der Fließmittel den getrockneten Trägern gegenüber zeigt, daß es offenbar in allen geprüften Fällen zu einer Sorption aller Komponenten des Lösungsmittelgemisches an der Oberfläche des Trägers kommt. Man erkennt weiter, daß auch im System Alkohol–Wasser die Wirkung der Träger nicht prinzipiell unterschiedlich sind.

Entmischung der Fließmittel am Chromatographie-Papier

Wie schon früher nachgewiesen werden konnte,[1] ist die Auswertung von freien Papierstreifen ungeeignet, und man kann auf diesem Wege nur Daten von sehr begrenzter Aussagekraft erhalten. Andererseits gibt aber die Technik der Papierchromatographie die besten experimentellen Möglichkeiten für das Studium der Veränderung in der Zusammensetzung der Fließmittel im Verlauf des chromatographischen Prozesses. Um diese Technik anwenden zu können und die störenden Einflüsse durch das selektive Abdampfen zu eliminieren, wurde für das Studium eine modifizierte Versuchsanordnung benutzt, die es ermöglichte, exakte Resultate auch bei Einsatz der Papierchromatographie zu erhalten. Das Ziel dieser Versuchsserie war die Ermittlung der quantitativen Zusammensetzung des Fließmittels in verschiedenen Phasen des Trennprozesses. Zunächst sollte festgestellt werden, ob die chromatographische Trennung unter Gleichgewichtsbedingungen an der Grenze zwischen der festen und der flüssigen Phase verläuft oder ob die Gleichgewichtseinstellung erst nach einer gewissen Zeit erfolgt, die u.U. für die eigentliche Trennung schon nicht mehr interessant ist.

Dazu wurde der zwischen den beiden Objektträgern befindliche Streifen Chromatographie-Papier in das zu untersuchende Lösungsmittelgemisch, z.B. Methanol-Wasser 9 + 1 bis 1 + 9, eingetaucht. Es wurde aufsteigend bis zum oberen Rand der Gläser bzw. im Durchfluß 24, 48 und 96 h entwickelt. Abbildung 3 zeigt die

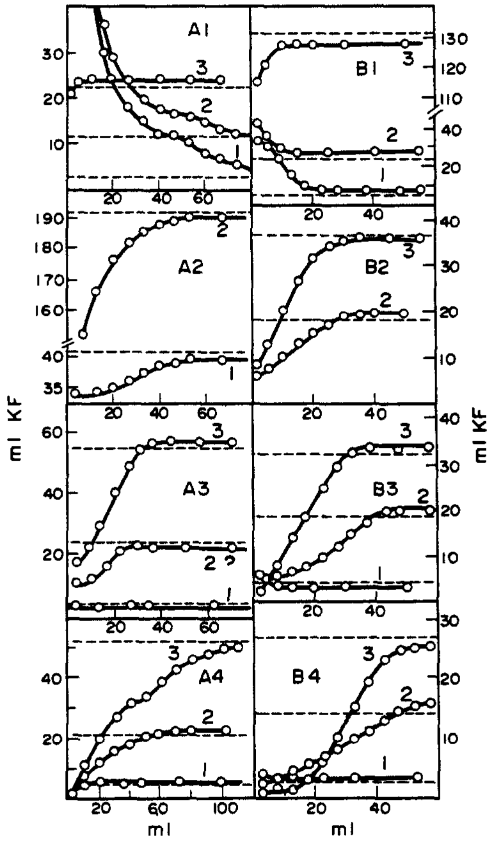

Abb. 2. Änderung des Wassergehalts im Filtrat.
A: Silicagelsäule. B: Aluminiumoxidsäule. KF = Karl Fischer Reagens.

Methanol-Wasser:	Kurve	A 1	1 2 3	B 1	1 2 3
	Mischung (Tabelle 1)		1 3 5		2 4 6
Äthanol-Wasser:	Kurve	A 2	1 2 -	B 2	2 3 -
	Mischung (Tabelle 1)		4 6 -		3 5 -
1-Propanol-Wasser:	Kurve	A 3	1 2 3	B 3	1 2 3
	Mischung (Tabelle 1)		1 3 6		2 4 5
1-Butanol-Wasser:	Kurve	A 4	1 2 3	B 4	1 2 3
	Mischung (Tabelle 1)		1 4 6		2 3 5

Abhängigkeit des Wassergehalts in der oberen, vorher markierten Zone des Chromatogramms von dem des ursprünglichen Gemisches bei Labortemperatur, bei 1°C und bei 46°C.

Wie das Bild zeigt, kommt es erst nach längerer Zeit zu einer Gleichgewichtseinstellung zwischen der mobilen und der stationären Phase, bei der ein Ausgleich in der Zusammensetzung des Lösungsmittelgemisches erfolgt. Man sieht weiter, daß die Temperatur die Verhältnisse kaum beeinflußt, denn der Charakter der Kurven ist auch bei 1°C und 46°C sehr ähnlich.

Um die Konzentrationsänderungen der einzelnen Komponenten des Gemisches über die ganze Länge des Chromatogramms zu erfassen, wurde ein Papierstreifen zwischen zwei Glasplatten 24 x 2 cm in dem zu untersuchenden Lösungsmittelgemisch entwickelt. Nachdem das Lösungsmittel die vorgegebene Strecke durchlaufen hatte, wurden die einzelnen Zonen des Chromatogramms abgebrochen, gewogen und der Wassergehalt durch Titration nach Karl Fischer bestimmt. Es wurden Methanol, Äthanol, 1-Propanol und 1-Butanol in praktisch wasser freier Form und im Gemisch mit 20% Wasser studiert. Die Versuche haben ganz ähnliche Resultate gezeigt. Als Beispiel sind in Abb. 4 die Ergebnisse der beiden Versuchsreihen mit 1-Propanol dargestellt. Bei den reinen Alkoholen ist der Wassergehalt im Verlauf des ganzen Chromatogramms praktisch konstant und die Wassermenge hängt auch nicht von der Art des Alkohols ab. Bei den 80% igen Alkoholen sinkt der Wassergehalt mit steigendem R_f-Wert.

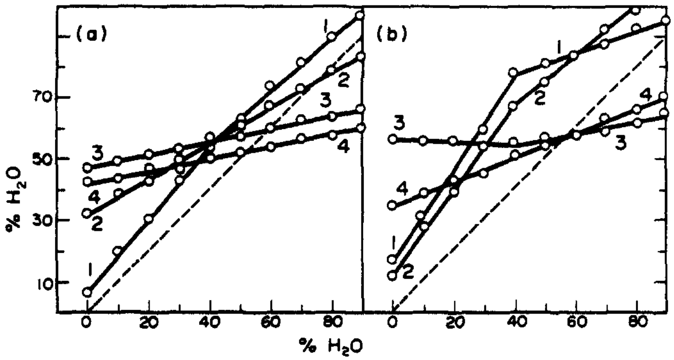

Abb. 3. Abhängigkeit des Wassergehalts in der oberen Zone des Chromatogramms von der Ausgangskonzentrat
A: Silicagelsaüle. B: Aluminiumoxidsäule.

	a 1	a 2	a 3	a 4	b 1	b 2	b 3	b 4
Entwicklungsdauer, *h*	0,5	24	48	72	0,5	0,5	72	72
Temperatur, °*C*	20	20	20	20	46	1	46	1

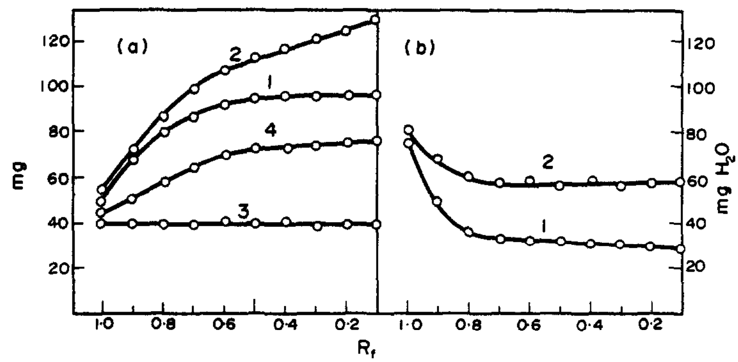

Abb. 4. Abhängigkeit der Masse des Fließmittels, des Wassergehalts und des Prozentgehalts an Wasser im Chromatogramm vom R_f-Wert.
a 1 Masse bei 1-Propanol, *mg*. a 2 Masse bei 80% igem 1-Propanol, *mg*. a 3 Wassergehalt bei 1-Propanol, *mg*. a 4 Wassergehalt bei 80% igem 1-Propanol, *mg*. b 1 Prozentgehalt an Wasser bei Verwendung von 1-Propanol. b 2 Prozentgehalt an Wasser bei Verwendung von 80% igem 1-Propanol.

Die angeführten Versuchsergebnisse haben gezeigt, daß die Konzentration der einzelnen Fließmittelkomponenten während des chromatographischen Prozesses nicht konstant ist. Diese Erkenntnisse, nämlich die selektive Sorption der Fließmittelkomponenten, die Verteilung der Fließmittel bei der Entwicklung und besonders der gleiche Charakter der Sorptionskurven an den einzelnen Trägersorten unterstützt die Meinung, daß in allen Fällen die Wechselwirkung zwischen dem Fließmittel und dem Träger dem gleichen Prinzip gehorchen. Es handelt sich dabei selbstverständlich um die komplexe Wirkung einer Reihe von Faktoren, deren Intensität dann den Typ der Trennung bestimmt.

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LITERATUR

1. J. Michal und G. Ackermann, *Talanta*, 1964, **11**, 441.
2. *Idem*, *ibid.*, 1964, **11**, 451.
3. *Idem*, *ibid.*, 1965, **12**, 171.
4. J. Michal, *Tschech. Patent*, 129173 (1968).

Zusammenfassung—Es wurde die selektive Sorption der Fließmittelkomponenten an verschiedenen Trägern im Verlauf des chromatographischen Prozesses studiert. Dabei ergab sich, daß keine prinzipiellen Unterschiede zwischen der Sorption der untersuchten Lösungsmittel an Silicagel, Aluminiumoxid und Papier (Cellulose) bestehen.

Summary—The selective sorption of components of the mobile phase on different solid supports during the course of the chromatographic process has been studied. It appears from the results, that there are no significant differences in behaviour of the various solvents investigated and silica gel, alumina, and paper (cellulose) as solid phases.

Résumé—On a étudié la sorption sélective des composants de la phase mobile sur différents supports solides au cours du processus chromatographique. Il apparaît des résultats qu'il n'y a pas de différences importantes dans le comportement des divers solvants étudiés et du gel de silice, de l'alumine et du papier (cellulose) comme phases solide.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON IN SEA-WATER BY SOLVENT EXTRACTION AS THE TERNARY COMPLEX IRON(II)–2-NITROSO-4-CHLOROPHENOL–RHODAMINE B

(*Received* 30 *August* 1973. *Accepted* 19 *November* 1973)

We recently reported the determination of iron in city water and river water with 2-nitroso-4-chlorophenol and Rhodamine B,[1] and have now extended the method to cover sea-water. Iron is one of the most interesting trace metal ions in sea-water and has been determined by various methods, most of which necessitate a preconcentration step, such as evaporation,[2] precipitation,[2] co-precipitation,[2,3] co-crystallization,[4,5] solvent extraction[6–9] or ion-exchange,[10–12] require large volumes of sample solution, and are time-consuming.

A few workers have determined iron in sea-water spectrophotometrically,[13,14] but the procedures are not satisfactory for the concentration of iron normally found in sea-water (2–20 μg/l). The method described here eliminates the preconcentration, requires very small volumes of sample solution, and provides rapidity, simplicity, and precision.

Die angeführten Versuchsergebnisse haben gezeigt, daß die Konzentration der einzelnen Fließmittelkomponenten während des chromatographischen Prozesses nicht konstant ist. Diese Erkenntnisse, nämlich die selektive Sorption der Fließmittelkomponenten, die Verteilung der Fließmittel bei der Entwicklung und besonders der gleiche Charakter der Sorptionskurven an den einzelnen Trägersorten unterstützt die Meinung, daß in allen Fällen die Wechselwirkung zwischen dem Fließmittel und dem Träger dem gleichen Prinzip gehorchen. Es handelt sich dabei selbstverständlich um die komplexe Wirkung einer Reihe von Faktoren, deren Intensität dann den Typ der Trennung bestimmt.

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Summary—The selective sorption of components of the mobile phase on different solid supports during the course of the chromatographic process has been studied. It appears from the results, that there are no significant differences in behaviour of the various solvents investigated and silica gel, alumina, and paper (cellulose) as solid phases.

Résumé—On a étudié la sorption sélective des composants de la phase mobile sur différents supports solides au cours du processus chromatographique. Il apparait des résultats qu'il n'y a pas de différences importantes dans le comportement des divers solvants étudiés et du gel de silice, de l'alumine et du papier (cellulose) comme phases solide.

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A few workers have determined iron in sea-water spectrophotometrically,[13,14] but the procedures are not satisfactory for the concentration of iron normally found in sea-water (2–20 μg/l). The method described here eliminates the preconcentration, requires very small volumes of sample solution, and provides rapidity, simplicity, and precision.

EXPERIMENTAL

Reagents

2-Nitroso-4-chlorophenol. Prepared as the copper complex by nitrosation of *p*-chlorophenol in acetic acid containing sodium acetate, copper sulphate, and sodium nitrite. The complex was decomposed by adding hydrochloric acid and the crude product was recrystallized three times from ethyl alcohol, and dissolved in toluene to give a 0·002*M* solution (yellow).

Rhodamine B. The dye was dissolved in distilled water and extracted into toluene to give a 0·01*M* solution (colourless).

Extracting solvent. The 2-nitroso-4-chlorophenol and Rhodamine B solutions were mixed in equal proportions and diluted fivefold with toluene to form the extracting solvent.

Standard iron(II) solution, 0·01M. Mohr's salt (392·2 mg) was dissolved in 100 ml of distilled water containing 1 ml of concentrated sulphuric acid and 1 g of hydroxylammonium chloride, and standardized by EDTA titration. This stock solution was accurately diluted before use.

Buffer solution (pH 4·7). Prepared from 1*M* acetic acid and 1*M* sodium acetate and adjusted to pH 4·7. Then 2 ml of 2·5% hydroxylammonium chloride solution and 5 ml of extracting solvent were shaken with 100 ml of buffer in a 200 ml separatory funnel for about 30 min. The organic phase was discarded and the extraction repeated until the organic phase remained yellow. If any Rhodamine B remained in the buffer, it was extracted by shaking with 10 ml of toluene for a few minutes and the extraction was repeated until the aqueous phase was colourless. This solution was used as the iron-free buffer solution.

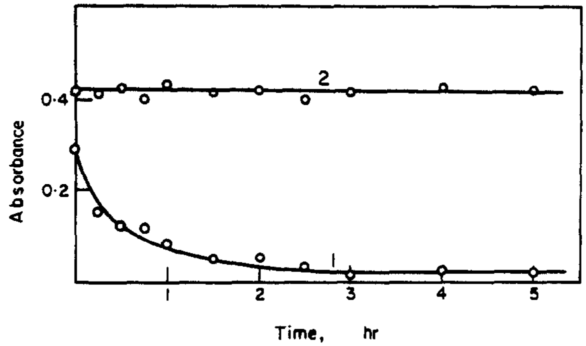

Fig. 1. Stability of iron in sea-water. 1. No HCl added. 2. Contains 2 ml of HCl (1 + 1) per litre. Reference, reagent blank.

Sodium chloride solution. Prepared by dissolving 313 g of sodium chloride in distilled water, diluting to 960 ml, adding 20 ml of 2·5% hydroxyl-ammonium chloride solution, 20 ml of buffer solution and 10 ml of extracting solvent, in that order, shaking the mixture for about 30 min and repeating the extraction until the organic phase remained unchanged. Any Rhodamine B in the aqueous phase was removed as for the buffer.

Hydrochloric acid (1 + 1). Prepared by mixing 50 ml of concentrated hydrochloric acid with 50 ml of distilled water in a 200 ml separatory funnel and shaking with 10 ml of methyl isobutyl ketone (MIBK) for a few minutes. The organic phase was discarded and the extraction repeated twice, then 10 ml of isopropyl ether were added and the extraction repeated three times. Up to 99·8% of the iron is removed by this method. This hydrochloric acid is used for acidifying sea-water samples.

Hydroxylammonium chloride solution, 2·5%.

EDTA solution, 0·01M.

All the reagents used were of analytical reagent grade.

Procedure

Acidify 1 litre of sea-water sample immediately with 2 ml of purified hydrochloric acid (1 + 1). Filter the sea-water samples through a 0·45 μm membrane filter previously washed by filtration of 500 ml of 0·01*M* hydrochloric acid. To an aliquot of <40 ml (or <90 ml) in a 100 ml separatory funnel, add 1 ml of 2·5% hydroxylammonium chloride solution and 5 ml of buffer solution, dilute with distilled water to 50 ml (or 100 ml), add 5 ml of extracting solution, shake the mixture for 30 min with a mechanical shaker and allow to stand for 10 min. Measure the absorbance of the organic phase at 558 nm in 1 cm glass cells against a reagent blank.

RESULTS AND DISCUSSION

In the previous work,[1] benzene was used as solvent. Toluene serves equally well and was used here. The composite reagent was used for convenience. The absorption spectrum remains virtually the same for the toluene medium. The optimal pH range was found to be 3·9–5·3 and the minimal shaking time was 20 min, a time of 30 min being selected for certainty. A waiting time before extraction was not necessary, but one after extraction was, so a period of 10 min was selected. The extracted species was very stable and its absorbance in the toluene phase did not change for at least one week at room temperature. Recovery of iron was found to be quantitative.

Table 1. Interferences

Ion	Added as	Tolerance limit, M	Ion	Added as	Tolerance limit, M
Cl^-	$NaCl$	0·5	Mn^{2+}	$Mn(NO_3)_2·6H_2O$	0·01
Br^-	$NaBr$	0·5	Cd^{2+}	$Cd(NO_3)_2·4H_2O$	0·01
I^-	KI	0·5	Hg^{2+}*	$Hg(NO_3)_2·H_2O$	0·01
NO_2^-	$NaNO_2$	0·5	Al^{3+}	$Al(NO_3)_3·9H_2O$	0·01
NO_3^-	$NaNO_3$	0·5	Cr^{3+}	$Cr(NO_3)_3·9H_2O$	0·01
ClO_3^-	$NaClO_3$	0·5	Bi^{3+}	$BiCl_3$	0·01
ClO_4^-	$NaClO_4$	0·5	In^{3+}	$InCl_3$	0·01
SCN^-	$KSCN$	0·5	Nd^{3+}	$NdCl_3$	0·01
CO_3^{2-}	Na_2CO_3	0·5	Ce^{3+}	$CeCl_3·7H_2O$	0·01
SO_4^{2-}	Na_2SO_4	0·5	Sc^{3+}	$ScCl_3$	0·01
$S_2O_3^{2-}$	$Na_2S_2O_3·5H_2O$	0·5	Y^{3+}	YCl_3	0·01
Li^+	$LiCl$	0·5	La^{3+}	$La(NO_3)_3·6H_2O$	0·01
Na^+	$NaCl$	0·5	Zr^{4+}	$ZrOCl_2$	0·01
K^+	KCl	0·5	Th^{4+}	$Th(NO_3)_4·4H_2O$	0·01
Cs^+	$CsCl$	0·5	V^{5+}	NH_4VO_3	0·01
Rb^+	$RbCl$	0·5	Cr^{6+}	$K_2Cr_2O_7$	0·01
Mg^{2+}	$MgCl_2$	0·05	S^{2-}	$Na_2S·9H_2O$	0·005
Ca^{2+}	$CaCl_2$	0·05	Pb^{2+}	$Pb(NO_3)_2$	0·005
Sr^{2+}	$Sr(NO_3)_2$	0·05	Zn^{2+}	$ZnCl_2$	0·005
Ba^{2+}	$Ba(NO_3)_2$	0·05	Ag^+	$AgNO_3$	5×10^{-4}
Cu^+	$CuCl$	0·01	Hg^{2+}	$Hg(NO_3)_2·H_2O$	5×10^{-4}
Ag^+*	$AgNO_3$	0·01	Ni^{2+}	$NiSO_4·6H_2O$	1×10^{-4}
Hg^+	$HgCl$	0·01	Cu^{2+}	$CuSO_4·5H_2O$	1×10^{-4}
Tl^+	$TlCl$	0·01	Sn^{2+}	$SnCl_2·2H_2O$	5×10^{-5}
			Co^{2+}	$Co(NO_3)_2·6H_2O$	2×10^{-5}

* Hydroxylammonium sulphate as reducing agent.

The absorbance obeyed Beer's law over the range 0–1 × $10^{-5}M$ iron(II). The apparent molar absorptivity was 9·0 × 10^4 l·mole^{-1}·cm^{-1}. The composition of the extracted species was found to be 1:3:1 iron(II):2-nitroso-4-chlorophenol–rhodamine B. When 5 ml of extracting solution were used with 2·23 μg of iron(II) in the aqueous phase, almost the same absorbances were obtained irrespective of the volume of aqueous phase between 5 and 100 ml. Thus, a 20-fold concentration can easily be achieved by choice of phase-volume ratio.

Interferences

Some metal ions, such as cobalt, copper and nickel, react with 2-nitroso-4-chlorophenol and to some extent are extracted along with iron(II). These metal ions and the other ions generally present in sea-water were examined in detail as shown in Table 1. Large amounts of tin(II), nickel, copper(II), and cobalt interfere, but the amounts found in sea-water are too small to interfere. Tin(II) interferes by decomposing the 2-nitroso-4-chlorophenol. Other ions in the amounts commonly present in sea-water do not interfere.

Effect of EDTA

The species extracted into toluene could not be decomposed by adding EDTA after the extraction, but when 1 ml of 0·01M EDTA was added before the extraction, the iron(II) was not extracted.

Table 2. Determination of total iron in sea-water

Sample*	Date of sampling	Sample taken, *ml*	Absorbance†	Iron, *μg/l.*
1	25 March 1973	20	0·202	31·3
	5 July 1973	20	0·414	64·1
2	30 March 1973	20	0·570	88·3
	22 June 1973	20	0·322	49·9
3	23 June 1973	40	0·184	14·3
4	13 July 1973	40	0·276	21·4
5	13 July 1973	40	0·164	12·7
	21 July 1973	20	0·061	9·4
		40	0·115	8·9
		80	0·229	8·9

* Sample 1: Seashore at Shibukawa, Okayama Prefecture, Japan. Sample 2: Seashore at Sanban, Okayama Prefecture, Japan. Sample 3: Seashore at Ushimado, Okayama Prefecture, Japan. Sample 4: Seashore at Tottori, Tottori Prefecture, Japan. Sample 5: Offshore at Uradome, Tottori Prefecture, Japan.

† Reference, reagent blank.

Filtration

When 1 litre of acid of the concentration used was filtered, trace amounts of iron were dissolved out from the membrane (about 0·6 μg per 47 mm diameter circle). Accordingly, it is necessary to wash the membrane filter with acid (500 ml of 0·01*M* hydrochloric acid) before use.

Amount of hydroxylammonium chloride

Some of the iron in sea-water exists as iron(III), so the efficiency of reduction of iron(III) with hydroxylammonium chloride was examined. Final concentrations of hydroxylammonium chloride from 0·02 to 1% were found equally effective, and conditions were adjusted to give a final concentration of 0·05%. The reduction was found to be rapid.

Table 3. Reproducibility of iron determination*

Sample volume, *ml*	20	40	80
Determinations	8	7	5
Mean of absorbance†	0·061	0·115	0·229
Standard deviation	$0{\cdot}003_{8}$	$0{\cdot}005_{7}$	$0{\cdot}006_{4}$
Relative std. devn., %	6	5	3

* Samples from offshore at Uradome, Tottori Prefecture, Japan.

† Reference, reagent blank.

Stability of iron in sea-water

The apparent iron content of sea-water stored in ordinary containers decreases gradually as shown in Fig. 1, but if the samples are acidified with 2 ml of hydrochloric acid (1 + 1) per litre, the iron content remains constant for at least a month. Accordingly, samples should be acidified immediately after collection. However, the iron can be recovered by acidifying the stored samples and leaving them for at least 4 hr.

Determination of total iron in sea-water

The results obtained for various sea-water samples are given in Table 2 and for reproducibility studies in Table 3. The amounts of iron found agree with those in recent papers.[6, 15, 16]

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Summary—Iron has been determined in sea-water by extraction of the ternary complex of iron(II) with 2-nitroso-4-chlorophenol and Rhodamine B at pH 4·7 and measurement at 558 nm. Toluene is used as the organic solvent. Any iron(III) is reduced with hydroxylammonium chloride.

Zusammenfassung—Eisen wurde in Meerwasser durch Extraktion des ternären Komplexes von Eisen(II) mit 2-Nitroso-4-chlorphenol und Rhodamin B bei pH 4,7 und Messung bei 558 nm bestimmt. Als organisches Lösungsmittel wird Toluol verwendet. Eisen(III), falls vorhanden, wird mit Hydroxylammoniumchlorid reduziert.

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DETERMINATION OF TRACE AND MINOR ELEMENTS IN ALLOYS BY ATOMIC-ABSORPTION SPECTROSCOPY USING AN INDUCTION-HEATED GRAPHITE-WELL FURNACE AS ATOM SOURCE—II*

(*Received* 27 *August* 1973. *Accepted* 3 *November* 1973)

An induction-heated graphite-well furnace used in conjunction with electrodeless discharge tubes as light-sources and the monochromator and detector of a Unicam SP90 atomic absorption spectrophotometer, has already been described for the determination of ppm quantities of bismuth in lead–base alloys, cast irons and stainless steels, and for the determination of cadmium at the ppm level in zinc–base alloys. Small samples of alloy, 5 or 6 mg in weight, were dropped into the furnace for these determinations. In this communication some further results are presented for the determination of zinc in aluminium and aluminium–silicon alloys and of aluminium, antimony and tin in steels.

EXPERIMENTAL

Apparatus

The apparatus has already been described in detail.[1] Temperatures were measured with a Land Disappearing Filament Pyrometer Type DFP 2C by looking down through the open valves into the base of the furnace. Temperatures could be measured with an accuracy of ± 10°C but are not corrected for the emissivity value of graphite

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* Part I: J. B. Headridge and David Risson Smith, *Talanta*, 1972, **19**, 833.

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EXPERIMENTAL

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The apparatus has already been described in detail.[1] Temperatures were measured with a Land Disappearing Filament Pyrometer Type DFP 2C by looking down through the open valves into the base of the furnace. Temperatures could be measured with an accuracy of ± 10°C but are not corrected for the emissivity value of graphite

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(0·90). The measured temperatures will be slightly lower than the true temperatures with an estimated maximum error of 35°C at 2500°C.

Electrodeless discharge tubes were made in the laboratory according to well-known procedures.[2-4]

Procedure

Use as a light-source either an electrodeless discharge tube or a hollow-cathode lamp of the element to be determined in the alloy samples. Weigh out 5 or 10 mg of standard alloys (similar to the samples) and the alloys to be analysed for the trace or minor element. Drop these samples consecutively into the furnace as described in the previous paper, measuring the absorbance of the vapour cloud for each sample. Construct a calibration graph for the standard samples and use this graph to determine the concentration of trace or minor element in the samples. If the rather tedious procedure of weighing 5 mg samples all to the nearest 0·1 mg is used, the abscissa of the calibration graph is "Concentration of the trace element". However it is easier to weigh out the samples accurately to the nearest 0·1 mg, but ensuring that their weights fall within the range of 4·5 to 5·5 mg, and to make simple calculations such that the abscissa reads "Weight of the trace element." Slight differences in the weights of samples do not appear to lead to any decrease in accuracy or precision for a determination.

Alloy samples

The alloys used for the construction of the calibration graphs, with the concentrations of minor or trace elements in parentheses, and the furnace temperatures, are shown in Table 1.

Samples weighing 5 mg were used throughout except for the calibration graph for zinc in aluminium alloys, where 10 mg samples were employed.

Table 1. Alloys and temperatures used for caibration graphs

Determination	Alloys used (concentrations in %)	Temperature, °C
Zn in Al alloys	BCS 268(0·05), BCS 181/2(0·07) BCS 182/2(0·10), BCS 216/2(0·20)	2350
Zn in Al-Si alloys	SS 504(0·06), SS 502(0·21), SS 505(0·24)	2350
Al in steels	BCS 320(0·013), BCS 327(0·020), BCS 325 (0·028), BCS 329(0·058), BCS 322(0·093)	2450
Sb in steels	BCS 325(0·002), BCS 326(0·005), BCS 329(0·018), BCS 328(0·026)	2400
Sn in steels	BCS 321(0·014), BCS 323(0·024), BCS 218/3(0·042), BCS 325(0·046), BCS 320(0·085)	2400

RESULTS AND DISCUSSION

Suitable calibration graphs were obtained for zinc in aluminium and aluminium–silicon alloys, and aluminium, antimony and tin in steels. They all had convex curvature except that for tin, which was linear. Alloys SS 503, BCS 328, BCS 330 and BCS 239/3 were analysed eight, ten, eight and seven times respectively for the accuracy and precision data shown in Table 2.

The amounts and concentrations of these elements in their respective matrices required to give 1% absorption when heated in the induction furnace, as calculated from the calibration graphs, are shown in Table 3.

Table 2. Accuracy and precision of analyses

Determination	Line, *nm*	Relative standard deviation, %	Content by this method, %	Content by independent method, %
Zn in Al–Si alloy*	307·6	4·2	0·148	0·15
Al in mild steel	309·3	7·1	0·046	0·048
Sb in mild steel	231·1	7·4	0·017	0·018
Sn in steel	284·0 286·3	9·4	0·032	0·030

* The less-sensitive resonance line for zinc was used.

Table 3. Amounts and concentrations of elements required for 1% absorption

Element	Matrix	Amount, *ng*	Concentration for 5-mg sample, *μg/g*
Zinc	Al-base	60	12
Aluminium	Mild steel	25	5
Antimony	Mild steel	4	0·8
Tin	Steel	50	10

The accuracy of the results is satisfactory, as can be seen from Table 2, provided that the compositions of the standards and the samples to be analysed are similar. This restriction also applies to certain other analytical methods using solid samples, such as emission spectrography and X-ray fluorescence spectroscopy. An incorrect result for the determination of the minor or trace element in a sample can be obtained if the sample contains a high concentration of another volatile element, compared with the standards. For example, the aluminium alloys BCS 268 (used in the construction of the calibration graph) and BCS 262 each contain 0·05% of zinc but 0·56% and 10·57% of magnesium respectively. Magnesium is a volatile element boiling at 1107°. The absorbance for zinc for BCS 262 is considerably greater than that for BCS 268, indicating that the volatile magnesium in high concentration sweeps out the zinc from the matrix more readily with BCS 262 and leads to a higher peak concentration of zinc in the vapour cloud. An examination of the concentrations of major elements in alloys along with their boiling points will show if any interference effects might be expected.

The precision of the results is similar to that obtained by other workers using non-flame methods of atomization. The precision should be improved if a semimicro balance is used to weigh the samples.[1] The sensitivity of the method for zinc will be greatly increased by using the more sensitive resonance line at 213·9 nm. However, no suitable alloy samples of sufficiently low zinc content were available for the construction of a calibration graph using this line. The sensitivities of the method for the determination of aluminium, antimony and tin in steels will be improved if the temperature of the furnace can be raised by several hundred degrees. The maximum temperature of the furnace was 2500°C but iron boils at 3000°C and the results from the previous study[1] showed that the best sensitivity is obtained at a temperature just above the boiling point of the base element when the element to be determined is more volatile.

By use of aqueous salt solutions dispensed onto carbon or tungsten discs, suitable calibration graphs were also obtained for lead, magnesium, manganese and silver, the amounts for 1% absorption being 4, 0·03, 1·4 and 0·1 ng respectively. It should also be possible to determine trace amounts of these elements in alloys if suitable standards are available

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Summary—Results are presented for the atomic-absorption spectrophotometric determination of zinc in aluminium and aluminium–silicon alloys, and aluminium, antimony and tin in steels, by means of solid samples dropped into an induction-heated graphite-well furnace to produce the atomic vapour.

Zusammenfassung—Es werden Ergebnisse von atomabsorptionsspektrophotometrischen Bestimmungen von Zink in Aluminium und Aluminium–Silicium–Legierungen sowie von Aluminium, Antimon und Zinn in Stählen mitgeteilt. Dabei werden zur Erzeugung des atomhaltigen Dampfes die festen Proben in einen induktiv geheizten Graphit-Schachtofen fallen gelassen.

Résumé—On présente des résultats pour le dosage spectrophotométrique par absorption atomique du zinc dans l'aluminium et des alliages aluminium–silicium, et l'aluminium, l'antimoine et l'étain dans les aciers, au moyen d'échantillons solides projetés dans le logement en graphite d'un four chauffé par induction pour produire la vapeur atomique.

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SPECTROGRAPHIC ANALYSIS OF HIGH-PURITY NICKEL OXIDE FOR TWENTY-ONE TRACE IMPURITIES, WITH USE OF A NEW BUFFER

(*Received* 11 *July* 1973. *Accepted* 29 *October* 1973)

Only a few reports deal with the spectrographic analysis of high-purity nickel oxide. Krasil'schik and Yakovleva[1] have determined six impurities in high-purity nickel oxide, using a hollow-cathode discharge in a helium atmosphere. However, when a simultaneous determination of a large number of impurities is required, a spectrographic method employing a d.c. arc is generally used. Two methods[2,3] have been reported for the analysis of nickel by converting it into nickel oxide and analysing in the d.c. arc, with different buffers. The ASTM method[2] used graphite as buffer and estimated nine impurities, whereas Fujishiro and Sakai[3] used a mixture of germanium oxide and graphite as buffer for determination of seven impurities. For both methods the lowest determination limits ranged from 10 to 50 ppm. The present method determines simultaneously twenty-one trace impurities in high-purity nickel oxide with a lower limit of 1–10 ppm. This has been made possible by the use of a new buffer (a mixture of indium oxide and graphite in 1:2 ratio) which enhances the intensities of the analytical lines of many elements more than the earlier buffers do.

EXPERIMENTAL

Equipment

A JACO 3·4 m Ebert spectrograph with a grating having 1200 lines/mm and blazed at 330 nm was used with a dispersion of about 0·25 nm/mm. A d.c. arc source was run at 10 A to excite the sample. A 26 μm slit width was used with a 10% transmission filter. The spectra were recorded on Ilford N.30 plates. The line densities were measured on a non-recording microphotometer (Hilger Model L.451). Intensity ratios were calculated on the Respectra calculator (Dennert and Pape, Hamburg).

Preparation of standards

Synthetic standards were prepared by dry-mixing the spectroscopically-pure grade impurity compounds with high-purity nickel oxide supplied by Johnson–Matthey and Co. Spectroscopically-pure graphite (U.C.C. 200-mesh) and indium oxide (Johnson–Matthey) were used for preparation of the buffer.

Procedure

The nickel oxide sample and synthetic standards were mixed with an equal amount of the buffer (a mixture of indium oxide and graphite in the ratio 1:2). The charge, consisting of 40 mg of this mixture, was loaded into a $\frac{1}{4}$ in. electrode (Ultra Carbon Products) having a suitable cavity. Graphite electrodes (1/8 in. diameter, Ultra Carbon Corporation) were used as cathodes. The spectra excited by the d.c. arc (10 A) with an electrode spacing of 4 mm were recorded (exposure of 60 sec). Working curves were drawn for various elements and their concentrations in the sample were determined.

RESULTS AND DISCUSSION

Table 1 gives the impurity elements, analytical lines and concentration ranges. The determination limits for Si, Al, Mg and Na are slightly higher because of the presence of residuals in the blank. These residuals were found by the method of trial additions.

Résumé—On présente des résultats pour le dosage spectrophotométrique par absorption atomique du zinc dans l'aluminium et des alliages aluminium–silicium, et l'aluminium, l'antimoine et l'étain dans les aciers, au moyen d'échantillons solides projetés dans le logement en graphite d'un four chauffé par induction pour produire la vapeur atomique.

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Table 1 gives the impurity elements, analytical lines and concentration ranges. The determination limits for Si, Al, Mg and Na are slightly higher because of the presence of residuals in the blank. These residuals were found by the method of trial additions.

Table 1. Analytical lines and concentration ranges

Impurity element	Analytical line wavelength,* *nm*	Concentration range, *ppm*	Impurity element	Analytical line wavelength,* *nm*	Concentration range, *ppm*
Sn	242·95	5–100	Co	304·40	1–20
Si	251·43	5–50	Ba	307·16	10–100
Al	257·51	2–20	Ti	316·26	5–100
Fe	259·96	5–100	V	319·80	10–100
Mn	260·57	1–20	Mo	320·88	10–100
Pb	261·42	5–100	Cd†	326·11	5–100
Mg	277·67	2–20	Cu†	327·40	1–20
As	286·05	10–250	Na	330·23	2–25
Sb	287·79	5–100	Zn	330·26	10–100
Cr	289·68	10–200	Ag†	338·29	1–20
Bi	289·80	5–100			

* Internal standard lines were Ni 263·03 nm for the elements in the left-hand set of columns (Sn–Bi) and Ni 317·41 nm for the rest (Co–Ag).

† The 10% transmission step of the filter was used for measurement.

In order to get the optimum sensitivity for most of the twenty-one trace impurities, mixtures of graphite with various compounds such as AgCl, Ga_2O_3, ZnO, CuO, GeO_2 and In_2O_3 were tried and added to the nickel oxide in the ratio 1:1. The mixture of In_2O_3 and graphite was found to give optimum sensitivity for the majority of the elements. Different ratios of indium oxide to graphite were tried and the ratio 1:2 was found to give optimum performance for most of the elements. In comparison with the buffers used in earlier methods,[2,3] namely, graphite and a mixture of 20% GeO_2 in graphite, this new buffer enhanced the intensities of the analytical lines of Pb, Bi, Sn, Cr, Ba, V, Ag, Cu, As, Mg and Mn. In addition, the intensities of the analytical lines of the other elements were not reduced. The Cd 326·1 nm and Co 304·4 nm lines had a somewhat higher background owing to intense indium lines in the vicinity. A comparison of the intensities (intensity ratios) for these impurities, when measured with the buffers GeO_2 in graphite and In_2O_3 in graphite, is given in Table 2. The nickel 317·41 nm line has almost constant intensity for both the buffers and is used as an internal standard line. The intensity ratios for both the buffers were calculated from the spectra taken on the same plate under identical conditions. From Table 2 it is clear that the In_2O_3 and graphite mixture is superior to the GeO_2 and graphite mixture for the impurities mentioned above. The relative standard deviation of the method varied from 8 to 16% for different elements.

Table 2 Intensity ratios obtained with GeO_2 in graphite (*a*) and In_2O_3 in graphite (*b*) as the buffers*

	Standard I		Standard II		Standard III		Standard IV	
Element	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Sn	0·095	0·12	0·15	0·24	0·32	0·64	0·74	1·13
Mn	0·16	0·19	0·32	0·38	0·75	0·98	1·85	2·0
Pb	0·26	0·58	0·49	1·05	0·97	2·6	2·2	4·18
Mg	†	0·074	0·058	0·13	0·081	0·27	0·20	0·44
As	†	†	†	0·39	0·42	0·70	0·64	1·30
Cr	0·045	0·084	0·077	0·14	0·17	0·49	0·38	0·85
Bi	0·12	0·16	0·23	0·34	0·47	1·09	1·39	2·02
Ba	†	0·13	0·068	0·25	0·14	0·77	0·42	1·27
V	0·36	0·52	0·53	1·05	1·11	3·01	2·9	6·0
Cu	0·98	1·4	1·8	2·45	3·70	5·75	7·65	8·8
Ag	0·65	0·91	1·25	1·55	2·3	4·0	5·35	6·0

* The nickel 317·41 nm line which had almost constant intensity with both the buffers was used as the internal standard line Hence the Table shows the changes in intensities of the impurity lines.

† The impurity line was not seen at this concentration.

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Summary—A spectrographic method for the determination of twenty-one trace impurities in high-purity nickel oxide by the d.c. arc technique has been developed. A mixture of graphite and indium oxide in the ratio 2:1 is used as buffer. The lowest determination limits for various elements lie between 1 and 10 ppm with an average relative standard deviation of ±12%.

Zusammenfassung—Ein spektrographisches Verfahren zur Bestimmung von einundzwanzig Spuren-Verunreinigungen in hochreinem Nickeloxid mit Hilfe des Gleichstromlichtbogens wurde entwikkelt. Ein Gemisch aus Graphit und Indiumoxid im Verhältnis 2: 1 dient als Puffer. Die niedrigsten Nachweisgrenzen mehrerer Elemente liegen zwischen 1 und 10 ppm mit einer relativen Standardabweichung von durchschnittlich ±12%.

Résumé—On a élaboré une méthode spectrographique pour le dosage de vingt et une impuretés à l'état de traces dans l'oxyde de nickel de haute pureté par la technique de l'arc en courant continu. Un mélange de graphite et d'oxyde d'indium dans le rapport 2:1 est utilisé comme tampon. Les limites de détermination les plus faibles pour divers éléments se situent entre 1 et 10 ppm avec un écart type relatif moyen de ±12%.

Talanta, Vol. 21, pp. 654–660 Pergamon Press, 1974. Printed in Great Britain

REACTION OF COBALT WITH 2-NITROSO-5-DIETHYLAMINOPHENOL AND THE SOLVENT EXTRACTION OF ITS COBALT COMPLEX

(*Received* 5 *June* 1973. *Accepted* 17 *October* 1973)

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By comparison with nitroso-DMAP, the cobalt complex of nitroso-DEAP has slightly greater molar absorptivity, is much less soluble, and is much more readily extracted into 1,2-dichloroethane (DCE). Thus, the reagent is expected to be very useful for the preconcentration and determination of micro amounts of cobalt in very dilute solutions. In order to establish optimum conditions for its use the appropriate equilibrium constants have been measured.

EXPERIMENTAL

The reagents, apparatus and procedures for the determination of equilibrium constants, other than those listed below, have been described previously.[4]

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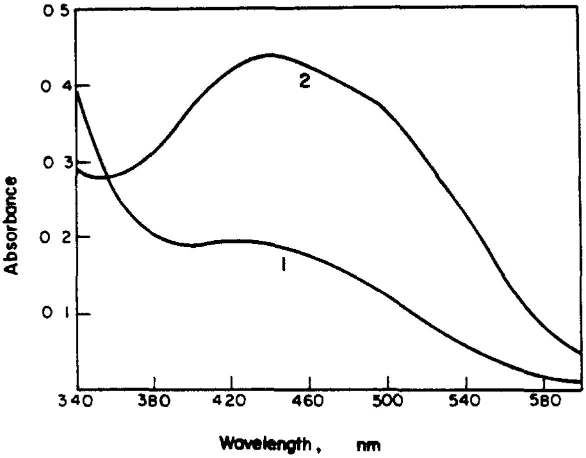

Fig. 1. Absorption spectra of the complex and the reagent in aqueous solution. (1) pH = 6·3, 10-cm cell, [Reagent] 3 × $10^{-6}M$; (2) [Reagent] 3 × $10^{-6}M$, [Co] 1 × $10^{-6}M$.

Reagent

Nitroso-DEAP was obtained in the same way as nitroso-DMAP. The purified nitroso-DEAP hydrochloride (nitroso-DEAP·HCl) is obtained as yellow needle-like crystals of the monohydrate ($C_{10}H_{15}N_2O_2Cl \cdot H_2O$). Elemental analysis gave: C 48·2%, H 6·6%, N 11·4%; $C_{10}H_{17}N_2O_3Cl$ requires C 48·3%, H 6·9%, N 11·3%.

Procedure

The solubility of the cobalt nitroso-DEAP and DMAP complexes in water were determined as follows. Various amounts of cobalt were added to an aqueous solution (pH 6·2) containing nitroso-DMAP or nitroso-DEAP (1 × $10^{-3}M$), and these solutions were shaken for about 5 hr at 25°C and filtered; 5 ml of the filtrate were shaken with 5 ml of DCE. The organic phase was washed with hydrochloric acid, and the absorbance measured. Figure 2 shows the results obtained. The nitroso-DEAP complex is not as soluble as that of nitroso-DMAP, so occasionally precipitation occurred at concentrations before the break-point. With nitroso-DMAP, the absorbances before the break-point are almost in agreement with the values expected from the molar absorptivity, but with nitroso-DEAP they are somewhat smaller. Therefore the solubility of the nitroso-DEAP complex was calculated from the absorbance after the break-point.

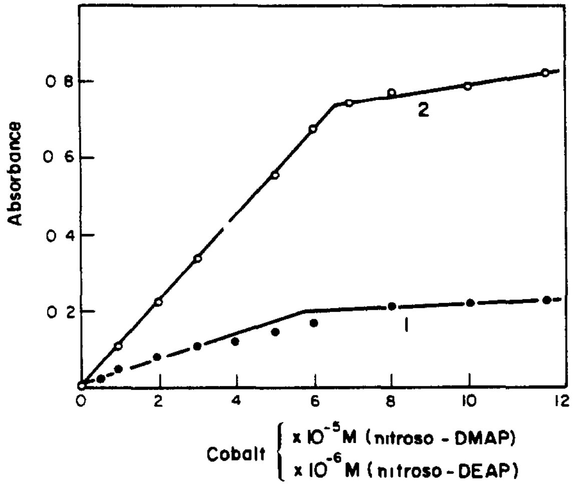

Fig. 2. Solubility of the cobalt complex in aqueous solution. (1) nitroso-DEAP, 1-cm cell, 462 nm; (2) nitroso-DMAP, 2-mm cell, 456 nm.

Table 1. The results obtained

	Nitroso-DMAP	Nitroso-DEAP
pK_{a1}	2·69 ± 0·03	2·83 ± 0·01 (μ 0·1)
pK_{a2}	8·40 ± 0·05	8·38 ± 0·03 (μ 0·2)
λ_{max} (MR$_3$), *nm*	445	442 (aqueous solution, pH 6·3)
λ_{max} (HR), *nm*	404	408 (1,2-dichloroethane)
λ_{max} (MR$_3$), *nm*	456	462 (1,2-dichloroethane)
ϵ_{MR_3}, $l \cdot mole^{-1} \cdot cm^{-1}$	6·0 × 10^4 at 456 nm	6·2 × 10^4 at 462 nm (1,2-dichloroethane)
log D_{HR}	1·42 ± 0·02	2·35 ± 0·02 (μ 0·1)
log K_{MR_3}	26·77 ± 0·12	24·73 ± 0·16 (μ 0·1)
log K_e	0·42 ± 0·22	−0·21 ± 0·20 (μ 0·1)
log D_{MR_3}	3·1	7·3
S_{MR_3}, M	6·5 × 10^{-5}	3·6 × 10^{-6}

D_X = partition coefficient of X, K_e = extraction constant, S_{MR_3} = solubility of MR$_3$.

RESULTS AND DISCUSSION

The experimental results are illustrated in Figs. 1–7 and the values of the constants calculated from them are given in Table 1. The reagent and complex have similar absorption spectra (Fig. 1) but the difference in the distribution ratios of reagent and complex at pH $< -1{\cdot}2$ or $> 12{\cdot}8$ can be exploited to remove the excess of reagent from the organic phase after complexation. Table 2 records the results of experiments to establish the best conditions for stripping.

Nitroso-DEAP is very similar to nitroso-DMAP in its synthesis, colour, crystal form, absorption spectra of the reagent and cobalt complex, *etc*., but differs in some respects, such as the solubility of the cobalt complex, the extractability of the reagent and the cobalt complex, *etc*. (Table 1). The greater pK_{a1} for nitroso-DEAP·HCl than for nitroso-DMAP·HCl is ascribed to the ethyl group having a stronger electron-donating effect than the methyl group. The solubility of nitroso-DEAP and its cobalt complex in DCE is larger than nitroso-DMAP. However, as nitroso-DEAP is very extractable into DCE, the extraction constant, K_e, is smaller.

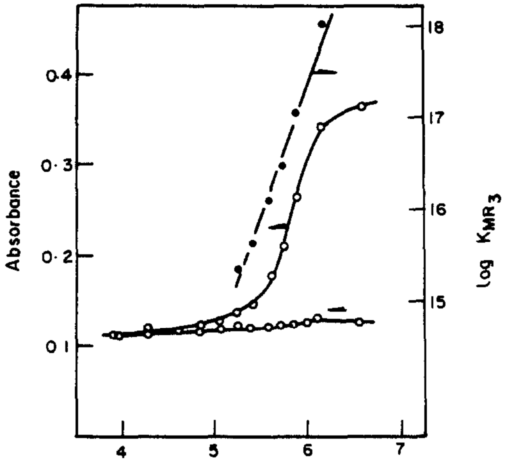

Fig. 3. Plots of absorbance *vs*. pH and of log K'_{MR_3} *vs*. pH.
(1) [Reagent] 3 × $10^{-6}M$; (2) [Reagent] 3 × $10^{-6}M$, [Co] 1 × $10^{-6}M$; (3) log K'_{MR_3} *vs*. pH, 10-cm cell, 500 nm.

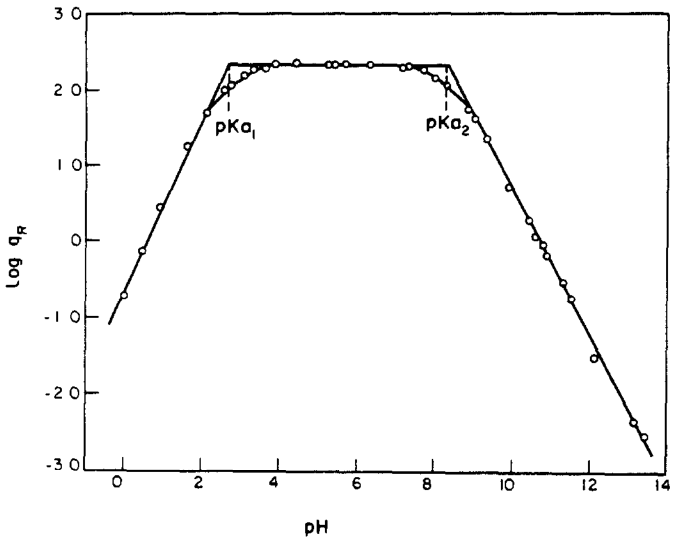

Fig. 4. Plot of log q_R *vs.* pH.

$$[\text{Reagent}]\ 1 \times 10^{-3}\,M.\ q_R = D_{HR} \Big/ \left\{1 + \frac{[H]_a}{K_{a1}} + \frac{K_{a2}}{[H]_a}\right\}$$

where $D_{HR} = [HR]_o/[HR]_a$ and subscripts o and a denote the organic and aqueous phases respectively.

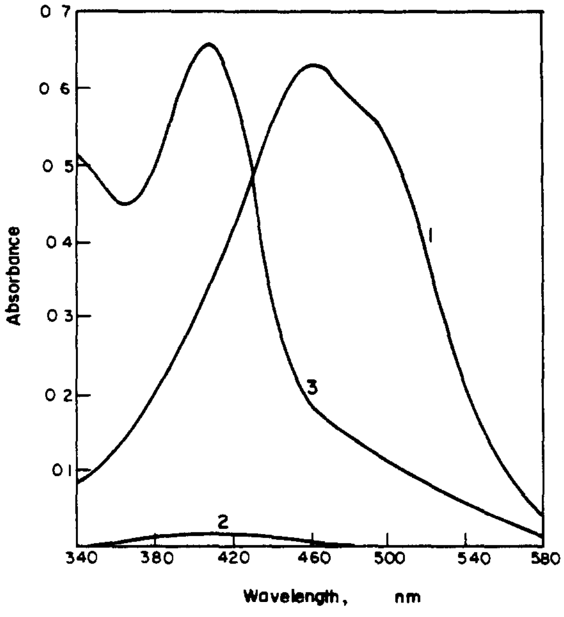

Fig. 5 Absorption spectra of the complex and the reagent in the organic phase. (1) Complex (1 × $10^{-5}M$), 1 cm cell; (2) reagent blank, 1 cm cell, both after washing with HCl (1 + 1). (3) [Reagent] 5 × $10^{-4}M$, 1 mm cell.

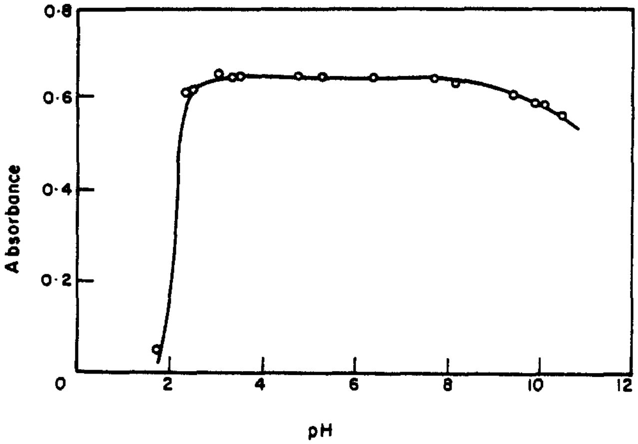

Fig. 6. Effect of pH on the extraction of cobalt.
[Reagent] $1 \times 10^{-3}M$; [Co] $1 \times 10^{-5}M$, 462 nm, 1 cm cell.

Determination of cobalt

For the determination of cobalt, nitroso-DEAP is used in a similar manner to nitroso-DMAP. Both reagents in DCE can be stripped with alkaline and acidic solutions. By treating the organic phase with hydrochloric acid, the excess of reagent and other metal complexes co-extracted into the organic phase are stripped. In case of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol *etc.*, the excess of the reagent and the other metal complexes in the organic phase must be removed with alkaline and acidic solutions, respectively. The molar absorptivity of the nitroso-DEAP complex is $6{\cdot}2 \times 10^4$ $1 \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ at 462 nm, which is probably larger than that of all other nitroso cobalt complexes used up to the present. Besides, as the partition coefficient of the cobalt complex is very large, nitroso-DEAP is especially advantageous for concentration of micro amounts of cobalt in very dilute solution by solvent extraction, and for subsequent determination of cobalt.

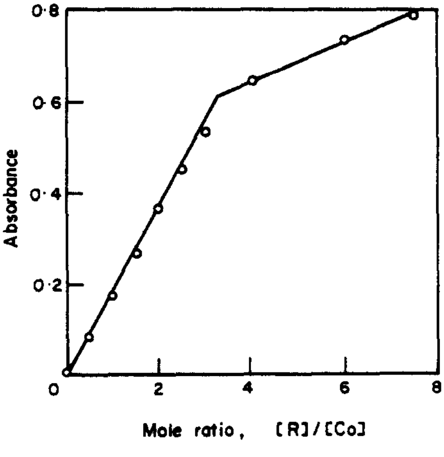

Fig. 7. Mole-ratio method for organic phase.
462 nm, 1 cm cell, pH 6·2, [Co] $1 \times 10^{-5}M$.

Table 2. Stripping of the organic phase with HCl and KOH

Extraction system	Stripping solution	Absorbance of organic phase after 1st wash	2nd wash	3rd wash
1*	1*N* KOH	0·189	0·100	0·125
	HCl (1 + 2)	0·034	0·013	0·007
	HCl (1 + 1)	0·016	0·007	0·004
	conc. HCl	0·026	0·007	0·005
2†	1*N* KOH	0·721(0·532)	0·724(0·624)	0·757(0·632)
	HCl (1 + 2)	0·654(0·620)	0·636(0·623)	0·638(0·631)
	HCl (1 + 1)	0·631(0·615)	0·622(0·615)	0·625(0·621)
	conc. HCl	0·357(0·331)	0·229(0·222)	—

Reagent solution $5 \times 10^{-3}M$, cobalt solution $1 \times 10^{-5}M$, reference 1,2-dichloroethane, λ 462 nm.

* Aqueous phase—H_2O (5 ml) + buffer solution (1 ml) + reagent solution (1 ml); organic phase—5 ml.

† Aqueous phase—cobalt solution (5 ml) + buffer solution (1 ml) + reagent solution (1 ml), organic phase—5 ml.

The values in parentheses were obtained by subtracting the reagent blank.

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Summary—2-Nitroso-5-diethylaminophenol (nitroso-DEAP) is a useful reagent for cobalt, with which it forms a 1:3 complex. Its pK_{a1} and pK_{a2} values are 2·83 and 8·38, and the formation constant, log K_{MR_3}, is 24·73. The reagent and complex may be extracted into 1,2-dichloroethane from water, the log of the respective partition coefficients being 2·35 and 7·3. The extracted cobalt complex is not stripped by 6*M* hydrochloric acid, whereas excess of the reagent is. The molar absorptivity of the complex in 1,2-dichloroethane is $6{\cdot}2 \times 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ at 462 nm, which is larger than that of other nitroso derivatives.

Zusammenfassung—2-Nitroso-5-diäthylaminophenol (Nitroso-DEAP) ist ein gutes Reagens für Kobalt, mit dem es einen 1:3:Komplex bildet. Seine pK_{a1}- und pK_{a2}-Werte betragen 2,83 bzw. 8,38, die Bildungskonstante log K_{MR_3} 24,73. Reagens und Komplex können aus Wasser in 1,2-Dichloräthan extrahiert werden; die Logarithmen der betreffenden Verteilungskoeffizienten betragen 2,35 und 7,3. Der extrahierte Kobaltkomplex wird durch 6*M* Salzäure nicht zurüchextrahiert, dagegen das überschüssige Reagens. Der molare Extinktionskoeffizient des Komplexes in 1,2-Dichloräthan beträgt $6{,}2 \times 10^4$ $l.mol^{-1}.cm^{-1}$ bei 462 nm, ein großerer Wert als bei anderen Nitrosoderivaten.

Résumé—Le 2-nitroso 5-diéthylaminophénol (nitroso-DEAP) est un réactif utile pour le cobalt, avec lequel il forme un complexe 1:3. Ses valeurs pKa_1 et pKa_2 sont 2,83 et 8,38, et la constante de formation, log K_{MR3} est 24.73. Le réactif et le complexe peuvent être extraits de l'eau en 1,2-dichloréthane, le log des coefficients de partage respectifs étant 2.35 et 7.3. Le complexe de cobalt

extrait n'est pas réextrait en acide chlorhydrique 6*M*, tandis que l'excès de réactif l'est. Le coefficient d'absorption moléculaire du complexe en 1,2-dichloréthane est 6.2×10^4 l.mole^{-1}.cm^{-1} à 462 nm, valeur qui est plus grande que celles des autres dérivés nitroso.

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TRACE ANALYSIS BY MICROWAVE EXCITATION OF SEALED SAMPLES—III
DETERMINATION OF 0·005–25 ng OF Te AND 0·25–25 ng OF Se IN 0·5 ml OF AQUEOUS SOLUTION

(*Received* 11 *July* 1973. *Accepted* 8 *October* 1973)

The determination of selenium and tellurium in (sub)nanogram amounts has become more important with the increasing awareness of the importance of these elements in biological systems.[1,2] Recent methods for this include atomic-absorption spectrometry using flameless atomizing systems[3,4,5] and (especially for tellurium) atomic fluorescence.[6] The results of these methods, however, leave room for improvement and no measurements below 1 ng/ml have been reported for these elements.

The use of the electrodeless discharge lamp (EDL) as a sampleholder for the determination of (sub)nanogram amounts of Cd, Tl, In, Hg, Zn and Pb has already been described.[7,8] The present paper investigates its use for the determination of traces of selenium and tellurium. The main problem considered is that of finding the most suitable matrix. This may consist of more than one component in order to maintain constant excitation conditions and at the same time suppress interfering band spectra. The matrix used will depend on the element concerned and thermodynamic data such as vapour pressure, solubility and stability of the element and its compounds (in our case oxides or halides).

EXPERIMENTAL

Apparatus

The vacuum apparatus and procedure for preparing the EDL's, the spectrometer, the monochromator, the detector and the microwave generator are the same as before.[7,8] The signals were corrected for a background value, measured immediately afterwards at a wavelength 0·3 nm longer than that of the line. The cavity used was the ¼-wave type (E.M.S. 214 L), the quartz used was "Vitreosil" (Thermal Syndicate). A nominal volume of 100 μl of matrix + sample solution was added to the EDL.

Tellurium

A tellurium tube was prepared[9,10] containing 1 mg of metallic tellurium and 1 mg of iodine. This tube gave an intense tellurium spectrum with the strongest lines at 238·3 and 238·6 nm; these lines were used in further investigations.

In the literature it was found that tellurium tetrachloride has favourable values for its solubility, thermodynamic stability and vapour pressure. Therefore in the first experiments 100 ng of tellurium tetrachloride were used in a matrix solution (slightly acidified to prevent hydrolysis) containing 2·5 μg of sodium chloride and 2·5 μg of lithium chloride, in order to maintain constant excitation conditions, and about 1 mg of germanium as a getter in order to prevent interfering band spectra.[7] With this matrix however, the EDL did not show any Te lines. Replacing the germanium getter by boron did not give any result either. As seen above, addition of iodine to tellurium gave an intense Te-spectrum. It could therefore be expected that addition of iodine to the tellurium tetrachloride introduced, would also give results, but because of its high volatility the iodine causes difficulty if used for quantitative purposes. Potassium iodide does not give such difficulties, however, and because it was found that an EDL containing potassium iodide showed exactly the same spectrum as an EDL containing iodine, potassium iodide was used in further experiments. Moreover, in the 200–300 nm region no interfering band spectra appeared, so there was no necessity to use a getter.

The optimum amount of the iodide and the optimum power (65 W, incident power minus reflected power) were determined. Some filler-gases were tested: helium and hydrogen were equally good, but oxygen was useless. Different kinds of quartz were tested, "Vitreosil" was found satisfactory. Other types could also be used.

Selenium

The strongest selenium line from an EDL (1 mg of selenium) was at 204 nm. From thermodynamic data it can be concluded that selenium may be determined when present as SeO_2, SeF_4 or $SeCl_4$ in the EDL.

extrait n'est pas réextrait en acide chlorhydrique $6M$, tandis que l'excès de réactif l'est. Le coefficient d'absorption moléculaire du complexe en 1,2-dichloréthane est 6.2×10^4 l.mole^{-1}.cm^{-1} à 462 nm, valeur qui est plus grande que celles des autres dérivés nitroso.

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The determination of selenium and tellurium in (sub)nanogram amounts has become more important with the increasing awareness of the importance of these elements in biological systems.[1,2] Recent methods for this include atomic-absorption spectrometry using flameless atomizing systems[3,4,5] and (especially for tellurium) atomic fluorescence.[6] The results of these methods, however, leave room for improvement and no measurements below 1 ng/ml have been reported for these elements.

The use of the electrodeless discharge lamp (EDL) as a sampleholder for the determination of (sub)nanogram amounts of Cd, Tl, In, Hg, Zn and Pb has already been described.[7,8] The present paper investigates its use for the determination of traces of selenium and tellurium. The main problem considered is that of finding the most suitable matrix. This may consist of more than one component in order to maintain constant excitation conditions and at the same time suppress interfering band spectra. The matrix used will depend on the element concerned and thermodynamic data such as vapour pressure, solubility and stability of the element and its compounds (in our case oxides or halides).

EXPERIMENTAL

Apparatus

The vacuum apparatus and procedure for preparing the EDL's, the spectrometer, the monochromator, the detector and the microwave generator are the same as before.[7,8] The signals were corrected for a background value, measured immediately afterwards at a wavelength 0·3 nm longer than that of the line. The cavity used was the ¼-wave type (E.M.S. 214 L), the quartz used was "Vitreosil" (Thermal Syndicate). A nominal volume of 100 μl of matrix + sample solution was added to the EDL.

Tellurium

A tellurium tube was prepared[9,10] containing 1 mg of metallic tellurium and 1 mg of iodine. This tube gave an intense tellurium spectrum with the strongest lines at 238·3 and 238·6 nm; these lines were used in further investigations.

In the literature it was found that tellurium tetrachloride has favourable values for its solubility, thermodynamic stability and vapour pressure. Therefore in the first experiments 100 ng of tellurium tetrachloride were used in a matrix solution (slightly acidified to prevent hydrolysis) containing 2·5 μg of sodium chloride and 2·5 μg of lithium chloride, in order to maintain constant excitation conditions, and about 1 mg of germanium as a getter in order to prevent interfering band spectra.[7] With this matrix however, the EDL did not show any Te lines. Replacing the germanium getter by boron did not give any result either. As seen above, addition of iodine to tellurium gave an intense Te-spectrum. It could therefore be expected that addition of iodine to the tellurium tetrachloride introduced, would also give results, but because of its high volatility the iodine causes difficulty if used for quantitative purposes. Potassium iodide does not give such difficulties, however, and because it was found that an EDL containing potassium iodide showed exactly the same spectrum as an EDL containing iodine, potassium iodide was used in further experiments. Moreover, in the 200–300 nm region no interfering band spectra appeared, so there was no necessity to use a getter.

The optimum amount of the iodide and the optimum power (65 W, incident power minus reflected power) were determined. Some filler-gases were tested: helium and hydrogen were equally good, but oxygen was useless. Different kinds of quartz were tested, "Vitreosil" was found satisfactory. Other types could also be used.

Selenium

The strongest selenium line from an EDL (1 mg of selenium) was at 204 nm. From thermodynamic data it can be concluded that selenium may be determined when present as SeO_2, SeF_4 or $SeCl_4$ in the EDL.

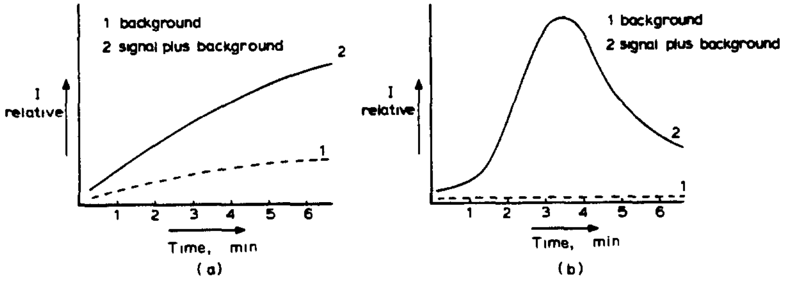

Fig. 1. Time-dependence of signal with (a) 2 μg of KI (b) 5 μg of KI.

Tubes were tested which contained: (1) SeO_2 added as a neutral solution of H_2SeO_3; (2) SeO_2 + HCl (1*M*) from which $SeCl_4$ will be formed during evaporation in the vacuum line; (3) $SeCl_4$ with various potassium halides. Tubes containing $SeCl_4$ + KI gave the best results. The amount of potassium iodide and the acidity were optimized but the selenium-emission signal was always less intense than the corresponding tellurium signal. Some improvement could be achieved by adding a small amount of potassium fluoride to the matrix.

RESULTS

Tellurium

The dependence of the signal on time for 10 ng of $TeCl_4$ differed according to the amount of potassium iodide present (Fig. 1). With a matrix of 5 μg of KI or more, a maximum always appeared in the emission signal about 3 min after switch-on of the EDL. This maximum appeared to be fairly reproducible, but some EDL's did not give the expected signal, probably because of contamination from the quartz.[8] Using 50 μg of KI gave the same results as with 5 μg but all EDL's gave the signal expected and no interferences from the quartz were found. Presumably the type of quartz used is less critical if more iodide is used. The results are listed in Table 1, for 50 μg of KI in the matrix. The volume was 123 μl, but 500 μl can be used without difficulty. From a calibration curve concentrations may be found with a relative standard deviation of about 20%.

Table 1. Maximum emission intensities, Te 238·6 nm line, measured 3 min after switch-on

Amount of Te, *ng*	Signal × 10^{-3}*	Amount of Te, *pg*	Signal*
25	11·1	25	23, 24
10	4·53, 3·32	10	16, 16
	7·15, 5·26	5	8, 10
2.5	1·37, 1·66	blank†	3, 4, 3, 6
1	0·423, 0·551	blank‡	0, 0
0·25	0·162, 0·142		
0·10	0·051, 0·062		

* Calculated scale divisions at highest amplification.
† The glassware had been used for Te determinations for some time.
‡ Completely different glassware was used.

Selenium

The selenium signal showed about the same dependence on time as the tellurium signal (Fig. 1); here too, maximum intensity was found 2–3 min after switch-on. Some results are listed in Table 2, each EDL containing 1 μg of $SeCl_4$ and 5 or 25 μg of halide.

The values suggest that the best matrix should be 5 μg of potassium iodide but no reliable results were obtained with such small quantities. Experiments with "Pursil 453" quartz[8] gave no improvement; presumably the difficulties found here cannot be attributed to the type of quartz.

Table 2. Influence of potassium halides on the Se signal

Halide	5 μg KX Signal × 10^{-3}*	25 μg KX Signal × 10^{-3}*
KF	0·391	0·094
KCl	1·16	0·563
KBr	157	4·80
KI	453	191

* Calculated scale divisions at highest amplification.

In quantitative experiments 40 μg of potassium iodide were used, resulting in a more reliable system, but with lower sensitivity. A somewhat better sensitivity could be achieved when 2 μg of potassium fluoride were also added, so the final matrix became 40 μg of KI + 2 μg of KF. The results for this system are listed in Table 3.

Table 3. Maximum emission intensities 2–3 min after switch-on. (Se 204·0 nm line)

Amount of Se, *ng*	Signal × 10^{-2}*	Amount of Se, *ng*	Signal × 10^{-2}*
25	13·4, 13·8, 18·0	1	0·51, 0·51, 0·56
10	3·98, 5·71, 4·50, 5·02, 5·02	0·5	0·27, 0·25, 0·29
2·5	1·07, 0·89, 0·80	0·25	0·12, 0·07, 0·10

* Calculated scale divisions at highest amplification.

Measurement of 0·1 ng was impossible because the rapid variation of signal with time made subtraction of a reliable background value impossible. A 500 μl matrix volume can be used. The relative standard deviation is about 20%.

DISCUSSION

So far in these experiments, only pure salt solutions have been analysed. When an actual sample is to be analysed, removal of the tellurium and selenium (*e.g.* by distillation of the chlorides) may be required. This will be investigated in further experiments. The lowest amount of Te and Se which can be measured in 0·5 ml are 5 and 250 pg respectively.

The temperature of the outer wall of our EDL's was measured and found to be about 1000°C. There may be a correlation between the rapid fall of the signal after the maximum is reached and the high temperature of the quartz. Temperature regulation of the EDL may improve the results, but has not yet been investigated.

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Summary—Traces of tellurium and selenium can be determined by optical emission spectrometry using microwave exitation in electrodeless discharge lamps. In 0·5 ml aqueous solution samples, freeze-dried in electrodeless discharge lamps, 10^{-5} ppm Te and 5×10^{-4} ppm Se can be determined with a relative deviation of about 20%.

Zusammenfassung—Spuren Tellur und Selen können durch optische Emissionsspektrometrie mit Mikrowellenanregung in elektrodenlosen Entladungsröhren bestimmt werden. In Proben von 0,5 ml wäßriger Lösung, die in elektrodenlosen Entladungsröhren gefriergetrocknet wurden, können 10^{-5} ppm Te und $5 \cdot 10^{-4}$ ppm Se mit einter relativen Standardabweichung von etwa 20% bestimmt werden.

Résumé—On peut doser des traces de tellure et de sélénium par spectrométrie d'émission optique en utilisant l'excitation micro-ondes dans des tubes à décharge sans électrode. Dans 0,5 ml d'échantillons en solution aqueuse, séchés par évaporation de la glace dans des tubes à décharge sans électrode, on peut doser 10^{-5} ppm de Te et 5×10^{-4} ppm de Se avec un écart type relatif d'environ 20%.

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BROMINE CYANIDE AS TITRIMETRIC OXIDANT IN NON-AQUEOUS MEDIA

(*Received* 26 *June* 1973. *Accepted* 8 *October* 1973)

Bromine cyanide has recently been developed as a titrimetric oxidant in acidic aqueous medium for the determination of several inorganic compounds.[1–6] In the present study, the work has been extended to its use in non-aqueous solvents such as acetonitrile, glacial acetic acid, 1:1 acetic acid–acetic anhydride mixture, methanol and ethanol. The study is significant because iodine need not be added, in contrast to the corresponding titrations in aqueous medium,[1–6] and because few, if any, bromine compounds (other than bromine itself) have been used in non-aqueous medium.[7]

EXPERIMENTAL

Reagents

Bromine cyanide,[1] arsenic(III) chloride, antimony(III) chloride,[8] sodium sulphide,[1] phenylhydrazine, chloralhydrazine, 1,1-methylphenylhydrazine, benzalazine,[3] ethylthiourea, isopropylthiourea, allylthiourea, α-phenylthiourea, benzylthiourea, *o*-tolylthiourea,[4] sodium methyldithiocarbamate, sodium dimethyldithiocarbamate, sodium ethyldithiocarbamate, sodium diethyldithiocarbamate, sodium isopropyldithiocarbamate and ethanol[5] were prepared and/or purified according to the methods referred to earlier. All the other chemicals used were of analytical grade. The solvents were distilled before use.

The solutions of bromine cyanide and the reductants ($2{\cdot}5 \times 10^{-2}M$) were prepared in glacial acetic acid, 1:1 acetic acid–acetic anhydride mixture, methanol, ethanol or acetonitrile by direct weighing and then diluting to the required volume.

General procedure

An aliquot of reductant solution (2–10 ml) was diluted to 50 ml with the solvent. Anhydrous sodium acetate (3–4 g) was added to the titrand in the titrations of hydrazines in glacial acetic acid and 1:1 acetic acid–acetic

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EXPERIMENTAL

Reagents

Bromine cyanide,[1] arsenic(III) chloride, antimony(III) chloride,[8] sodium sulphide,[1] phenylhydrazine, chloralhydrazine, 1,1-methylphenylhydrazine, benzalazine,[3] ethylthiourea, isopropylthiourea, allylthiourea, α-phenylthiourea, benzylthiourea, *o*-tolylthiourea,[4] sodium methyldithiocarbamate, sodium dimethyldithiocarbamate, sodium ethyldithiocarbamate, sodium diethyldithiocarbamate, sodium isopropyldithiocarbamate and ethanol[5] were prepared and/or purified according to the methods referred to earlier. All the other chemicals used were of analytical grade. The solvents were distilled before use.

The solutions of bromine cyanide and the reductants ($2{\cdot}5 \times 10^{-2}M$) were prepared in glacial acetic acid, 1:1 acetic acid–acetic anhydride mixture, methanol, ethanol or acetonitrile by direct weighing and then diluting to the required volume.

General procedure

An aliquot of reductant solution (2–10 ml) was diluted to 50 ml with the solvent. Anhydrous sodium acetate (3–4 g) was added to the titrand in the titrations of hydrazines in glacial acetic acid and 1:1 acetic acid–acetic anhydride mixture media. After each addition of oxidant, the mixture was thoroughly stirred and the potential noted, the potentiometric titration outfit described earlier being used.[1] The titrations were repeated at least thrice at each concentration level.

Some typical results are given in Table 1.

Table 1. Potentiometric determination of various reductants with bromine cyanide

Reluctant	Taken; mg	Found, mg	Mean relative deviation %	$\Delta E/\Delta V$, mV per 0·02 ml	Taken, mg	Found, mg	Mean relative deviation %	$\Delta E/\Delta V$, mV per 0·02 ml
	Acetic acid medium				1:1 Acetic acid–acetic anhydride mixture			
Potassium iodide	12·20	12·19	0·29	33	15·25	15·27	0·35	37
Sodium sulphide	40·40	40·45	0·16	24	40·40	40·43	0·05	29
Sodium sulphite	33·20	33·23	0·12	20	49·80	49·74	0·03	21
Ammonium thiocyanate	23·84	23·80	0·08	63	37·76	37·80	0·09	60
Tin (II) chloride	29·30	29·25	0·04	66	29·30	29·25	0·00	65
Arsenic (III) chloride	25·38	25·42	0·07	43	50·76	50·82	0·08	46
Antimony (III) chloride	28·80	28·78	0·02	31	57·60	57·58	0·07	28
Hydrazine hydrate	46·36	46·42	0·06	63	31·26	31·21	0·07	47
Phenylhydrazine	39·63	39·55	0·05	15	28·20	28·17	0·09	13
1,1-Methylphenyl hydrazine	15·94	15·96	0·12	24	33·30	33·36	0·05	10
Chloral hydrazine	23·16	23·12	0·08	19	34·74	34·79	0·08	17
	Ethanol medium				Acetonitrile medium			
Sodium methyldithiocarbamate	17·91	17·94	0·06	25	30·24	30·22	0·05	23
Sodium dimethyldithiocarbamate	22·00	22·05	0·14	53	17·98	17·96	0·18	82
Sodium ethyldithiocarbamate	27·00	27·03	0·03	34	17·10	17·11	0·11	93
Sodium diethyldithiocarbamate	21·00	21·03	0·10	38	19·52	19·48	0·06	79
Sodium isopropyldithiocarbamate	30·21	30·23	0·23	43	30·99	30·95	0·04	99
	Methanol medium							
Thiourea	40·96	40·91	0·04	39				
Ethylthiourea	50·56	50·58	0·23	31				
Isopropylthiourea	53·10	53·17	0·12	17				
Allylthiourea	10·36	10·34	0·00	26				
α-Phenylthiourea	17·68	17·66	0·09	38				
Benzylthiourea	30·80	30·77	0·14	53				
o-Tolylthiourea	25.00	24·97	0·08	25				

RESULTS AND DISCUSSION

The solution of bromine cyanide in glacial acetic acid, 1 : 1 acetic acid–acetic anhydride mixture, acetonitrile, methanol or ethanol is stable and does not undergo decomposition or change in reactivity with time. The titre does not change more than 1% even after 2 months.

Determination of inorganic ions

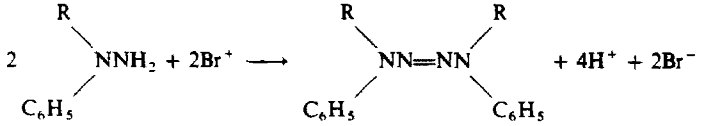
Bromine cyanide reacts in 1:1 molar ratio with sulphide and sulphite in glacial acetic acid and 1:1 acetic acid–acetic anhydride mixture, forming sulphur and sulphate respectively. Tin(II), arsenic(III) and antimony(III) are oxidized to tin(IV), arsenic(V) and antimony(V) respectively in these media even in the absence of anhydrous sodium acetate, which has to be added in the corresponding titrations with iodine cyanide.[8] Thiocyanate reacts with bromine cyanide in 2:1 molar ratio, forming thiocyanogen. All the titrations are reversible and bromine cyanide is reduced directly to bromide in every case. It may be mentioned that thiocyanate reduces iodine cyanide in these media only to elementary iodine[8] and the titration is not possible in aqueous medium with either oxidant. The behaviour of bromine cyanide in glacial acetic acid and 1 : 1 acetic acid–acetic anhydride is somewhat different from that of iodine cyanide in these media;[8] there is neither colour change nor formation of the corresponding complex trihalide ion during these titrations. However, when iodine is titrated with bromide cyanide, the colour changes from yellow to orange, indicating that the iodide is first oxidized to iodine and then to the complex tri-iodide,(I_3^-), but there is no abrupt potential change corresponding to the formation of iodine as there is in aqueous medium.[1] When the iodide is completely oxidized to tri-iodide, the solution acquires a yellowish-brown colour and there is an abrupt rise in potential at a BrCN/KI molar ratio of 1:3.

The titration is selective for iodide and as little as 2 mg can be determined in the presence of 100 times excess of chloride and bromide. The titrations of iodide, sulphide, sulphite, thiocyanate and tin(II) are faster than those of arsenic(III) and antimony(III).

Determination of hydrazines

Bromine cyanide reacts with hydrazine hydrate, phenylhydrazine, 1,1-methyl phenylhydrazine and chloralhydrazine in 1:1 molar ratio in glacial acetic acid. The solution remains colourless, indicating the reduction of bromine cyanide to bromide. The behaviour of bromine cyanide is similar to that of iodine cyanide in the corresponding titrations[3] and the reactions may, therefore, be explained by the following equations:

$$2\,N_2H_4 + 2\,Br^+ \rightarrow NH_3 + N_3H + 4\,H^+ + 2\,Br^- \qquad (1)$$



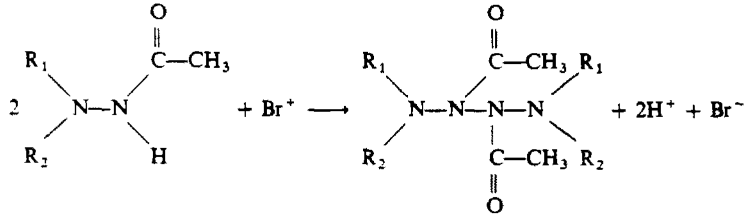
$$2\,\mathrm{R(C_6H_5)NNH_2} + 2Br^+ \longrightarrow \mathrm{R(C_6H_5)NN{=}NN(C_6H_5)R} + 4H^+ + 2Br^- \qquad (2)$$

$$2\,CCl_3CH(OH)NHNH_2 + 2\,Br^+ \rightarrow CCl_3CH(OH)NHNH(OH)CHCCl_3 + N_2 + 4H^+ + 2\,Br^- \qquad (3)$$

The evolution of nitrogen was observed only in the titration of chloralhydrazine.

These hydrazines, however, react with bromine cyanide in 1 : 1 glacial acid–acetic anhydride mixture in 2 : 1 molar ratio except for hydrazine hydrate which consumes an equimolar amount of the oxidant. The stoichiometric ratios in this medium are different from those in aqueous[3] and glacial acetic acid medium because the hydrazines are acetylated in presence of acetic anhydride.[9,10] These acetyl derivatives are then oxidized by bromine cyanide:

$$2\,CH_3CONHNH_2 + 2\,Br^+ \rightarrow CH_3CONHNHCOCH_3 + N_2 + 4\,H^+ + 2\,Br^- \qquad (4)$$



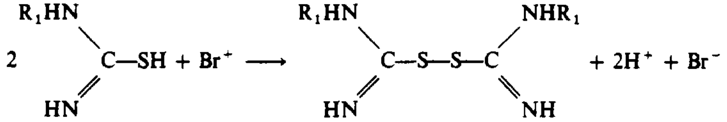
$$2\,\mathrm{R_1R_2N{-}N(H)C({=}O)CH_3} + Br^+ \longrightarrow \mathrm{R_1R_2N{-}N(C({=}O)CH_3){-}N(C({=}O)CH_3){-}NR_1R_2} + 2H^+ + Br^- \qquad (5)$$

where $R_1 = H, CH_3$ and $R_2 = C_6H_5$ or $CCl_3CH(OH)$.

The titrations are slow, reversible, accurate and possible in both media only in the presence of molar concentrations of anhydrous sodium acetate. Benzalazine, which reacts with iodine cyanide in both media,[3] could not be titrated with bromine cyanide under similar conditions. The mode and progress of the reaction are thus governed largely by the nature of the solvent and the oxidant. Since the media are acidic, there is no chance of air oxidation of the hydrazines, which is the main source of error in their determination in aqueous medium.[7] All attempts to determine the hydrazines in solvents such as ethanol, formamide and acetone have failed.

Determination of thioureas

Thiourea and its derivatives cannot be titrated with bromine cyanide in glacial acetic acid or 1 : 1 acetic acid–acetic anhydride mixture, even in presence of anhydrous sodium acetate, although the corresponding titrations with iodine cyanide are quantitative.[4] However bromine cyanide reacts with thiourea, ethylthiourea, isopropylthiourea, allylthiourea, α-phenylthiourea, benzylthiourea and *o*-tolylthiourea in methanol in molar ratio 1:2 and itself is reduced to bromide:



(6)

where R_1 = hydrogen, alkyl or aryl.

This is significant because in aqueous medium only the alkylthioureas react quantitatively (and even then an indirect method has to be used) and the titrations are not of any analytical interest.[4] Iodine cyanide reacts with alkyl and aryl thioureas in methanol medium in molar ratio 1:2 and 1:1 respectively.[4] The bromine cyanide titrations in methanol are quick and the change in potential at the equivalence point is appreciable. The thioureas can be titrated with bromine cyanide only in slightly acid media and all attempts to determine them in solvents such as acetone and ethyl acetate have failed.

Determination of dithiocarbamates

Bromine cyanide reacts with sodium methyl-, ethyl-, dimethyl-, diethyl- and isopropyldithiocarbamates in the molar ratio 1:2 in ethanol and acetonitrile.

$$2R_1R_2NCS_2^- + Br^+ \longrightarrow R_1R_2N\overset{\overset{S}{\|}}{C}\text{—S—S—}\overset{\overset{S}{\|}}{C}NR_2R_1 + Br^- \qquad (7)$$

where R_1 = alkyl or aryl, and R_2 = hydrogen or alkyl.

The titrations are fast, reversible and quantitative. The titrations of dithiocarbamates with bromine cyanide in ethanol are faster than the corresponding titrations with iodine cyanide and require about 20–25 min with manual recording of the potential.

The use of non-aqueous solvents for these determinations is advantageous because the oxidation product need not be extracted with petroleum ether, carbon tetrachloride or chloroform as is the case in aqueous medium.[5] Unlike iodine cyanide,[5] bromine cyanide does not oxidize the dithiocarbamates quantitatively in acetone medium. The titrations are also unsuccessful in acidic solvents such as glacial acetic acid even in presence of anhydrous sodium acetate, and also in stronger donor solvents like formamide and dioxan.

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Summary—Bromine cyanide has been used for the potentiometric determination of sulphide, sulphite, thiocyanate, iodide, tin(II), arsenic(III), antimony(III), hydrazine hydrate, phenylhydrazine, 1,1-methylphenylhydrazine and chloralhydrazine in glacial acetic acid and 1:1 acetic acid–acetic anhydride mixture, of thiourea, ethylthiourea, isopropylthiourea, allylthiourea, benzylthiourea, α-phenylthiourea and *o*-tolylthiourea in methanol, and of sodium methyl-, ethyl-, dimethyl-, diethyl- and isopropyldithiocarbamates in ethanol and acetonitrile media. The behaviour of bromine cyanide in these non-aqueous solvents has been compared with its behaviour in aqueous medium and with that of iodine cyanide in these non-aqueous solvents.

Zusammenfassung—Bromcyanid wurde verwendert zur potentiometrischen Bestimmung von Sulfid, Sulfit, Thiocyanat, Jodid, Zinn(II), Arsen(III), Antimon(III), Hhydrazinhydrat, Phenylhydrazin, 1,1-Methylphenylhydrazin und Chloralhydrazin in Eisessig und in einem 1:1-Gemisch aus Essigsäure und Acetanhydrid, von Thioharnstoff, Äthylthioharnstoff, Isopropylthioharnstoff, Allylthioharnstoff, Benzylthioharnstoff, α-Phenylthioharnstoff und *o*-Tolylthioharnstoff in Methanol; sowie der Methyl-, Äthyl-, Dimethyl-, Diathyl- und Isopropyldithiocarbamate von Natrium in Äthanol und Acetonitril. Das Verhalten von Bromcyanid in diesen nichtwäßrigen Lösungsmitteln wurde verglichen mit seinem Verhalten in wäßriger Lösung und mit dem von Jodcyanid in diesen nichtwäßrigen Lösungsmitteln.

Résumé—On a utilisé le bromure de cyanogène pour le dosage potentiométrique de sulfure, sulfite, thiocyanate, iodure, étain (II), arsenic (III), antimoine (III), hydrate d'hydrazine, phénylhydrazine, 1,1-méthylphénylhydrazine, et chloralhydrazine en acide acétique glacial et dans un mélange de 1:1 acide acétique-anhydride acétique, de thiourée, éthylthiourée, isopropylthiourée, allylthiourée, benzylthiourée, α-phénylthiourée et *o*-tolylthiourée en méthanol, et de méthyl-, éthyl-, diméthyl-, diéthyl- et isopropyldithiocarbamates de sodium en milieux éthanol et acétronitrile. Le comportement du bromure de cyanogène dans ces solvants non-aqueux a été comparé à son comportement en milieu aqueux et à celui de l'iodure de cyanogène dans ces solvants non-aqueux.

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PRELIMINARY COMMUNICATION

CATALYTIC EFFECT OF COPPER ON THE HEXACYANOFERRATE(III)–CYANIDE REDOX REACTION

(*Received* 19 *December* 1973 *Accepted* 10 *January* 1974)

Cyanide is oxidized by hexacyanoferrate(III), according to the equation:

$$2Fe(CN)_6^{3-} + CN^- + 2OH^- \rightarrow 2Fe(CN)_6^{4-} + CNO^- + H_2O$$

This reaction involves a two-electron transfer, and is therefore slow, in good agreement with the empirical law reported by Adamson.[1] However, we have verified that the reaction rate is notably increased if copper is present in the solution. An attempt is being made to apply this catalytic activity to the kinetic determination of copper and in this paper, a preliminary study is reported.

EXPERIMENTAL

Reagents

Cupric nitrate solutions were obtained by dilution from a 0·01*M* standard solution; 2·0*M* sodium cyanide and $5 \times 10^{-3}M$ potassium hexacyanoferrate(III) were prepared from reagent grade products.

Procedure

In a 50 ml volumetric flask, 25 ml of 2·0*M* sodium cyanide and different volumes of $10^{-3}M$ cupric nitrate were diluted with water to nearly 40 ml. Then 5 ml of $5 \times 10^{-3}M$ potassium hexacyanoferrate(III) were added with stirring, and the volume was quickly adjusted to 50 ml. The time was measured from the moment of adding the $Fe(CN)_6^{3-}$ solution. All the solutions were previously heated to 25° in a thermostat, and this temperature was maintained in the reaction cell during the experiment.

The reaction rate was followed by measuring the decrease of the characteristic maximum of $Fe(CN)_6^{3-}$ at 422 nm, with time. The other species in solution do not interfere practically at this wavelength.

RESULTS AND DISCUSSION

In all the runs it was verified that, after an initial period of about 10 min, plots of $1/[Fe(CN)_6^{3-}]$ against time were straight lines, showing a second-order dependence on hexacyanoferrate(III) concentration. The pseudo second-order rate constant k_2 was a linear function of the total copper concentration for fixed pH and cyanide concentration. The rate constant in 1·0*M* cyanide media (pH 11·4) was measured for copper concentrations varying from 10^{-7} to $10^{-3}M$. A value of k_2 corresponding to the uncatalysed reaction was obtained by extrapolating the straight line to zero copper concentration. The detection limit in the experimental conditions was somewhat higher than $10^{-7}M$. The computed relative standard deviation from ten determinations of $4 \times 10^{-5}M$ copper was about ±3%.

We are now making a kinetic study of the uncatalysed reaction by spectrophotometric and amperometric methods. The reaction rate increases with ionic strength, alkalinity and cyanide concentration, while it is decreased as the hexacyanoferrate(II) concentration increases. From knowledge of the kinetics, mechanisms and activation energy values of both the uncatalysed and catalysed reactions, an attempt will be made to determine the best experimental conditions to obtain the greatest sensivity and the smallest detection limit. Interferences will also be studied.

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Summary—The oxidation of cyanide with hexacyanoferrate(III) is a thermodynamically possible but kinetically slow reaction, which is catalysed by copper(II). The catalysed reaction has a second-order dependence on hexacyanoferrate(III) concentration, and the pseudo second-order rate constant increases linearly with the copper concentration, at least in the range from 10^{-7} to $10^{-3}M$.

Zusammenfassung—Die Oxidation von Cyanid durch Hexacyanoferrat(III) ist eine thermodynamisch mögliche, jedoch langsame Reaktion; sie wird durch Kupfer(II) katalysiert. Die katalysierte Reaktion hängt nach der zweiten Ordnung von der Hexacyanoferrat(III)-Konzentration ab; die Geschwindigkeitskonstante pseudo-zweiter Ordnung steigt linear mit der Kupferkonzentration an, wenigstens im Bereich von 10^{-7} bis $10^{-3}M$.

Résumé—L'oxydation du cyanure par l'hexacyanoferrate(III) est une réaction thermodynamiquement possible mais cinétiquement lente, qui est catalysée par le cuivre(II). La réaction catalysée a une dépendance du second ordre par rapport à la concentration en hexacyanoferrate(III), et la constante de vitesse de pseudo second ordre croît linéairement avec la concentration en cuivre, au moins dans le domaine de 10^{-7} à $10^{-3}M$.

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ANALYTICAL DATA

COPPER(II), LEAD AND ZINC COMPLEXES OF ETHYLENEDIAMINE-*N*,*N'*-DIACETIC ACID

(*Received* 13 *September* 1973. *Revised* 18 *January* 1974. *Accepted* 23 *January* 1974)

EDTA has already been thoroughly investigated as a selective titrant in complexometry. Ethylenediaminetriacetic acid is reported to be unstable[1,2] and is thus of limited utility. Ethylenediaminediacetic acid (EDDA), which is stable, has not been studied in depth. It exists as two stable isomers: *N*,*N'*-EDDA and *N*,*N*-EDDA. Although the latter is reported to be stable,[3,4] we have not yet managed to prepare it pure enough for use as analytical reagent. Complex formation with *N*,*N'*-EDDA has been little studied,[5–7] and this paper extends the range.

EXPERIMENTAL

Reagents

Commercial EDDA was recrystallized four times from aqueous ethanol and the white product dried for 2 hr at 80°C. Further recrystallization did not alter the properties of the product. The metal ions were added as solutions of the p.a. nitrates, standardized by EDTA titration, and the salts were checked for freedom from excess of acid or base. Sodium nitrate, p.a., was added to obtain a constant ionic strength of 0·1.

Apparatus

Potentials were measured with a Dynamco DM 20225 instrument connected to the electrode system through an amplifier built in this laboratory. The electrode system was arranged as described previously,[8] with an Ag/AgCl reference electrode, and an Orion 90–02 double-junction reference electrode with 0·1*M* sodium nitrate in the outer chamber. All solutions were kept at 25 ± 0·1°C and stirred with a magnetic stirrer. Nitrogen was bubbled through all solutions before and during titrations. All potentiometric measurements were repeated at least twice and results varying by more than 1 mV repeated until satisfactory reproducibility was obtained.

Method

Solutions with different initial concentration ratios of metal ions and EDDA were titrated with standard CO_2-free sodium hydroxide or nitric acid, the hydrogen ion concentration being determined with the electrode system:

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,0{\cdot}1M\ \mathrm{NaCl}\,|\,0{\cdot}1M\ \mathrm{NaNO_3}\,|\ \text{test solution}\,|\ \text{glass electrode}$$

and the metal-ion concentrations with analogous electrode systems.

The electrode systems were calibrated at least twice daily by measuring the potentials after successive additions of standard nitric acid to 0·1*M* sodium nitrate and applying a least-squares treatment to the results. By this procedure the liquid-junction potential was included in the numerical value of the standard potential, and was assumed to remain constant

Interpretation

The calculations were done by the pit-mapping[9] procedures discussed previously.[8] The initial concentrations of the various species are limited by the solubility of the ligand and the precipitation of the metal hydroxides. Titrations were not performed when precipitation occurred. To exclude erroneous results due to invisible solid phase, titrations were stopped before the point of precipitation, and the solutions were therefore too acid (as calculated from the published hydrolysis constants) for the hydroxides to form. It is thus reasonable to assume the absence of soluble simple hydroxo-species.

It was assumed that no species containing more than one EDDA ion exists in significant quantities. Only the ligand species X^{2-}, HX^-, H_2X, H_3X^+ and H_4X^{2+} are assumed to be possible, and of these H_4X^{2+} was assumed to be absent under the given experimental conditions. The formation constant found for H_3X^+ was very low and that species exists only in very acidic solution, and is therefore unimportant for complexation studies.

Table 1. Protonation of EDDA (H_2X), 25°, μ = 0·1 ($NaNO_3$)

Reaction	log K	Std. devn.
$X^{2-} + H^+ = HX^-$	9·17	0·03
$HX^- + H^+ = H_2X$	6·36	0·02
$H_2X + H^+ = H_3X^+$	1·54	0·16
$H_3X^+ + H^+ = H_4X^{2+}$	no complex	—

Table 2. Stabilities of the metal complexes studied.* Results from glass electrode measurements at 25° and μ = 0·1 ($NaNO_3$)

Reaction	log β	Std. devn.
$Cu^{2+} + X^{2-} = CuX$	17·47	0·02
$H^+ + Cu^{2+} + X^{2-} = CuHX^+$	20·87	0·05
$OH^- + Cu^{2+} + X^{2-} = Cu(OH)X^-$	6·34	0·05
$2Cu^{2+} + X^{2-} = Cu_2X^{2+}$	20·85†	0·14
$Pb^{2+} + X^{2-} = PbX$	11·71	0·01
$H^+ + Pb^{2+} + X^{2-} = PbHX^+$	15·60	0·02
$OH^- + Pb^{2+} + X^{2-} = Pb(OH)X^-$	12·27	0·02
$2Pb^{2+} + X^{2-} = Pb_2X^{2+}$	15·02	0·01
$Zn^{2+} + X^{2-} = ZnX$	11·71	0·01
$H^+ + Zn^{2+} + X^{2-} = ZnHX$	15·48	0·03
$OH^- + Zn^{2+} + X^{2-} = Zn(OH)X$	11·98	0·03
$2Zn^{2+} + X^{2-} = Zn_2X^{2+}$	14·91	0·01

* Doubtful species studied (the most probable values of the constants are given in parentheses): Zn_2HX^{3+}, $Zn_2(OH)X^+$ (6·7), Cu_2X^{2+} (18·8) +, Cu_2HX^{3+} (23·8), CuH_2X^{2+} (24·1), $Cu_2(OH)X^+$ (0·3), Pb_2HX^{3+} (16·8), $Pb_2(OH)X^+$ (5·8), PbH_2X^{2+} (20·1), ZnH_2X^{2+} (19·8).

† From work with both glass and ion-specific electrodes.

RESULTS

The results are given in Tables 1 and 2. The association constants of EDDA agree with previously reported values,[5–7] considering the difference in ionic medium. The formation of the species H_3X^+ has not previously been reported. Previously reported constants[6] for the copper(II) and zinc complexes are somewhat lower than those reported in the present paper. This is explained by considering the difference in temperature, ionic medium, and the fact that the protonated and hydroxo-species were not previously considered.

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Summary—From potentiometric measurements with glass and ion-specific electrodes, the formation constants of the complexes of ethylenediamine-*N,N'*-diacetic acid (EDDA, H_2X) and Cu^{2+}, Pb^{2+} and Zn^{2+} have been determined at 25·0° and ionic strength of 0·1 ($NaNO_3$). The formation constants of the protonated species of EDDA were determined from separate measurements. The following species and log β values were found (standard deviations in parentheses): HX^- 9·17 (0·03); H_2X 6·36 (0·02); H_3X^+ 1·54 (0·16); CuX 17·47 (0·02); CuHX 20·87 (0·05); Cu(OH)X 6·34 (0·05); Cu_2X 20·85 (0·14); PbX 11·71 (0·01); PbHX 15·60 (0·02); PbOHX 12·27 (0·02); Pb_2X 15·02 (0·01); ZnX 11·71 (0·01); ZnHX 15·48 (0·03); Zn(OH)X 11·98 (0·03); Zn_2X 14·91 (0·01). (Stepwise constants are given for HX^-, H_2X and H_3X^+.)

Zusammenfassung—An Hand potentiometrischer Messungen mit Glas- und ionenspezifischen Elektroden wurden die Bildungskonstanten der Komplexe von &thylendiamin-N,N'-diessigsäure (EDDA, $H_2Ö$) und Cu^{2+}, Pb^{2+} und Zn^{2+} bei 25,0° und einer Ionenstärke von 0,1 ($NaNO_3$) ermittelt. Aus weiteren Messungen wurden die Bildungskonstanten der protonierten Formen von EDDA bestimmt. Folgende log β-Werte wurden für die genannten Apezies gefunden (Standardabweichungen in Klammern): $HÖ^-$ 9,17 (0,03); $H_2Ö$ 6,36 (0,2); $H_3Ö^+$ 1,54 (0,16); CuÖ 17,47 (0,02); CuHÖ 20,87 (0,05); Cu(OH)Ö 6,34 (0,05); $Cu_2Ö$ 20,85 (0,14); PbÖ 11,71 (0,01); PbHÖ 15,60 (0,02); Pb(OH)Ö 12,27 (0,02); $Pb_2Ö$ 15,02 (0,01); ZnÖ 11,71 (0,01); ZnHÖ 15,48 (0,03); Zn(OH)Ö 11,98 (0,03) $Zn_2Ö$ 14,91 (0,01). (Für $HÖ^-$, $H_2Ö$ und $H_3Ö^+$ sind Konstanten für die einzelnen Bildungsstufen angegeben).

Résumé—A partir de mesures potentiométriques avec des électrodes de verre et des électrodes spécifiques d'ions, les constantes de formation des complexes de l'acide éthylènediamine-N,N'-diacétique (EDDA, H_2X) avec Cu^{2+}, Pb^{2+} et Zn^{2+} ont été déterminées à 25,0° et à une force ionique de 0,1 ($NaNO_3$). Les constantes de formation des espèces protonées de l'EDDA ont été déterminées à partir de mesures séparées. Les espèces et valeurs de log β suivantes ont été trouvées (écarts types entre parenthèses): HX^- 9,17 (0,03); H_2X 6,36 (0,02); H_3X^+ 1,54 (0,16); CuX 17,47 (0,02); CuHX 20,87 (0,05); Cu(OH)X 6,34 (0,05); Cu_2X 20,85 (0,14); PbX 11,71 (0,01); PbHX 15,60 (0,02); PbOHX 12,27 (0,02); Pb_2X 15,02 (0,01); ZnX 11,71 (0,01); ZnHX 15,48 (0,03); Zn(OH)X 11,98 (0,03); Zn_2X 14,91 (0,01); (On donne les constantes par palier pour HX^-, H_2X et H_3X^+).

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FORMATION CONSTANTS OF ALKALINE-EARTH METAL COMPLEXES WITH SEMI-XYLENOL ORANGE AND SEMI-METHYLTHYMOL BLUE

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In earlier papers,[1,2] the bivalent transition metal complexes with Semi-Xylenol Orange (SXO) and Semi-Methylthymol Blue (SMTB) were investigated. This paper gives the results of a similar study of the complexes of the alkaline-earth metals with SXO and SMTB.

RESULTS AND DISCUSSION

From the results of potentiometric and spectrophotometric investigations conducted as described previously,[1,2] it was found that the reactions shown in Table 1 occur. The absorption spectra of these metal complexes are almost the same as those of the parent indicator species (L^{4-}: $\lambda_{max} = 576$ nm, $\epsilon = 6{\cdot}20 \times 10^4$ l. mole^{-1}.cm^{-1}; MgL^{2-}: $\lambda_{max} = 572$ nm, $\epsilon = 6{\cdot}00 \times 10^4$; CaL^{2-}: $\lambda_{max} = 577$ nm, $\epsilon = 7{\cdot}90 \times 10^4$; SrL^{2-}: $\lambda_{max} = 578$ nm, $\epsilon = 7{\cdot}31 \times 10^4$; BaL^{2-}: $\lambda_{max} = 579$ nm, $\epsilon = 7{\cdot}06 \times 10^4$ for SXO systems, L^{4-}: $\lambda_{max} = 607$ nm, $\epsilon = 3{\cdot}65 \times 10^4$; MgL^{2-}: $\lambda_{max} = 599$ nm, $\epsilon = 3{\cdot}02 \times 10^4$; CaL^{2-}: $\lambda_{max} = 611$ nm, $\epsilon = 4{\cdot}03 \times 10^4$; SrL^{2-}: $\lambda_{max} = 613$ nm, $\epsilon = 4{\cdot}38 \times 10^4$; BaL^{2-}: $\lambda_{max} = 614$ nm, $\epsilon = 4{\cdot}01 \times 10^4$ for SMTB systems). The wavelengths of the absorption maxima increase as the stabilites of the complexes decrease, for SXO and SMTB systems, *i.e.*, in the order MgL^{2-}, CaL^{2-}, SrL^{2-}, BaL^{2-}

Distribution diagrams for the ligand and complex species have been calculated from the formation constants and are shown in Fig 1 for SMTB systems. As seen from Fig. 1, a fair amount of ligand cannot react with Ba(II)

Summary—From potentiometric measurements with glass and ion-specific electrodes, the formation constants of the complexes of ethylenediamine-*N*,*N*′-diacetic acid (EDDA, H_2X) and Cu^{2+}, Pb^{2+} and Zn^{2+} have been determined at 25·0° and ionic strength of 0·1 ($NaNO_3$). The formation constants of the protonated species of EDDA were determined from separate measurements. The following species and log β values were found (standard deviations in parentheses): HX^- 9·17 (0·03); H_2X 6·36 (0·02); H_3X^+ 1·54 (0·16); CuX 17·47 (0·02); CuHX 20·87 (0·05); Cu(OH)X 6·34 (0·05); Cu_2X 20·85 (0·14); PbX 11·71 (0·01); PbHX 15·60 (0·02); PbOHX 12·27 (0·02); Pb_2X 15·02 (0·01); ZnX 11·71 (0·01); ZnHX 15·48 (0·03); Zn(OH)X 11·98 (0·03); Zn_2X 14·91 (0·01). (Stepwise constants are given for HX^-, H_2X and H_3X^+.)

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Distribution diagrams for the ligand and complex species have been calculated from the formation constants and are shown in Fig 1 for SMTB systems. As seen from Fig. 1, a fair amount of ligand cannot react with Ba(II)

Table 1. Formation constants of magnesium(II), calcium(II), strontium(II) and barium(II) complexes with SXO and SMTB at 25 ± 0·1°, μ = 0·1(KNO$_3$)

Reaction		log K							
		Mg(II)		Ca(II)		Sr(II)		Ba(II)	
		SXO	SMTB	SXO	SMTB	SXO	SMTB	SXO	SMTB
$M^{2+} + L^{4-} \rightleftharpoons ML^{2-}$	K^{M}_{ML}	6·89	7·05	6·53	6·52	5·30	5·34	4·75	4·54
$M^{2+} + HL^{3-} \rightleftharpoons MHL^{-}$	K^{M}_{MHL}	2·91	2·48	2·79	2·22	2·13	1·60	1·82	1·29
$ML^{2-} + OH^{-} \rightleftharpoons M(OH)L^{3-}$	$K^{OH}_{M(OH)L}$	2·43	2·35						
$H^{+} + ML^{2-} \rightleftharpoons MHL^{-}$	K^{H}_{MHL}	6·92	7·55	7·16	7·82	7·73	8·38	7·97	8·87

and Sr(II) at high pH even if excess of metal ion is present. Distribution of the complex MHL$^-$ depends on that of the ligand species HL^{3-}. Thus the initial formation of the complex MHL$^-$ may be given by

$$H_2L^{2-} \rightleftharpoons HL^{3-} + H^+$$

$$M^{2+} + HL^{3-} \rightleftharpoons MHL^-.$$

The conversion from H$_2$L^{2-} into HL^{3-} involves the dissociation of a proton from the phenol group[2] and the proton remaining on the ligand is attached to the nitrogen atom of the iminodiacetate group. Accordingly the arrangement of the complex MHL$^-$ is given by formula **I**. This arrangement is unexpectedly different from that of the complex MHL$^-$ for the bivalent transition metals, Co(II), Ni(II), Cu(II) and Zn(II) (formula **II**).[1,2] From **I** it seems that the nitrogen atom is very near to the metal ion, and it is clearly assumed that the formation of the complex ML^{2-} (formula **III**) occurs easily, while in arrangement **II**, the phenol group is far from the metal ion, and the conversion from MHL$^-$ into ML^{2-} does not go so easily. The complexes of the transition metals are formed at low pH, but ML^{2-} is found at higher pH.[1,2] On the other hand, in the case of alkaline earth metals,

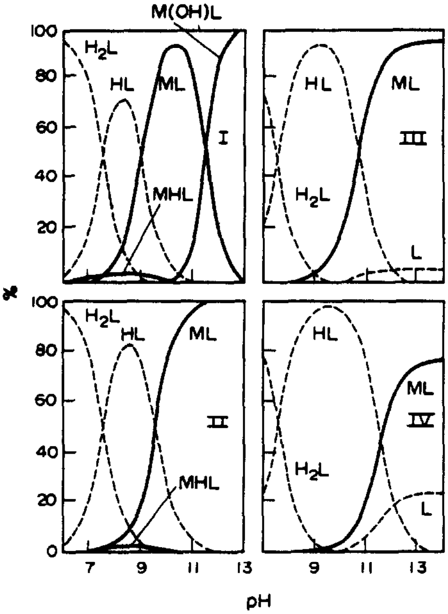
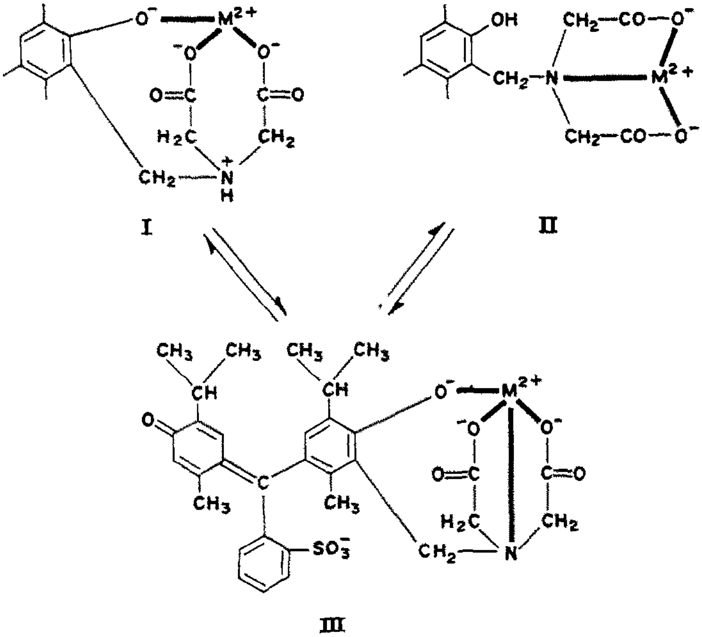


Fig. 1. Distribution diagrams showing the proportions of Mg(II), Ca(II), Sr(II) and Ba(II) complexes with SMTB as a function of different pH values for 10:1 mixtures of alkaline-earth metal ion and SMTB.

The percentages are relative to total ligand (T_L = 2·0 × 10^{-5}*M*). I, Mg(II)–SMTB; II, Ca(II)–SMTB; III, Sr(II)–SMTB; IV, Ba(II)–SMTB.

the formation of the complex MHL^- is immediately followed by the dissociation of the proton and the formation of ML^{2-}.



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2. T. Yoshino, S. Murakami and M. Kagawa, *ibid.*, 1974, **21**, 199.

Summary—Potentiometric and spectrophotometric studies on the interactions of Semi-Xylenol Orange and Semi-Methylthymol Blue and alkaline-earth metal ions are reported. Two complex species, MHL^- and ML^{2-}, for each indicator and element have been found to be formed in aqueous solutions, and the formation constants and the arrangements of these complexes have been determined

Zusammenfassung—Es wird über potentiometrische und spektrophotometrische Untersuchungen über die Reaktionen zwischen Semixylenolorange, Semimethylthymolblau und den Erdalkalimetallionen berichtet. In wäßriger Lösung bilden sich mit jedem Indikator und jedem Element zwei Komplexspezies: MHL^- und ML^{2-}. Die Bildungskonstanten und die Anordnungen dieser Komplexe wurden ermittelt.

Résumé—On rapporte les études potentiométriques et spectrophotométriques sur les interactions de l'Orangé Semi-Xylénol et du Bleu de Semi-Méthylthymol et des ions alcalino-terreux. On a trouvé que deux espèces complexes, MHL^- et ML^{2-} se forment en solutions aqueuses pour chaque indicateur et élément, et l'on a déterminé les constantes de formation et les arrangements de ces complexes.

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FORMATION CONSTANTS OF ALKALINE-EARTH METAL COMPLEXES WITH XYLENOL ORANGE AND METHYLTHYMOL BLUE

(*Received* 7 *January* 1974. *Accepted* 17 *January* 1974)

The complexes of the alkaline-earth metals with Xylenol Orange (XO) and Methylthymol Blue (MTB) have not previously been thoroughly investigated. In the present work, the reactions between these indicators and elements in aqueous solutions are investigated over a wide pH range potentiometrically and spectrophotometrically, as described previously.[1]

RESULTS AND DISCUSSION

Alkaline-earth metals react with XO and MTB above pH about 6 in aqueous solutions, and form the complex species listed in Table 1 together with their formation constants. The complex formation equilibria are very complicated, so the distribution curves for the various dissociated forms of the ligand and for the metal complex were calculated, and the diagrams for MTB systems containing 1:1 and 10:1 mole ratios of metal ion to ligand are shown in Fig. 1. Even in the "1:1" solution, a fair amount of the binuclear complex M_2L^{2-} is formed above pH about 9, whereas in the "10:1" solution, the 1:1 complex species are predominant in relatively weakly alkaline medium. The contributions of the complexes, MH_2L^{2-} and M_2HL^-, are very small both in the "1:1" and "10:1" solutions. At high pH, the behaviour of Mg(II) differs from that of the other three metals because of formation of hydroxo-complexes. For Sr(II) and Ba(II), the stabilities are small, resulting in complex formation at higher pH than for Mg(II) and Ca(II), and that a fair amount of the free ligand species HL^{5-} and L^{6-}, which are negligible in the systems of Mg(II) and Ca(II), exists in the solutions.

The distribution of the complex MH_2L^{2-} depends on that of the ligand species H_2L^{4-} as seen in a distribution diagram for each "10:1" solution. Accordingly the initial formation of the complex MH_2L^{2-} may be given by the following equilibria.

$$H_3L^{3-} \rightleftharpoons H_2L^{4-} + H^+$$

$$M^{2+} + H_2L^{4-} \rightleftharpoons MH_2L^{2-}.$$

The conversion from H_3L^{3-} into H_2L^{4-} corresponds to the dissociation of a proton from the phenol group, and the two protons remaining on the ligand are those attached one to each nitrogen atom of the iminodiacetate groups.[1,2] The metal ion may combine with one of the phenol groups and with two carboxyl groups of the iminodiacetate group at the same side of the sulphonphthalein as the phenol groups (formula I). It is natural to consider

Table 1. Formation constants of magnesium, calcium, strontium and barium complexes with Methylthymol Blue at 25 ± 0·1°, $\mu = 0{\cdot}1(KNO_3)$

		log *K*							
		Mg(II)		Ca(II)		Sr(II)		Ba(II)	
Reaction		XO	MTB	XO	MTB	XO	MTB	XO	MTB
$M^{2+} + L^{6-} \rightleftharpoons ML^{4-}$	K^M_{ML}	9·02	8·87	8·65	8·25	7·71	7·05	6·67	6·93
$M^{2+} + HL^{5-} \rightleftharpoons MHL^{3-}$	K^M_{MHL}	7·10	6·73	6·82	6·21	5·44	5·19	5·04	5·09
$M^{2+} + H_2L^{4-} \rightleftharpoons MH_2L^{2-}$	$K^M_{MH_2L}$	3·09	2·63	2·97	2·42	2·24	1·96	2·02	2·11
$M^{2+} + ML^{4-} \rightleftharpoons M_2L^{2-}$	$K^M_{M_2L}$	6·14	5·80	6·02	5·38	4·89	4·58	4·57	4·65
$M^{2+} + MHL^{3-} \rightleftharpoons M_2HL^-$	$K^M_{M_2HL}$	2·6	2·3	2·5	2·1	2·1	1·9	2·0	1·9
$H^+ + ML^{4-} \rightleftharpoons MHL^{3-}$	K^H_{MHL}	10·3	10·8	10·4	10·9	10·4	11·1	10·5	11·2
$H^+ + MHL^{3-} \rightleftharpoons MH_2L^{2-}$	$K^H_{MH_2L}$	6·56	7·04	6·71	7·35	7·36	7·93	7·54	8·06
$H^+ + M_2L^{2-} \rightleftharpoons M_2HL^-$	$K^H_{M_2HL}$	6·8	7·3	6·9	7·7	7·6	8·3	8·0	8·5
$ML^{4-} + OH^- \rightleftharpoons M(OH)L^{5-}$	$K^{OH}_{M(OH)L}$	2·43	2·69						
$M_2L^{2-} + 2OH^- \rightleftharpoons M_2(OH)_2L^{4-}$	$K^{OH}_{M_2(OH)_2L}$	3·21	3·44						

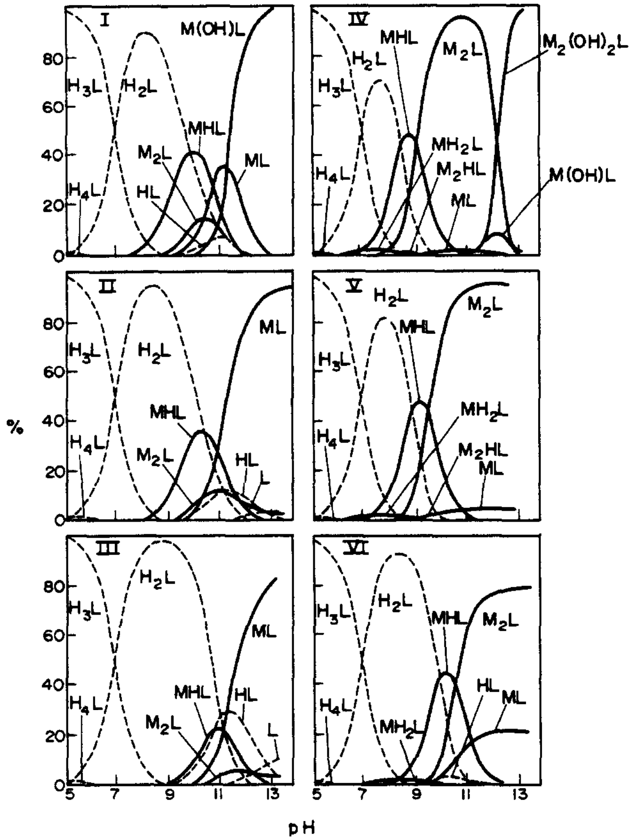
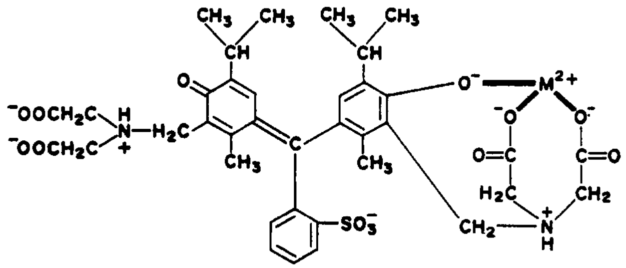
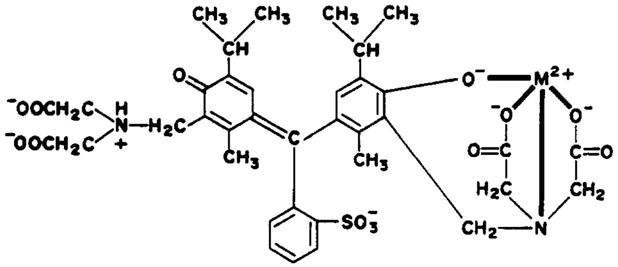


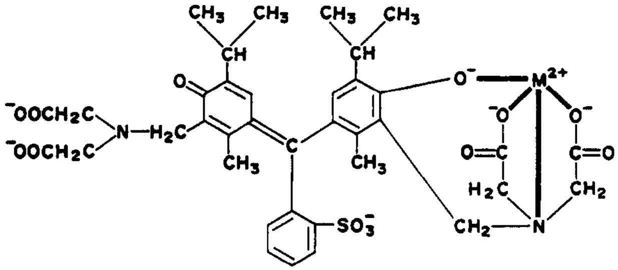
Fig. 1. Distribution diagrams showing the proportions of Mg(II), Ca(II) and Ba(II) complexes with MTB as a function of pH for 1:1 and 10:1 mixtures of alkaline-earth metal ions and MTB. The percentages are relative to total ligand (T_l = 2·0 × $10^{-5}M$). *I*, Mg(II)–MTB(1:1); *II*, Ca(II)–MTB(1:1); *III*, Ba(II)–MTB(1:1); *IV*, Mg(II)–MTB(10:1); *V*, Ca(II)–MTB(10:1); *VI*, Ba(II)–MTB(10:1).



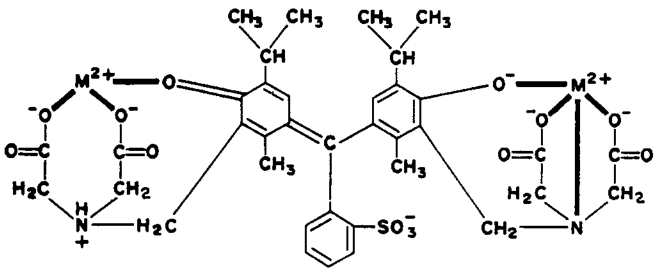
I MH_2L^{2-}



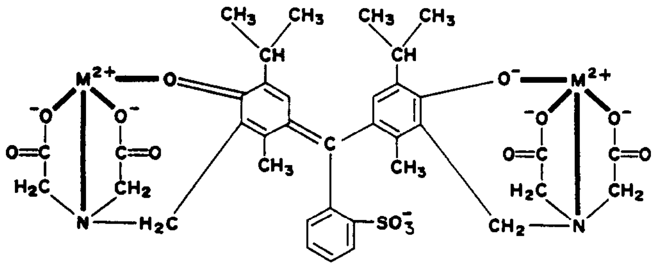
II MHL^{3-}



III ML^{4-}



IV M_2HL^{-}



V M_2L^{2-}

that the protons further dissociated from MH_2L^{2-} are from the nitrogen atoms of the iminodiacetate groups co-ordinated to the metal ion, and the structures of the complexes MHL^{3-} and ML^{4-} are given by formulas **II** and **III**, respectively.

The initial binuclear complex M_2HL^- is formed in the relatively high pH region and its distribution depends on that of the complex MHL^{3-}, as seen in the diagram for the "10: 1" solution, although this complex is negligible when the metal ion is Sr(II) or Ba(II). The equilibria of the complex formation are probably given by

$$MH_2L^{2-} \rightleftharpoons MHL^{3-} + H^+$$

$$M^{2+} + MHL^{3-} \rightleftharpoons M_2HL^-.$$

From the arrangement of the complex MHL^{3-}, it is assumed that the second metal ion combines with two carboxyl oxygen atoms and the phenol oxygen atom which remain unco-ordinated at the opposite side of the first chelate ring in formula **II**, and the arrangement of the complex M_2HL^- is given by formula **IV**. The formation of M_2L^{2-} occurs just after the formation of MHL^{3-}. Its equilibrium may be given mainly by

$$M^{2+} + MHL^{3-} \rightleftharpoons M_2L^{2-} + H^+$$

and its structure is probably given by formula **V**.

Acknowledgement—The authors wish to thank Messrs. T. Fujiwara and A. Hesaka for their help in the experimental work.

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Summary—The complexes of the alkaline-earth metals with Xylenol Orange and Methythymol Blue have been studied. Three 1:1 and two 2:1 (metal:ligand) complex species for each indicator and each element have been found to be formed in aqueous solutions, and the formation constants and the arrangements of these complexes have been determined.

Zusammenfassung—Die Komplexe der Erdalkalimetalle mit Xylenol-orange und Methylthymolblau wurden untersucht. Drei 1 : 1-und zwei 2 : 1-(Metall : Ligand) Komplexspezies wurden für jeden Indikator und jedes Element in wäßriger Lösung gefunden; die Bildungskonstanten und die Anordnungen dieser Komplexe wurden ermittelt.

Résumé—On a étudié les complexes des métaux alcalino-terreux avec l'Orangé Xylénol et le Bleu de Méthylthymol. On a trouvé que trois espèces complexes 1 : 1 et deux espèces 2 : 1 (métal :coordinat) se forment en solutions aqueuses pour chaque élément et chaque indicateur, et l'on a déterminé les constantes de formation et les arrangements de ces complexes.

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PROTOLYTIC REACTIONS OF 3,3'-DIMETHYLNAPHTHIDINE AND 3,3'-DIMETHOXYBENZIDINE

(*Received* 22 *October* 1973. *Accepted* 2 *December* 1973)

In the course of investigation of the characteristics of redox indicators[1] the dissociation constants of diprotonated 3,3'-dimethylnaphthidine and 3,3'-dimethoxybenzidine in aqueous solution, have been determined for the reactions

$$BH_2^{2+} + H_2O \xrightleftharpoons{K_{a1}} BH^+ + H_3O^+$$

$$BH^+ + H_2O \xrightleftharpoons{K_{a2}} B + H_3O^+$$

where B is the free indicator base.

that the protons further dissociated from MH_2L^{2-} are from the nitrogen atoms of the iminodiacetate groups co-ordinated to the metal ion, and the structures of the complexes MHL^{3-} and ML^{4-} are given by formulas **II** and **III**, respectively.

The initial binuclear complex M_2HL^- is formed in the relatively high pH region and its distribution depends on that of the complex MHL^{3-}, as seen in the diagram for the "10:1" solution, although this complex is negligible when the metal ion is Sr(II) or Ba(II). The equilibria of the complex formation are probably given by

$$MH_2L^{2-} \rightleftharpoons MHL^{3-} + H^+$$

$$M^{2+} + MHL^{3-} \rightleftharpoons M_2HL^-.$$

From the arrangement of the complex MHL^{3-}, it is assumed that the second metal ion combines with two carboxyl oxygen atoms and the phenol oxygen atom which remain unco-ordinated at the opposite side of the first chelate ring in formula **II**, and the arrangement of the complex M_2HL^- is given by formula **IV**. The formation of M_2L^{2-} occurs just after the formation of MHL^{3-}. Its equilibrium may be given mainly by

$$M^{2+} + MHL^{3-} \rightleftharpoons M_2L^{2-} + H^+$$

and its structure is probably given by formula **V**.

Acknowledgement—The authors wish to thank Messrs. T. Fujiwara and A. Hesaka for their help in the experimental work.

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Summary—The complexes of the alkaline-earth metals with Xylenol Orange and Methythymol Blue have been studied. Three 1:1 and two 2:1 (metal:ligand) complex species for each indicator and each element have been found to be formed in aqueous solutions, and the formation constants and the arrangements of these complexes have been determined.

Zusammenfassung—Die Komplexe der Erdalkalimetalle mit Xylenol-orange und Methylthymolblau wurden untersucht. Drei 1 : 1-und zwei 2 : 1-(Metall : Ligand) Komplexspezies wurden für jeden Indikator und jedes Element in wäßriger Lösung gefunden; die Bildungskonstanten und die Anordnungen dieser Komplexe wurden ermittelt.

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PROTOLYTIC REACTIONS OF 3,3′-DIMETHYLNAPHTHIDINE AND 3,3′-DIMETHOXYBENZIDINE

(*Received* 22 *October* 1973. *Accepted* 2 *December* 1973)

In the course of investigation of the characteristics of redox indicators[1] the dissociation constants of diprotonated 3,3′-dimethylnaphthidine and 3,3′-dimethoxybenzidine in aqueous solution, have been determined for the reactions

$$BH_2^{2+} + H_2O \overset{K_{a1}}{\rightleftharpoons} BH^+ + H_3O^+$$

$$BH^+ + H_2O \overset{K_{a2}}{\rightleftharpoons} B + H_3O^+$$

where B is the free indicator base.

Preliminary spectrophotometric studies in the acidity range from $2M$ sulphuric acid to pH 8 indicated that no individual peaks occur for the protonated forms in the accessible spectral range, but the molar absorptivities change significantly. For 3,3′-dimethoxybenzidine maximal absorbance is observed at 300 nm, and for 3,3′-dimethylnaphthidine at 330 nm, the molar absorptivities for the basic and diprotonated forms being:

$$\text{3,3}'\text{-dimethoxybenzidine (300 nm)}, \varepsilon_B = 1{\cdot}68 \times 10^4 \text{ l.mole}^{-1}.\text{cm}^{-1}, \varepsilon_{BH_2^{2+}} = 1{\cdot}80 \times 10^3 \text{ l.mole}^{-1}.\text{cm}^{-1};$$

$$\text{3,3}'\text{-dimethylnaphthidine (330 nm) } \varepsilon_B = 7{\cdot}33 \times 10^3 \text{ l.mole}^{-1}.\text{cm}^{-1}; \varepsilon_{BH_2^{2+}} = 0.$$

The molar absorptivity of the BH^+ species could not easily be found because of the small difference between the two pK_a values. Therefore the computer programme developed by Albert and Serjeant[2] has been applied, which by successive approximation allow the calculation of pK_{a_1}, pK_{a_2} and ε_{BH^+}. The original FORTRAN IV programme has been translated for our purposes into ALGOL IV.

EXPERIMENTAL

The spectra of $5 \times 10^{-5}M$ 3,3′-dimethoxybenzidine were recorded for sulphuric acid media and formate or acetate buffers having ionic strength 0·033, in 1 cm cuvettes. The spectra of 3,3′-dimethylnaphthidine in 3 cm cuvettes were obtained for $2 \times 10^{-5}M$ solutions prepared by appropriate dilution of an ethanolic solution of the base with sulphuric acid or formate or acetate buffer, at ionic strength $I = 0{\cdot}1$.

RESULTS

The pK_{a_1} and pK_{a_2} values found were $2{\cdot}83 \pm 0{\cdot}07$ and $4{\cdot}05 \pm 0{\cdot}12$ for 3,3′-dimethoxybenzidine and $2{\cdot}62 \pm 0{\cdot}03$ and $3{\cdot}33 \pm 0{\cdot}09$ for 3,3′-dimethylnaphthidine. The molar absorptivities found for the monoprotonated species were $9{\cdot}34 \times 10^3$ l.mole^{-1}.cm^{-1} at 300 nm for 3,3′-dimethoxybenzidine, and $3{\cdot}75 \times 10^3$ l.mole^{-1}.cm^{-1} at 330 nm for 3,3′-dimethylnaphthidine.

The molar absorptivities of the basic and diprotonated forms indicate that for 3,3′-dimethoxybenzidine the condition given by Albert and Serjeant[2] is not satisfied ($\varepsilon_{BH_2^{2+}}/\varepsilon_B \approx 0{\cdot}1$ instead of $< 0{\cdot}05$). However the convergence of the successive approximations shows that the calculated constants are not much different from the true values. The indicated precision of the pK_a values has been calculated on the basis of the standard deviation of the series of measurements at a probability level of 95%.

The calculated values for 3,3′-dimethyoxybenzidine are in fair agreement with the values for unsubstituted benzidine[1] (3·43 and 4·65), indicating that the methoxy substituent introduces a shift of 0·60 in both pK_a values.

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Summary—The dissociation constants of diprotonated 3,3′-dimethylnaphthidine (DMN) and 3,3′-dimethoxybenzidine (DMB) have been determined spectrophotometrically. They are: p$K_{a_1} = 2{\cdot}62 \pm 0{\cdot}03$, p$K_{a_2} = 3{\cdot}33 \pm 0{\cdot}09$ for DMN; p$K_{a_1} = 2{\cdot}83 \pm 0{\cdot}07$; p$K_{a_2} = 4{\cdot}05 \pm 0{\cdot}12$ for DMB. The molar absorptivities (l.mole^{-1}.cm^{-1}) of all forms of the indicators have been also determined: $\varepsilon_B = 1{\cdot}68 \times 10^4$, $\varepsilon_{BH^+} = 9{\cdot}34 \times 10^3$, $\varepsilon_{BH_2^{2+}} = 1{\cdot}80 \times 10^3$ at 300 nm for DMB; $\varepsilon_B = 7{\cdot}33 \times 10^3$, $\varepsilon_{BH^+} = 3{\cdot}73 \times 10^3$, $\varepsilon_{BH_2^{2+}} = 0$ at 330 nm for DMN.

Zusammenfassung—Die Dissoziationskonstanten von diprotoniertem 3,3′-Dimethylnaphthidin (DMN) und 3,3′-Dimethoxybenzidin (DMB) wurden spektrophotometrisch bestimmt. Sie betragen: p$K_{a1} = 2{,}62 \pm 0{,}03$, p$K_{a2} = 3{,}33 \pm 0{,}09$ für DMN; p$K_{a1} = 2{,}83 \pm 0{,}07$, p$K_{a2} = 4{,}05 \pm 0{,}12$ für (DMN) und 3,3′-Dimethoxybenzidin (DMB) wurden spektrophotometrisch bestimmt. Sie betragen: p$K_{a1} = 2{,}62 \pm 0{,}03$, p$K_{a2} = 3{,}33 \pm 0{,}09$ für DMN; p$K_{a1} = 2{,}83 \pm 0{,}07$, p$K_{a2} = 4{,}05 \pm 0{,}12$ für DMB. Die molaren Extinktionskoeffizienten (in l.mol^{-1}.cm^{-1}) aller Formen der Indikatoren wurdenebenfallsgemessen: $\epsilon_B = 1{,}68 \times 10^4$, $\epsilon_{BH+} = 9{,}34 \times 10^3$, $\epsilon_{BH_2}{}^2 + = 1{,}80 \times 10^3$ bei 300 nm für DMB; $\epsilon_B = 7{,}33 \times 10^3$, $\epsilon_{BH}{}^+ = 3{,}73 \times 10^3$, $\epsilon_{BH_2}{}^{2+} = 0$ bei 330 nm für DMN.

Resume—On a determine spectrophotometriquement les constantes de dissociation des 3,3′-diméthylnaphtidine (DMN) et 3,3′-diméthoxybenzidine (DMB). Elles sont: $pK_{a_1} = 2{,}62 \pm 0{,}03$; $pK_{a_2} = 3{,}33 \pm 0{,}09$ pour la DMN; $pK_{a_1} = 2{,}83 \pm 0{,}07$; $pK_{a_2} = 4{,}05 \pm 0{,}12$ pour la DMB. Les coefficients d'absorption molaires ($l.mole^{-1}.cm^{-1}$) de toutes les formes des indicateurs ont aussi été déterminés: $\varepsilon_B = 1{,}68 \times 10^4$, $\varepsilon_{BH^+} = 9{,}34 \times 10^3$, $\varepsilon_{BH_2^{2+}} = 1{,}80 \times 10^3$ à 300 nm pour la DMB; $\varepsilon_B = 7{,}33 \times 10^3$. $\varepsilon_{BH^+} = 3.73 \times 10^3$. $\varepsilon_{BH_2^{2+}} = 0$ à 330 nm pour la DMN.

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ANNOTATION

ABSORPTION CHARACTERISTICS OF XYLENOL ORANGE

(*Received* 3 *October* 1973. *Accepted* 3 *November* 1973)

Xylenol Orange has been extensively used for the spectrophotometric determination of numerous metallic ions in aqueous solutions.[1] Several workers[2, 3] have measured the various dissociation constants of Xylenol Orange in aqueous solutions. They have reported nine different ionic forms having absorption maxima at different wavelengths. In acidic solutions, Xylenol Orange has maximum absorption near 434 nm and in alkaline solutions the absorption peak is at 580 nm.[3] Earlier, Murakami *et al.*[3] had shown that in alkaline solutions the absorption spectrum of Xylenol Orange changes with the variation in pH of the solution. Later Kovalenko *et al.*[4] stated that the absorbance of Xylenol Orange at 580 nm in alkaline solutions is independent of the pH of the solution. During radiation chemistry studies, we wanted to use the intense absorption of Xylenol Orange at 580 nm for analytical purposes.[5] It was necessary therefore to reinvestigate the absorption characteristics of Xylenol Orange.

EXPERIMENTAL

The tetrasodium salt of Xylenol Orange (B.D.H. Laboratory Reagent) was tested for purity according to Murakami *et al.*[3] and dried in a vacuum desiccator and a known amount dissolved in triply distilled water to give about 1·0mM concentration. A stock buffer solution was prepared that was 0·25M in each of sodium carbonate and sodium bicarbonate in triply distilled water. This buffer was diluted tenfold to give a pH of 10·0.

RESULTS

The variation of absorbance with pH is shown in Fig. 1. From this figure it is seen that the intensity of the peak at 434 nm is independent of the acidity below about pH 6 and that the intensity of the peak at 580 nm is dependent on the pH of the solution. Actually there is no conflict between the results of Murakami *et al.*[3] and Kovalenko *et al.*[4] The latter workers made their measurements near pH 9 and 13, and as the molar absorption coefficient of Xylenol Orange at these pH values is nearly the same, as seen from Fig. 1, they probably came to the (erroneous) conclusion that the molar absorption coefficient of Xylenol Orange at 580 nm is independent of the pH of the solution above pH 9. If only they had made measurements at some points between pH 9 and 13, they also would have observed the depression near pH 11·5 as shown in Fig. 1.

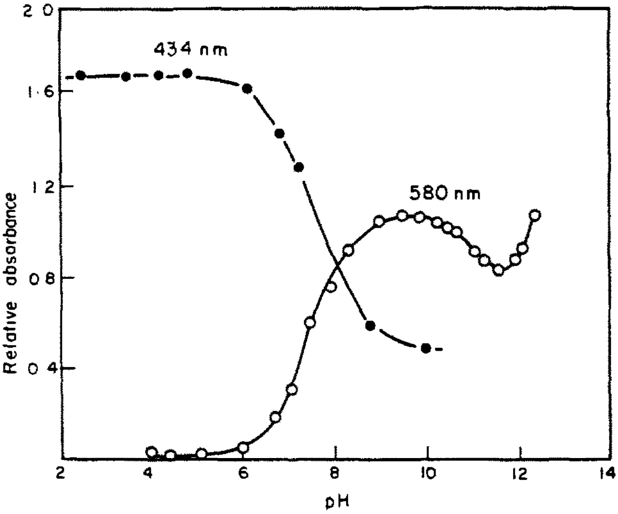

Fig. 1. Relative absorbance of Xylenol Orange solution at 434 and 580 nm at different pH values
● 113μM Xylenol Orange, ○ 34·6μM Xylenol Orange.

For determination of Xylenol Orange, the solution was buffered to pH 10·0 with 0·025*M* sodium carbonate–0·025*M* sodium bicarbonate mixture. The plot of absorbance at 580 nm against Xylenol Orange concentration was linear. The molar absorption coefficient of Xylenol Orange at 580 nm and pH 10·0 is $3{\cdot}12 \times 10^4$ l. mole^{-1}. cm^{-1}.

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Summary—Absorption characteristics of Xylenol Orange have been reinvestigated for the purpose of its spectrophotometric estimation. The molar absorption coefficient of Xylenol Orange at 580 nm and pH 10·0 is $3{\cdot}12 \times 10^4$ l.mole^{-1}, cm^{-1}.

Zusammenfassung—Die Lichtabsorptions-Kenngrößen von Xylenol-orange wurden neu gemessen, um dieses spektrophotometrisch bestimmen zu können. Der molare Extinktionskoeffizient von Xylenolorange bei 580 nm und pH 10,0 beträgt $3{,}12 \times 10^4$ l.mol^{-1}.cm^{-1}

Résumé—On a réétudié les caractéristiques d'absorption de l'Orangé Xylénol en vue de son dosage spectrophotométrique. Le coefficient d'absorption molaire de l'Orangé Xylénol à 580 nm et à pH 10,0 eest $3{,}12 \times 10^4$ l.mole^{-1}.cm^{-1}.

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CARBOXYLIC ACIDS AS METAL EXTRACTANTS

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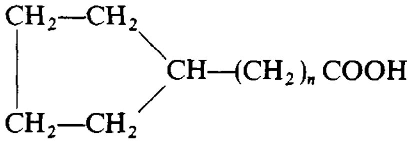
Summary—One of the problems in the extraction of trace elements is that matrix elements must usually be masked, involving the addition of large amounts of extra reagent and thus increasing the risk of contamination. If the maxtrix element is to be removed, an extraction system of high capacity is needed to avoid dilution effects. In this respect, long-chain or substituted carboxylic acids show great promise. A literature review on their use as metal extractants is presented.

With the ever-increasing importance of trace analysis and the imminent threat of exhaustion of the richer ores and the consequent need for efficient extraction of metals from low-grade ores, attention is being turned to extraction systems with high capacity and good recycling properties, for extraction of matrix metals in trace analysis (for enrichment in trace metals) and of commercially useful metals in ore-treatment plants.

Carboxylic acids are one such type of system and this paper presents a review of their applications. For convenience they are divided into naphthenic acids, mixed-acid fractions, unbranched aliphatic acids, and miscellaneous acids.

EXTRACTION WITH NAPHTHENIC ACIDS

Naphthenic acids are saturated monocyclic carboxylic acids having the general formula[1]



The ring is almost invariably five-membered.

The extraction of Fe(III), Cu(II), Zn(II), Mn(II) and Co(II) from aqueous sulphate solutions at 25° by naphthenic acids in gasoline has been investigated as a function of pH.[2] The pH was varied by gradual neutralization of the solutions with sodium hydroxide, the $pH_{1/2}$ values obtained being Fe 2·1, Cu 2·9, Zn 5·3–5·7, Mn 5·9 and Co 6·1. A study of the separation of Cu, Zn and Na sulphates with naphthenic acids in kerosene (1·0*M*) showed that copper could be separated at pH 5·0–5·5 or 5·5–6·0, then zinc at pH 7–8.[3] The composition of the cobalt naphthenate was obtained by measurement of the distribution coefficient between water and petroleum ether at various pH and organic acid (HR) concentration values and was $CoR_2H_2R_2$ and $CoR_22H_2R_2$.[4] In the presence of sodium the compounds $Na[CoR_2(HR)_2]$ and $Na_2[CoR_2(HR_2)_2]$ were obtained. With the same acid

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and either ether or hexane as diluent only a moderate separation of elements was found throughout the rare earths.[5] The extraction was stoichiometric, six moles of acid being used per mole of rare earth oxide at pH 7·6. Thorium and uranium were extracted preferentially over all tervalent rare earths.

With colorimetry or polarography used to analyse the phases for metals, the distribution coefficients of In, Te, Sb, Sn, As, Ge, V, Fe, Tl, Cd and Zn between aqueous phases of constant ionic strength and naphthenic acid phases were determined.[6] The naphthenic acids were C_5–C_7 or C_{12}–C_{16} fractions dissolved in kerosene. The pH was adjusted by the addition of sodium carbonate to the mineral acid solutions. In general, distribution coefficients increased with increasing pH in curves of increasing slope. The pH at the steepest part of the slope depended on the acidity of the metal as follows: Sn(II) 3·0, In(III) 3·5, Sn(IV) 3·5, Cu(II) 5·5, Zn(II) 6·5, but the curves of Te(IV), Tl(I), As(III), Ge(IV) and V(V) were less regular. Very low distribution coefficients for As(III), Ge(IV), V(V) indicated their presence as unextracted anionic species.

Alekperov *et al.*[7–20] have studied the extraction of metals with naphthenic acids. Gallium and aluminium were extracted at pH 3–5 with naphthenic acids (average molecular weight 215) in 1:1 kerosene–ether.[7] In the presence of sodium chloride (120–200 g/l.) the extraction curve of aluminium was shifted by 0·5 pH units to the acid side compared to unsalted water, while that of gallium was displaced by more than 1 pH unit to the acid side in sodium sulphate solution (1·0*M*), the curve for aluminium being unmoved. With the same concentration of sodium sulphate and a naphthenic acid concentration of 233 g/l. the maximum separation factors were 7·9 (Al:Ga 1·5:1, pH 3·56, *D* values 0·602 and 4·72) and 6·50 (Al:Ga 100:1, pH 3·68, *D* values 1·05 and 6·8). Higher alcohols, ether, ethyl acetate and a benzene–ethyl acetate mixture were satisfactory diluents but a precipitate formed in the system when kerosene was used. For Al(III), Ga(III), In(III), Zr(IV), Th(IV), UO_2(II), Y(III), Sc(III), Gd(III) and La(III), the distribution coefficient has been shown to vary with pH in their extraction with naphthenic acids of average molecular weights 170, 190 and 270 in kerosene.[8] Cerium and yttrium ($10^{-11}M$) were extracted at pH 4–6 by solutions of naphthenic acids in kerosene (0·05–0·50*M*).[9] The extraction curve of Y was displaced by 0·04 pH units to the basic side, compared with Ce(III). For the plots of log distribution coefficient *vs.* pH and *vs.* log concentration of naphthenic acid, the gradients were about 3. The dependence of degree of extraction on pH for different concentrations of these two metals with a 1*M* solution of naphthenic acids in kerosene has been investigated.[10] The time of equilibration was 20 min, temperature 15–17° and ratio of aqueous to organic phase 5:1. For both metals the maximum extraction (95–98%) occurred at pH 5. The extraction was examined in various organic solvents and the coefficient of separation of yttrium and cerium depended on the solvent used and was at a maximum (about 11) for isoamyl alcohol at pH 4·8–5·2. The extraction of uranium with 1*M* solutions of naphthenic acids (HR) in kerosene, heptane or benzene began at pH 3·3 and reached a maximum at pH 4·0–4·5.[11] Emulsions which formed at pH values of more than 6 could be destroyed by the addition of higher alcohols. The presence of sodium chloride and sodium sulphate displaced the extraction curve to lower and higher pH values respectively, and both salts increased the maximum degree of extraction of uranium. At a given pH value the extraction was approximately constant for HR:UO_2 ratios greater than 8. The extracted complex was probably $UO_2R_2 . n$HR. The presence of aniline and other low molecular-weight amines markedly increased the distribution coefficient. The absorption maxima of the extracted complex between 350 and 560 nm were shifted 10–20 nm towards the red from the corresponding maxima of a uranyl nitrate solution and in the presence of aniline, with benzene as diluent, the maxima were strongly displaced towards the ultraviolet region.

For 1*M* solutions of naphthenic acid (average molecular weight 200) in kerosene, extraction curves as a function of pH were determined for the rare earth metals.[12] It was found that the $pH_{1/2}$ value increased with decreasing metal concentration, and decreased from lanthanum to europium, then increased from gadolinium to ytterbium. Owing to complex formation the value also increased in the presence of chloride and more so with sulphate. The maximum and minimum differences in values for adjacent rare earths were 0·15 and 0·02 pH units respectively. In the extraction of the cerium subgroup rare-earth metals with 1*M* solutions of naphthenic acids in ligroin, the partition coefficients were pH-dependent.[13] The pH of the metal chloride solutions (0·5 g/l.) was adjusted by the addition of sodium hydroxide solution and the ratio of aqueous to organic phase was 4:1. The $pH_{1/2}$ values decreased in the order La(III) > Ce(III) > Pr(III) > Nd(III) > Sm(III) > Eu(III) which showed that the extraction of these metals could be combined with their separation.

The effect of pH, nature of solvent and metal concentration on the extraction of the alkaline-earth metals with naphthenic acids showed that their extraction constants (*K*) increased in the order Mg < Ca < Sr < Ba.[14] The p*K* values were 13·9, 12·63, 11·28 and 9·77 respectively. This was also the order of decreasing limiting pH value at which the metals started to extract. This pH value increased with increasing polarity of the solvent. For strontium, the distribution coefficient was dependent on the nature of the solvent and increased with increasing concentration of metal, apparently because of association in the organic phase. Except for calcium, the curves for degree of extraction *vs.* pH for traces of metals were flatter than for macro amounts. The addition of minimal amounts of low molecular-weight amines (ethylamine, butylamine or aniline) to the organic phase led to quantitative extraction of all the alkaline-earth metals in trace quantities. This effect was used to concentrate strontium and barium from natural waters for analysis.

Again with 1*M* solutions of naphthenic acids in kerosene and pH values specific for each metal, the extraction was found to decrease in the order Pb(II), Cd(II), Zn(II), Hg(II), Tl(I) for these cations.[15] The order did not change with variation of the Cd:Zn and Tl:Pb ratios. Chloride and large amounts of sulphate interfered in the cadmium and zinc extractions respectively. Under the same conditions and with the volume ratio of organic to aqueous phase equal to 1:4 and equilibration time 30 min, the $pH_{1/2}$ values of In(III), Cd(II) and Zn(II) were 2·97, 5·39 and 5·51 respectively.[16] All three metals could be back-extracted into hydrochloric acid (0·1*M*). Under similar conditions and with naphthenic acids of average molecular weights 200, 274 and 324 in kerosene, iron was extracted at pH values greater than 1·5, quantitatively at pH 5·5.[17] The $pH_{1/2}$ value increased with increasing molecular weight of acid, owing to lowering of the acid dissociation constant. The extraction was studied as a function of the concentration of naphthenic acids (HR). With micro quantities of iron the compounds $FeR_3(HR)$ or $FeR_3(HR)_2$ were formed, but with macro quantities hydrolysed forms were recovered. The co-extraction of ruthenium with Fe(III), Co and Cu naphthenates was examined as a function of pH.[18] With iron, maximum co-extraction occurred at pH 2·85 and decreased at pH values greater than 4. With cobalt and copper the degrees of co-extraction were 85% and 60% at pH values of 6·5 and 6·0 respectively. The co-extraction increased in the series Cu < Co < Fe. In the presence of iron the degree of co-extraction decreased from 96% to 1% with decrease in acid con- concentration from 1·0 to 0·05*M* in benzene. With 1*M* solutions of naphthenic acids (average molecular weight 220) in kerosene, the extractions were investigated of the isotopes ^{59}Fe, ^{51}Cr, ^{54}Mn, ^{60}Co, ^{90}Sr, ^{91}Y, ^{144}Ce, ^{147}Pm in the form of chlorides; ^{134}Cs, ^{95}Zr, ^{95}Nb as nitrates; and ^{106}Ru as the nitrosonitrate.[19] The solutions were $10^{-10}M$ in metal, and the pH was adjusted by the addition of potassium hydroxide solution. The ratio of aqueous to organic phase was 5:1, and the time of equilibration was 30 min. At pH 7, the degree of extraction of the sum of the twelve radioactive isotopes that can practically be found in waste waters, was 80% in one extraction cycle. This could be increased by the addition of a minimal amount of ferric ion to the initial aqueous solution (*e.g.*, 10 mg/l. increased the degree of extraction to 96%). Each element could be quantitatively extracted in a determined pH range apart from ruthenium and niobium. With the same extractant and an aqueous to organic phase ratio of 4:1, the extraction of some 45 metal solutions (1 g/l.) was investigated.[20] The characteristic extraction curves, equilibrium constants and $pH_{1/2}$ values were determined, which gave rise to the following extraction sequence: Fe(III) > Th(IV) > Zr(IV) > U(IV) > In(III) > Tl(III) > Ga(III) > UO_2(II) > Sc(III) > rare earth metals > Al(III) > Pb(II) > Be(II) > Cr(III) > Mn(II) > Cd(II) > Zn(II) > Cu(II) > Nb(V) > Pd(II) > VO(II) > Ag(I) > Ni(II) > Sr(II) > Hg(II) > Co(II) > Ca(II) > Tl(I) > Mg(II) > Ru(III) > Cs(I).

The suitability of commercially available naphthenic acid under certain conditions for the extraction of metals from aqueous solutions has been noted.[21] The great stability of the reagent makes it suitable for use in continuous extraction processes. From solutions of constant ionic strength, the extraction of Cu, Ni and Co by naphthenic acid in benzene has been studied as a function of pH, metal concentration and reagent concentration.[22] The extracted species were $Ni_2R_4.4HR$ and $Co_2R_4.4HR$ where HR is the organic acid. With copper, the empirical formula was $CuR_2.RH$ but there was evidence of dimer formation.

At suitable pH values, copper was effectively separated from Co, Ni and Zn, and zinc from Co, Ni and Mn with naphthenic acid in benzene, toluene or preferably kerosene.[23]

The extraction of the uranyl cation at a pH not more than 0·5 pH unit below that producing hydrolysis, or in suspension as the hydrolysis product, has been investigated.[24] In one extraction, 60% of the uranium in a $0{\cdot}1M$ solution was removed by an equal volume of $1{\cdot}0M$ naphthenic acid in kerosene at pH 3·5. The same reagent has been used to obtain pure cadmium from mixtures of cadmium and zinc, the latter being selectively extracted.[25] The effects of temperature, pH, salt concentration and diluent were examined. This selective extraction of zinc from cadmium was also observed from chloride solution but was reversed from sulphate solution.[26] The enhanced extraction of copper due to mixed complex formation above pH 6·5 with naphthenic acid ($0{\cdot}1M$) and nonylphenol (0–$0{\cdot}5M$) in benzene from ammonium nitrate solution ($3{\cdot}0M$) has been reported.[27] There was no further enhancement with greater concentrations of nonylphenol. Spectral measurements indicated mixed complex formation when a mixture of naphthenic acid and LIX63 (an α-hydroxy oxime) was used to extract copper and cobalt.[28] With copper the organic phase was pale green compared to dark green (naphthenic acid alone) and brown (LIX63 alone). It would appear that while naphthenic acid complexed the copper, the LIX63 acted as a solvating agent.

The economic advantage as well as the low aqueous solubility and high solubility of metal naphthenates in hydrocarbons and the narrow pH range in which each metal was extracted was noted for the extraction of non-ferrous metals with naphthenic acids.[29] Tervalent metal ions could be selectively extracted by using only an excess of the acid. The metal ions extracted form the series Fe(III), Al(III), Cu(II), Zn(II), Co(II), Ni(II), Mn(II), Ca(II), Mg(II), Na(I), in order of increasing pH value of the aqueous phase after extraction. With a tenfold increase in metal concentration the same series was obtained, except for interchange of Ni and Mn and of Ca and Mg.

EXTRACTION WITH CARBOXYLIC ACID FRACTIONS

The extraction of ^{134}Cs by a C_7–C_9 carboxylic acid fraction was investigated at 25° as a function of pH and nitrate concentration.[30] With constant nitrate concentration, the degree of extraction increased from pH 1·5 to pH 5–6, then decreased. On dilution of the acid with benzene or iso-octane, a linear increase in extraction with increasing acid concentration was observed. With increasing nitrate concentration the degree of extraction decreased owing to decrease of both the acid solubility in the aqueous phase and the activity coefficient of caesium. The formula $CsR.7HR$ was assumed, where R is the organic radical. The distribution of Fe(III) between aqueous solutions of nitrate (initially 10 g/l.) and C_7–C_9 fatty acids in the pH range 0·48–2·5 showed[31] that the distribution coefficient D increased with increasing pH according to $\log D = 0{\cdot}74 + 2{\cdot}10\,\mathrm{pH}$. Practically no iron was present in the aqueous phase at pH 2·5. The volume ratio of aqueous to organic phase was 5:1. The formation of compounds of the type $FeR_3.HR$ was assumed. The dependence of the extraction coefficient on pH for ^{134}Cs, ^{95}Nb, ^{95}Zr, Fe(III) and U(VI) in their extraction with C_7–C_9 fatty acids (6·55*N*) has been determined.[32]

The graphs of log distribution coefficient *vs.* pH for the extraction of Fe(III), Th(IV), UO_2(II), Al(III), Fe(II), Mn(II) and Mg(II) with a C_7–C_9 fatty acid fraction were found to be linear with gradient equal to the charge of the metal ion, indicative of a cation-exchange mechanism.[33]

A great deal of research on the extraction of metals with carboxylic acids has been carried out by Gindin *et al.* Using a C_7–C_9 acid fraction in kerosene (400 g/l.) they showed that the sulphates of Ci(II), Cu(II), Ni(II) and Fe(III) could be separated on an extraction column.[34] With the same extractant under alkaline conditions, metal chlorides or sulphates of Co, Ni, Zn, Cd, Cu, Pb and Al were separated.[35] The relationship $\log D = K + n\mathrm{pH}$ was derived where D is the distribution coefficient, n is the charge on the extracted cation and K is a constant dependent on the basic character of the cation. For bivalent cations, K decreased in the order Pb, Cu, Cd, Zn, Ni, Co. The same relationship between distribution coefficient and pH was found for Bi, Sb and Ag between acid nitrate and C_7–C_9 monocarboxylic acid (undiluted).[36] Graphs of log D *vs.* pH showed the extracted species to be CoR_2, AgR, BiR_3 (where HR is the organic acid) and the $\mathrm{pH}_{1/2}$ values were Bi 0·45, Sb 2·30, Ag 3·50, Co 4·80. Antimony was extracted as hydrolysed forms. The following exchange extraction series was given in order of decreasing extraction into the organic phase: Sn(IV), Bi(III), Fe(III), Pb(II), Al(III), Cu(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II), Mg(II), Na(I).[37] This was also, in general, the order of increasing basic character, where the more basic of two metals was taken as that which forms a precipitate of basic salt or hydroxide at a higher pH value, ionic activities being equal. To this series were added Ag(I),[36] H(I) and Ca(II),[38] Ca(II)[39] and Sb(III), Ti(IV), Sn(II), Ca(II), Ba(II), Ga(III), Cr(III), Y(III), Ce(III), In(III), Ag(I), La(III), Cs(I), Rb(I), K(I) and Li(I),[40] to give the cation-exchange series in order of increasing $\mathrm{pH}_{1/2}$ value H(I), Sn(IV), Bi(III), Fe(III), Ti(III), Sn(II), Sb(III), Pb(II), Ga(III), Cr(III), In(III), Cu(II), Al(III), Y(III), Ce(III), Ag(I), La(III), Cd(II), Zn(II), Ca(II), Ba(II), Ni(II), Cs(I), Rb(I), K(I), Cd(II), Mn(II), Mg(II), Na(I), Li(I).* The exchange reaction of a cobalt soap with Sn(IV), Fe(III), Pb(II), Al(III), and Cu(II) proceeded almost to completion (more than 99% exchange) but with Cd(II) and Zn(II) was less complete.[37] With nickel, the separation coefficient $\beta_{Ni/Co}$ was constant (1·8–1·9) and was independent of reagent concentration,[37] mineral acid anion, composition of fatty acid and the presence of other metals, but decreased with increase in temperature. In the exchange reactions of Co with Mn, Mg and Na, the organic phase was enriched with cobalt. Dilution of the organic acid in kerosene did not influence the exchange reactions. The rate of mass transfer was proportional to the concentration product of the reactants.[38] The separation coefficients were Ni–Co 1·8, Zn–Co 5·0, Cd–Co 35·0, Co–Mn 1·4, Cu–Co 100–500, Fe–CO 10^4, Co–Na 100–200.[39] The degree of extraction of Ca, Cr and Ce was independent of metal concentration and the $pH_{1/2}$ values for Y, Ce and Ca were not altered by the presence of sodium perchlorate (2*M*) in the aqueous phase.[40]

The exchange series was the basis of a method for the preparation of pure cobalt.[41] A cobalt solution was extracted countercurrently with a cobalt-(C_7–C_9 fraction) soap, to remove impurities such as Fe(III), Ni(II) and Cu(II) before pure cobalt was obtained by electrolysis. Although the distribution coefficients of metals between aqueous and carboxylic acid phases were markedly influenced by pH, the metal anion did not interfere in the process.[42]

A method has been described for the chemical and spectroscopic determination of micro impurities in high-purity salts of scarce alkali metals.[43] A solution of lithium nitrate in demineralized water, adjusted to pH 6–7, was mixed for 2–3 min with a C_7–C_9 fatty acid fraction, thus concentrating the impurities. After separation, the organic phase was stripped with nitric acid, which was then added to carbon black, evaporated in a platinum vessel and transferred to a carbon electrode. The arc spectrum was examined at 2300–3000 Å for Al, Bi, Ga, In, Cd, Cu, As, Sn, Pb, Sb, Ag, Cr, Fe and Ti. The nitrates of Rb, Cs and K were examined similarly, but with extraction at pH 4–5.

The possibility of separation of iron from cobalt and of zinc from copper by the addition of C_7–C_9 fatty acids and sodium hydroxide or carbonate to the aqueous metallic solution has been shown.[44] The pH values for separation were Fe 2·0–2·5, Cu 4·1–4·2, Co 7–9, Zn 6·2.

The use of C_7–C_9 fatty acids in chloroform for the separation of iron and copper from cobalt[45] and nickel[46] has been proposed. At pH 5·6 cobalt was not extracted, iron was completely removed by a double extraction but 10–12 extractions were necessary for the complete separation of copper. For both cobalt and nickel, the last traces of copper could be removed by diethyldithiocarbamate in chloroform at pH 3–4 and 2–3 respectively. Iron alone could be separated from acetate buffer when thiourea was used to complex the copper.[47]

An extractability series for cations with a C_7–C_9 carboxylic acid fraction was given as ($pH_{1/2}$ values in parenthesis) Bi(III) (0·46) > Fe(III) (0·99) > Sb(III) (2·3) > Pb(II) (2·5) > Lanth.(III) (2·6) > Cu(II) (3·14) > Al(III) (3·19) > Ag(I) (3·5) > Cd(II) (3·75) > Zn(II) (4·32) > Ni(II) (4·56) > Co(II) (4·68) > Mn(II) (4·74) > Mg(II) (4·93) > Na(I) (5·1).[48] Separation was improved by the addition of salting-out agents. The lanthanides were extracted at pH 2·0–3·5, selectively in presence of complexones.

With 1*M* C_7–C_9 fatty acid fraction solution in benzene as extractant, at pH 6 ^{95}Zr was extracted from ^{95}Nb which was masked by the addition of hydrogen peroxide.[49] The co-

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* Cadmium was given twice in this series in both the original paper and in *Chemical Abstracts*.

extraction of niobium increased with increasing zirconium concentration, owing to the former being trapped as part of a micelle which formed on extraction of the latter. With the same extractant (0·1–1·0M) the non-equilibrium distribution coefficients of zirconium were found to depend on the order and speed of mixing of the metal, sodium hydroxide, acetate and fatty acid solutions.[50] Equilibrium was not reached in one week. The distribution coefficients increased with organic acid chain lengths up to C_7–C_9 then decreased, increased non-linearly with organic acid or zirconium concentration and decreased with increase in mineral acid or acetate concentration. The value increased for small amounts of Y, Nb, Mn(II) and Sr if zirconium was present, but caesium was not co-extracted. Zirconium was separated as a colloid and could be separated from Y, Mn, Cu, Ni and Na_2SO_4 (2M) by fatty acid extraction followed by stripping with Complexone III at pH 6 or with 0·1M nitric acid, the other elements remaining in the organic phase. With variation of solvent, the following degrees of extraction were obtained with a 0·1M organic acid solution: nitrobenzene 50%, chloroform 42%, benzene 38%, heptane 27%, ether 23%, trichloroethylene 22%, toluene 16%, IBMK 7%, ethyl acetate 0·3%.

In the extraction of mercury from 5M nitric acid by C_7–C_8 fraction fatty acids, the proposed mechanism, supported by infrared absorption analysis of the organic phase, was absorption of the metal into the organic phase by the partial oxidation products of the hydrocarbons, formed by reaction with the nitric acid.[51] With a C_7–C_9 fraction organic acid in the extraction of the rare-earth elements, the addition of sodium carbonate or hydroxide was necessary to induce transfer between the phases.[52] The effect of solvent on the extraction of La, Pr, Ne and Gd showed that the influence of diluents decreased in the series: heptyl alcohol, decyl alcohol, isoamyl acetate, *m*-xylene, 2,2′-dichlorodiethyl ether, carbon tetrachloride and kerosene, which was also the order of decrease of hydrogen-bond formation.[53]

In the extraction of alkali metals with carboxylic acids, the distribution coefficents increased linearly with pH up to pH 6.[54] By use of exchange reactions, each metal in the series Fe, Cu, Ni, Co, Ca and Na was found to extract all those to its right from the organic phase, which was a solution of industrial fatty acids (C_5–C_6, C_7–C_9, C_{10}–C_{16} fractions) in an inert solvent such as kerosene.[55] This series was extended to Fe(III), Pb(II), Cu(II), Zn(II), Ni(II), Co(II), Mn(II), Na(I).[56] The addition of alkali was necessary to achieve extraction, and a relationship was found between the distribution coefficient and the pH of the aqueous phase. The solubility of the corresponding soaps in water was proportional to the cube root of the metal hydroxide solubility product. The exchange extraction was described as a hydrolytic method without precipitate formation and was applicable to the separation of closely similar metals such as cobalt and nickel.

When freshly prepared metal carbonates, dissolved in fatty acid in kerosene (400 g/l.), were extracted with water or mineral acid, the distribution coefficients increased with increasing initial organic phase concentration but decreased with increasing solubility of the respective salts in water.[57] The aqueous phase solubility increased in the order Fe(III) < Cu(II) < Ni(II) < Co(II) < Mn(II) < Na(I).

The countercurrent exchange extraction of copper and iron impurities in a nickel solution with C_{10}–C_{13} aliphatic acids containing nickel has been reported.[58]

With a C_{12}–C_{16} fatty acid fraction (HR) in kerosene, the extraction of indium from acidic solution increased with increasing pH, indium concentration and organic acid concentration, equilibrium being reached in 15–20 min.[59] The formula of the extracted complex was $[In_2(OH)R_5 . 5HR]_x$.

EXTRACTION WITH ALIPHATIC LONG-CHAIN ACIDS

The pH-dependence of the degree of extraction of iron with propionic acid in chloroform solution in the absence and presence of 2,2'-bipyridyl, antipyrine, quinoline, pyridine, 2-aminopyridine and *n*-butylamine has been investigated. At pH 4 the degree of extraction was 30%, but increased with the addition of amines. One mole of iron was found to coordinate one mole of pyridine, quinoline, butylamine or aminopyridine, and three moles of antipyrine or bipyridyl.[60]

Between the pH values of 9·3 and 9·5 beryllium was more than 90% extracted by butyric acid in chloroform, but only 70–80% extraction occurred with ethyl acetate, ether or benzene as solvent.[61] The optimum acid concentration was 10–15 ml per 50 ml of chloroform; higher concentrations led to decreased extraction. Iron(III) and aluminium were completely extracted, but could be masked by the addition of EDTA.[62]

A method has been described for the separation of thorium from Ca, Mg, Ba, Pb, Zn, Cd, Be, Ni and Co by extraction of a solution containing less than 100 mg of Th in 80 ml with butyric acid in chloroform (1:100, 20 ml).[63] After three extractions at pH 4·8–5·0 the combined extracts were evaporated to dryness, the residue was dissolved in nitric acid and the thorium determined by EDTA titration. The interfering metals were Mn, Ti, Cr, Bi, Fe, Zr, U, Al, Ce and more than 100 mg of Cu.

The separation and subsequent gravimetric determination of beryllium in ores by extraction into chloroform as the butyrate has been reported.[64] When complexed with EDTA, Al, Ti, Fe, Pb, Sn and Cr remained in the aqueous phase. The beryllium butyrate was formed by boiling the solution at pH 9–10 in presence of butyric acid and sodium chloride. The organic phase was stripped with acid and beryllium hydroxide was then precipitated in the aqueous phase, collected, ignited and weighed. A similar method was developed for the separation of the rare-earth metals from Fe, Al, Ti, Ta, Zr, Nb, Sn, W and Mo by extraction with butyric acid in presence of sulphosalicylic acid as masking agent and subsequent gravimetric determination with Arsenazo I or III.[65] The method was applied to the extraction with butyric acid at pH 9–10 of rare earths from silicate ores for subsequent chemical or spectrophotometric determination,[66] and later extended to include thorium in the extraction of rare earths at pH 2·0–2·3.[67] A similar method was developed for the separation of scandium from Fe, Al, Ti, Zr, Be, Nb, Ta, Mo, W, Ca and Mn by extraction with butyric acid in presence of sulphosalicylic acid at pH 4·7–5·7.[68] Scandium was also separated from the rare earths (including Y) by extraction with 0·5 or 2·0*M* butyric acid in isobutyl alcohol at pH 4·1–4·4 or 3·4–3·7 respectively. When thorium was present it could be determined spectrophorometrically with Arsenazo III in 6*M* hydrochloric acid without interference from scandium or in 1*M* acetic acid along with scandium. The distribution coefficients of the lanthanides, Th, Sc and U between saturated aqueous solutions of ammonium nitrate and butyric acid were found to increase with increase in the pH of the aqueous phase.[69] The maximum values obtained were for a mixture of lanthanides (212 at pH 3·9), Th (3000 at pH 2·55), Sc (357 at pH 2·95) and U (258 at pH 2·25). At pH 2·0–2·35 the values for Th, Sc, U and the lanthanides were 99–199, 2·3–32, 42–79 and 0·005–0·027 respectively, allowing separation of Th, Sc and U from the lanthanides by pH control. The extraction of Ca, Sr and Ba with butyric acid in chloroform (2:1) took place at higher pH than for the rare-earth elements, and was more effective from concentrated sodium chloride than ammonium nitrate solution.[70] Thus, these metals and magnesium could be separated from the rare earths by pH control.

The effect of pH on the extraction of iron and copper with solutions of n-butyric and α-bromobutyric acids in chloroform (1·0*M*) has been examined in the presence and absence of pyridine, 2-aminopyridine, n-butylamine and antipyrine.[71] The presence of amines extended the pH range for the complete extraction of iron and increased the degree of extraction of copper. Iron could be completely extracted from more than a thousandfold amount of cobalt and nickel in a single extraction with n-butyric acid in chloroform (1·0*M*) in presence of pyridine and antipyrine. Copper, in the presence of pyridine, was separated from a similar excess of cobalt in two extractions. The amines were found to be components of the extracted compounds.

Pietsch has examined the possibility of extracting Th(IV), Pb(II) and Fe(III) with caproic (n-hexanoic, capronic) acid into chloroform.[72] The degrees of extraction and optimum pH values were 88% (pH 6·5), 98% (pH 7·6) and 85–95% (pH 5·5) respectively. With hexanoic acid (HR) the compositions of the metal caproates were PbR_2 and ThR_2, but iron gave a chain structure.

By use of radioactive isotopes of thorium, its extraction into chloroform in presence of 8-hydroxyquinoline-2-aldoxime and hexanoic acid was examined.[73] With the former complexing agent in perchlorate solution at pH 3·1, thorium formed two extractable compounds with metal to reagent molar ratios 1:1 or 1:3. Examination of the ternary coloured system by means of a triangular diagram has shown that the metal to reagents ratio in the mixed complex was 1:2:2.

The extraction and photometric determination of iron in copper and its alloys has been reported.[74] At pH 6–7, Fe(II) was completely extracted into hexanoic acid (1·0*M*) (HR) and 2,2′-bipyridyl (0·1*M*) (A) in chloroform and measured at 520 nm (ϵ 1·41 × 10^4 l.mole^{-1}. cm^{-1}). The copper was masked by EDTA. Beer's law was obeyed from 0·01 to 1·10 ppm. The extracted compound was FeA_2R_2.

The extraction of iron with capronic and α-bromocapronic acids in the absence and presence of pyridine, 2-aminopyridine, quinoline, antipyrine, n-butylamine, 1,10-phenanthroline and 2,2′-bipyridyl has been investigated.[75] One mole of iron was found to co-ordinate one mole of antipyrine, two moles of n-butylamine or 2-aminopyridine and three moles of phenanthroline or bipyridyl (*cf.* extraction with propionic acid[60]).

The extraction of iron(III) from nitric, hydrochloric and sulphuric acids with caproic acid in petroleum ether (1:1) was studied as a function of pH.[76] The equilibration time was 10 min. The pH at the beginning of extraction was 1·5–2·0 from hydrochloric and nitric acid solutions, 0·5–0·7 pH units higher from sulphuric acid and even higher from acetic acid. The presence of less than 100 mg/ml of the corresponding neutral salt did not alter the pH-dependence of extraction. When the iron concentration was increased from 0·05 to 5 g/l., the pH at the beginning of extraction decreased from 2 to 1·5 from chloride and nitrate solutions and from 2·5 to 2·0 from sulphate solution. This increase in extraction pH with decrease in initial concentration of iron, and also with decrease in the caproic acid concentration for constant concentration of iron, had been reported earlier.[77] With the same extractant, the extraction of calcium from solutions of its nitrate and chloride was possible at pH values greater than 4·2.[78] The distribution coefficient decreased with decrease in calcium concentration. The pH of extraction was displaced towards the acid region with increase of the concentration of caproic acid. The calcium to caproic acid ratio of the extracted species varied from 1:1·1 to 1:1·6. Identification of the major indium species extracted from aqueous sodium perchlorate solution with hexanoic acid in chloroform was proposed.[79] The extraction of Cu(II), Co(II), Fe(III), Fe(II) (all 10^{-3}*M*) and Ti(IV) (4 × 10^{-4}*M*) by 0·1*M* n-enanthic (heptanoic) acid in chloroform or isobutyl alcohol in the presence of various amines was examined as a function of pH.[80] The pH values for complete extraction were (amine and its concentration in parenthesis) Cu(II) 10 (pyridine, 0·5*M*), 9 (butylamine, 0·5*M*), 8 (1,10-phenanthroline, 0·062*M*), 9 (ethylenediamine, 0·5*M*); Co(II) 8 (pyridine, 0·5*M*), 9–10 (butylamine, 0·5*M*), 10 (1,10-phenanthroline, 0·062*M*), 10 (ethylenediamine, 0·5*M*); Fe(III) 8 (1,10-phenanthroline, 0·062*M*), 10 (2,2′-bipyridyl, 0·125*M*); Fe(II) 10 (1,10-phenanthroline, 0·062*M*); Ti(IV) 10 (diantipyrylmethane, 0·05*M*).

The presence of pyridine has been found to greatly extend the pH range for quantitative extraction of cobalt and copper with heptanoic acid in chloroform.[81] Comparison of the absorption spectra in presence and absence of pyridine showed its involvement in the extracted compounds. Copper was completely extracted from cobalt at pH 4–5 with heptanoic acid (1·0*M*) and pyridine (0·5*M*) in chloroform. An extension in the pH range for complete extraction in presence of pyridine was also found for nickel, with the same extractant.[82] The molecule of the extracted nickel compound contained two molecules of pyridine. The presence of up to 1·0*M* quinoline did not influence the pH limits for the complete extraction of Cu, Co and Ni with heptanoic acid, but the addition of 0·1 mole of 1,10-phenanthroline per litre shifted the extraction curves to the acid region.[83] Both quinoline and phenanthroline were involved in the extracted metal compounds.

In the presence of complexing agents, the extraction of Fe(III) and Cu(II) by caprylic (octanoic) acid in chloroform (1·0*M*) as a function of pH has been investigated.[84] In the presence of citrate and tartrate less than 0·3% Fe(III) was extracted but glycerol and mannitol had no effect. Between the pH values of 6·5 and 7·2 copper was extracted in presence of tartrate, but citrate suppressed the extraction.

Cobalt and nickel caprylates existed as dimers in the organic phase and their distribution coefficients decreased with decreasing pH.[85] Depending on the concentration of sodium caprylate, its equilibrium ratio at 25° between water and caprylic acid varied between 0·991 and 7·90.[86] The hydration number was found to be 8.

The extraction of Co(III) ammines with caprylic acid in the pH range 3–6 was examined.[87] Ammonia and ammonium nitrate were present in the aqueous phase for pH adjustment. For the complex compounds the plot of log distribution coefficient *vs.* pH was linear at low pH, but at higher pH the slope was less positive owing to aquation and alkaline hydrolysis. With carboxylic acids unspecified in the abstract this linear relationship was also destroyed when polymerization occurred, the distribution ceofficient being dependent on the overall concentration of metal.[88] In the extraction of cobalt with caprylic acid in decane, the variation of $pH_{1/2}$ with original concentration of metal indicated partial polymerization.[89] The solvation number for cobalt and nickel was 2 and for sodium 4; dimers were solvated to a considerably lesser degree. The extraction of Fe(III), Pb, Zn, Co and Ni from 3–10*M* hydrochloric acid with caprylic acid in n-decane showed the order of extractability to be Co < Zn < Pb < Fe(III).[90] Nickel was not extracted. The extractions of Pb, Zn and Co were independent of increasing hydrochloric acid concentration, but that of iron increased. The extracted species was identified as $HFeCl_4.(HR)_8$, and the distribution ratio of iron was dependent on the organic acid (HR) concentration. The use of different diluting agents in the extraction of cobalt and nickel with caprylic acid showed that the dimerization of the extracted complex increased in the order isoamyl alcohol < nitrobenzene < chloroform < α-chloronaphthalene < benzene < decane.[91] No correlation was found between dimerization and conductivity of the diluting agent. The dissociation in the organic phase of extracted metal–organic acid species was found to be a function of both the distribution coefficient and the concentration of metal.[92] The equilibrium constants of the following processes have been calculated, where HR is the organic acid.[93]

$$M^{2+}_{aq} + 2[(HR)_2]_{org} + qH_2O \rightleftharpoons [MR_2 . 2HR(H_2O)_q]_{org} + 2H^+_{aq}$$

$$2[(MR_2 . 2HR)]_{org} \rightleftharpoons [(MR_2)_2]_{org} + 2[(HR)_2]_{org}$$

$$2Na^+_{aq} + 5[(HR)_2]_{org} \rightleftharpoons 2[(NaR . 4HR)]_{org} + 2H^+_{aq}$$

$$(K_{Na\text{-}H} = 10^{-12 \cdot 4}).$$

When nickel was extracted with capric (decoic) acid (HR) in benzene, the extracted species were $NiR_2.4HR$ and $(NiR_2.2HR)_2$.[94] With the same extractant the species $(CuR_2.HR)_2$, $(CoR_2.2HR)_2$ and $(FeR_3)_3$ prevailed down to a metal concentration of about $10^{-4}M$, but at lower concentrations $CoR_2.4HR$ was extracted.[95]

In the extraction of copper with capric acid in benzene, the extracted species was identified as $(CuR_2.HR)_2$ and from acetate buffer as $Cu(R.Ac.HR)_2$, where R and Ac are the acid radical and acetate respectively.[96]

In the pH range 6·3–10·3 copper was quantitatively extracted by n-capric acid in ethyl acetate (5%), but Mn(II), Pd(II), Fe(III) and Ru(III) interfered.[97] The precipitates of nickel and cobalt were gathered by the organic phase and settled at the interface. When butyraldehyde was used as solvent, the extraction of nickel and palladium was prevented, but rhodium interfered. With butyric acid in benzene only Cu, Mn and Fe were extracted, but ruthenium was extracted in the presence of copper.

The extraction of metals as stearates (octadecoates) into an organic phase was reported as early as 1934.[98] At least 0·5 g of calcium stearate was extracted from graphite by 10 ml of trichlorobenzene at its boiling point. The method was also applicable to aluminium and magnesium stearates, which were more soluble.

Stearic acid has been proposed as a new extraction reagent for the separation of metals.[99] After heating of the solid acid in the metal ion solution to above its melting point, with vigorous shaking, the metals were separated in the cooled, solid organic phase. The extractabilities of iron, copper and various fission products were studied at various pH values.

For palmitic (hexadecoic) acid in paraffin the distribution ratios of macro quantities of Fe(III), Al(III), Ca(II), Mg(II), UO_2(II) and micro quantities of ^{137}Cs, ^{90}Sr, ^{90}Y, ^{106}Ru, ^{144}Ce and ^{95}Zr–^{95}Nb in presence of 0·1*M* uranyl nitrate were studied as a function of the degree of alkalinity (the molar ratio of base added to metal salt).[100] At a value of 0·04 for this factor, zirconium could be separated from uranium, and both these metals could be separated from Fe(III), Al(III), Ca(II), Mg(II) and other fission products at a degree of alkalinity of 2·0. On addition of hydroxide, hydrolytic complexes were formed with Fe, Al, Mg and U. Beryllium stearates and palmitates were found by ebullioscopic measurement to exist as double molecules in solvents such as benzene, toluene, xylene, chloroform and acetic acid.[101] The association was influenced by the polarity of the solvent.

With a mixture of heptanoic, octanoic and nonanoic acids (average molecular weight 140) in kerosene (2·86*M*), the variation of extraction constants with metal ionic radius for the alkali metals passed through a maximum at potassium.[102] The extractability of the metals increased in the order Li < Na < Cs < K and the logarithm of the distribution coefficient increased with pH up to about pH 7.

The time of separation of phases in the extraction of potassium and rubidium with the salts of various organic acids was found to increase with increasing number of carbon atoms in the organic radical.[103] The capronates of these metals formed very stable emulsions on attempted separation.

The distribution ratio in the extraction of zirconium at low concentrations (10^{-6}–$10^{-8}M$) with fatty acids in benzene was measured radiometrically and depended on organic acid concentration and chain-length, pH and type of solvent.[104] Equilibrium was reached after 20 min. Of caprylic, pelargonic (nonoic), lauric (dodecoic), caproic and valeric acids, caprylic gave the highest distribution coefficient at about pH 6, but all increased with pH from pH 4–5 to 6–7, then decreased except for lauric, which reached a maximum at pH 9–10, then decreased. Little difference was observed in the extraction from chloride and nitrate solution. Although a colloidal extraction mechanism was not proposed, a possible mechanism suggested was that the zirconium existed as a colloid in the aqueous phase. The process was likened to detergent action, save that the soap chains would have their anionic ends towards a central colloid particle and their hydrophobic ends towards benzene. A similar mechanism had previously been proposed for the extraction of ferric hydroxide with oleic (*cis*-heptadec-8-ene-1-carboxylic acid) or C_7–C_9 fraction fatty acid in kerosene.[105] Relatively high extraction of metal was found for an organic acid to metal ratio of 1:100, and with decrease in iron concentration, the amount of organic phase precipitate decreased, with corresponding increase in the supposedly chemically bound iron in the clear organic phase. Hence the formation of polymeric, chain-type adsorbent layers which hold the colloidal hydroxide precipitate in the organic phase was postulated, the resultant micelles complexing with fatty acid anions. The extraction of zirconium and hafnium ($5 \times 10^{-4}M$) with 8-hydroxyquinoline-2-aldoxime ($2 \times 10^{-3}M$) in presence of acetic, propionic, butyric, valeric, hexanoic, heptanoic, octanoic, nonanoic and decanoic acids ($2 \times 10^{-1}M$) from hydrochloric acid solution was investigated.[106] The extraction decreased with increase in hydrochloric acid concentration (0·05–0·4*M*) and increased with organic acid chain length up to hexanoic acid, then decreased. The extraction of zirconium and hafnium with the same reagent and carboxylic acids (respective concentration ratios 1:10:1000) showed that the degree of extraction increased with decrease in concentration of hydrochloric acid (0·4–0·05*M*).[107] An increase was also observed with increasing length of alkyl group up to C_5H_{11}, after which extraction decreased. Except from 0·05*M* hydrochloric acid, zirconium was more easily extracted than hafnium.

The extraction of zinc (10^{-3}–$10^{-7}M$) from sodium perchlorate solution (0·1*M*) into organic solvents (benzene, chloroform, IBMK) with C_1–C_{10} aliphatic monocarboxylic acids in 1-aminobutane has been investigated.[108] The degree of extraction increased with increasing acid molecular weight and concentration, pH and 1-aminobutane concentration, but was independent of zinc concentration. Similar work with thulium showed that the degree of extraction increased with increasing acid molecular weight and concentration, and pH up to a value of about 6.[109] With hexanoic acid the species extracted into IBMK was $TmR_3(HR)$ and into chloroform $TmR_3(HR)_5$, where HR is hexanoic acid. In both cases the predominant aqueous species were Tm(III) and Tm(OH)(II).

In the extraction of Sn(IV) with equimolar concentrations of 8-hydroxyquinoline and various organic acids (*e.g.* butyric, valeric, caproic) in chloroform, the logarithm of the distribution coefficient ranged between 0·5 and 2·9 and was at a maximum between the pH values of 1 and 6, depending on the nature of the extractant.[110]

Carboxylic acids such as caproic, caprylic, capric, lauric, cyclohexanecarboxylic and cyclo-octanecarboxylic have been used in the extraction of Fe(III), Cu(II), Co(II) and Ni(II) from acidified solutions.[111] Selective extraction of cobalt and nickel was achieved by using a solution of 3-n-decyl-1,2-dichlorocyclobutane-1,2-dicarboximide in cumene, chloroform or mixed with "versatic acid" as auxiliary extractant. Zinc was also extracted by these reagents. The extractability of some 20 metals at pH 2–10 with a series of C_3–C_{10} carboxylic acids in chloroform was examined.[112] With the lower members of the series few metals were extracted, but the number increased with increasing molecular weight of the acid. For a particular metal, however, the degree of extraction did not necessarily increase linearly with acid chain length, but in some cases decreased after reaching a maximum with an intermediate member of the series. A similar trend in the extractability of cations had previously been recorded for perfluorocarboxylic acids.[113] With perfluorobutyric acid, tervalent cations [*e.g.*, Fe, Al, Cr] and a few bivalent cations [*e.g.*, Ca, Mg, Fe, Pb, Zn] could be separated from univalent ones. The extractions were dependent on pH and the anion present in the aqueous phase.

Fatty acids (oleic, caproic, caprylic and pelargonic) have been proposed for the quantitative extraction of uranium, the degrees of extraction for various ratios of uranyl nitrate to sodium hydroxide solution having been investigated.[114] The distribution was independent of the concentration of sodium nitrate as salting-out agent. Cerium and strontium did not interfere. A dimeric copper species was reported as being extracted from perchlorate solution (0·1*M*) by n-(C_4–C_{10}) carboxylic acids in benzene.[115] Although the distribution coefficient increased with increasing acid molecular weight, the extraction constant did not alter. This was explained by the distribution coefficients of metal carboxylates and carboxylic acids increasing to the same extent with increasing chain-length.

Evidence, based on cryoscopic and spectral measurements, has been produced that some cupric alkanoates, when soluble, exist as dimers in dioxan.[116] Their resolved frequencies at certain wave-numbers, for chloroform solutions, were independent of the alkanoate used.[117] Cupric propionate was shown to exist in the chloroform phase as a dimer,[118] since it gave dimerization constants (k) of the form

$$k = \frac{[\mathrm{Cu}]_{\mathrm{aq}}}{\sqrt[4]{[\mathrm{Cu}]_{\mathrm{org}}}}$$

corresponding to $2\mathrm{CuR}^+ + 2\mathrm{R}^- \rightleftharpoons \mathrm{Cu_2(R)_4}$ where HR is propionic acid. Spectroscopic measurements showed that the dimer was unhydrated and unsolvated. However, k was later found to vary with the concentration of propionic acid,[119] which showed that the extracted species was in fact solvated according to

$$2\mathrm{CuR}^+ + 2\mathrm{R}^- + 2\mathrm{HR} \rightleftharpoons \mathrm{Cu_2R_4(HR)_2}$$

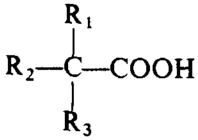
This accounted for the insensitivity of the absorption spectra to change of extracting solvent. Comparison of the solubility of cupric alkanoates with the concentration of free acid showed that the formula above was also true for acetate, isobutyrate and crotonate, and spectroscopic evidence showed the structure to be probable for other acids used.

MISCELLANEOUS ACIDIC EXTRACTANTS

Extractions of Fe(III), Al, Be, Ga, In and Sc ions as their benzoates into ethyl acetate, butyl or amyl alcohol have been achieved at pH 7 with sodium benzoate solution (25%).[120]

Complexes of Pu(IV) with salicylic acid (pH 2–3) and 3,5-dinitrobenzoic acid (pH 3) were extractable into amyl acetate, and with cinnamic acid (pH 2·5–4·5) into amyl alcohol.[121] With the same three acids in chloroform or IBMK complete separation of thorium from lanthanum was possible and, under closely controlled conditions, extraction of thorium from uranium.[122] IBMK was an excellent solvent and chloroform a poor one. The extraction of thorium and uranium with salicylic acid, methoxybenzoic acid and cinnamic acid into the same solvents showed that with salicylic acid (H_2R) the complexes extracted into IBMK were probably $Th(HR)_4 . H_2R$ and $UO_2(HR)_2 . H_2R$, but on replacement of the phenolic with a methoxy group no association of the extra acid molecule occurred.[123] The aqueous and organic species involved in the extraction of uranium with salicylic acid and methoxybenzoic acid into IBMK have been formulated.[124]

"Versatic 911" is a mixture of saturated tertiary monocarboxylic acids of C_9, C_{10} and C_{11} chain-length, manufactured from C_9–C_{11} olefines.[1] The formula is



$$R_2—\overset{R_1}{\underset{R_3}{C}}—COOH$$

where at least one R group is methyl. A 1*M* solution of Versatic 911 (a tertiary monocarboxylic acid) in kerosene was used for the extraction of iron at concentrations <4 g/l.[125] For greater concentrations most of the iron could be removed by precipitation and the remainder by extraction.

The optimum pH values for the extraction of metals with "Versatic 9" (prepared from C_9 olefins) were Fe 2·0–2·6, Cu 3·6–4·7, Zn 4·7–5·6, Co and Ni 5·5–6·5, Cd 4·7–7·5.[126] For pH variation, the acidic aqueous phases were gradually neutralized with ammonium hydroxide, sodium hydroxide and sodium carbonate.

Industrially manufactured organic acids "S.R.S.-100" (prepared from C_{15} olefins) and Versatic 9 have been used in the extraction of some transition metals at controlled pH.[127] With S.R.S.-100 in benzene (1:2) the pH values for extraction were Fe(III) 3·15, Co(II) 8·2, Ni(II) 8·3, Mn(II) 7·95 and Cu(II) 6·15, whereas with Versatic 9 they were Co 8·1, Ni 7·5, Fe 3·15 (95%), Mn 7·05 and Cu 6·2. There was little difference between the acids except that the rate of extraction was greater with Versatic 9. Variation of the metal concentration indicated no polymerization in the organic phase. Xylene and toluene showed similar properties to benzene as diluent but butanol and di-isopropyl ether decreased the degree of extraction, as did dilution of the organic acid. With both acids the order of extraction was Fe(III) > Cu(II) > Mn(II) > Co(II) > Ni(II), and phosphate, tartrate, citrate, oxalate, fluoride and EDTA interfered. This work was extended to include other bivalent metals, for which the recommended pH values for quantitative extraction were Pd 5·45, Pb 6·9, Zn 7·1, Cd 8·2, Ba 8·75, Sr and Ca 8·8, Mg 9·2 and Hg 9·8, permitting separations by pH control.[128] At pH 6·1, 90% of Fe(II) was extracted. On addition of sodium, ammonium and lithium chlorides, the degrees of extraction increased for Zn, Cd and Hg but decreased for the others. The effect of diluent and acid concentration was similar to that in the previous work on bivalent metals.

For the tervalent ions of Ga, In, Th, La, Bi and Sb, extractions with S.R.S.-100 in benzene were quantitative except for Sb (65%) and Ga (97·2%, but more than 99% with undiluted acid at pH 4·6).[129] The pH values for quantitative extraction were In 5·4, Th 6·2, La

8·2 and Bi 7·0. With antimony, partial neutralization was employed to prevent hydroxide precipitation. The presence of ammonium, magnesium and sodium chlorides gave increased degrees of extraction for Ga, In and Tl but decreased ones for Bi and La. The order of extraction was Ga > In > Tl > Bi > La > Sb.

For the quadrivalent ions Ce, Zr and Th the effects of diluent and acid concentration were similar to the previous work reported for bivalent ions.[130] With S.R.S.-100 quantitative extraction took place at the pH values Zr 2·4 (98·5%), Th 6·0, Ce 4·3. With Versatic 9, however, only 73·5% of zirconium was extracted at pH 2·9. The three metals have been individually separated from many others, and interfering metals investigated.

The distribution of copper between water and a toluene phase containing excess of pivalic (trimethylacetic) acid showed the extracted species to be mainly polymeric; only about 10% of the monomeric complex was present in the organic phase.[131] The distribution coefficient was measured for various pivalic acid concentrations, as a function of pH, and for fixed pivalic acid concentration with variation in the concentration of copper.

The extraction of cobalt soaps with heptane and subsequent photometric determination was the basis of a sensitive and selective ultramicro method for the determination of free fatty acids in serum.[132]

A review on the use of carboxylic acids as metal extractants proposed their use on an industrial scale and pointed out their economic advantage,[133] and a theoretical treatment of the extraction of metal ions from aqueous solutions has been published.[134]

The extraction of zirconium and hafnium with organic acids, amines and organophosphorus ethers was the subject of a review.[135] Extractions with carboxylic acids not specified in Chemical Abstracts have been reported.[136–138]

The rare earths were extracted selectively by carboxylic acids from weakly acidic or neutral solutions in the presence of complexones.[136] In the separation of lanthanum and praseodymium with carboxylic acids in presence of EDTA at pH 4·3–4·8, an increase in the contact time from 0·1 to 18 hr led to an increase in the separation coefficient $\beta_{\mathrm{Pr/La}}$ from 3·22 to 5·37.[137] With a contact time of 3 hr, an increase in the molar ratio of total metal to EDTA increased the aqueous concentration of praseodymium but β remained constant. Equilibrium extraction curves as a function of acidity were obtained for the cerium and yttrium group rare earths (in particular La, Ce, Pr, Nd, Sm, Gd, Ho and Er) in their extraction with carboxylic acids in presence of tri-isoamylphosphine oxide.[138] With variation of mineral acid, the salting-out ability of the acidic anions was graded nitrate > chloride > sulphate. Increase of temperature enlarged the pH range of extraction toward values below those corresponding to hydrolysis. Dilution of the organic acid displaced the extraction curve to a higher pH to an extent which increased with increasing tendency for hydrogen-bond formation of the diluent and its affinity for a proton. The extraction of lanthanum was complete in 3–5 min at pH greater than 1·5. The maximum distribution coefficient was obtained with a concentration of tri-isoamylphosphine oxide of 0·35*M*.

Phenylacetic acid has been reported to have a high extraction capacity for iron, copper and uranium at pH 6.[139] In the presence of nitrilotriacetic acid only uranium was extracted.[140]

The selective extraction of copper from hexamine-buffered solution with phenylacetic acid in chloroform (1·0*M*) has been reported.[141] Iron and uranium were masked with ammonium fluoride. The co-extraction of Au(III), Pt(IV) and Pd(II) did not interfere with the photometric determination at 700 nm. Beer's law was obeyed from 100 to 1000 μg of Cu per 5 ml and sulphate, chloride and nitrate did not interfere. The method was adapted to the removal of Fe, Cu and U before determination of manganese with formaldoxime

Phenylacetic acid was found to be superior to diphenylacetic, naphthylacetic and naphthoxyacetic acids as an extractant for Cu, Co, Ni, Pb, Cd, Zn, Mn, Fe, Al, In, Ga.[142] It was found that increase in the molecular weight of the acid led to decrease in selectivity of extraction and, in some cases, decrease in the solubility of metal salts in chloroform.

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Zusammenfassung—Eines der Probleme bei der Extraktion von Spurenelementen besteht darin, daß die Hauptbestandteile im allgemeinen maskiert werden müssen; dabei werden große Mengen von fredem Reagens zugegeben und damit das Risiko der Verunreinigung erhöht. Muß das Matrix-Element entfernt werden, so ist ein Extraktionssystem hoher Kapazitat erforderlich, um Verdünnungseffekte zu vermeiden. In dieser Hinsicht sinh langkëttige oher substituierte Carbonsäuren recht vielversprechend. Es wird eine Literaturübersicht über deren Verwendung als Extraktionsmittel für Metalle gegeben.

Résumé—L'un des problèmes dans l'extraction d'éléments à l'état de traces est que les éléments de la matrice doivent habituellement être dissimulés, ce qui implique l'addition de grandes quantités de réactif supplémentaire et accroît ainsi le risque de contamination. Si l'élément de la matrice doit être éliminé, un système d'extraction de grande capacité est nécessaire pour éviter les effets de dilution. De ce point de vue, les acides carboxyliques à longue chaîne ou substitués offrent de grands espoirs. On présente une revue de la littérature sur leur emploi comme agents d'extraction des métaux.

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SPECTROPHOTOMETRIC DETERMINATION OF PENTAERYTHRITOL TETRANITRATE (PETN) IN WASTE WATER FROM LEAD STYPHNATE PRIMER PLANTS

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Summary—An accurate spectrophotometric method is proposed for the determination of pentaerythritol tetranitrate (PETN) in waste water from lead styphnate primer plants by use of phenoldisulphonic acid. The waste water is filtered through a sintered glass crucible and the PETN is determined in the filtrate and the residue. In the determination of PETN in the filtrate, sodium hydroxide is added and the PETN is extracted with methylene chloride (in alkaline solution, styphnate and TNT are not extracted). The methylene chloride solution is then evaporated to dryness, the residue is treated with a solution of phenoldisulphonic acid in sulphuric acid, water and ammonia are added, and the yellow colour is measured. In the determination of PETN in the residue, the PETN is dissolved in acetone, an aliquot of the acetone solution is treated with water and sodium hydroxide, the PETN is extracted with methylene chloride and the colour is developed as above. Various factors affecting the determination were investigated. The solubility of PETN in water was studied.

PETN (pentaerythritol tetranitrate) is an important explosive that has innumerable uses in Ordnance. Also, it is used as a vasodilator in medicine.

This laboratory undertook an investigation on the determination of PETN in waste waters, particularly waste waters from lead styphnate primer plants. There is little information in the literature on the determination of PETN in waste water. Golubeva[1] determined PETN in waste water from industrial production centres by extracting with chloroform, evaporating to dryness, adding a solution of phenoldisulphonic acid in sulphuric acid, diluting, adding ammonia and measuring the yellow colour. This method, of course, really measures the nitrate produced by hydrolysis of the PETN in sulphuric acid. Goldman[2] determined PETN and other organic nitrates in air by passing the air through alcohol and applying the phenoldisulphonic acid method. Allert,[3] the Association of Official Analytical Chemists (AOAC),[4] and Sarnoff[5] determined PETN and other organic nitrates in pharmaceuticals by dissolving the sample in acetic acid and applying the phenoldisulphonic acid method. AOAC[4] also determined PETN in pharmaceuticals by use of column chromatography, followed by infrared determination of the PETN in chloroform solution. Yagoda and Goldman[6] determined PETN and other organic nitrates in air by aspirating the air through triethylene glycol, adding *m*-xylenol and sulphuric acid to form 4-hydroxy-1,3-dimethyl-5-nitrobenzene, which was steam-distilled and determined spectrophotometrically. Bandelin and Pankratz[7] determined PETN and other organic nitrates in pharmaceuticals by extracting with acetone, evaporating to dryness, and applying the ferrous sulphate colorimetric method for nitrate. Hankonyi and Karas-Gašparec[8] determined PETN and other organic nitrates in pharmaceuticals by hydrolysing the PETN in boiling 1*M* sodium hydroxide solution to form nitrite which was then reacted with *p*-nitroaniline to form the diazonium ion which in turn was reacted with azulene to give an azo dye.

Yagoda[9] and Oettingen *et al.*[10] determined PETN in biological materials by extracting with ether and applying the *m*-xylenol method. Parihar, Sharma and Verma[11] investigated thin-layer chromatography for the determination of PETN in explosives.

None of these methods was directly applicable to the problem of determining PETN in waste water from lead styphnate primer plants. The phenoldisulphonic acid, *m*-xylenol, ferrous sulphate, azulene and infrared methods are subject to interference from other organic nitrates. The thin-layer technique would be difficult to apply quantitatively to pollution wastes. Gas chromatography is not useful for determining PETN, since PETN is decomposed in chromatographic columns to a variety of products.

An investigation was therefore undertaken to develop a method for the determination of PETN in waste water from lead styphnate primer plants. It seemed that the best method of approach would be to modify the phenoldisulphonic acid method.

EXPERIMENTAL

Apparatus

Witt filtration apparatus and Bailey crucible holders (Arthur H. Thomas Co., Catalogue Numbers 4196 and 5116-F).

Beckman Model B spectrophotometer (or equivalent).

Reagents

Concentrated sulphuric acid (*sp. gr.* 1·84).

Fuming sulphuric acid (15% *free* SO_3).

Ammonia solution (*sp. gr.* 0·90).

Methylene chloride, ACS grade.

Sodium hydroxide solution (0·4%).

Phenoldisulphonic acid reagent. Dissolve 50 g of pure white phenol in 300 ml of concentrated sulphuric acid contained in a 1-litre glass-stoppered flask, add 150 ml of fuming sulphuric acid, mix, and heat on a steam-bath at full heat for 2 hr.

Standard PETN solution No. 1 (1 *ml* ≡ 1·0 *mg of PETN*). *Dissolve* 0·2000 *g of PETN in acetone and dilute to* 200 *ml in a volumetric flask with acetone.*

Standard PETN solution No. 2 (1 *ml* ≡ 0·2 *mg of PETN*). Accurately dilute standard PETN solution No. 1 fivefold with acetone.

Preparation of calibration curve

Add 0·0, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of standard PETN solution No. 2 to 100 ml beakers. Add 60 ml of water and 10 ml of 0·4% sodium hydroxide solution and allow to stand for 15–20 min. Decant into 125 ml separatory funnels and wash the beakers with water, collecting the washings in the separatory funnels. Wash the beakers with 25 ml of methylene chloride, decanting the washings into the separatory funnels. Shake the separatory funnels for 1 min, allow the layers to separate and draw off the bottom (methylene chloride) layers into the original beakers. Extract twice more with methylene chloride (using 20 ml portions) and combine the extracts with the first extract in the original beakers. Discard the aqueous solutions in the separatory funnels and rinse the funnels with water. Transfer the methylene chloride solutions to the separatory funnels, wash the beakers with water and collect the washings in the funnels. Add 25 ml of water to the separatory funnels, shake for 1 min allow the layers to separate and draw off the bottom (methylene chloride) layers into the original beakers. Discard the aqueous solutions.

Evaporate the methylene chloride solutions to dryness at a temperature not above 50°. Allow to cool. Add by means of a graduated cylinder 3 ml of phenoldisulphonic acid reagent quickly around the sides of the beaker. Allow to stand for 1 hr at room temperature, swirling occasionally. Add 50 ml of water and 10 ml of ammonia solution and cool to room temperature. Wash into 100 ml volumetric flasks and dilute to the mark with water. Measure the absorbance at 410 nm against the reagent blank and plot absorbance against mg of PETN.

Procedure

Collect a 250–1000 ml sample of the waste water in a stoppered bottle. Swirl and filter it through a tared Coor filtering crucible of fine porosity into a clean dry suction flask. Transfer some or all of the filtrate to a dry beaker and use this to wash the residue from the beaker to the crucible. Do not wash with water. After transferring the residue, measure the total volume of the filtrate by means of a graduated cylinder and then transfer the filtrate to a dry stoppered flask. Dry the crucible in an oven at 60° for 4 hr, cool in a desiccator and weigh.

Pipette a 50-ml portion of the filtrate into a 100-ml beaker, add 10 ml of water and 10 ml of 0·4% sodium hydroxide solution and allow to stand for 15–20 min. If (as is usually the case) the solution remains clear or is only slightly turbid on adding the alkali, proceed with the extraction and development of the colour as described under preparation of calibration curve. If a large amount of precipitate (lead or barium styphnate) forms on addition of the alkali, discard the solution, take another 50-ml portion, extract it three times with methylene chloride, evaporate the methylene chloride, add 60 ml of water and 10 ml of 0·4% sodium hydroxide and proceed with the extraction and development of the colour. Calculate the number of mg of PETN in the 50-ml aliquot by referring to the calibration curve.

Insert the crucible containing the weighed residue into the crucible holder and place a 250-ml beaker in the suction flask of the Witt filtering apparatus.

Note. It is important to use a Witt-type filtering apparatus in order to prevent the acetone from coming into direct contact with rubber.

Wash the crucible with a volume of acetone sufficient to dissolve the PETN. Transfer the filtrate to a 100- or 500-ml volumetric flask and dilute to the mark with acetone. Pipette an aliquot containing preferably 0·4–0·8 mg of PETN into a 100 ml-beaker. If the aliquot is larger than 5 ml, evaporate to a volume of 2–5 ml. Add 60 ml of water and 10 ml of 0·4% sodium hydroxide solution, allow to stand for 15–20 min, and proceed with the extraction and development of the colour as described under the preparation of the calibration curve.

Calculate as follows:

$$\text{Amount of residue } (mg/l.) = \text{residue } (mg) \times \frac{1000}{\text{total volume of aqueous solution } (ml)}$$

$$\text{PETN in aqueous solution } (mg/l.) = \frac{\text{PETN as read}}{\text{from curve } (mg)} \times \frac{1000}{\text{aliquot of aqueous solution taken } (ml)}$$

$$\begin{matrix}\text{PETN in residue}\\ (mg/l.)\end{matrix} = \begin{matrix}\text{PETN as read}\\ \text{from curve } (mg)\end{matrix} \times \frac{\begin{matrix}\text{volume of diluted}\\ \text{acetone extract } (ml)\end{matrix}}{\begin{matrix}\text{aliquot of acetone}\\ \text{extract } (ml)\end{matrix}} \times \frac{1000}{\begin{matrix}\text{total volume of}\\ \text{aqueous solution } (ml)\end{matrix}}$$

$$\text{Total PETN } (mg/l.) = \text{PETN in aqueous solution } (mg/l.) + \text{PETN in residue } (mg/l.)$$

DISCUSSION AND RESULTS

Conditions for development of the colour

The reaction between the phenoldisulphonic acid reagent and PETN involves as a first step the formation of nitric acid by hydrolysis of the PETN by the sulphuric acid. The nitrate then reacts with the phenoldisulphonic acid to produce nitrophenoldisulphonic acid, which is then converted into yellow nitrophenoldisulphonate ion on the addition of ammonia.[12,13]

It was found that for the determination of small amounts of PETN after an extraction procedure (using methylene chloride) it was desirable that the solutions stand for 1 hr at room temperature after addition of the phenoldisulphonic acid reagent. Allert[3] found that the colour developed fully if the solution was warmed for 10 min on the steam-bath after addition of the reagent. We have found that Allert's conclusions are correct when pure PETN solutions are analysed, but the heating is undesirable when working with PETN residues after an extraction because of occasional charring of extraneous organic matter left after the extraction.

The effect of the amount of phenoldisulphonic acid was investigated, since there is disagreement concerning this factor.[13,14] Various volumes of phenoldisulphonic acid were added to aliquots of potassium nitrate solution (0·6 mg of nitrate) that had been evaporated to dryness. Water was added and the solutions were cooled. Ammonia was added until the yellow colour appeared (this required about 6·5 ml of ammonia solution) and 5 ml excess of ammonia solution was added. The solutions were cooled, the volumes made up to 100 ml and the transmittances measured at 410 nm. The transmittances obtained for addition of 2, 3, 5, 8, 10, 12 and 15 ml of phenoldisulphonic acid reagent were 36. 36. 35. 36, 34, 34 and 34, respectively. These results indicated that the amount of reagent was not critical. It was decided to use 3 ml of the reagent (this amount readily covered the bottom of the 100 ml beaker in which the evaporation was conducted). It is recommended that the reagent be added quickly around the sides of the beaker from a graduated cylinder to prevent any localized reaction.

The effect of the amount of ammonia was studied by using 3 ml of phenoldisulphonic acid reagent and 0·6 mg of nitrate. In this study, various volumes of ammonia solution were added, in a single step. The transmittances obtained for 7, 10, 12·5, 15, 20 and 25 ml of ammonia solution were 36, 36, 36, 36, 38 and 28, respectively. These results showed that the amount of ammonium hydroxide was not critical over the range 7–15 ml; a volume of 10 ml is recommended.

The colour was stable overnight. All measurements were made at 410 nm, as suggested by many previous investigators. The absorption spectrum is available elsewhere.[12]

The calibration curve obtained by carrying PETN through the extraction procedure was reasonably similar to the calibration curve obtained by evaporating aliquots of a standard solution of PETN in acetone to dryness and proceeding directly with the colour development. Nevertheless, it is recommended that the calibration curve be prepared by using the extraction procedure.

Separation of PETN from waste water

It would be expected that some PETN in waste water would be in solution and some in suspension. It was decided to filter the waste water sample and determine the PETN in the residue and in the filtrate. It is recommended that the residue be weighed since the amount of residue is of importance in pollution considerations.[15,16]

To determine the PETN in the filtrate it was necessary first to separate the PETN by extraction with a solvent. It was obvious that a satisfactory solvent should be immiscible with water, have a reasonably high solubility for PETN, be preferably heavier than water to facilitate extraction in a separatory funnel and be easily volatilized. Methylene chloride fulfils all these criteria admirably.

After the extraction of the PETN, the methylene chloride was removed by evaporation. The manner of evaporation is of importance. It has been stated by previous investigators[4,5,7,9,17] that in evaporating chloroform, diethyl ether, or acetone solutions of PETN, excessive heat should not be used (a maximum temperature of 50° is frequently mentioned), otherwise loss of PETN can occur. We confirmed that there can be losses of PETN on rapid evaporation on a steam-bath, particularly when working with small amounts of PETN. These losses apparently occur during the actual evaporation before the residue is dry. Heating dry PETN in a beaker at the full heat of the steam-bath for 1 hr did not cause losses due to volatilization or decomposition. This is in keeping with the observation that PETN does not decompose or volatilize at 100° over a period of several days.[18,19]

Some investigators recommend that a vacuum oven or vacuum desiccator be used to remove the last traces of chloroform or diethyl ether after the evaporation to dryness.[4,7,17] We found this vacuum treatment was not necessary if the methylene chloride extraction was used. Equally satisfactory results were obtained if the methylene chloride was evaporated at room temperature or by heating on a steam-bath at a temperature below 50°. When chloroform solutions of PETN were allowed to evaporate at room temperature (overnight), high results for PETN were obtained spectrophotometrically, apparently because of non-volatile material from the chloroform (this solvent is much less volatile than methylene chloride).

The important question arises as to what is the solubility of PETN in water. The figures given in the literature are as follows:

Investigator	*Solubility (mg/100 ml)*
Desvergnes[20]	10 (19°)
Department of Army[21]	4·3 (25°)
Leslie[22]	0·15 (ambient temperature)
Merrill[23]	0·21 (ambient temperature)

All the investigators except Merrill used a gravimetric technique to determine the solubility. Merrill employed a radiometric technique, using PETN labelled with ^{14}C.

We determined the solubility of PETN in water by shaking an excess of PETN with water at 20° for several hr, filtering 100 ml through a Whatman No. 42 filter paper, extracting with methylene chloride, evaporating to dryness and determining the PETN spectrophotometrically by the phenoldisulphonic acid method. The result was 0·19 mg/100 ml (average of three determinations). This result agreed with those of Leslie[22] and Merrill[23] but differed drastically from the results of other investigators.

Military grade PETN[24] was used in all our investigations. Before use, the PETN (which is customarily shipped wet) was transferred to a Buchner funnel, washed several times with water and dried at 60° for 6 hr.

It was expected that the solubility of PETN would be greater in water containing styphnate, inorganic nitrate and other salts than in pure water (as shown by the results in Table 3).

Elimination of interferences in the determination of PETN in solution

The methylene chloride extraction was found to eliminate interference from inorganic nitrate, inorganic nitrite and sodium acetate (the last two substances are not ingredients of lead styphnate primers but are used in the manufacture of lead styphnate), but not the marked interference from styphnate, which was also extracted by the methylene chloride and produced a yellow colour with phenoldisulphonic acid; nor did it eliminate the lesser but still significant interference from trinitrotoluene (TNT), which was extracted with methylene chloride and produced a yellow-pink colour with phenoldisulphonic acid that slowly increased in intensity after addition of ammonia.

It was found that the interference from styphnate and TNT could be eliminated by adding 10 ml of 0·4% sodium hydroxide solution (to give a sodium hydroxide concentration of about 0·015*M*), allowing to stand for 15–20 min, and then proceeding with the extraction with methylene chloride. The styphnate ion does not change colour significantly on addition of the alkali but TNT forms a red complex that requires about 15 min to develop. PETN is not significantly hydrolysed by 0·015*M* alkali at room temperature in 15–20 min. It has been stated[25,26] that PETN is not significantly hydrolysed by heating with sodium hydroxide 1*M* at 60° for 24 hr but this claim seems open to question.

When large amounts of styphnate ion, lead salts and barium salts are present, a precipitate is sometimes obtained on adding the alkali to the aliquot of aqueous solution. When this occurs, it is necessary to discard the solution, take another aliquot, extract with methylene chloride (without alkali), evaporate the methylene chloride, add the water and alkali and proceed as in the regular method.

Determination of PETN in the residue

In order to determine the PETN in the residue obtained by filtering the waste water, it is necessary to dissolve out the PETN with acetone. The solubility of PETN in acetone is quite high (about 25%),[21,27] so this extraction offers no difficulty. In earlier experiments, an aliquot of the acetone filtrate was evaporated to dryness, water was added and the methylene chloride extraction was performed. However, it was found that the caked material formed on the bottom of the beaker by this means led to difficulties. This trouble was overcome by treating a 5 ml aliquot of the acetone extract directly with 60 ml of water and 10 ml of 0·4% sodium hydroxide solution and then extracting with the methylene chloride. If the aliquot of the acetone solution was greater than 5 ml, it was evaporated to 2–5 ml before addition of water and sodium hydroxide solution.

Table 1. Results for PETN in synthetic filtrates from waste samples

PETN added, *mg*	Other contaminants added	PETN found, *mg*
0·00	5 mg TNR	0·01
0·40		0·42
1·00		0·97
0·00	5 mg TNT	0·01
0·40		0·39
1·00		1·02
0·00	5 mg TNT + 5 mg TNR	0·02
0·40		0·42
1·00		1·02
0·00	50 ml sat. Pb styphnate soln	0·01
0·40		0·42
1·00		0·97
0·00	5 mg Ba $(NO_3)_2$	0·00
0·40		0·41
1·00		0·98
0·00	50 ml sat. tetracene soln	0·00
0·40		0·40
1·00		1·03
0·00	5 mg TNR + 5 mg $Ba(NO_3)_2$	0·01
0·40		0·42
1·00		0·98
0·00	5 mg $Ba(NO_3)_2$ + 50 ml of sat. Pb styphnate soln	0·00*
0·40		0·42*
1·00		1·02*
0·00	5 mg gum arabic	0·02
0·40		0·42
1·00		0·96
0·00	5 mg Na acetate	0·00
0·40		0·44
1·00		1·01
0·00	5 mg $NaNO_2$	0·00
0·40		0·42
1·00		1·02

* Preliminary extraction technique used.

Such ingredients of primers as antimony sulphide, tetracene, aluminium powder and calcium silicide are essentially insoluble in water and acetone and remain in the crucible.

Results for synthetic and actual waste samples

Synthetic filtrates from waste samples were prepared by adding portions of PETN standard solution No. 2 containing 0·2, 0·4 and 1·0 mg of PETN to 100 ml beakers and then adding various combinations of the following: 1 ml of 5-mg/ml trinitroresorcinol (TNR) solution in acetone, 1 ml of 5 mg/ml TNT solution in acetone, 1 ml of 5 mg/ml barium nitrate solution in water, 1 ml of 5 mg/ml gum arabic solution in water, 1 ml of 5 mg/ml sodium acetate solution in water, 1 ml of 5 mg/ml sodium nitrite solution in water, 50 ml of saturated lead styphnate solution (equivalent to about 20 mg of lead styphnate since the solubility of lead styphnate in water is about 0·04%[21]), and 50 ml of a saturated tetracene solution (the solubility of tetracene in water is very low).

These synthetic solutions were immediately diluted to about 60 ml with tap-water, 10 ml of 0·4% sodium hydroxide solution were added, and the procedure was applied. The samples containing barium nitrate and lead styphnate required the preliminary extraction with methylene chloride. The results obtained are shown in Table 1. The recoveries were satisfactory.

Synthetic residues from waste samples were prepared by accurately weighing portions of PETN in sintered crucibles and then adding approximate amounts of lead styphnate, antimony sulphide, tetracene, aluminium powder and calcium silicide. These ingredients were in the approximate ratios to be found in common lead styphnate primers. Barium nitrate was not included, since it would be found in the filtrate and not in the residue. The synthetic residues were subjected to the acetone extraction, the solutions were diluted to 100 ml in a volumetric flask, 5 ml aliquots were taken, and the samples were analysed as in the recommended procedure. The results obtained are shown in Table 2. The recoveries were satisfactory.

Table 2. Results for PETN in synthetic residues from waste samples

PETN present, *mg*	Other contaminants present, *mg*	PETN found, *mg*
28·4	160 Pb styphnate + 70 Sb_2S_3 + 20 tetracene + 35 Al powder + 35 $CaSi_2$	27·0
28·7		29·2
17·4		18·2

Table 3. Results for PETN in actual waste samples

	Sample 1	Sample 2
Total filterable residue, *mg/l*	75·9	42·0
PETN in solution, *mg/l*,	1·5	4·2
PETN in residue, *mg/l*	10·9	3·6
Total PETN in solution and residue, *mg/l*.	12·4	7·8

The results obtained for PETN in two actual waste samples are shown in Table 3. Also shown are the results for total filterable residue. It is realized, of course, that meaningful sampling is a difficult problem, particularly insofar as filterable residue is concerned.

The method described in this paper will probably have application to the determination of PETN in other materials besides waste water.

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Zusammenfassung—Eine genaus spektrophotometrische Methode zur Bestimmung von Pentaerythrit-tetranitrat (PETN) in Abwässern von Bleistyphnat-Zünderfabriken mit Phenoldisulfonsäure wird vorgeschlagen. Das Abwasser wird durch einen Glasfiltertiegel filtriert und PETN im Filtrat und im Rückstand bestimmt. Bei der Bestimmung von PETN im Filtrat wird Natriumhydroxid zugegeben und PETN mit Methylenchlorid extrahiert (in alkalischer Lösung werden Styphnat und TNT nicht extrahiert). Die Methylenchloridlosung wird dann zur Trockne eingedampft, der Rückstand mit einer Lösung von Phenoldisulfonsäure in Schwefelsäure behandelt, Wasser und Ammoniak zugegeben und die gelbe Farbe gemessen. Zur Bestimmung von PETN im Filterrückstand wird das PETN in Aceton gelost, ein abgemessener Teil der Acetonlösung mit Wasser und Natriumhydroxid behandelt, das PETN mit Methylenchlorid extrahiert und die Farbe wie oben entwickelt. Es wurden mehrere Faktoren untersucht, die Einfluß auf die Bestimmung haben. Die Löslichkeit von PETN in Wasser wurde untersucht.

Résumé—On propose une méthode spectrophotométrique précise pour le dosage du tétranitrate de pentaérythritol (PETN) dans les eaux usagées des usines d'amorces au styphnate de plomb par emploi d'acide phénoldisulfonique. L'eau usagée est filtrée à travers un creuset en verre fritté et le PETN est dosé dans le filtrat et le résidu. Dans le dosage du PETN dans le filtrat, on ajoute de la soude et extrait le PETN au chlorure de méthylène (en solution alcaline, le styphnate et le TNT ne sont pas extraits). La solution de chlorure de méthylène est alors évaporée à sec, le résidu est traité par une solution d'acide phénoldisulfonique en acide sulfurique, on ajoute de l'eau et de l'ammoniaque, et l'on mesure la coloration jaune. Dans le dosage du PETN dans le résidu, on dissout le PETN dans l'acétone, traite une partie aliquote de la solution acétonique par l'eau et la soude, extrait le PETN au chlorure de méthylène et développe la coloration comme précédemment. On a étudié divers facteurs qui influencent le dosage. On a étudié la solubilité du PETN dans l'eau.

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MUTUAL INTERFERENCE OF GOLD, PLATINUM AND PALLADIUM IN ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—It is shown that the mutual interference between the chlorides of Au, Pt and Pd in AAS using aqueous solutions nebulized into an air–acetylene flame, can be eliminated by using the dithizonates of these metals. This releasing action is ascribed to the formation of noble metal dithizonates. It is further shown that complex formation with dithizone favours the atomization of Au and that such an effect should be considered as due to complexation rather than to some bulk effect of the organic matrix.

The atomic-absorption spectroscopic (AAS) analysis of noble metals is subject to interferences.[1–10] In order to remove these some investigators suggest releasing agents such as copper sulphate,[1,9] a mixture of copper and cadmium sulphates,[4,9] uranyl chloride,[5,9] lanthanum chloride[6,9,10] or a sodium and copper sulphate mixture.[8] Others propose the use of hotter flames (premixed N_2O–C_2H_2 flames)[9,10] or the use of a concentric furnace tube to increase the exhaust-gas temperature.[3] Finally, solvent extraction has also been suggested.[7,11]

The purpose of this work was to study the use of dithizone in the AAS analysis of mixtures of Au(III), Pt(IV) and Pd(II). This investigation originated both from the interference problem just mentioned and from the fact that the industrial preparation of noble metals through cation-exchange techniques often gives solutions which contain Au, Pt and Pd as well as Ir, Rh, Sb, Sn, Te, Se, Pb, Bi, As and traces of Ag. The use of dithizone in acid medium makes it possible to extract only Au, Pt, Pd, Bi, Ag and Sn amongst all these elements.[12] We shall show that dithizone dissolved in methyl isobutyl ketone (MIBK) eliminates the mutual AAS interference between Au, Pt and Pd and that this releasing action seems to be related to dithizonate formation.

EXPERIMENTAL

Equipment and reagents

Two AAS instruments were used, a Hilger & Watts Atomspek with laminar-flow burner having a 130 × 0·5 mm slot, and a laboratory-assembled instrument built from a 0·5 m Ebert scanning spectrometer, power supplies and detection system (Jarrell–Ash). Westinghouse hollow-cathode lamps, a Hamamatsu (R 106) photomultiplier, a laminar-flow Techtron burner (AB-51) with a 100 × 0·5 mm slot, and a new nebulizer of a pneumatic sonic type constructed in the laboratory and connected to a heated nebulizing chamber, the whole nebulizer assembly giving very high efficiencies ($>85\%$) and allowing work with known constant liquid flow-rates.[13]

All reagents were of analytical grade The noble metals were generously donated by the Metallurgie Hoboken–Overpelt Company (Hoboken, Belgium). Their purity was $>99{\cdot}98\%$ for the gold and $>99{\cdot}99\%$ for the palladium and platinum

Table 1. Optimum instrumental conditions used on the Hilger & Watts apparatus

Parameter	Analytical solution					
	Au		Pd		Pt	
	dithizonate in MIBK	chloro-complex in H_2O	dithizonate in MIBK	chloro-complex in H_2O	dithizonate in MIBK	chloro-complex in H_2O
Wavelength, *nm*	242·8	242·8	247·6	247·6	265·9	265·9
Lamp current *mA*	6	6	15	15	5	10
Acetylene flow-rate, *l./min*	0·75	1·25	0·5	1·25	0·5	1·25
Air flow-rate, *l./min*	8·5* + 1·5†	8·5 + 1·5	8·5 + 1·5	8·5 + 1·5	8·5 + 2·0	8·5 + 1·5
Observation height, *mm*§	6	0·5	8	2·5	7	1
Slit-width, *mm*	0·012	0·015	0·030	0·030	0·015	0·015

* Air-flow used for nebulization of the solutions in the sprayer. This part of the total air supply is kept constant to equalize the nebulization characteristics.

† Additional air for adjustment of final air to fuel ratio.

§ Distance between the burner surface and the optical axis.

Instrumental conditions

The experiments performed with the Hilger & Watts apparatus were done under preselected optimum instrumental conditions,[18] given in Table 1. When using the Jarrell–Ash equipment we used the conditions summarized in Table 2. The flames used were both air–acetylene, the composition being given in the same tables.

Preparation of solutions and extraction conditions

Solutions of the noble metals were prepared by dissolving the pure metals in *aqua regia* and expelling the excess of nitric acid by repeated evaporations with concentrated hydrochloric acid. Care must be taken not to evaporate to dryness because appreciable losses of gold can occur when this happens.[14] The stock solutions thus prepared each contained 1000 mg of noble metal per litre. Dilutions were made with distilled water and extractions carried out with a 0·015% w/v solution of dithizone in MIBK. The pH was adjusted to 1·0 for the Au(III) and Pd(II) extractions.[12] The extraction of Pt has to be preceded by a quantitative reduction of Pt(IV) to Pt(II), since only Pt(II) can form extractable compounds with dithizone.[12] The reduction is carried out with a 35% w/v solution of stannous chloride in water.[15] In order to prevent the formation and subsequent extraction of Sn(II) dithizonate the pH was lowered to about 0.[11] Unfortunately, under such circumstances Sn(IV) is extracted as the chloro-complex into MIBK.[16] The extraction of copper was performed at pH 4·0, by using a stock solution containing 1000 mg of Cu per litre as $CuSO_4$ and a 0·030% w/v solution of dithizone in MIBK.

Table 2. Instrumental conditions used on the transformed Jarrell–Ash instrument

Wavelength	242·8 nm
Lamp current	10 mA
Acetylene flow-rate	1·34 l./min
Air flow-rates	13 l./min (6 for nebulization)
Slit-width	0·100 mm
Slit-height	10 mm
Cross-section of parallel light beam	1 mm high, 2 mm broad
Temperature of the nebulizing chamber	165°
Solution flow-rate	1·00 ml/min
Concentration of Au in all solutions	10 mg/l.

Under these conditions only primary dithizonates were obtained for the metals concerned.[12] Extraction was done the same way for all the metals: 10 ml of sample solution with an adequate metal concentration were shaken in a 100 ml separatory funnel for 3 min in the presence of 15 ml of dithizone/MIBK solution. This operation was performed three times. The extracts were collected in a 50 ml volumetric flask and diluted to volume with dithizone solution. The extraction yields were tested by analysing the residual aqueous phase by AAS. It was found that Au and Pd were extracted nearly quantitatively, Pt > 97% and Cu > 98%.

RESULTS AND DISCUSSION

Sensitivities

Aqueous solutions of the chloro-complexes of Au, Pd and Pt, MIBK solutions of their primary dithizonates and an MIBK solution of gold chloride show the AAS sensitivities (concentration in ppm giving 1% absorption) given in Table 3 and that, as is well known,[19] the use of organic matrices results in improvement in the sensitivity. Table 3 further shows that complexation further improves the sensitivity.

Table 3. AAS sensitivities for chloro-complexes and primary dithizonates

	Sensitivities, *ppm* for 1% absorption		
	Chloro-complex		Primary dithizonate
Element	in water	in MIBK	in MIBK
Au	0·22	0·14	0·07
Pd	0·28	—	0·13
Pt	3·0	—	1·20

Interferences

Series of aqueous and MIBK solutions were prepared, each containing a constant amount of one of the noble metals and increasing amounts of one of the other two. The mixed dithizonate solutions were obtained by mixing the individual dithizonate solutions.

Figure 1 illustrates the mutual interferences between Au, Pd and Pt as their chloro-complexes in aqueous solution. It is obvious that these elements show negative mutual interferences. Similar results were obtained by other investigators.[1–10] The interferences with Pt can be reduced considerably although not completely by adding as much as 20 g of copper per litre (in the form of $CuSO_4$).[1] A condensed-phase chemical interference is suggested in which more or less volatile Pt-compounds are formed.[10]

The results of a similar interference study on the dithizonates of the same noble metals are summarized in Fig. 2. The full curves show a positive interference by the added noble metal dithizonates. In further experiments copper dithizonate was added in concentrations as low as 5 mg/l. (dashed lines). As seen in Fig. 2 the interference with the signal of Au and Pt disappears completely and the absorption by Pd is nearly free of interference. The question now arises whether the observed positive interferences in Fig. 2 are not merely due to complexation with dithizone itself.

Complexation and atomization in flames

In order to throw some light on this matter absorption profiles in flames were recorded for solutions of Au in MIBK, prepared by extraction with increasing amounts of dithizone.

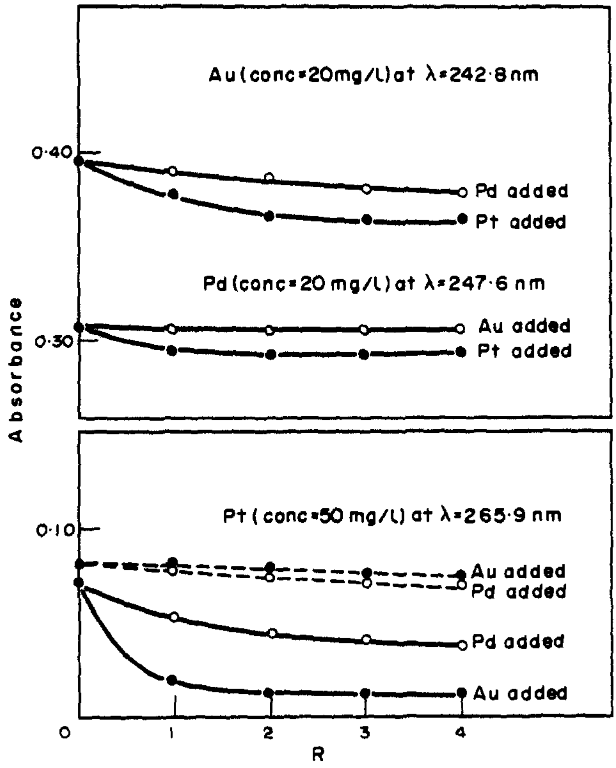

Fig. 1. Absorbances of Au, Pd and Pt (as chlorides in water) measured as a function of the weight ratio R, of added element to determined element.
---- in the presence of 20 g of Cu per litre (as $CuSO_4$). —— in absence of $CuSO_4$.

The use of MIBK allows quantitative extraction of both gold(III) chloride[16] and dithizonate. In this way solutions are obtained which contain the chloride or dithizonate or a mixture of both, depending on the dithizone content.

It is important to realize that the same solvent, MIBK, is used throughout and that therefore any effect on the atomic absorption from addition of dithizone should be ascribed to this addition and not to some solvent effect. All the following measurements were performed with the Jarrell–Ash instrument, while all previous data were obtained with the Atomspek equipment. The results are given in Fig. 3. Maximum net absorbances are plotted against the concentration of added dithizone. These maximum values were taken from the absorption profiles corrected for the blank. Typical profiles are shown in Fig. 4.

The total concentration of gold was kept constant at $5{\cdot}07 \times 10^{-5}M$. For comparison, results for Au taken from Fig. 2 are incorporated in Fig. 3 (dashed lines), after correction for the gold concentration factor and conversion of the weight ratio of interferent to gold (R values) into dithizone concentrations.

Figure 3 reveals that the absorbance increases considerably with increasing dithizone concentration. Comparing this with the results of Fig. 2, it is likely that the increase in

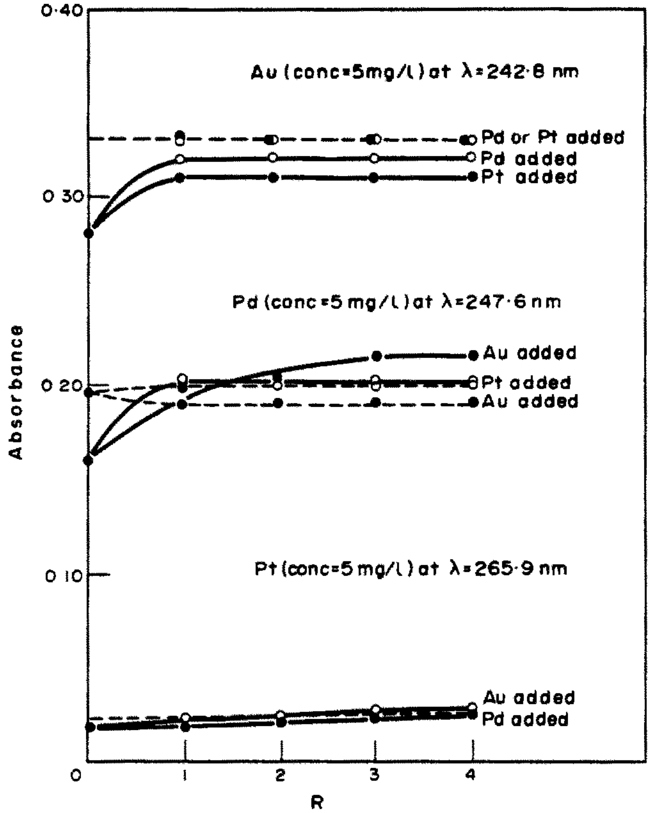

Fig. 2. Absorbances of Au, Pd and Pt (as primary dithizonates in MIBK) measured as a function of the weight ratio *R*, of added element to determined element.
----- in the presence of 5 mg of Cu per litre (as Cu dithizonate). —— in absence of Cu dithizonate

absorbance observed here originates from the dithizone through ligand-exchange equilibria of the following kind:

$$[\mathrm{AuCl}_n\mathrm{L}_{(3-n)}]_o + m[\mathrm{L}^-]_w \rightleftharpoons [\mathrm{AuCl}_{(n-m)}\mathrm{L}_{(3-n+m)}]_o + m[\mathrm{Cl}^-]_w \qquad \text{(I)}$$

$$[(\mathrm{Cu, Pd, Pt})\mathrm{Cl}_{(r-m)}\mathrm{L}_{(2-r+m)}]_o + m[\mathrm{Cl}^-]_w \rightleftharpoons [(\mathrm{Cu, Pd, Pt})\mathrm{Cl}_r\mathrm{L}_{(2-r)}]_o + m[\mathrm{L}^-]_w \qquad \text{(II)}$$

the overall equilibrium being

$$[\mathrm{AuCl}_n\mathrm{L}_{(3-n)}]_o + [(\mathrm{Cu, Pd, Pt})\mathrm{Cl}_{(r-m)}\mathrm{L}_{(2-r+m)}]_o \rightleftharpoons$$
$$[\mathrm{AuCl}_{(n-m)}\mathrm{L}_{(3-n+m)}]_o + [(\mathrm{Cu, Pd, Pt})\mathrm{Cl}_r\mathrm{L}_{(2-r)}]_o \qquad \text{(III)}$$

where subscripts o and w indicate the organic and water phases respectively. The more the chloride ligands are replaced by dithizone ligands (L^-) the better the atomization becomes.

This explanation is in line with the fact that the stability of metal–dithizone complexes decreases in the order Pd(II) > Au(III) ≫ Cu(II).[17] The influence of this on the atomization process was checked by the following experiment. Two aqueous solutions were prepared, one containing 10 mg each of gold and palladium per litre and the other containing only 10 mg of gold per litre, the metals being present as their chloro-complexes. These

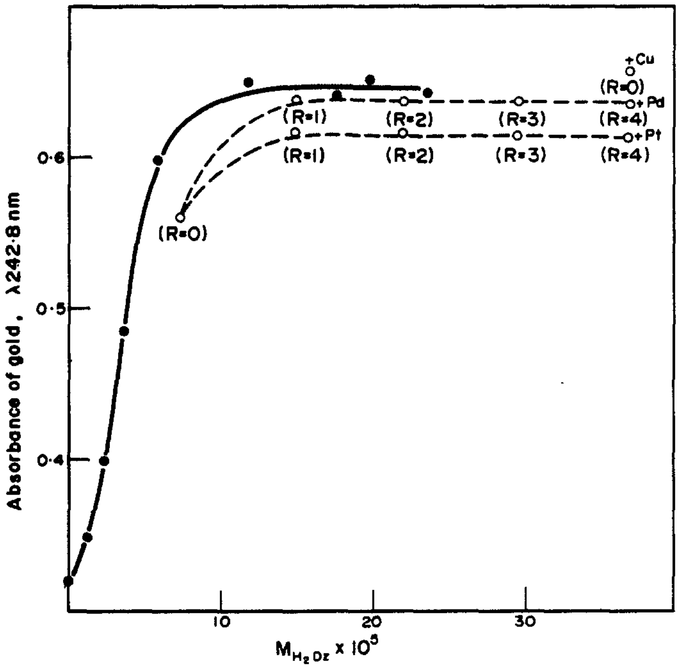

Fig. 3. Influence of the concentration of dithizone on the atomization of gold. Corresponding weight ratios for the data of Fig. 2 are given in brackets.

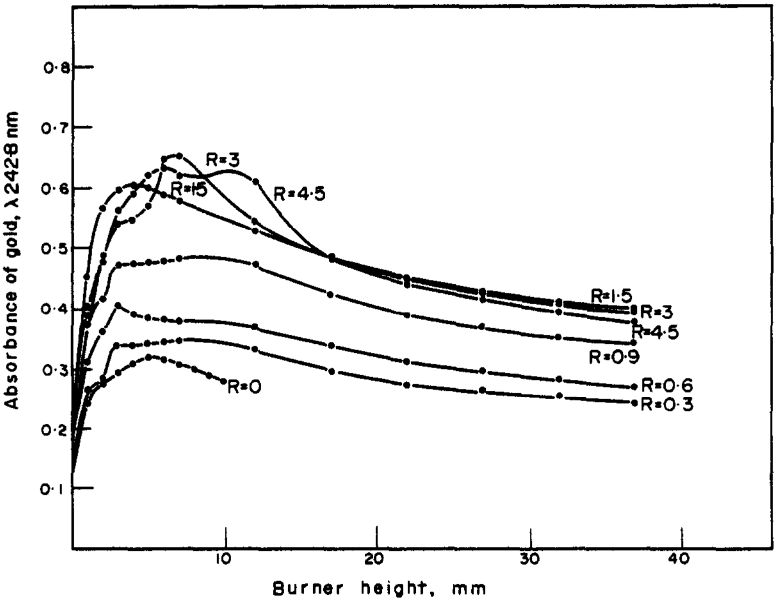

Fig. 4. Typical height profiles of absorbance corrected for the blank, for different weight ratios *R* of dithizone to gold.

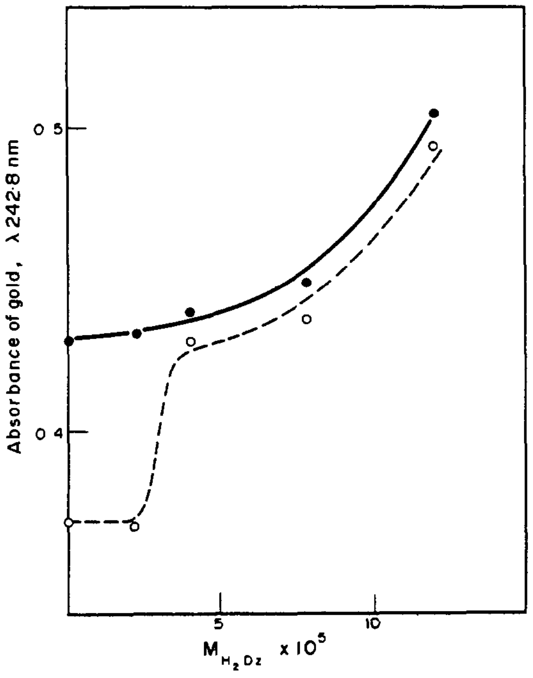

Fig. 5. Influence of Pd on the atomization of Au in the system dithizone/MIBK. Full line: without Pd. Dashed line: with Pd.

solutions were divided into several equal parts which were extracted with MIBK solutions containing increasing amounts of dithizone.

The results for the two series of solutions show that in the presence of palladium the gold atomization remains constant for concentrations of dithizone up to about 6 mg/l. (Fig. 5). This behaviour is in agreement with the order of decreasing stability of dithizone complexes. The reactions occurring during the extraction process would thus be:

$$[H_2Dz]_o \leftrightharpoons [HDz^-]_w + [H^+]_w$$

$$[PdCl_4^{2-}]_w + [AuCl_4^-]_w + (n+m)[HDz^-]_w \leftrightharpoons [PdCl_{2-n}HDz_n]_o + [AuCl_{3-m}HDz_m]_o + (3+n+m)[Cl^-]_w$$

where n and m increase with increasing concentration of H_2Dz, but n much faster than m.

Figures 3 and 5 are not identical as far as shape and absolute numerical values are concerned, although the shapes turn out to be fairly similar, if the dithizone concentration range is increased sufficiently for Fig. 5. The difference in numerical values between Figs. 3 and 5 is due to the use of different capillaries in the nebulizer[13] and is thus to be considered as an artifact which does not modify the conclusions of the present work.

The experiments illustrated in Figs. 3 and 5 clearly show the superiority of an organic ligand to an inorganic one in atomic-absorption spectroscopy. Ruling out the influence of the organic solvent further indicates that the observed increase in atomization must be due to a change of properties on the molecular scale, rather than to some bulk property (*e.g.*, viscosity, surface tension, volatility) of the solution.

Therefore the phenomenon of increase in atomization of an element by addition of a chelating substance should be defined as a complexation effect. Further work on this effect and its origin (thermal stability, volatility or some other property of the complexes) is being carried out.

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Zusammenfassung—Die gegenseitige Störung der Chloride von Au, Pt, und Pd bei der Atomabsorptionsspektrometrie mit wäßrigen Lösungen, die in eine Luft–Acetylen-Flamme zerstäubt werden, kann vermieden werden, wenn man die Dithizonate dieser Metalle verwendet. Die freisetzende Wirkung wird der Bildung von Edelmetalldithizonaten zugeschrieben. Es wird ferner gezeigt, daß die Komplexbildung mit Dithizon die Bildung von Au-Atomen begünstigt und daß ein solcher Effekt eher auf die Komplexbildung zurückgeführt werden sollte als auf einen allgemeinen Effekt der organischen Matrix.

Résumé—Il est montré que les interférences mutuelles entre les chlorures de Au, Pt et Pd en spectrométrie d'absorption atomique en utilisant des solutions aqueuses nébulisées dans une flamme air-acétylène, peuvent être éliminées en employant les dithizonates de ces métaux. Cette action d'élimination est attribuée à la formation de dithizonates de métaux nobles. Il est montré de plus que la formation de complexe avec la dithizone favorise l'atomisation de Au et qu'une telle influence devrait être considérée comme dûe à la complexation plutôt qu'à quelque effet de masse de la matrice organique.

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IMPROVED LINEAR TITRATION PLOTS FOR WEAK-ACID TITRATIONS

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Summary—Linear titration plot functions are derived for the following types of titration: weak monobasic acid–strong base, weak dibasic acid–strong base and weak acid–weak base. These functions are compared with the corresponding Gran functions, where possible, and the effects of the following sources of error are discussed: the neglect of activity coefficients, errors in equilibrium constants and the presence of a hydrolysable salt.

The potentiometric titration of a weak acid with a strong base is the more difficult, the smaller the dissociation constant of the acid; not only does the point of inflexion of a pH–degree of titration curve become harder to identify, but as shown by Meites and Goldman,[1] for sufficiently weak acids the point of inflexion does not coincide with the equivalence point. Gran[2] has applied a graphical linear extrapolation method to such titrations, but, despite its general usefulness, the approximations involved in producing the simple form of the expression can result in curvature in two cases: at the low-pH end of the titration of a moderately strong acid and near the equivalence point in the titration of a very weak acid. Johansson[3] has proposed a modified, but still approximate, function to deal with the stronger acids at low pH, but curvature, although much reduced, is still present. For the titration of the salt of a weak acid with a strong acid Dyrssen, Jagner and Wengelin[4] use different Gran plots in different parts of the titration curve, having first analysed the curve by means of the computer program HALTAFALL.[5] Ingman and Still[6] have derived a graphical method which eliminates both kinds of curvature in the titration of a monobasic weak acid with a strong base at constant ionic strength.

All these methods except Ingman and Still's involve sorting the data into groups to each of which an appropriate Gran function may be applied, a process which may require the rejection of some of the data. Combination of the charge- and mass-balance equations and equilibrium constants for a system gives a continuous function applicable to any part of a titration curve. Ingman and Still's function for the titration of a weak monobasic acid with a strong base was derived in this way, but with the aid of a computer more complicated functions can be used, and we have written an ALGOL program to deal with the following types of titration: weak acid–strong base, dibasic weak acid–strong base and weak acid–weak base. Improved functions for strong acid–strong base and precipitation titrations[7] are also covered, as are Gran functions, where applicable. Previously, activity coefficients have been either rendered unnecessary by means of a constant ionic medium or neglected; our program calculates activity coefficients iteratively and applies them when necessary to all the functions above.

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THEORY

For convenience, charges have been omitted from ionic symbols; f_i is the activity coefficient of the ith species, V_e the equivalent volume of base and V the volume of base added. K_w is the thermodynamic autoprotolysis constant of water and, assuming $f_H = f_{OH} = f_\pm$, [OH] is given by $K_w/\{H\}f_H$, $\{H\}$ being the hydrogen ion activity.

Weak acid–strong base titrations

V_0 ml of a solution of a monobasic weak acid, HA, of concentration c mole/l., are titrated with a solution of a strong base, BOH, of concentration m mole/l. The *association* constant of the acid is defined as:

$$K_A = [HA]f_{HA}/(\{H\}[A]f_A). \tag{1}$$

The mass- and charge-balance equations are as follows:

total acid, $$T_A = [HA] + [A] = [A](1 + Z) = m.V_e/(V_0 + V) \tag{2}$$

total base, $$T_B = [B] = m.V/(V_0 + V) \tag{3}$$

electroneutrality, $$[H] + [B] = [A] + [OH] \tag{4}$$

Z is defined as $K_A\{H\}f_A/f_{HA}$. Substituting for [B] and [A] in equation (4) gives:

$$[H] + T_B = [OH] + T_A/(1 + Z)$$

which on rearrangement results in the two equations below:

$$T_A - T_B = ([H] - [OH])(1 + Z) + Z.T_B = m(V_e - V)/(V_0 + V)$$

$$T_A - T_B = [H] - [OH] + Z.T_A/(1 + Z) = m(V_e - V)/(V_0 + V).$$

Expressing [H] and [OH] in terms of the experimental quantity $\{H\}$, substituting for T_B or T_A as appropriate and multiplying by $(V_0 + V)$, we can derive the functions F_A (to be used if m is known) and F_B (to be used if c is known) which can be calculated from the equilibrium constants, K_A, K_w, and the experimental data V_0, V, $\{H\}$ and either m or c. Both F_A and F_B when plotted against V are linear and intercept the V-axis at $V = V_e$:

$$F_A = (V_0 + V)(1 + Z)(\{H\} - K_w/\{H\})/f_H + ZmV$$

$$F_B = (V_0 + V)(\{H\} - K_w/\{H\})/f_H + ZcV_0/(1 + Z).$$

In the presence of a known concentration, s, of the salt of a weak base, a further function can be derived. Let the salt have the general formula SH_hX_x, where S is a monoacidic weak base of charge σ (=0 or −1), h (=0 or 1) is the number of protons per molecule of salt removable by titration, X is a univalent ion of the charge sign necessary to maintain electrical neutrality and $x = |h + \sigma|$. The following additional equations can be written:

$$K_S = [SH]f_{SH}/(\{H\}[S]f_S)$$

$$T_S = [S] + [SH] = [S](1 + Y) \quad \text{where} \quad Y = K_S\{H\}f_S/f_{SH}$$

$$[X] = x.T_S.$$

By assigning a charge i ($= \pm 1$) to X, only one system of equations is necessary, regardless of whether X is a cation ($h + \sigma < 0$) or an anion ($h + \sigma > 0$):

$$i[\mathrm{X}] = -(h + \sigma)T_S.$$

The electroneutrality equation becomes:

$$[\mathrm{B}] + [\mathrm{H}] + (\sigma + 1)[\mathrm{SH}] + \sigma[\mathrm{S}] + i[\mathrm{X}] = [\mathrm{OH}] + [\mathrm{A}].$$

Substituting for [B], [SH], [S], [A] and i[X], we obtain:

$$T_B + [\mathrm{H}] + (\sigma + 1)YT_S/(1 + Y) + T_S/(1 + Y) - (\sigma + h)T_S = [\mathrm{OH}] + T_A/(1 + Z).$$

Multiplying by $(1 + Z)$ and collecting terms gives:

$$T_A - T_B = (1 + Z)\{[\mathrm{H}] - [\mathrm{OH}] - [h - Y/(1 + Y)]T_S\} + Z.T_B = m(V_e - V)/(V_0 + V).$$

Further substitution and rearrangement gives F_S, a function of the known quantities V_0, m, s, K_A, K_S and K_w and the experimental variables V and $\{\mathrm{H}\}$.

$$F_S = (V_0 + V)(1 + Z)(\{\mathrm{H}\} - K_w/\{\mathrm{H}\})/f_H - s.V_0(1 + Z)[h - Y/(1 + Y)] + Z.m.V$$
$$= m(V_e - V):$$

A plot of F_S *vs.* V is linear and intercepts the V-axis at $V = V_e$. In the above, the case $\sigma = 0$, $h = 1$ corresponds to, say, an ammonium salt with $\mathrm{X} = \mathrm{Cl}^-$; $\sigma = -1$, $h = 0$ corresponds to a salt such as sodium acetate, with $\mathrm{X} = \mathrm{Na}^+$; $\sigma = 0$, $h = 0$ corresponds to a weak base such as ammonia, and $\sigma = -1$, $h = 1$ to a second acid similar to the first. In all cases, setting $K_A = 0$ reduces the functions F_A, F_B and F_S to the corresponding plots for the titration of strong acids.[7]

Weak dibasic acid–strong base titrations

V_0 ml of an acid, $\mathrm{H}_h\mathrm{AX}_x$, of concentration c mole/l. are titrated with a strong base, BOH, of concentration m mole/l. X is a univalent ion with the charge sign necessary to maintain electrical neutrality, h is the number of protons removable by titration, a is the negative charge on A and $x = |h - a|$. If charge i is assigned to X, the following equations can be written:

$$K_1 = [\mathrm{HA}]f_{\mathrm{HA}}/(\{\mathrm{H}\}[\mathrm{A}]f_{\mathrm{A}}) \quad (5)$$

$$K_2 = [\mathrm{H_2A}]f_{\mathrm{H_2A}}/(\{\mathrm{H}\}[\mathrm{HA}]f_{\mathrm{HA}}) \quad (6)$$

$$T_A = [\mathrm{H_2A}] + [\mathrm{HA}] + [\mathrm{A}] = [\mathrm{A}](1 + Z + W) \quad (7)$$

$$i[\mathrm{X}] = -(h - a)T_A \quad (8)$$

$$[\mathrm{H}] + [\mathrm{B}] + i[\mathrm{X}] = [\mathrm{OH}] + a[\mathrm{A}] + (a - 1)[\mathrm{HA}] + (a - 2)[\mathrm{H_2A}] \quad (9)$$

Z is defined as $K_1\{\mathrm{H}\}f_A/f_{HA}$ and W as $K_1K_2\{\mathrm{H}\}^2f_A/f_{H_2A}$. Proceeding as before, by substituting for [B], i[X], [A], [HA] and [H$_2$A] in equation (9), we obtain:

$$[\mathrm{H}] + T_B - (h - a)T_A = [\mathrm{OH}] + a.T_A - T_A.Z/(1 + Z + W) - 2T_A.W/(1 + Z + W).$$

Collecting terms and rearranging gives the two equations:

$$h.T_A - T_B = h([\mathrm{H}] - [\mathrm{OH}])/(h - R) + R.T_B/(h - R) = m(V_e - V)/(V_0 + V)$$

$$h.T_A - T_B = [\mathrm{H}] - [\mathrm{OH}] + R.T_A = m(V_e - V)/(V_0 + V)$$

where $R = (Z + 2W)/(1 + Z + W)$. These equations can be converted into the functions F_{DA} (for use when m is known) and F_{DB} (for use if c is known), which when plotted against V will be linear and intercept the V-axis at $V = V_e$.

$$F_{DA} = h(V_0 + V)(\{\mathrm{H}\} - K_w/\{\mathrm{H}\})/[f_H(h - R)] + R.m.V/(h - R) = m(V_e - V)$$

$$F_{DB} = (V_0 + V)(\{\mathrm{H}\} - K_w/\{\mathrm{H}\})/f_H + R.c.V_0 = m(V_e - V).$$

The functions above deal comprehensively with dibasic acid titrations: *e.g.*, for dicarboxylic acids $a = h = 2$; for acid salts of dicarboxylic acids $a = 2$, $h = 1$; for amino-acid salts such as glycine hydrochloride $a = 1$, $h = 2$; for simple amino-acids such as glycine $a = h = 1$. If K_2 is set to zero, the functions reduce to those for a monobasic weak acid and, if $K_1 = K_2 = 0$, to those for strong acid–strong base titrations.[7]

Weak acid–weak base titrations

V_0 ml of a weak acid, HAX_{1-a} of concentration c mol l^{-1}, are titrated with a weak base, $\mathrm{P}_b\mathrm{B}$, of concentration m mol l^{-1}. X and P are univalent ions not involved in the equilibria, a is the negative charge on A, and b is the negative charge on B. Besides equations (1) and (2), we can write the following:

$$K_B = [\mathrm{BH}]f_{BH}/(\{\mathrm{H}\}[\mathrm{B}]f_3) \tag{10}$$

$$T_B = [\mathrm{BH}] + [\mathrm{B}] = [\mathrm{B}](1 + E) = m.V/(V_0 + V) \tag{11}$$

$$[\mathrm{P}] + [\mathrm{H}] = [\mathrm{OH}] + a[\mathrm{A}] + (a - 1)[\mathrm{HA}] + [\mathrm{X}] + b[\mathrm{B}] + (b - 1)[\mathrm{BH}]. \tag{12}$$

E is defined as $\mathrm{K_B}\{\mathrm{H}\}f_B/f_{BH}$. Combining equations (1), (2) and (10)–(12) and rearranging, we obtain

$$\begin{aligned} T_A - T_B &= ([\mathrm{H}] - [\mathrm{OH}])(1 + Z) - T_B + E.T_B(1 + Z)/(1 + E) \\ &= ([\mathrm{H}] - [\mathrm{OH}])(1 + E)/E + T_A\{1 - [1 + E]/[E(1 + Z)]\}. \end{aligned}$$

A plot F_{WA} (if m is known) or F_{WB} (if c is known) against V is linear with an intercept on the V-axis at $V = V_e$.

$$F_{WA} = (V_0 + V)(\{\mathrm{H}\} - K_w/\{\mathrm{H}\})(1 + Z)/f_H - m.V(1 - E.Z)/(1 + E).$$

$$F_{WB} = (V_0 + V)(\{\mathrm{H}\} - K_w/\{\mathrm{H}\})(1 + E)/(f_H.E) - c.V_0[1 - E.Z]/[E(1 + Z)].$$

With $K_A = 0$ the functions reduce to those for strong acid–weak base titrations, with $K_B = 0$ to those for weak acid—strong base titrations, and with $K_A = K_B = 0$ to those for strong acid—strong base titrations.[7]

DISCUSSION

Comparison with the Gran function

The question of activity coefficients is discussed below and for the purposes of this comparison it is convenient to assume that all activity coefficients are equal to unity and that concentrations can be used instead of activities.

Monobasic weak acids. Gran's functions for the titration of a monobasic weak acid, when normalized with respect to the functions F_A and F_B, are in the acidic and alkaline halves of the titration respectively:

$$G = m.K_A.V[\mathrm{H}]$$

$$G' = (V_0 + V)K_w/[\mathrm{H}].$$

Table 1 shows the ratio F_A/G for acids of different strengths at various pH values in the titration of 100 ml of 0·01*M* acid with 0·1*M* strong base and Table 2 the values of F_A/G' for the alkaline regions of the titration curves. It can be seen that the Gran alkaline function, G', works well, except for the weakest acid, and that the Gran acidic function, G, is more accurate for the weaker acids than for the stronger. If for the purposes of computer calculation of the titration results the functions are fitted to a straight line by the method of least squares, the effect of the deviations in the G-function is to bias the result to give an excessive equivalent volume of base. Curvature in the G'-function leads to an underestimate of the equivalent volume of base. It may be noted that the change from one Gran function to the other is determined by the relative magnitudes of the two terms in each of the functions F_A and F_B rather than by whether the solution is acid or alkaline.

Table 1. Ratio F_A/G as a function of pH for acids of different strengths (100 ml of 0·01*M* acid titrated with 0·1*M* base)

	Acid association constant, *l./mole*			
pH	10^2	10^4	10^6	10^8
2·22	69·01	—	—	—
2·40	5·61	—	—	—
3·00	2·48	—	—	—
3·40	2·23	1·32	—	—
4·00	2·14	1·04	—	—
5·00	2·10	1·01	1·01	—
6·00	2·00	1·01	1·00	1·01
7·00	1·00	1·00	1·00	1·00
8·00	—	—	0·99	1·00
9·00	—	—	—	0·99

Table 2 Ratio F_A/G' as a function of pH for acids of different strengths (100 ml of 0·01*M* acid titrated with 0·1*M* base)

	Acid association constant, *l./mole*			
pH	10^2	10^4	10^6	10^8
8·00	−1·00	−0·91	89·10	476·0
9·00	−1·00	−0·99	−0·09	82·33
10·00	−1·00	−1·00	−0·99	−0·10
11·00	−1·00	−1·00	−1·00	−0·99
12·00	−1·00	−1·00	−1·00	−1·00

In order to determine the range of validity of the Gran function, G, at the low-pH end of the titration, the following procedure has been adopted. It is assumed that the approximations inherent in Gran's function are valid, i.e., for a weak acid before the end-point,

$$[\mathrm{A}] = T_A/n, \quad [\mathrm{HA}] = T_A(n-1)/n, \quad [\mathrm{H}] = (n-1)/K_A$$

where $n = V_e/V$. The ratio of the F and Gran functions is

$$F_A/G = 1 + (V_0 + V)([H] - [OH])(1 + K_A[H])/(K_A . m . V[H]).$$

The condition for good agreement is defined as:

$$F_A/G \leqslant 1 + D$$

where D is a discrimination factor. Since in the defined conditions $[H] > [OH]$, D is positive. If [OH] is negligible, on substituting for [H] and V and simplifying we obtain

$$1 + \frac{n(V_0 + V_e/n)}{mV_e(n - 1)/n} \leqslant 1 + D.$$

Rearrangement gives the condition

$$n^2(V_0 + V_e/n) \leqslant D . m . K_A . V_e$$

For a particular set of titration conditions, the limiting value of n for a prescribed value of D is the positive root of the quadratic

$$n^2 + r . n - D . K_A . m . r = 0$$

where $r = V_e/V_0$. Maximum values of n for different conditions and values of D are listed in Table 3. For $K_A . m < 10^3$ agreement between the functions is poor and for $K_A . m > 10^5$ it is good.

Table 3. Maximum values of n for agreement between Gran and F-functions in weak monobasic acid–strong base titrations

	$D = 10^{-2}$			$D = 10^{-3}$		
$K_A . m$	$r = 0{\cdot}1$	0·5	1·0	$r = 0{\cdot}1$	0·5	1·0
10^3	*	2·0	2·7	*	*	*
10^4	3·1	6·8	9·5	*	2·0	2·7
10^5	10	22	31	3·1	6·8	9·5

* $n < 1$.

Dibasic weak acids. Gran's method for dibasic weak acids assumes that the dissociation of the acid occurs in two distinct steps, each of which can be treated as the dissociation of a monobasic acid. After the first equivalence point, V_1, has been passed, the Gran function, G_D, when normalized with respect to the F-functions is as follows

$$G_D = m(V_e - V) = m . K_2(V - V_1)[H].$$

It can be seen that it is necessary to know one of the equivalent volumes, even approximately, in order to calculate the other. When the acid association constants are so similar that two steps in the neutralization curve cannot be detected, *e.g.*, tartaric acid, the procedure becomes less accurate. Comparisons of F_{DA} and G_D (calculated for an arbitrary value $V_1 = 5$ ml) and F_{DA} and G (calculated with $K_A = K_1$) at different pH values for a theoretical titration of 100 ml of 0·005M dibasic acid with 0·1M strong base are given in Table 4 for acids with various combinations of similar association constants. The Gran dibasic function is less satisfactory, the closer the two constants, and comparison of F_{DA}/G_D ratios with F_A/G ratios at corresponding pH values in Table 1 for monobasic acids with association constants equal to the K_1 values of the dibasic acids shows that the Gran procedure is a poorer approximation in the case of dibasic acids

Table 4. Ratios $R_1 = F_{DA}/G_D$ and $R_2 = F_{DA}/G$ as functions of pH for dibasic acids with different combinations of association constants. (100 ml of 0·005M acid titrated with 0·1M base)

	K_1, K_2, *l./mole*							
	$10^4, 10^2$		$10^4, 10^3$		$10^5, 10^4$		$10^6, 10^4$	
−log[H]	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
3·3	1·63	0·16	—	—	—	—	—	—
4·0	1·04	0·34	1·35	0·40	—	—	—	—
4·3	1·02	0·41	1·14	0·44	—	—	—	—
5·0	1·01	0·48	1·03	0·49	1·33	0·40	—	—
5·3	1·01	0·49	1·03	0·50	1·13	0·44	1·47	0·16
6·0	1·00	0·50	1·02	0·50	1·02	0·49	1·03	0·34
6·3	—	—	1·02	0·50	1·01	0·49	1·01	0·40
7·0	—	—	1·00	0·50	1·00	0·50	1·00	0·48
7·3	—	—	—	—	—	—	1·00	0·49

that with monobasic ones. Treating the dibasic acid as a monobasic one and using the G-function is a poorer approximation, which grows worse as the difference between the two association constants increases.

Ingman and Still[6] treated a dibasic acid as a monobasic acid, but included the hydrolysis correction term $(V_0 + V)([H] - [OH])$ in their equation. Their results for β-alanine are not very accurate (−2·4% error in the equivalence volume) and when we reprocessed their data with the F_A-function and the equilibrium constants obtained by Irving, Williams, Ferrett and Williams[8] the error was reduced to 0·03% in the opposite direction. Two titrations of (+)-tartaric acid, and calculations using the constants obtained by Dunsmore and Midgley,[9] gave answers −0·06 and +1·3% in error.

The effect of neglecting activity coefficients

If the ionic strength varies in the course of the titration of a weak acid, the effect of not allowing for changes in activity coefficients depends not only on the concentration of the acid and the degree of dilution during the titration, but also on whether the titration is on the acidic or basic side of the equivalence point, on the function being used and on the association constant of the acid.

On the basic side of the equivalence point the functions F_A and F_B approximate closely to the function for a strong acid titration, and the treatment given previously[7] for this case will not be repeated. On the acidic side the effect is more complex. The uncorrected functions F'_A and F'_B are defined as follows ($Z' = K_A\{H\}$).

$$F'_A = (V_0 + V)(\{H\} - K_w/\{H\})(1 + Z') + Z'.m.V$$

$$F'_B = (V_0 + V)(\{H\} - K_w/\{H\}) + Z'.c.V_0/(1 + Z')$$

Table 5 shows the ratios F_A/F'_A and F_B/F'_B of the corrected and uncorrected functions for the titration of 100 ml of 0·01M acid with 0·1M base for acids of different association constants. The ratios are given for corresponding hydrogen ion *concentrations*. Omitting activity coefficients decreases the contribution of the first term in each function and increases the contribution of the second. For the strongest acid represented in Table 5 the first term is dominant and therefore $F_A/F'_A > 1$ and $F_B/F'_B > 1$, while the converse is true for the other acids. In all cases F'_B is a better approximation than F'_A. At the equivalence

Table 5. Ratios $R_A = F_A/F'_A$ and $R_B = F_B/F'_B$ of functions with and without activity coefficient corrections at different pH values for acids of different strengths. (100 ml of 0·01M acid titrated with 0·1M base.)

	Association constant, *l. mole*							
	10^2		10^4		10^6		10^8	
$-\log[H]$	R_A	R_B	R_A	R_B	R_A	R_B	R_A	R_B
2·3	1·05	1·03	—	—	—	—	—	—
3·0	1·02	1·02	—	—	—	—	—	—
3·3	1·01	1·01	0·96	1·00	—	—	—	—
4·0	1·01	1·01	0·93	0·96	—	—	—	—
4·3	1·01	1·01	0·92	0·94	0·99	1·00	—	—
5·0	1·01	1·01	0·91	0·92	0·97	1·00	—	—
5·3	1·01	1·01	0·91	0·91	0·95	0·99	1·00	1·00
6·0	1·01	1·00	0·91	0·91	0·93	0·96	0·99	1·00
6·3	—	—	0·91	0·91	0·92	0·94	0·98	1·00
7·0	—	—	—	—	0·91	0·91	0·97	1·00
7·3	—	—	—	—	0·91	0·91	0·95	0·99
8·0	—	—	—	—	0·90	0·90	0·93	0·96
8·5	—	—	—	—	—	—	0·92	0·94
9·0	—	—	—	—	—	—	0·90	0·91

point the ionic strength is almost the same for all the acids, but at the start of the titration the ionic strength is highest (and the activity coefficient smallest) in the solution of the strongest acid. The weaker the acid, the more the activity coefficient changes during the titration, which is reflected in the ratios of corrected and uncorrected functions. Unlike the uncorrected strong acid function,[7] the uncorrected weak acid functions do not pass exactly through the equivalence point.

The effect of neglecting activity coefficients in the Gran function, G, is almost identical to that observed with the F_A-function in the range in which the Gran function is useful (and therefore approximates to F_A). For most titrations the neglect of activity coefficients in the Gran function compensates to some extent for the other approximations involved and a more accurate result is obtained.

The effect of an error in the association constant

If the association constant used in calculating the functions F_A and F_B is inaccurate, it is possible that these functions may be less accurate than the Gran functions. To facilitate comparison, activity coefficients are assumed to be equal to unity in all the following cases.

On the acidic side of the equivalence point, we can define the function ϕ_A, which uses the inaccurate "constant" K'_A.

$$\phi_A = (V_0 + V)([H] - [OH])(1 + K'_A[H]) + m.K'_A.V[H]$$

It does not matter if large values of the difference $(\phi_A - F_A)$ appear during a titration, provided that ϕ_A/F_A is effectively constant, *i.e.*, that ϕ_A intercepts the V-axis at $V \approx V_e$ and does not deviate significantly from linearity even though the slope of the plot differs from that of F_A. In the region under discussion it is the second term of each of F_A and ϕ_A that is normally dominant (otherwise the G-function is useless anyway) and in order to compare differences between F_A and ϕ_A and F_A and G it is necessary to put ϕ_A on the same basis as the other functions, which are defined in terms of the true constant K_A, by introducing the normalizing factor K_A/K'_A.

If the function ϕ_A is to be a better approximation than the G-function, the condition is, for $K'_A > K_A$,

$$(F_A - \phi_A K_A/K'_A)/(F_A - G) = (1 - K_A/K'_A)/(1 + K_A[H]) \leqslant 1$$

i.e., $-K_A/K'_A \leqslant K_A[H]$, which is always the case and so ϕ_A is always better than G.

For $K'_A < K_A$, the condition is given below.

$$(\phi_A K_A/K'_A - F_A)/(F_A - G) = (K_A/K'_A - 1)/(1 + K_A[H]) \leqslant 1$$

i.e., $K_A/K'_A \leqslant 2 + K_A[H]$. Thus ϕ_A is better than G if $K'_A \geqslant 0{\cdot}5K_A$ and may be so for even less accurate values of K'_A, depending on the magnitude of $K_A[H]$.

On the basic side of the equivalence point, the comparison is clearer if the function F_B (numerically equal to F_A) is taken. The function ϕ_B, with use of the inaccurate "constant", is defined below.

$$\phi_B = (V_0 + V)([H] - [OH]) + K'_A . c . V_0[H]/(1 + K'_A[H]).$$

Since F_B and ϕ_B are dominated by their first terms, there is no need for normalization, and assuming that $[OH] \gg [H]$, the required condition is, for $K'_A < K_A$,

$$(F_B - \phi_B)/(F_B + G') = 1 - K'_A(1 + K_A[H])/K_A(1 + K'_A[H]) \leqslant 1.$$

This condition is always fulfilled and ϕ_B is always better than G'. For $K'_A > K_A$, the condition becomes the following.

$$(\phi_B - F_B)/(F_B + G') = -1 + K'_A(1 + K_A[H])/K_A(1 + K'_A[H]) \leqslant 1$$

i.e., $K'_A/K_A \leqslant 2 + K'_A[H]$. ϕ_B is better than G' if $K'_A \leqslant 2K_A$ and may be so for less accurate values of K'_A, depending on the magnitude of $K'_A[H]$. It follows that even an inaccurate F-function is better than at least one of the Gran functions and that, provided $0{\cdot}5 \leqslant K'_A/K_A \leqslant 2$, it is better than both.

Scope of the method

It has been shown that functions can be derived for the titration of monobasic and dibasic acids without limitations due to the size of the acid association constants. The power of similar functions to deal with otherwise different titrations is illustrated for two other cases. Figure 1 shows the function F_{WA} for the titration of a weak acid with a weak base, when the conventional pH curve has a point of inflexion well removed from the equivalence point. Figure 2 shows the effect of the presence of a known quantity of the salt of a weak base (which most commonly would be an ammonium salt) on the pH curve and Gran plots for a weak acid–strong base titration; the function F_S which allows for this interference is linear.

CALCULATION

Calculation of the functions is greatly facilitated by the use of a computer and we have written an ALGOL program, available on request, for use with the English Electric–Leo–Marconi KDF. 9 computer. This program deals with functions for strong acid–strong base and precipitation titrations,[7] as well as those described here.

The best straight line through the titration points is determined by the method of least squares. If the ionic strength changes in the course of the titration, activity coefficients can be calculated iteratively, if required. Initially the ionic strength is approximated by

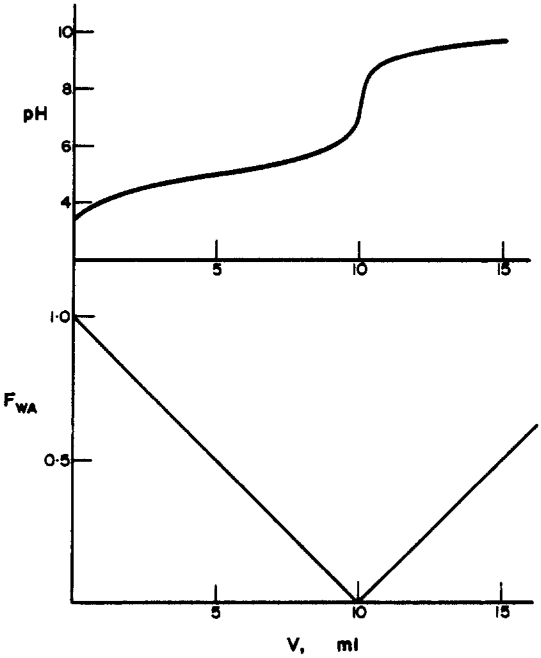

Fig. 1. Titration of 100 ml of 0·01*M* weak acid ($K_A = 10^5$ l./mole) with 0·1*M* weak base ($K_B = 10^9$ l./mole). After the equivalence point the F_{WA} function is reflected.

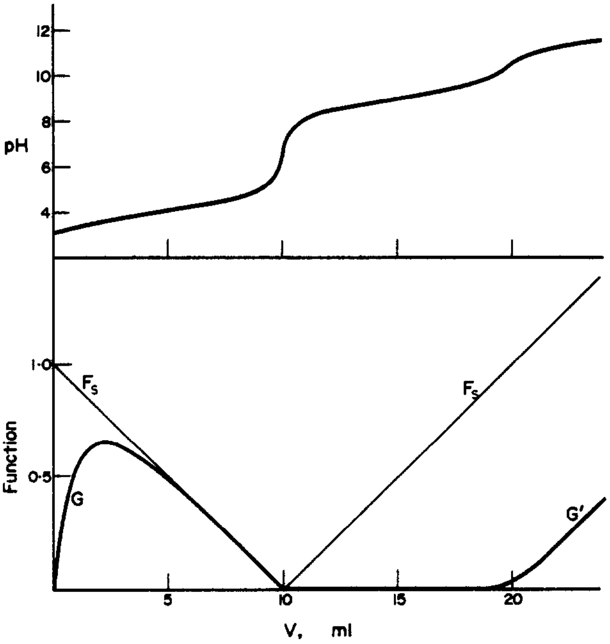

Fig. 2. Titration of 100 ml of 0·01*M* weak acid ($K_A = 10^4$ l./mole) + 0·01*M* salt of weak base ($K_S = 10^9$ l./mole) with 0·1*M* strong base. After the equivalence point the F_S function is reflected.

$I = u \cdot V_0/(V_0 + V)$, where u is an estimate of the sample concentration obtained from a conventional pH step curve, or from previous experience, or from a guess. Iteration proceeds until successive results agree within 0·1%. Activity coefficients are calculated from the equation below, where A and B are the Debye–Hückel parameters, a and b are adjustable parameters to be supplied to the program and z is the charge on the ion.

$$-\log f_z = A \cdot z^2(I^{1/2}/(1 + B \cdot a \cdot I^{1/2}) - b \cdot I)$$

The functions developed here require more calculation per datum than the Gran functions and also demand a knowledge of the appropriate equilibrium constants and of the calibration of the electrode, although the latter should be known in any analytical procedure. The linearity of the F-functions, however, means that fewer points are needed to define them and that a least-squares analysis can be done on all the data, without rejecting points at the operator's discretion. For automatic analysis by computer of titration data, the F-functions have the advantage of being continuous and there is no need to assign data to one of two or more groups.

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Zussamenfassung—Lineare Funktionen zur Wiedergabe der Titrationskurven werden für folgende Titrationstypen abgeleitet: schwache einbasige Säure–starke Base, schwache zweibasige Säure–starke Base und schwache Säure–schwache Base. Diese Funktionen werden, wo möglich, mit den entsprechenden Gran-Funktionen verglichen, und der Einfluß folgender Fehlerquellen wird diskutiert: die Vernachlässigung der Aktivitätskoeffizienten, Fehler in den Gleichgewichtskonstanten und die Gegenwart eines hydrolysierbaren Salzes.

Résumé—Les fonctions des courbes de titrage linéaires sont établies pour les types suivants de titrages: acide monobasique faible–base forte, acide dibasique faible–base forte et acide faible–base faible Ces fonctions sont comparées avec les fonctions de Gran correspondantes, dans les cas où c'est possible, et l'on discute des influences des sources d'erreur suivantes: négligence des coefficients d'activité, erreur dans les constantes d'équilibre et la présence d'un sel hydrolysable.

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SUBSTOICHIOMETRIC EXTRACTION WITH HEXAFLUOROACETYLACETONE AND TRI-*n*-OCTYLPHOSPHINE OXIDE IN CYCLOHEXANE

DETERMINATION OF MANGANESE BY NEUTRON ACTIVATION

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Summary—Traces of manganese have been determined quantitatively by neutron activation and substoichiometric extraction with a mixture of hexafluoroacetylacetone and tri-*n*-octylphosphine oxide in cyclohexane. When applied to calcium carbonate, the specific example cited here, it was necessary to make a prior separation of manganese by extraction with a mixture of pyrrolidinedithiocarbamic acid and diethylammonium dithiocarbamate in chloroform to avoid interferences from calcium. Replicate determination of sub-ppm amounts of manganese in a sample of calcium carbonate showed a relative standard deviation of 6·9% while measurements on a solution prepared by dissolving a refined-silicon standard, SRM 57, indicated a relative error of 6·0%.

In spite of the proven applicability of non-destructive gamma-ray spectroscopy for multi-elemental trace determination, separations and chemical treatment are required in many practical analyses to obtain the necessary selectivity and sensitivity. Such techniques, based on the principle of substoichiometric separation, have been particularly useful in activation analysis.[1]

Several of these methods have been reported for the determination of manganese. Perezhogin extracted permanganate with a substoichiometric amount of tetraphenylarsonium chloride in order to determine manganese in high-purity lead.[2] This procedure required a preliminary separation of manganese as the dioxide followed by a substoichiometric extraction into 1,2-dichloroethane. A similar method was applied for the determination of this impurity in gallium arsenide.[3] In this case after removal of Ga and As, a preliminary separation of Mn^{2+} was performed by extraction with a mixture of thenoyltrifluoroacetone (HTTA) and sodium diethyldithiocarbamate. The direct extraction of Mn^{2+} at pH 8–8·5 in the presence of appropriate masking agents has also been accomplished with a substoichiometric amount of HTTA.[4]

The determination of traces of manganese has been particularly important in evaluating various methods for preparing ultrapure calcium carbonate, a raw material required for the fabrication of optical waveguides.[5] It has been demonstrated in a previous paper that a mixture of hexafluoroacetylacetone (HHFA) and tri-*n*-octylphosphine oxide (TOPO) in cyclohexane offers particular advantages for substoichiometric extraction of Mn^{2+} and other cations.[6] A new method for the determination of manganese in calcium carbonate by neutron activation and substoichiometric extraction with this reagent is reported in this paper.

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EXPERIMENTAL

Reagents

Tri-*n*-octylphosphine oxide (Eastman Kodak) was used without further purification. Hexafluoroacetylacetone (Peninsular Chemresearch, Inc.) was freshly distilled before use. Sodium acetate buffers were prepared by mixing appropriate amounts of reagent grade chemicals. Carrier solutions of Mn^{2+} were prepared by dissolving accurately weighed quantities of the pure metal in "Ultrex" (J. T. Baker Chemical Company) nitric acid and diluting to volume with demineralized quartz-distilled water. Carrier-free ^{54}Mn was purchased from New England Nuclear. Batches of ultrapure calcium carbonate, prepared by special processes, were obtained from several commercial suppliers. A stock solution of 10% pyrrolidinedithiocarbamic acid (HPDC) in chloroform was made by pipetting 5·7 ml of pyrrolidine and 4·1 ml of carbon disulphide into 50 ml of chloroform in a 100-ml volumetric flask and diluting to volume with solvent. The diethylammonium salt of diethyldithiocarbamic acid (HDEDC) was purchased from J. T. Baker Chemical Company.

Procedures

Extraction with HHFA–cyclohexane and HHFA–TOPO–cyclohexane. Aqueous phases for the extraction of manganese into HHFA–cyclohexane were prepared by adding to 10-ml volumetric flasks 2·0 mg of Mn carrier and ^{54}Mn tracer and diluting to volume with various sodium acetate buffers that had previously been saturated with cyclohexane. Aliquots (5 ml) of these aqueous phases were placed in 15-ml centrifuge tubes and shaken vigorously for 2 hr with an equal volume of 0·07*M* HHFA in cyclohexane. (A convenient method for reproducibly preparing cyclohexane solutions of this concentration consisted of equilibrating freshly-distilled HHFA, at 25 ± 1°, pipetting 1·0 ml into 20 ml of cyclohexane in a 100-ml volumetric flask and diluting to volume with solvent.)

After equilibrium was reached the tubes were centrifuged for 2 min to facilitate separation of the phases. Aliquots of each phase were pipetted into polypropylene test-tubes and counted in a 3 × 3 in. well-type sodium iodide detector. In a similar procedure the distribution of Mn^{2+} into 0·07*M* HHFA–0·01*M* TOPO mixture in cyclohexane was measured as a function of pH.

Substoichiometric extractions. To measure the substoichiometric extraction of Mn^{2+} as a function of pH, aqueous phases were prepared by mixing 2·0 mg of Mn^{2+} carrier plus tracer in 10-ml volumetric flasks and diluting to 9·5 ml with sodium acetate–acetic acid buffer (pH 4·75) pre-equilibrated with an equal volume of 0·07*M* HHFA in cyclohexane. The pH of the aqueous phase was adjusted to the desired value by dropwise addition of 8·0*M* hydrochloric acid or 1·0*M* ammonia and the solution was diluted to volume with buffer.

Corresponding organic phases were prepared by adding appropriate amounts of 0·1 *M* TOPO to a volumetric flask and diluting to volume with the organic phase that remained after equilibrating the buffer with 0·07*M* HHFA in cyclohexane. Aliquots (5 ml) of each phase were equilibrated and equal volumes of each phase were counted in the manner described previously.

The substoichiometric extraction of Mn^{2+} was also investigated by equilibrating different volumes (2–8 ml) of an aqueous phase containing 0·2 mg of $Mn^{2+} + {}^{54}Mn$ per ml with a constant volume (4 ml) of TOPO–cyclohexane mixture. The concentration of TOPO in the organic phase was held constant at 25 or 50% of the stoichiometric amount required for complete extraction of carrier from the aqueous phase of smallest volume.

The effect of the concentration of HHFA on the substoichiometric extraction of Mn^{2+} was followed by extracting 5-ml aqueous phases (0·00364*M* in Mn^{2+}) with equal volumes of cyclohexane in which the concentration of TOPO was kept constant at 0·001*M* and the concentration of HHFA was varied from 0·0007 to 0·07*M*.

The effect of Fe^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Sc^{3+} and Ca^{2+} on the substoichiometric isolation of Mn^{2+} was determined by introducing 1–100 μg of each cation (up to 6000 μg for Ca^{2+}) into 5 ml aqueous phases containing 0·2 mg of Mn^{2+} per ml and ten extracting with equal volumes of 0·07*M* HHFA–0·001*M* TOPO in cyclohexane. Non-radioactive carriers and/or suitable radioisotopes of the elements were employed. The activity of ^{54}Mn in the organic phases at equilibrium was compared with the corresponding activity extracted from aqueous phases containing no interfering elements.

Mass-action effect and mole-ratio studies. The mass-action effect of TOPO on the extraction of trace manganese ($10^{-8}M$) in the presence of 0·01*M* HHFA in the organic phase was studied by varying the concentration of TOPO in the organic phase while keeping all other extraction conditions constant.

Mole-ratio experiments were performed to determine the influence of TOPO concentration on the extraction of macro-quantities of Mn^{2+}. In this case 5·0 ml aqueous phases (0·004*M* in $Mn^{2+} + {}^{54}Mn$) were equilibrated with equal volumes of organic phases in which the concentration of HHFA was kept constant at 0·07 *M* and the concentration of TOPO was varied from 0·001 to 0·014*M*.

Extraction rates and reagent stability. The rate of extraction of Mn^{2+} under substoichiometric conditions was investigated by starting a set of phases to equilibrate at the same time and then removing samples after 5, 15, 30, 60 and 120 min of equilibration. The γ-ray activities of ^{54}Mn in the organic phases were 16,132, 17,782, 18,051, 18,441 and 17,798 cpm respectively. However, for most experiments at least 1 hr of equilibration was allowed to ensure attainment of equilibrium, although 15 min should be long enough.

The stability of the substoichiometric reagent was monitored by mixing a 5-ml aliquot of aqueous phase (0·2 mg of Mn^{2+} per ml) with an equal volume of freshly prepared 0·001*M* TOPO, equilibrating for 30 min and measuring the degree of extraction, and repeating this procedure periodically with the same stock TOPO solution over a period of several hours The results [age of solution (hr), γ-ray activity from ^{54}Mn in the organic phase (cpm): 0, 18,050; 1, 18,440; 2, 17,800; 6, 18,317; 11·5, 17,659] indicate that the reagent is stable for several hours after preparation

Separation of ^{54}*Mn from solutions of calcium nitrate.* A 5·0*M* stock solution of calcium was prepared from pure calcium carbonate and high-purity nitric acid. Six 10-ml aqueous phases at pH 5–7 were prepared containing 0·2 g of calcium, 1·0 mg of Mn^{2+} carrier, 50 mg of ascorbic acid, and some ^{54}Mn. These phases were shaken for 10 min in 60-ml separatory funnels with 10 ml of chloroform containing 1% pyrrolidinedithiocarbamic acid and 0·5% diethylammonium diethyldithiocarbamate; 30 sec of manual shaking or 5 min of vigorous equilibration on a mechanical wrist-action shaker was sufficient for quantitative extraction of manganese.

Each organic phase was transferred to another funnel and manganese was stripped into 10 ml of 4·0*M* hydrochloric acid pre-equilibrated with chloroform (5 min on the mechanical shaker or 1 min of manual shaking). Completion of stripping was indicated by the disappearance of the brownish-purple colour of the organic phase. The aqueous phases from the stripping were washed with 10 ml of chloroform, then neutralized with concentrated sodium hydroxide solution to pH 5–7 and extracted with one 10-ml portion of chloroform, one 10-ml volume of cyclohexane and one 5-ml portion of 0·07*M* HHFA in cyclohexane

This sequence of extractions was followed by adjusting the pH of the aqueous phases to 5–6 and substoichiometrically extracting Mn^{2+} by shaking for 10 min with 5·0 ml of 0·002*M* TOPO in cyclohexane. Portions of the organic and aqueous phases were centrifuged and measured volumes were counted to determine the efficiency and reproducibility of the extractions.

Irradiations. Samples of calcium carbonate (~0·5 g) were weighed in a positive-pressure, filtered-air clean-room and sealed in cleaned polyethylene tubes. Solutions of Mn^{2+} (10·7 ng/ml) were prepared by diluting standardized stock solutions with demineralized quartz-distilled water. Portions (3–5 ml) of these were sealed in polyethylene tubes and used as comparison standards. Samples and standards were irradiated simultaneously for 20 min in a thermal flux of 10^{13} $n.cm^{-2}.sec^{-1}$ at the Industrial Reactor Laboratory in Plainsboro, New Jersey The irradiated samples were quantitatively transferred to 100-ml plastic beakers containing 5 ml of water and 1 ml of Mn^{2+} carrier solution (1 mg/ml). The sample was dissolved by dropwise addition of 1·0*M* hydrochloric acid, then 50 mg of ascorbic acid were added, the pH was adjusted to 5–7 with 1·0*M* sodium hydroxide and Mn^{2+} separated as described for calcium solutions.

In a second beaker, 1 or 2 ml of the irradiated standard solution of Mn^{2+}, a sample of non-irradiated calcium carbonate (equal in weight to the irradiated sample) and 1 mg of Mn^{2+} carrier were treated in the same way as the sample

Samples of SRM 57 (~0·1 g), an NBS refined-silicon standard, containing 96·80% Si, 0·034% Mn, 0·65% Fe, 0·02% Cu, 0·002% Ni, 0·025% Cr, 0·025% Zr, 0·10% Ti, and traces of Al, Ca, and Mg, were dissolved in Teflon bombs at 150 with a mixture of 10 ml of hydrofluoric acid and 1·0 ml of nitric acid. The solution was heated nearly to dryness after the addition of 1 ml of perchloric acid. The residue was dissolved in demineralized water, 1 ml of "Ultrex" nitric acid was added, and the mixture was diluted to 10 ml in a volumetric flask. A portion of this solution was accurately diluted tenfold and 2-ml samples were irradiated for 20 min along with 3-ml samples of a comparison standard.

Next, 0·5 ml of the SRM solution and 1·0 ml of the reference solution were pipetted into 50-ml polyethylene beakers containing 1 mg of Mn^{2+} carrier, 30 mg of sodium cyanide, and either 50 mg of ascorbic acid or 25 mg of hydroxylammonium chloride. After 0·5 ml of non-irradiated SRM solution had been added to the beaker containing the reference solution, manganese was separated first by the HPDC/HDEDC method and subsequently substoichiometrically isolated.

THEORY OF SUBSTOICHIOMETRIC EXTRACTIONS BY ADDUCT FORMATION

The extraction of Mn^{2+} with excess of HHFA into cyclohexane *via* the reaction,

$$Mn^{2+} + 2HHFA \rightleftharpoons Mn(HFA)_{2,(o)} + 2H^+, \tag{1}$$

is very inefficient, as shown by curve *B* in Fig. 1. The synergic combination, HHFA–TOPO, extracts Mn^{2+} completely from the aqueous phase at pH > 2·5 (see *A* in Fig. 1). Thus, TOPO establishes the degree of extraction according to the tendency for the adduct reaction,

$$Mn(HFA)_{2(o)} + m\text{TOPO}_{(o)} \rightleftharpoons Mn(HFA)_2(\text{TOPO})_{m,(o)}, \tag{2}$$

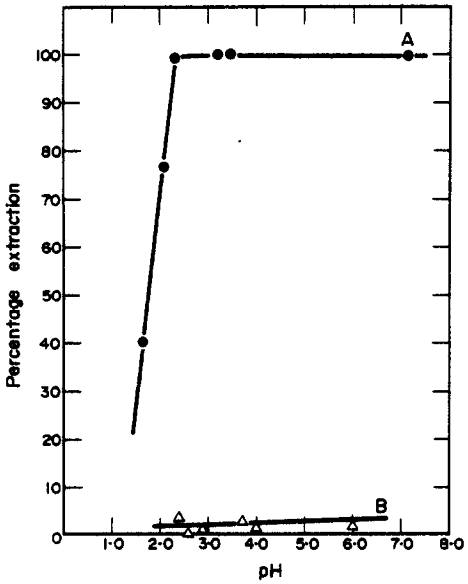

Fig. 1. Dependence of the extraction of Mn^{2+} ($3{\cdot}64 \times 10^{-3}$ *M*) on pH with (*A*) 0·07 *M* HHFA–0·01*M* TOPO–cyclohexane and (*B*) 0·07*M* HHFA–cyclohexane.

to occur in the organic phase. Depending on the stability constant for the adduct complex, given by

$$\beta_n = \frac{[\mathrm{Mn(HFA)_2(TOPO)}_m]_{(0)}}{[\mathrm{Mn(HFA)_2}]_{(0)}[\mathrm{TOPO}]^m_{(0)}}, \tag{3}$$

or on the magnitude of the extraction constant,

$$K = \frac{[\mathrm{Mn(HFA)_2(TOPO)}_m]_{(0)}[\mathrm{H}^+]^2}{[\mathrm{Mn}^{2+}]\,[\mathrm{HHFA}]^2[\mathrm{TOPO}]^m_{(0)}}, \tag{4}$$

for the reaction

$$\mathrm{Mn}^{2+} + 2\mathrm{HHFA} + m\mathrm{TOPO}_{(0)} \rightleftharpoons \mathrm{Mn(HFA)_2(TOPO)}_{m,(0)} + 2\mathrm{H}^+, \tag{5}$$

a substoichiometric amount of TOPO can be used to transfer always the same quantity of Mn^{2+} into the organic phase.

If at least 99% of the manganese in the organic phase is in the form $Mn(HFA)_2(TOPO)_m$ and the TOPO (initially 0·001*M* in the organic phase) has reacted to the extent of 99% or better during equilibration of the organic phase with an equal volume of aqueous phase (0·002*M* Mn^{2+}) to produce a single adduct-species, reproducible substoichiometric extractions can be performed provided the stability constants, β_1 and β_2 for the mono- and di-adduct complexes are $> 10^7$ and $> 10^{12}$ respectively,[6] and that the pH of the aqueous phase provides for production of enough $Mn(HFA)_2$ to react with all the TOPO.

The threshold pH at which 50% extraction can be achieved is derived from the value of *K*. Under the conditions of 99% reaction of TOPO (initial concentration 0·001*M*), equal phase volumes, Mn^{2+}, and di-adduct formation in the organic phase, equation (4) becomes

$$\mathrm{pH} \geqslant -1/2 \log K - \log[\mathrm{HHFA}] + 5. \tag{6}$$

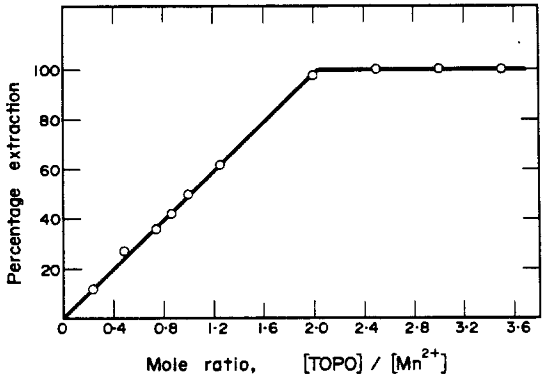

Fig. 2. Dependence of the extraction of Mn^{2+} on the molar ratio of TOPO in the organic phase to $[Mn^{2+}]$ in the aqueous phase ($3·64 \times 10^{-3}M$).

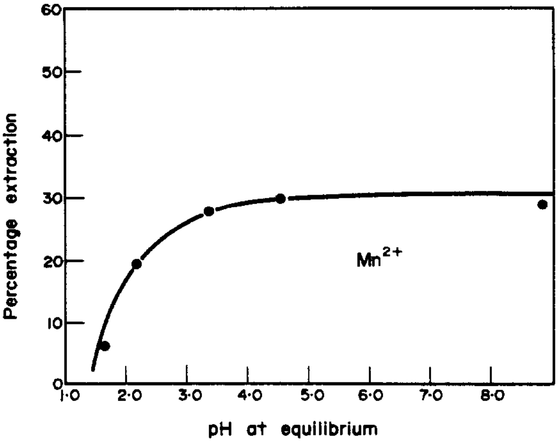

Fig 3 Substoichiometric extraction of Mn^{2+} ($3·64 \times 10^{-3}M$) with 0·07*M* HHFA–0·002*M* TOPO–cyclohexane.

Table 1 Dependence of substoichiometric extraction of Mn^{2+} on [HHFA]

[HHFA], *M*	^{54}Mn activity in organic phase*	Distribution ratio	Extraction, %
0·0007	2033	0·016	1·6
0·0014	3080	0·024	2·3
0·0021	4702	0·037	3·6
0·0042	7565	0·060	5·7
0·0063	17,281	0·150	13·0
0·0070	17,134	0·152	13·2
0·0105	17,460	0·153	13·2
0·0350	18.738	0·164	14·1
0·0704	19,260	0·169	14·4

* [Mn] = 0·00364*M*, [TOPO] = 0·001*M*, $V_a = V_0$ = 5 ml.

Replicate extractions of trace amounts of $^{54}Mb^{2+}$ ($10^{-8}M$; aqueous phase at pH 2·18, ionic strength 0·1) into cyclohexane with excess of HHFA (0·01*M*) as a function of the concentration of TOPO ($1·0 \times 10^{-4}$–$8·0 \times 10^{-2}M$) gave slopes between 1·2 and 1·7 on log–log plots. Deviations of these slopes from 2·0 are probably related to aqueous phase complexation of Mn^{2+} by HHFA.[7] The formation of the di-adduct was confirmed by the mole-ratio plot in Fig. 2.

It was estimated from the log–log graph that the extraction constant for reaction (5) was about $6·3 \times 10^4$. Substitution of this value into expression (6) suggests that substoichiometric extractions should be possible above a threshold pH of 3·8 which closely approximates the experimental value of 4·0 (Fig. 3).

The influence of the concentration of HHFA on the substoichiometric isolation of Mn^{2+} is demonstrated by Table 1. Although a large excess of HHFA is used in combination with substoichiometric amounts of TOPO, the minimum HHFA concentration required for the extraction is the amount needed to generate an HFA^- concentration greater than the initial concentration of Mn^{2+} in the aqueous phase when 50% of the stoichiometric amount of TOPO is present initially in the organic phase.

RESULTS AND DISCUSSION

The precision obtained for substoichiometric extractions of Mn^{2+} (in the absence of other metal ions) is shown in the first column of Table 2. The effects of traces of other transition metal cations are shown in Table 3. It is seen that the total concentration of ions capable of participating in adduct reactions with TOPO can approach 10 μg without significantly affecting the isolation of Mn^{2+} from an aqueous phase containing 1·0 mg of manganese carrier. Thus, direct substoichiometric extraction of manganese can be applied after irradiation of 1 g samples of highly pure reagents and materials containing less than 10 ppm of transition elements.[6] Interferences from other metal ions at this concentration can be reduced further by adding 10 mg of Mn^{2+} carrier and extracting with 0·02*M* TOPO. Samples with matrix or major elements that react with HHFA or TOPO will require preliminary separations.

Owing to the large interference by calcium, a preliminary separation was required before manganese could be determined in calcium carbonate. The results are shown in Tables 4 and 5.

Table 2. Reproducibility of substoichiometric extractions of Mn^{2+} under ideal conditions

Activity of ^{54}Mn in organic phase*, *cpm*	Mn in aqueous phase†, *mg*	Activity of ^{54}Mn in organic phase†, *cpm*
18,202	0·4	18,299
18,312	0·8	18,518
18,343	1·0	18,401
18,939	1·2	18,268
18,084	1·4	18,554
18,720	1·6	18,160
18,468		
18,731		

* $V_a = V_0 = 3$ ml, pH = 4·4, [TOPO] = 0·0018*M*, $[Mn^{2+}] = 0·0037\ M$.
† $V_0 = 3$ ml, pH = 4·2, [TOPO] = 0·002*M*.

Table 3. Effect of various cations on the substoichiometric extraction of Mn^{2+}

Element	Amount of cation in aqueous phase, *μg*	Interference ratio*
^{54}Mn	none†	1·000
^{59}Fe	100	1·394
^{60}Co	100	1·149
^{64}Cu	100	7·707
Fe^{3+}	10	1·112
Co	10	1·090
Zn	10	1·143
Sc	3	1·043
Co, Fe^{3+}	3	1·017
Ni	3	0·994
Ca	6000	1·740

$$* \text{ Ratio} = \frac{^{54}\text{Mn activity isolated in absence of cation}}{\text{activity separated in presence of cation.}}$$

† $[Mn]_a = 0{\cdot}20$ mg/ml, pH = 4·0, $V_a = V_0 = 5$ ml, $[TOPO]_{(0)} = 0{\cdot}002M$.

Table 4. Separation of ^{54}Mn from $Ca(NO_3)_2$ solutions

Preliminary extraction*		Stripping†	Substoichiometric extraction§	
pH	*E*‡	*E*‡	pH	^{54}Mn activity in organic phase, *cpm*
7·7	99·9	95·4	4·1	34,235
7·7	99·6	97·5	4·2	34,072
7·7	99·6	97·5	4·4	33,930
7·9	99·7	97·9	4·9	33,075
7·9	99·8	97·6	5·0	35,283
7·9	99·9	100	4·0	33,927
				34,087¶

* 1% HPDC–0·5% HDEDC–$CHCl_3$, $[Mn^{2+}] = 0{\cdot}1$ mg/ml, $V_a = 10$ ml.
† 4·0*M* HCl.
‡ Extraction, %.
§ 0·07*M* HHFA–0·002*M* TOPO–cyclohexane.
¶ Mean value, standard deviation 711.

Table 5. Determination of Mn in $CaCO_3$

Sample, *g*	^{56}Mn activity isolated, *cpm* Sample	Standard	[Mn] found, *ng**
0·509	24,628	22,076	242·6
	21,941	20,706	230·5
0·554	24,372	21,967	221·7
	20,464	21,071	194·1†
0·504	23,015	20,171	250·6
	21,425	22,198	212·0
		21,365‡	231·5§

* NaI detector, detection limit 0·1 *ng* of Mn.
† Value rejected.
‡ Mean value, standard deviation = 837 *cpm*.
§ Mean value, standard deviation = 15·5 *ng*.

Table 6. Determination of Mn^{2+} in solutions prepared by dissolving samples of SRM 57

	^{56}Mn γ-ray activity in organic phase, *cpm*		
Set*	Standard†	Sample	[Mn^{2+}], *μg/ml*‡
I	37,474	47,101	0·280
	37,134	48,395	0·287
		49,241	0·292
II	40,442	59,046	0·324
	40,389	59,478	0·326
			0·302§

* Results for sets I and II obtained with different TOPO concentrations.

† [Mn^{2+}] = 0·1107 *μg/ml.*

‡ Two ~ 0·1 samples of SRM 57 dissolved and diluted to 100 ml. 0·5-ml aliquots of these solutions were analysed.

§ Mean, standard deviation = 0·022 *μg/ml.*

There being no reference CaCO$_3$ standard certified for traces of manganese, NBS SRM 57 (0·034% Mn) was selected to test the accuracy of the method. The results reported in Table 6 demonstrate the precision and accuracy of the method. Atomic-absorption determinations of the manganese (2·90 μg/ml in the test-solution) agreed closely with the mean value 0·303 ± 0·017 μg/ml found by activation analysis of a tenfold dilution of the test-solution. Analysis of 0·1-g samples of the SRM by atomic absorption showed a mean value of 0·031% Mn, which agrees reasonably well with the NBS value, 0·034 ± 0·003%. Based on the NBS recommended value, the amount of manganese in 0·5-ml samples of the diluted test-solution would be 0·17 μg, with a relative uncertainty of ±7·6%. The results by activation analysis were 0·151 ± 0·009 μg. Because of either small losses of manganese during sample dissolution and fuming or uncertainties in the manganese value recommended for SRM 57, a total error of 6–12% is indicated for this analytical procedure for determinations of 0·2 ppm of manganese.

CONCLUSIONS

The reagent hexafluoroacetylacetone–tri-*n*-octylphosphine oxide–cyclohexane has been shown to be suitable for precise and accurate substoichiometric determinations of traces of manganese by neutron activation. The γ-ray activity from the 0·847-MeV photopeak is sufficient for the determination of 2·0 ng of Mn by this method. Owing to the number of cations that can form adducts with it, this reagent has broad applicability in activation analysis.

Although preliminary separation of the element to be determined will often be required, direct substoichiometric separations of Mn^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and rare earths from certain reagents and materials of high purity should be possible.[6]

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Zusammenfassung—Manganspuren wurden quantitativ durch Neutronenaktivierung und unterstöchiometrische Extraktion mit einem Gemisch von Hexafluoroacetylaceton und Tri-n-octylphosphinoxid in Cyclohexan bestimmt. Bei der Anwendung auf Calciumcarbonat, dem hier aufgeführten Beispiel, war es notwendig, Mangan vorher durch Extraktion mit einem Gemisch von Pyrrolidindithiocarbaminsäure und Diäthylammoniumdithiocarbamat in Chloroform abzutrennen, um Störungen durch Calcium zu vermeiden. Mehrfachbestimmungen von Manganmengen unter 1 ppm in einer Calciumcarbonatprobe zeigten eine relative Standardabweichung von 6,9%, während Messungen an der Lösung eines Standards aus gereinigtem Silicium, SRM 57, einen relativen Fehler von 6.0% ergaben.

Résumé—On a dose quantitativement des traces de manganèse par activation de neutrons et extraction substoechiométrique avec un mélange d'hexafluoracétylacétone et d'oxyde de tri-*n*-octylphosphine en cyclohexane Dans l'application au carbonate de calcium, l'exemple spécifique cité ici, il a été nécessaire d'effectuer une séparation préalable du manganèse par extraction avec un mélange d'acide pyrrolidinedithiocarbamique et de dithiocarbamate de diéthylammonium en chloroforme pour éviter des interférences du calcium. Un dosage répété de quantités de manganèse à l'échelle de la sub-ppm dans un échantillon de carbonate de calcium a montré un écart type relatif de 6,9% tandis que des mesures sur une solution préparée en dissolvant un étalon de silicium purifié SRM 57, ont montré une erreur relative de 6,0%

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DETERMINATION OF CADMIUM IN BIOLOGICAL MATERIALS BY ATOMIC ABSORPTION

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Summary—A variety of biological samples such as blood, urine, hair, nail and kidneys has been analysed cadmium. Tantalum ribbon flameless and conventional flame-aspiration atomic-absorption techniques were employed for the analysis.

Among the heavy metals of toxicological importance, cadmium has received considerable attention. Some investigators have gone as far as saying that cadmium has probably more lethal possibilities than any other heavy matal.[1] Cadmium is a common air and water pollutant, especially from smelters. It is also present in cigarette smoke.[2] Diagnosis of cadmium exposure may be difficult.[3,4] With this problem in mind, the present work has been geared to the determination of cadmium in a variety of biological samples, especially with regard to micro-sampling.

Four analytical techniques have been commonly applied to cadmium analyses, including ultraviolet and visible spectrophotometry, neutron activation, optical emission spectrography and atomic-absorption spectrometry.[5] Of these techniques, atomic-absorption spectrometry has received the greatest attention because of its excellent sensitivity for cadmium. Pulido, Fuwa and Valee, using long-path absorption cells to increase sensitivity, were able to determine cadmium in urine and serum by direct aspiration.[6] More commonly used atomic-absorption techniques involve chelation and extraction of cadmium into an organic solvent. Blood (after trichloroacetic acid precipitation of protein), urine, and tissue (after digestion with nitric–perchloric acid mixture and dissolution) are adjusted to a pH of 6·0–7·5, sodium diethyldithiocarbamate is added and then methyl isobutyl ketone (MIBK)[7] is used for extraction. Other methods for tissue analysis involve acid digestion or dry ashing followed by acid dissolution of the residue and ultimately direct aspiration of the acid solution.[4,8] All of these methods, however, require at least 5 ml of whole blood or 1–2 g of tissue. Few microtechniques have been developed for the analysis of biological samples for cadmium. One recent method is based on solvent extraction in blood.[9] No methods have been reported for the determination of cadmium in biopsy tissue.

In this paper, methods are presented which have been developed for the determination of cadmium in urine by conventional flame aspiration atomic-adsorption spectrometry and in blood by flameless atomic-adsorption spectrometry. In addition, since some results have been reported concerning high levels of cadmium in hair from exposed animals,[5] a micro flameless atomic-absorption method has been developed for the determination of cadmium in organ biopsy samples. Assay of biopsy samples may be of significant value

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in the light of previous data indicating that analysis of blood and urine may be of no value in diagnosing excessive exposure to cadmium.

EXPERIMENTAL

Apparatus

All flame atomic-absorption measurements were made with an Instrumentation Laboratory (I.L.) Model 253-02 Atomic Absorption Spectrophotometer. For the flameless atomic-absorption measurements, the burner head was replaced with an I.L. Model 355 Flameless Sampler. Procedures for the optimization and use of the flameless sampler have been described previously.[10] The background correction mode was used as described in the I.L. Instruction Manual. The operation and application of the background correction mode was described in earlier papers.[11] Important instrumental parameters are given in Table 1.

Table 1. Instrumental parameters

Spectrometer		
Mode		Automatic background correction
Hollow-cathode lamp	A	Cadmium
	B	Hydrogen continuum
Lamp current	A	5 mA
	B	10 to 15 mA
Photomultiplier		R372 (run at 530 V)
Slit-width		320 μm
Wavelength		228·8 nm
Flameless sampler		
Mode		Automatic
Purge gas		Argon
Gas flow-rate		10 ft^3/hr
"Dry" setting		4–5 turns
"Dry" time		30–60 sec
"Analyze" setting		8·0 turns
Height of measurement		2 mm

Polypropylene test-tubes, 5 ml and 15 ml size (Falcon Plastics), were used throughout the sample preparations. The tubes were soaked overnight in 5% w/v Triton X-100 solution before use.

Reagents

The following solutions were used in the present work. Formamide, 1% w/v ammonium pyrrolidinedithiocarbamate solution (APDC), 1% w/v saponin solution and water-saturated MIBK for blood analysis. For hair, nail and tissue dissolution, nitric acid (Baker "Ultrex") and 10% v/v hydrogen peroxide were used. A 1000 μg/ml standard cadmium solution was prepared from cadmium metal.

Sample preparation

Urine. Samples were collected in polyethylene bottles and acidified by addition of 10 ml of concentrated hydrochloric acid per l.

Blood. To 0·1 ml of heparinized whole blood were added one drop of 1% w/v saponin solution, 0·1 ml of formamide, 0·1 ml of 1% APDC, and 0·2 ml of water-saturated MIBK. The samples were mixed after each addition and for at least 1 min following the addition of the MIBK and then centrifuged. The blank and cadmium standard of 0·005 μg/ml, prepared from water and standard solution, respectively, were treated similarly.

Hair and nails. Samples were soaked in 0·3% Triton X-100 solution for 30 min followed by three successive washes with the Triton X-100 solution and then three successive washes with demineralized water, then dried. To 10 mg of sample was added 1 ml of 8*M* nitric acid in a plastic test-tube. The tubes were capped lightly and placed in a water-bath at 80–90°. After 5–10 min, 0·5 ml of 10% hydrogen peroxide was added and the tubes were left in the water-bath for an additional 5–10 min, cooled, and diluted to a volume of 5 ml. Blank and standard (Cd 0·005 μg/ml) were prepared in a similar acid matrix.

Tissue samples. A 5–10 mg portion of tissue sample was weighed into a plastic test-tube and 1·0 ml of concentrated nitric acid was added. The tubes were capped lightly and placed in a water-bath at 80–90°. After 5–10 min, 1·0 ml of 10% v/v hydrogen peroxide was added and the tubes returned to the water-bath for an additional 5–10 min. Blank and standard (Cd 0·005 μg/ml) were prepared in a similar acid matrix.

Determinations

Urine cadmium was determined by simple aspiration of the sample. The method of standard additions was used for standardization.

For blood, hair, nail and tissue analysis, 25 μl of the sample extract or solution were placed on the tantalum ribbon. For very low cadmium levels, more sample, up to 100 μl, can be used.

RESULTS AND DISCUSSION

Contamination

During the early stages of this work, severe problems were encountered with sample contamination when the flameless atomic-absorption technique was employed, because of the extreme sensitivity of atomic-absorption for cadmium (4 pg). Glass test-tubes were found unsatisfactory despite repeated soakings in acid and 5% Triton X-100 solution. Plastic tubes were far more satisfactory but still required cleaning. Soaking in 8*M* nitric acid overnight was found inadequate. However, excellent results were obtained when the tubes were soaked overnight in 5% w/v Triton X-100 solution. The tubes used were polypropylene with snap caps, which could be capped lightly during heating, thus preventing any loss.

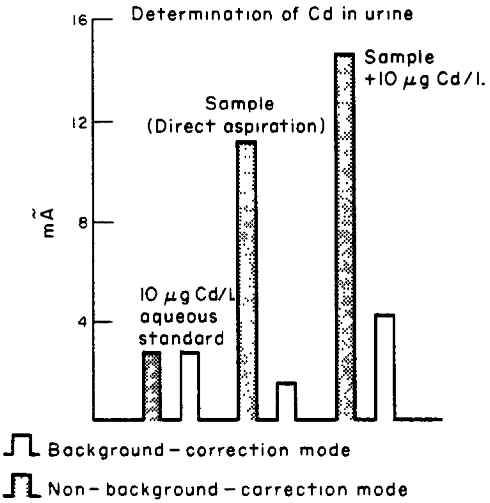

Fig. 1. Determination of Cd in urine.

Reagent-grade nitric acid was found to have a cadmium content of 5–10 μg/ml and could not be used, but Baker "Ultrex" nitric acid contained less than 1μg/ml and was very satisfactory.

The APDC, MIBK and other reagents used for the determination of cadmium in blood were found to be virtually free from cadmium contamination. Under the conditions mentioned above, very low blanks were observed in all cases.

The determination of cadmium in urine has suffered considerable difficulty in the past from interferences by alkali metal salts in the sample. This has led to erroneously high values for cadmium in urine, 20–50 μg/l.[5] Because of the high salt content, most urine cadmium analyses are performed by a solvent extraction technique. Figure 1 shows results for determination of cadmium in urine by direct aspiration in the non-background-correction mode and the automatic background-correction mode. A significant amount of background signal is evident. This also shows the utility of the background-correction mode.

Thus, use of the automatic background-correction mode coupled with high scale-expansion (100 X) and signal integration makes possible the direct determination of cadmium in urine. The cadmium value which we have obtained, 4 μg/l, is consistent with normal data previously published, Table 2. More data concerning normal levels of cadmium in the body may be found in reference 5.

Table 2. Normal values of cadmium in biological materials

Sample	Average	Range
Urine,[14] *μg/100 ml*	0·85	0·3–5·0
Blood,[14] *μg/l.*	1·6	0·5–11·0
Liver,[8] *ppm*	2·03	1·19–3·71
Kidney,[8] *ppm*	11·2	2·1–22·0

Blood analysis

The extraction procedure presented here for the blood samples is merely an adaptation of a method used for the determination of lead in blood, reported earlier.[12,13] Results obtained from four normal blood samples by using the method described are given in Table 3. These results yielded a cadmium result of 0·3 μg/100 ml. The results presented for the normal blood samples are consistent with those previously published, Table 3. Lead can also be determined in the same extract.

Table 3. Cadmium in whole blood (*μg/100 ml*)

Sample A*	0·3
Sample B	0·4
Sample B + 1·0 μg Cd/100 ml	1·6
Sample C	0·2
Sample C + 1·0 μg Cd/100 ml	1·3
Sample D	0·4
Sample D + 1·0 μg Cd/100 ml	1·3

* Results for Sample A were verified by standard additions.

Hair and nail analysis

Analytical results obtained from the determination of cadmium in hair and nails are given in Table 4. In all cases, duplicate determinations gave good agreement. Normal levels of cadmium in hair are not well documented, since variations occur with sex, age, sampling site, colour of hair, and especially external contamination. The value of hair analysis as a measure of cadmium intoxication is not understood and is disputed.[5] A 10-mg sample of hair is used since at least this amount of hair is necessary for the sample to be representative. Ca, Mg, Na and K can be determined by aspiration in this same sample as well as Cu, Cr, Mn, Zn, Fe and Pb by flameless atomic-absorption.

Tissue analysis

The most important analyses conducted were those performed on the tissue samples. The goal here was to establish whether or not biopsy tissue analysis could be used as a means of determining toxic exposure to cadmium. Autopsy samples of kidney and liver organs were sampled in triplicate from different portions of the organ. At the same time

Table 4. Cadmium in hair and nails

Sample	Cd, *ppm*	Sample	Cd, *ppm*
Hair No. 1	4·1	Hair No. 5	3·2
	3·7		2·4
Hair No. 2	1·0	Hair No. 6	3·4
	0·8		4·5
Hair No. 3	1·7	Hair No. 7	4·5
	2·5		4·9
Hair No. 4	2·4	Hair No. 8	1·7
Nails No. 9	2·2	Nails No. 10	0·32
	2·5		

a 2-g sample was taken from the organ for conventional flame-aspiration atomic-absorption analysis. The results obtained are summarized in Table 5. It is important to notice the large spread in the three different analyses of the same organ. To ascertain whether the range of values obtained was due to variation in cadmium concentration at different locations in the organ, or due to poor reproducibility of the method, NBS SRM No. 1157, bovine liver, was analysed by the method presented. The results of the triplicate cadmium determinations are shown in Table 6. The accuracy and precision of the analysis were found to be excellent and thus it is obvious that the variation in cadmium concentrations observed is attributable to the heterogeneous distribution of cadmium in the organ. Although a significant variation in cadmium concentration at different organ locations is

Table 5. Cadmium in kidney and liver autopsy samples, *ppm*

		Cadmium	
Sample	Weight of sample, *mg*	Flameless	Flame
A (Kidney)	9·8	127	
	5·2	150	150
	10·3	167	
B (Kidney)	18·4	42	
	18·2	64	69
	13·8	92	
C (Liver)	27·2	2·2	
	11·0	4·8	3·0
	12·5	2·8	
D (Kidney)	12·7	2·1	
	11·5	4·4	5·0
	8·5	5·3	

Table 6. Accuracy and precision of method. (NBS SRM 1157 Bovine Liver)

Present method, *ppm**	NBS data, *ppm*
0·27 ± 0·02	0·27 ± 0·04
0·27 ± 0·02	
0·25 ± 0·04	

* Results based on 50-mg sample and aqueous standards Precision data based on 10 readings.

apparent, this does not rule out the validity of the method as a diagnostic tool, since in the case of individuals suffering from cadmium poisoning a considerably higher than normal organ cadmium level is observed.

Acknowledgement—The authors would like to express their appreciation to Dr. George Lewis and his colleagues at the Boston V. A. Hospital for providing the autopsy samples used in this work.

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Zusammenfassung—Eine Anzahl biologischer Proben wie Blut, Urin, Haare, Nägel, Leber und Nieren wurden auf ihren Cadmium-gehalt analysiert. Zu der Analyse wurden das flammenlos Atomabsorptionsverfahren mit Tantalband und das übliche Verfahren mit Ansaugen der Probe in die Flamme verwendet.

Résumé—On a analysé une variété d'échantillons biologiques tels que sang, urine, cheveux, ongles, foie et reins pour le cadmium. On a employé les techniques d'absorption atomique sans flamme au ruban de tantale et à aspiration de flamme ordinaire.

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SOME CHELATING ION-EXCHANGE RESINS CONTAINING KETOIMINOCARBOXYLIC ACIDS AS FUNCTIONAL GROUPS

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Summary—A series of ion-exchange resins containing —$COCH_2N\,[(CH_2)_mCOOH_2]_2$ groups has been synthesized. Additional analogues were prepared by means of the reaction of the carbonyl group with phosphorus trichloride or thioglycollic acid. The properties of these resins and the selectivity for different metal ions have also been investigated.

A great deal of work has been done on the preparation of ion-exchange resins containing various complexing functional groups.[1–4] During recent years attention has been paid to exchangers with amino- or imino-acids as ligand groups. Dowex A-1 or Chelex 100 are typical representatives. The presence and arrangement of the two carboxyl groups and the tertiary nitrogen atom confer upon the resins a strong preference for complexing copper and other heavy metal cations.

Little is known of the synthesis of derivatives having a carbonyl group as an additional co-ordinating site. Schwarzenbach[5] reported a monomeric compound, *N*-acetoiminodiacetic acid. Ando[6] synthesized a chelating monomeric agent aminoacetone-*N*,*N*-diacetic acid and explained the increase in the chelate stability by the contribution of the carbonyl co-ordination. No reports have been found on exchange resins containing similar functional groups.

This report describes the synthesis, basic characteristics, and selectivity of some new chelating resins (Fig. 1). Besides the resins based on iminodicarboxylic acids, compounds with a keto group as an extra co-ordinating site were prepared. The reactive carbonyl group permits the preparation of further exchange resins having two or more different complexing groups.

EXPERIMENTAL

Synthesis of resins

Compound I. To 150 g of macroreticular polystyrene–divinylbenzene copolymer (4% DVB)†, previously extracted with chloroform, in 1050 ml of carbon disulphide were added 391 g of anhydrous aluminium chloride. To the stirred mixture 196 g of acetyl chloride were added dropwise over 2 hr. The mixture was stirred for 10 hr at room temperature and finally for 3 hr at 37°. The solid phase was filtered off, washed with acetone, and hydrolysed in concentrated hydrochloric acid and ice. The temperature for hydrolysis was kept below 5° The acetylated copolymer was washed several times with, in succession, hydrochloric acid (1 + 1), water, 0·2*M* sodium hydroxide, water, acetone and ethanol. The slightly yellow product was dried in air.

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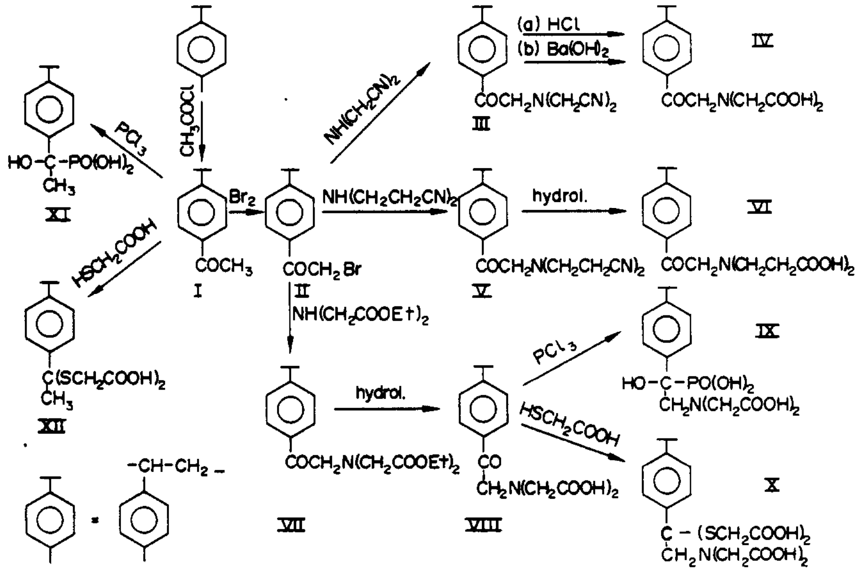

Fig. 1. Diagram of resin synthesis and theoretical formulae.

Compound II. Bromine (110 g) was added dropwise over a period of 2 hr to a stirred suspension of 160 g of acetylated copolymer previously dried over phosphorus pentoxide, in 500 ml of glacial acetic acid. The temperature was kept below 5° with an ice-bath. After the reaction mixture had been stirred for 7 hr the solid phase was filtered off and washed with ice water, acetone and ethyl acetate.

Compound III. To a suspension of 30 g of compound II in 200 ml of *N,N'*-dimethylformamide were added 100 g of iminodiacetonitrile. The mixture was stirred for 8 hr at 90–100°. After cooling, the solid was filtered off and washed with water and acetone.

Resin IV. (*a*) Compound III (15 g) was heated for 5 hr, with stirring, in 150 ml of concentrated hydrochloric acid. (*b*) Compound III (10 g) was hydrolysed in a mixture of 150 ml of water, 100 ml of ethanol and 30 g of barium hydroxide octahydrate for 6 hr at 80–90°. After the hydrolysis step, both products were washed with water, hydrochloric acid (1 + 1), and 0·2*M* sodium hydroxide, and converted into the hydrogen form with 5% hydrochloric acid.

Compound V. To a stirred mixture of 30 g of compound II and 100 ml of boiling ethyl acetate, were added 60 g of iminodipropionitrile in 100 ml of ethyl acetate over a period of 60 min. The mixture was kept at just below boiling point for 15 hr. After cooling, compound V was filtered off.

Resin VI. Compound V was hydrolysed for 5 hr in a mixture of 150 ml of water, 70 g of barium hydroxide and 70 ml of ethanol. After hydrolysis the resin was washed in 1*M* hydrochloric acid, water and 0·5*M* sodium acetate, and converted into the hydrogen form with 1*M* hydrochloric acid. The final product was dried in air. In a similar manner a resin with higher cross-linking (10% DVB) was obtained.

Compound VII. The same procedure as that used for the synthesis of compound V was employed, but instead of iminodipropionitrile, 110 g of iminodiacetic acid dimethyl ester were used.[6] The mixture was kept at just below boiling point for 18 hr.

Resin VIII. The hydrolysis of compound VII was carried out in a similar fashion to that described for resin VI.

Resin IX. Compound VIII (15 g) was dried for 6 days over phosphorus pentoxide. The dry resin was suspended in 100 ml of phosphorus trichloride. After 2 hr (for swelling of the resin), 60 g of glacial acetic acid were added. The mixture was allowed to stand for 6 days with occasional stirring. The solid phase was filtered off and hydrolysed in a mixture of ice and water. After washing with water and 0·2*M* sodium hydroxide, the resin was converted into the hydrogen form and dried in air.

Resin X. Compound VII (10 g, dried over phosphorus pentoxide) was added to a mixture of 190 ml of chloroform and 20 g of anhydrous zinc chloride; 65 g of 85% thioglycollic acid solution were added over a period of 50 min. The mixture was heated under reflux for 8 hr. After cooling, the solid phase was filtered off and washed with acetone, dioxan, and water. After a final washing with 5% acetic acid and water, the resin was dried in air.

Resin XI. This was synthesized from compound I by using phosphorus trichloride as a phosphorylating agent.

Resin XII. This was prepared from compound I by the reaction with thioglycollic acid.

Titration curves

Air-dried resin in the hydrogen form (0·150–0·200 g) was shaken in polyethylene flasks for a period of 7 days with 2*M* potassium chloride solution containing different amounts of 0·10*M* potassium hydroxide at constant ionic strength The total volume of the solution was 20·0 ml.

Determination of distribution coefficients

Distribution studies were performed in 100 ml polyethylene flasks with approximately 0·200 g of air-dried resin in the hydrogen form, and 50 ml of solution containing the metal (2×10^{-2} *N*) as the nitrate, and ammonium acetate (0·25*M*). The pH of the solution was adjusted with hydrochloric acid or ammonia solution. Batches were equilibrated by shaking for 8 days. The pH and metal content in each solution were then determined. The results are expressed as distribution coefficients. *D*:

$$D = \frac{\text{meq of metal/g of dry resin}}{\text{meq of metal/ml of solution}}$$

Breakthrough curves

The dry ion-exchange resin (particle size 0·10–0·16 mm) was soaked in water and packed in glass tubes. Resin columns of about 5 mm dia and 60 mm length were used. Before each experiment the column was washed with 0·2*M* ammonium acetate until the pH of the effluent and wash-solution was identical. Perchloric acid was added to adjust the pH of the wash-solution. A similarly buffered solution containing metal nitrate ($5 \times 10^{-2}N$) and ammonium acetate (0·1*M*) was passed through the column at the rate of 0·25 ml/min. Fractions 1·25 ml in volume were collected for analysis.

Analytical procedures

The content of the elements investigated was determined complexometrically or spectrophotometrically. The nitrogen content in various resins was estimated by the Kjeldahl method The amount of phosphorus was determined gravimetrically as ammonium phosphomolybdate after decomposition of the resins with a mixture of sulphuric acid and perchloric acid. For the sulphur content the resins were fused in a sodium carbonate–sodium nitrate mixture, and the sulphur was determined as barium sulphate. The water content was estimated by drying the exchange resins (hydrogen form) to constant weight at 80° over phosphorus pentoxide.

RESULTS AND DISCUSSION

Synthesis

A summary of all resin syntheses is shown in Fig. 1. The yields were usually 70–90%, but for resins X and XI the yield of the reaction with thioglycollic acid was only about 25%.

The freshly prepared resins are yellow or slightly brown, with the exception of resin XII which is white. The mechanical stability of the resins is very good and their chemical stability varies with the type of resin. With the exception of resins X and XII, all the exchangers are stable in neutral or acidic solution at room temperature. In alkaline solution a slight degradation was observed. In the presence of Cu^{2+} ions at 80°, changes in resin VIII were also observed. This was probably due to a reaction between the carbonyl group and Cu^{2+} ions. No such changes were observed with Ca^{2+} instead of Cu^{2+}.

Resins X and XII, containing sulphur in their functional groups, have lower chemical stability than the other exchangers. In water a slight hydrolysis of the functional groups was observed. When 200 ml of 2*N* sulphuric acid were used for the column washing (10 g of resin X) the sulphur content decreased by approximately 25%. Nevertheless these resins may be used for separations in slightly acidic or neutral solution.

To avoid using elemental bromine for the preparation of compound II, other syntheses were investigated, *e.g.*, by reacting styrene–DVB copolymer with monochloroacetyl chloride, but the yield of resins prepared from the chloro-analogue of compound II was lower than from the bromo-compound II. The exchange capacities of these products were only

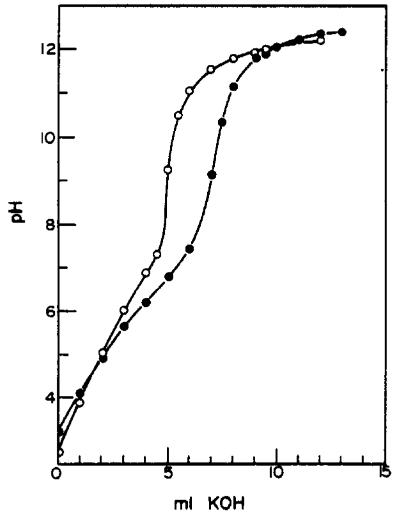

Fig. 2. Titration curves: ● resin VI (×4); ○ resin VI (×10).

about 1·5 meq/g of dry resin. A low exchange capacity was also obtained if iminodiacetonitrile instead of an iminodiacetic acid dimethyl ester was used (resin IV). Resins XI and XII were prepared only for comparison of the titration curves with those of resins IX and X.

The contents of nitrogen, phosphorus and sulphur were lower than the theoretical values of these elements, calculated from structural formulae of the resins.

Titration curves

The titration curves shown in Figs. 2–4 indicate that the synthesized resins are dibasic polyacids. The first inflection point for the curve of resin VI is very indistinct, as are all those for resin X (Fig. 4). The titration curves of these resins (Fig. 4) are affected by the degradation of sulphur-containing groups.

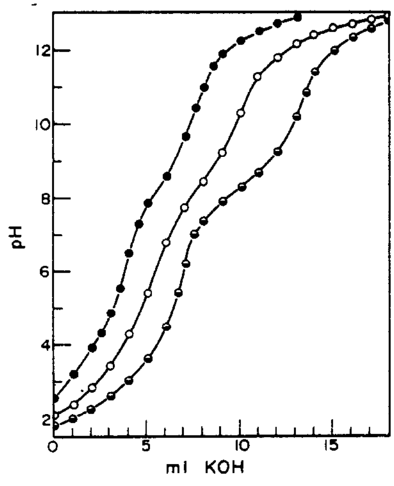

Fig. 3. Titration curves: ● resin VIII; ○ resin IX; ○ resin XI.

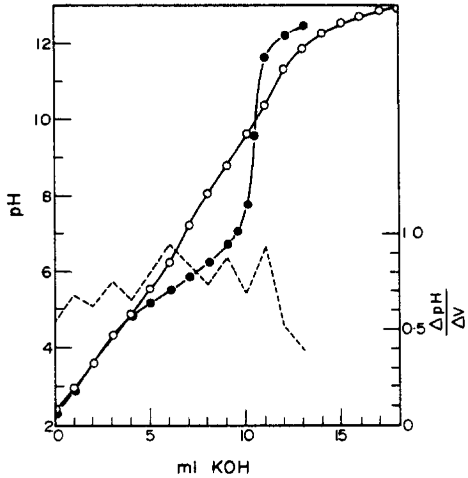

Fig. 4. Titration curves: ○ resin X: ● resin XII. ΔpH/ΔV shown for resin X.

Titration curves for resins VIII and IX are presented in Fig. 3. For comparison of resins with and without phosphonic acid groups, the titration curve for resin XI (containing only phosphonic active groups) is also included in Fig. 3. It is not possible to differentiate the individual dissociation steps of iminodiacetic and phosphonic groups in the curve for resin XI.

Table 1 Characteristic properties of synthetic exchange resins.

Resin no.	N, %	P, %	S, %	Exchange capacity *meq/g* 1st equiv.	2nd equiv.	Apparent dissociation constant pK_1	pK_2
VI [×4]	2·58	—	—	2·00	3·98		>6·6
VI [×10]	2·72	—	—	1·30	2·62		>6·8
VIII	3·03	—	—	2·62	5·26	3·8	8·5
IX	2·44	7·25	—	3·62	7·25	3·1	8·0
X	2·52	—	3·9	—	5·74	3·7	8·5
XI	—	—	—	4·37	8·72	2·6	8·2
XII	—	—	—	—	5·82	—	—

According to the values of the first dissociation constants, all the exchange resins prepared can be classed as medium strength cation-exchangers. Values of their apparent dissociation constants are shown in Table 1. Titration curves of Chelex 100, resin VIII, and resin IX in the presence of metal ions were obtained and are shown in Fig. 5.

The application of selective chelating exchange-resins is limited by the slow exchange-rate of various ions (pH effect). In Fig. 6 are shown the time dependences for the sorption of the cations at several pH values on resin VIII.

The equilibrium sorption of various cations at different pH values is presented in Tables 2–6. Anomalies in the sorption of Cu^{2+} ions have been noted; the *D* values found were too low and did not correspond to those which were obtained from dynamic experiments.

For transition elements, lower *D* values were generally found at higher pH values (probably because of the formation of amine complexes).

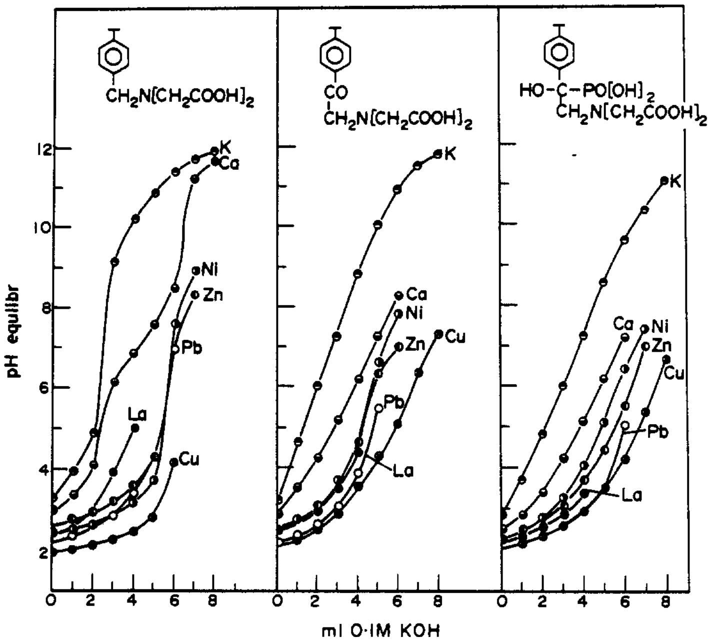

Fig. 5. Titration curves of Chelex 100, resin VIII and resin IX in the presence of metal ions.

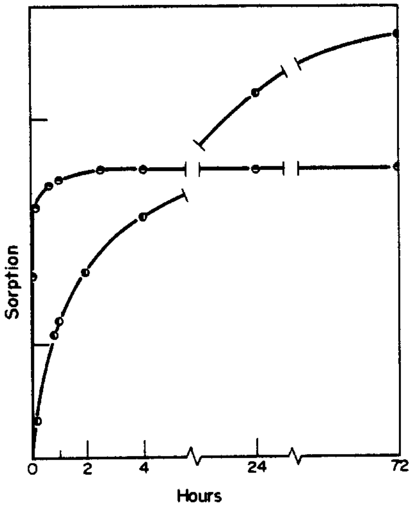

Fig. 6. Rate of exchange of calcium and thorium ions on resin VIII.
● Ca^{2+} at pH 5·0; ◐ Th^{4+} at pH 2·5; 0·1*M* ammonium acetate as support electrolyte.

Selectivity

On the basis of equilibrium batch experiments it is possible to show a qualitative order of selectivity of the exchangers.

Resin VI (× 4), pH 3·0: Th > U(VI) > Pb > La > Zn > Ni > Co > Ca > Sr > Mg.
Resin VI (× 10), pH 3·0: U(VI) > Th > Pb > La > Ni > Co > Ca > Sr > Mg.

Resin VIII. pH 3·0: Th > Pb > Ni > U(VI) > Ca > Zn > Dc > Co > Ca > Sr > Mg.
Resin IX. pH 3·0: Th ≫ U(VI) > Pb > Fe(III) > La > Zn > Ni >
Co > Cd > Ca > Sr > Mg.
Resin X. pH 3·0: Th > Zn > (Cu).

The data in Tables 2 and 3 indicate the influence of the cross-linking of the resin matrix on the order of selectivity for Th, U and Pb. The great differences of selectivity for thorium and uranyl ions on resin IX and resin VIII are the result of the presence of —$PO(OH)_2$ groups in resin IX. With increasing pH, the differences in selectivity values generally decrease, but all resins showed increases in the selectivity for Zn^{2+} ions, with a maximum at pH 6·5–8·0, depending on the nature of the resin.

The pH-dependence of the breakthrough curves of various ions was studied for only two resins. Their selection was based on the results as shown in Fig. 7 and 8.

Table 2. pH-dependence of the distribution coefficient *D* of several metal ions on resin VI. (4% DVB. 0·25*M* ammonium acetate as support electrolyte)

Ion \ Equilibrium pH	1·5	2·0	2·5	3·0	3·5	4·0	5·0	6·0	7·0	8·0	8·5
Th(IV)	110	168	207	250	318	403	600				
Cu(II)	3	13	30	76	148	215	380	723		882	830
Pb(II)		5	50	100	162	219	355				
U(VI)	28	56	126	204	233	208	238				
Cd(II)				2	20	60	157	300	492	608	405
Zn(II)				16	50	93	197	328	526	632	540
La(III)	5	33	47	85	142	215	381	475			
Co(II)				2	20	47	87	116	140	170	175
Ni(II)				5	28	52	93	123	140	150	145
Ca(II)				1	5	33	74	103	129	132	134
Sr(II)					1	18	62	96	118	124	125
Mg(II)						1	47	83	106	112	114
Fe(III)	125	100	95								

Table 3. pH-dependence of the distribution coefficient *D* of several metal ions on resin VI. (10% DVB. 0·25*M* ammonium acetate as support electrolyte)

Ion \ Equilibrium pH	1·5	2·0	2·5	3·0	3·5	4·0	5·0	6·0	7·0	8·0	8·5
Th(IV)	44	55	60	66	70	75					
Cu(II)		1	37	74	107	135	212	335		455	305
Pb(II)		2	35	60	83	98	117	125			
U(VI)		2	25	93	110	116					
Cd(II)			5	7	30	55	136	178	217	237	228
Zn(II)					50	75	158	177	233	258	270
La(III)			25	55	82	105	157	234			
Co(II)			2·5	13	25	42	75	92	106	133	150
Ni(II)			2·5	15	28	47	78	95	106	113	111
Ca(II)			1	11	21	33	60	85	103	112	113
Sr(II)				1	11	21	48	73	93	102	104
Mg(II)					1	5	35	65	87	97	98

Table 4. pH-dependence of the distribution coefficient *D* of several metal ions on resin VIII. (0·25*M* ammonium acetate as support electrolyte)

Ion \ Equilibrium pH	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0	7·5	8·0	8·5	9·0
Th(IV)	370	600	958	1350	1650	2020										
Pb(II)	190	490	850	1275	1418	1490	1525									
U(VI)	95	187	265	310	330	312	265									
La(III)	10	55	155	275	415	620	920									
Fe(III)	10	25	35	45												
Ni(II)		80	225	360	478	570	653	728	783	826	840	803	660	555	515	
Cu(II)		60	105	142	150	155	160	160	155	128						
Zn(II)		5	110	270	450	620	730	795	850	950		1270	1185	1020	750	400
Cd(II)			55	200	340	530	730	850	985	1050	1085	1115		1020		
Co(II)			65	200	253	500	580	605	575	540	518	505	500	496	493	
Ca(II)				10	66	115	165	250	400	485	572	660	745	827	890	895
Sr(II)					40	72	110	165	255	392	422	628	700	745	760	775
Mg(II)					25	50	75	100	130	170	235	315	410	510	545	553

Table 5. pH-dependence of the distribution coefficient *D* of several metal ions on resin IX. (0·25*M* ammonium acetate as support electrolyte)

Ion \ Equilibrium pH	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0	7·5	8·0	8·5
Th(IV)	1100	3250	9880	18,200	21,150										
U(VI)	340	620	1100	1700	2120	1600	1215								
Fe(III)	200	320	630	1020											
La(III)		230	450	910	1350	2200	3300	5000							
Pb(II)		210	700	1320	1900	2230									
Cu(II)		120	170	260	320	350	420	470	560	620	640	660			
Zn(II)		80	210	390	655	930	1200	1560	2100	3620	6200				
Cd(II)		5	50	110	170	250	365	370	620	750	955	1160	1380	1635	1880
Ni(II)			205	305	405	505	590	660	710	755	800	840	880	910	970
Co(II)			90	200	300	400	480	540	560	620	815	1080	1385	1735	2250
Ca(II)			40	80	145	210	290	420	500	670	900	1200	1550	1920	2300
Sr(II)			20	60	100	140	180	220	280	360	470	600	740	885	1050
Mg(II)			5	30	55	80	105	130	160	195	230	280	330	400	500

Table 6. pH-dependence of the distribution coefficient *D* of several metal ions of resin X. (0·25*M* ammonium acetate as support electrolyte)

Ion \ Equilibrium pH	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0	7·5	8·0	8·5
Th(IV)	260	310	390	540	875	1330									
Cu(II)	45	65	80	120	165	215	245	250	250	250	250	250	250	225	170
Zn(II)		10	65	145	220	300	375	450	530	610	685	760	760	660	570

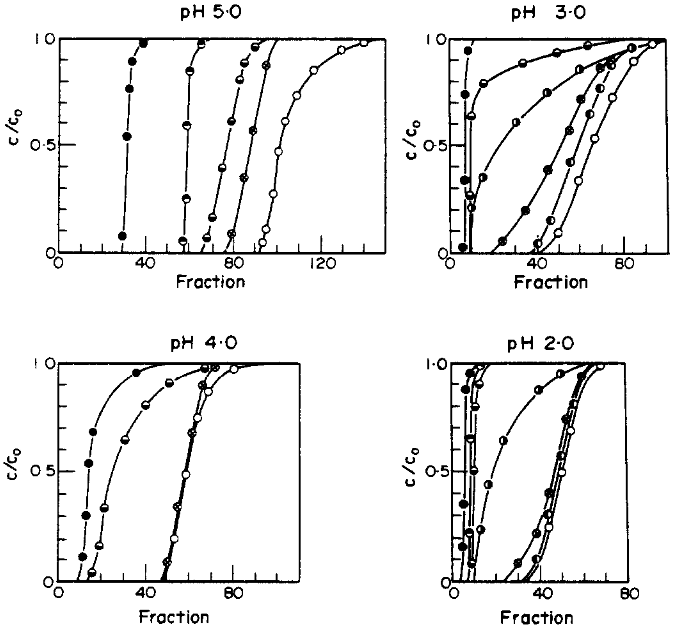

Fig. 7. pH-dependence of breakthrough curves of various ions on resin VIII, with 0·1*M* ammonium acetate as support electrolyte.
○ Cu^{2+}, ● Mg^{2+}, ⊖ Ca^{2+}, ⊗ Pb^{2+}, ◒ Zn^{2+}, ◑ La^{3+}, ◐ Th^{4+}

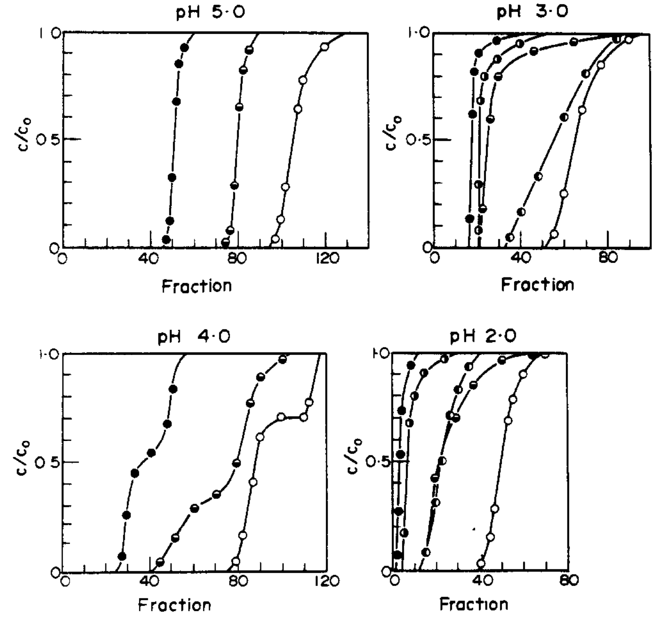

Fig. 8. pH-dependence of breakthrough curves of various ions on resin IX, with 0·1*M* ammonium acetate as a support electrolyte.
○ Cu^{2+}, ● Mg^{2+}, ⊖ Ca^{2+}, ◒ Zn^{2+}, ◑ La^{3+}, ◐ Th^{4+}

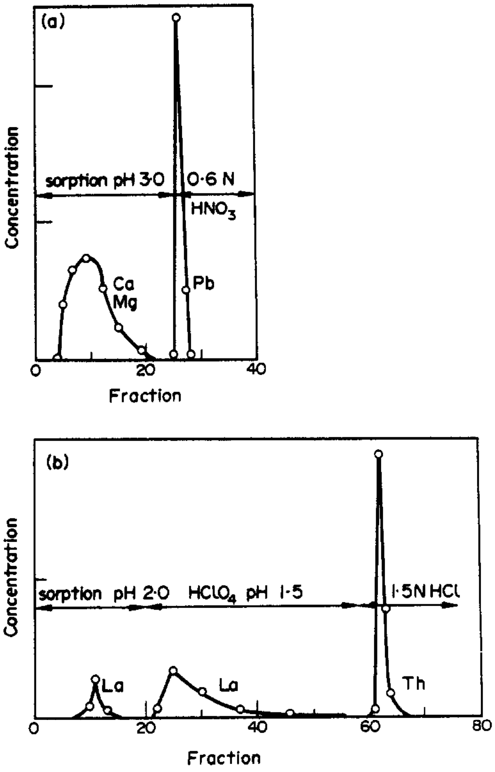

Fig. 9. Separation of binary mixtures on resin VIII.
A: Ca + Mg from Pb; *B*: La from Th. Column 0·5 × 15 cm, flow-rate 0·5 ml/min. Column preconditioned with 0·1*M* ammonium acetate at pH 3·0.

The selectivity of both resins decreases in the order Cu > Th > La > Zn > Ca > Mg. The difference in selectivity at various pH values for different ions was utilized for the separation of some binary mixtures of ions. The conditions for sorption were chosen such that only one type of ion was quantitatively sorbed, other ions being sorbed slightly or not at all.

Separation of mixtures

The optimum pH range for separation of different mixtures was found to be 2·0–3·0. Under these conditions, Ca^{2+}, Mg^{2+} and Sr^{2+} passed quantitatively through the column, Zn^{2+} and La^{3+} ions being partly sorbed. For their elution hydrochloric or perchloric acid at pH 1·5–1·8 was used. If thorium was separated on resin IX the last traces were removed from the resin with a 1–2% solution of ammonium carbonate. Other elements sorbed (Cu^{2+}, Pb^{2+}) were sharply eluted with 1·0–1·5*M* hydrochloric or perchloric acid.

The data in Tables 2–6 give a great deal of information for possible separation of metal ions in mixtures. For instance, magnesium may be separated from calcium and strontium with resins VI, VIII, and X at certain pH values based on their separation factors. Some results of separations of various binary mixtures are presented in Fig. 9 and Table 7.

Table 7. Separation of mixtures.

Resin	Metal	Taken, *mg*	Found, *mg*	Error, *mg*
VIII	Th	11·53	11·50	−0·03
	Mg	2·50	2·50	0·00
VIII	Cu	6·46	6·44	−0·02
	Mg	2·50	2·50	0·00
IX	Cu	6·46	6·42	−0·04
	Mg	2·50	2·50	0·00
VIII	Cu	6·46	6·50	+0·02
	La	9·47	9·38	−0·09
VIII	Pb	21·14	21·60	+0·46
	Ca	4·06	4·00	−0·06
VIII	Pb	21·20	21·45	+0·25
	Mg + Ca	6·43	6·43	0·00
VIII	Pb	21·20	21·10	−0·10
	Zn	6·62	6·63	+0·01
VIII	Th	11·46	11·33	−0·13
	La	9·27	9·31	+0·04
VI	Cu	6·46	6·40	−0·06
	Mg	2·50	2·50	0·00
IX	Th	22·50	22·01	−0·49
	Ca, Mg, Sr	52·31	52·35	+0·04
VIII	Cu	12·92	12·88	−0·16
	Co	2·50	2·52	+0·02
VIII	Na 250 ml of 1*M* NaNO$_3$			
	Cu	3·22	3·19	−0·03

Separations were carried out at pH 3·0 or pH 2·0.

Table 8. Swelling properties of resins in water and hydrochloric acid.

Ion	Resin VIII, *ml/g*	Resin IX, *ml/g*	Swelling *medium*
Na^{+}	2·18	2·40	water
Ca^{2+}	2·06	2·06	water
Mg^{2+}	2·18	2·13	water
Sr^{2+}	2·03	2·06	water
Zn^{2+}	2·06	1·98	water
Ca^{2+}	2·00	2·00	water
Co^{2+}	2·05	2·06	water
Ni^{2+}	2·06	2·08	water
La^{2+}	2·01	2·00	water
UO$_2^{2+}$	1·98	1·96	water
Cu^{2+}	1·98	1·96	water
Pb^{2+}	1·98	1·94	water
Th^{4+}	2·00	1·90	water
H^{+}	1·95	1·90	water
H^{+} (control)	1·95	1·91	water
H^{+}	1·93	1·90	0·1*M* HCl
H^{+}	1·98	1·95	1·0*M* HCl
H^{+}	2·03	2·01	6·0*M* HCl
Water regain			
H^{+}	0·375	0·403	water

Swelling properties of the resins in water and hydrochloric acid

It is known that chelating resins such as Chelex 100 tend to swell considerably when complexed by multivalent metal ions, and the swelling properties of these new chelating resins were investigated both in water and in hydrochloric acid media.

Approximately 0·300 g of air-dried resin in the H^+ form was placed in water for 24 hr. The resin was then converted into the desired ionic form by an exchange reaction with a 0·1–0·15*M* solution of the appropriate metal nitrate in 0·15*M* ammonium acetate adjusted to pH 6·0. For La^{3+}, Co^{2+}, Pb^{2+}, and Th^{4+}, and pH was adjusted to 4·5–5·0. Approximately 80% of the resin capacity was converted into the desired ionic form; it is difficult to obtain 100%, conversion, because of hydrolysis. After rinsing with water, the resin was transferred to a 1·0-ml cylinder (readable to 0·01 ml) and gently tapped until no further packing could be detected. The results are shown in Table 8.

Generally the swelling volumes are in good agreement with the selectivity series of these resins. The ion for which the functional groups have lowest selectivity (Mg^{2+}) gives the highest swelling volume.

Usually the swelling volume of resins in the H^+ form in different concentrations of hydrochloric acid decreases with increasing acid concentration. The present results show the opposite trend. With Dowex A-1 as a reference resin, resins VIII and IX were treated in various hydrochloric acid solutions. It may be concluded that the two resins showed 5% swelling or less for most ions except Na^+ and Mg^{2+}.

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Zusammenfassung—Eine Reihe von Ionenaustauschharzen, die $—COCH_2N[(CH_2)_mCOOH_2]_2$-Gruppen enthalten, wurde hergestellt. Weitere analoge Verbindungen wurden durch Umsetzung der Carbonylgruppe mit Phosphortrichlorid oder Thioglykolsäure gewonnen. Die Eigenschaften dieser Harze und ihre Selektivität für verschiedene Metallionen wurden ebenfalls untersucht.

Résumé—On a synthétisé une série de résines échangeuses d'ions contenant des groupes $—COCH_2N[(CH_2)^mCOOH]_2$. On a préparé des analogues supplémentaires au moyen de la réaction du groupe carbonyle avec le trichlorure de phosphore ou l'acide thioglycolique. On a aussi étudié les propriétés de ces résines et la sélectivité pour différents ions métalliques.

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COMPLEXATION REACTIONS OF PYRIDINOLS

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Summary—Complexation of iron(III) with several pyridinols has been studied and used in selective detection and determination (spectrophotometric and chelatometric) of the metal. Iron(III)-pyridinol complexes are also used as indicators in acid-base titrations. A thiol group vicinal to a phenol group in a pyridine molecule provides a reagent that is a suitable ligand for palladium(II) determination. Stability constants of bivalent metal complexes with pyridinols have been determined potentiometrically.

Sommer and Bartušek[1] have reviewed the extensive work on metal complexes with hydroxy derivatives of benzene. It was thought of interest to study the chelating capabilities of similar co-ordinating centres on heterocyclic analogues of benzene. The presence of the heterocyclic nitrogen atom considerably affects the co-ordinating characteristics of the substituents and the properties of the resulting metal complexes. Several pyridinols (Table 1) were therefore examined and this communication reports the complexing abilities of these compounds and reviews the earlier work.

Table 1.

Pyridinol	Source	λ_{max}, *nm*	ϵ, *l.mole*$^{-1}$.*cm*$^{-1}$
2,3-Dihydroxypyridine (DHP)	Aldrich Chemical Co., U.S.A.	240; 298	$4{\cdot}4 \times 10^3$; $7{\cdot}5 \times 10^3$
2-Amino-3-hydroxypyridine (AHP)	Aldrich Chemical Co., U.S.A.	235; 300	$5{\cdot}8 \times 10^3$; $6{\cdot}6 \times 10^3$
5-Chloro-2,3-pyridinediol (CPD)	K & K Laboratories, U.S.A.	245; 305	$4{\cdot}4 \times 10^3$; $6{\cdot}1 \times 10^3$
3-Hydroxypyridine-2-thiol (HPT)	Fluka AG, Switzerland	275; 360	$9{\cdot}1 \times 10^3$; $1{\cdot}1 \times 10^3$
6-Methyl-2-hydroxypyridine-3-carboxylic acid (MPC)	K & K Laboratories, U.S.A.	235; 315	$6{\cdot}7 \times 10^3$; $9{\cdot}6 \times 10^3$
3-Hydroxypyridine-2-carboxylic acid (HPC)	Fluka AG, Switzerland	230; 300	$5{\cdot}6 \times 10^3$; $7{\cdot}2 \times 10^3$
3-Hydroxy-2-picolinamide (HPA)	Fluka AG, Switzerland	220; 300	$7{\cdot}6 \times 10^3$; $7{\cdot}4 \times 10^3$

2,3-*Dihydroxypyridine* (*DHP*)

This reagent was first applied to spectrophotometric determination of iron(III) by Katyal *et al.*[2] Later, more systematic studies of the ligand[3] and its complexing ability were reported by several workers.[4–7] The reagent was also used in chelatometric determination of iron.[8] The reagent is now used for chelatometric determination of vanadium, and its iron-complex in acid–base titrations, as described below.

Take an aliquot of vanadium(IV) solution containing 0·5–2·5 mg of the metal, add 10 ml of sodium acetate–hydrochloric acid buffer so that the pH is between 3·6 and 4·6, add about 4 ml of 1% DHP solution (in ethanol) and dilute to about 25 ml. Allow 5–10 min for full development of the reddish-brown colour, then titrate slowly with 0·01*M* EDTA added from a microburette. The disappearance of the colour shows the end-point.

Tolerances for other ions (in terms of w/w ratio to vanadium) are: CN^-, NO_3^-, Cl^-, Br^-, I^-, SO_4^{2-}, citrate, tartrate, BO_3^{3-} and Mg^{2+} (100-fold); IO_3^- (80-fold); Ca^{2+}, Sr^{2+} and Ba^{2+} (10-fold); Al^{3+} and Sn^{4+} (6-fold); Cu^{2+} and Ni^{2+} (5-fold if masked with CN^-). NO_2^-, $C_2O_4^{2-}$, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+} and Co^{2+} interfere.

DHP forms two stable complexes[2] with iron(III), a blue 1:1 complex up to pH 2·0 and a red 2:1 (DHP:iron) complex at pH >3·5. The colour change can be used for end-point indication in titrations of strong acid *vs.* strong base. Mix 2·5 ml of ferric perchlorate solution (iron 1 mg/ml) with 25 ml of 1% DHP solution (in ethanol). Adjust the pH to 7·0, without increasing the volume to >30 ml.

To 10·0 ml of ~ 0·1*M* strong acid add 0·5 ml of indicator; a deep blue colour develops instantly. Titrate with standard sodium or potassium hydroxide solution to the appearance of a red colour. The end-point is sharp, and reproducible within ±0·2%. The titrations can be done in the reverse direction. The apparent indicator constant, pK_i, is 2·3, which limits use of the indicator to titration of acids (or bases) that are ⩾0·1*N*. The indicator solution is stable for several weeks.

Filter paper impregnated with DHP can be used to detect iron(III). Whatman No. 1 paper is soaked for 1 hr in 1% DHP solution (in methanol), then dried at room temperature and cut into strips. A drop of acidified test solution (~ 2*M* in hydrochloric acid) is placed on the paper. Appearance of a blue spot which turns red on addition of 2 drops of 1*M* sodium hydroxide indicates iron is present. The minimum detectable concentration is 0·2 μg per drop. Amounts of foreign ions (in μg/ml) which do not interfere are: 10000 of CH_3COO^-, Cl^-, Br^-, I^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, As^{3+}, Bi^{3+}, Cr^{3+}, Mn^{2+}, Co^{2+} and Ni^{2+}; 5000 of citrate; 4000 of Pd^{2+}; 1000 of F^-, S^{2-}, NO_2^-, $S_2O_3^{2-}$, $C_2O_4^{2-}$, PO_4^{3-}, Li^+, Cu^{2+}, Tl^+, Sn^{4+}, Sb^{3+}, Ta^{5+}, Mo^{6+}, W^{6+}, Ru^{3+}, Os^{8+}, Ir^{3+} and Pt^{4+}; 500 of Th^{4+} and UO_2^{2+}; 200 of Be^{2+} and Nd^{3+}; 100 of Ga^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+} and V^{5+}.

2-*Amino*-3-*hydroxypyridine* (*AHP*)

AHP reacts similarly to DHP with iron(III) but the complexes are not very stable and the absorbance varies with time. Stability constants of bivalent metals with AHP, in aqueous and in 50% dioxan medium, have been reported. The order of stability is UO_2 > Cu > Be > Pb > Zn > Ni > Co > Mn.

AHP forms a violet-red 1:1 complex (λ_{max} 510–525 nm; ϵ 4·46 × 10^3 $l.mole^{-1}.cm^{-1}$) with ruthenium(III), which can be used for selective determination of the metal.[10]

5-*Chloro*-2,3-*pyridinediol* (*CPD*)

Addition of a few drops of an ethanolic solution of CPD to an acidic ferric solution results in a blue complex which changes to red at higher pH (boric acid–sodium hydroxide buffer). The characteristics of the two complexes are summarized in Table 2. The amounts of foreign ions (μg/ml) tolerated in estimation of 2·5 μg of iron per ml in 0·1*M* perchloric acid medium are: 500 of CH_3COO^-, NO_2^-, NO_3^-, Cl^-, Br^-, SO_4^{2-}, citrate, tartrate or BO_3^{3-}; 250 of Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Bi^{3+} or Mn^{2+}; 150 of Cu^{2+}, UO_2^{2+}, Co^{2+} or Ni^{2+}; 50 of Th^{4+}, As^{3+}, Sb^{3+} or Sn^{4+}; 20 of PO_4^{3-} or Pd^{2+}; 10 of F^-, $C_2O_4^{2-}$ or Zr^{4+}. I^-, IO_3^-, $S_2O_3^{2-}$, EDTA, Cr^{3+} and Mo^{6+} interfere. The red complex gives a rather more selective and sensitive determination of iron. The amounts

Table 2 Characteristics of iron(III) complexes

Characteristic	Pyridinol CPD	 CPD	 HPC	 HPA
Colour	Blue	Red	Yellow	Red
λ_{max}, *nm*	560	515	390–405	480–500
ε, *l mole*$^{-1}$ *cm*$^{-1}$	$2·5 \times 10^3$	$5·4 \times 10^3$	$3·7 \times 10^3$	$1·6 \times 10^3$
pH for formation	From 1*M* $HClO_4$ to pH 2·5	3–11	3·5–5·0	0·8
Medium	50% ethanol and 0·1*M* $HClO_4$	50% ethanol and pH ~ 9	Aqueous and pH ~ 4	50% ethanol and pH 1·5–3·0
Composition (iron:pyridinol)	1:1	1:2	1:1	1:1
Beer's-law range (iron concn., *μg/ml*)	Up to 10	Up to 5·6	Up to 7·9	Up to 11·5
Accurate range of determination, *μg/ml*	2·2–7·2	1·7–5·0	—	—
Molar excess of pyridinol needed for full colour development	12-fold	6-fold	10-fold	20-fold
Std. devn. from 10 observations (iron concn. in *ppm*; mean absorbance)	0·002 (2·78; 0·125)	0·003 (2·78; 0·260)	0·002 (4·14; 0·285)	0·001 (5·58; 0·160)
Apparent stability constant at 25°C	$4·8 \times 10^3$	$2·4 \times 10^8$	$8·0 \times 10^3$	$1·7 \times 10^4$

of foreign ions (μg/ml) tolerated in estimation of 2·5 μg of iron per ml at pH 9 are: 500 of CH_3COO^-, NO_2^-, NO_3^-, Cl^-, Br^-, I^-, IO_3^-, SO_4^{2-}, tartrate, Sr^{2+} or Ba^{2+}; 250 of $S_2O_3^{2-}$, PO_4^{3-}, Ag^+ or Ca^{2+}; 200 of Al^{3+}, As^{3+}, Sb^{3+} or Sn^{4+}; 100 of citrate, Pb^{2+} or Mn^{2+}; 50 of F^-, Zn^{2+}, Hg^{2+}, Th^{4+}, Bi^{3+}, Mo^{6+}, Co^{2+}, Ni^{2+} or Pd^{2+}; 25 of $C_2O_4^{2-}$, Cu^{2+} or Zr^{4+}. The presence of EDTA, Cr^{3+} or UO_2^{2+} interferes.

Both iron(III)–CPD complexes are easily decomposed by EDTA; this fact is utilized in chelatometric determination of iron at pH 1·4–3·2.

Adjust the pH of the iron solution (1–10 mg of iron) to 1·4–3·2 with hydrochloric acid or sodium acetate–hydrochloric acid buffer. Add 0·4–0·8 ml of CPD solution (0·004*M* in ethanol), dilute to about 20 ml, and titrate slowly with 0·01*M* EDTA until the blue (pH below 3·0) or red (pH above 3·0) colour completely disappears. When the amount of iron in the original solution exceeds 3·0 mg, the end-point is given by the appearance of the pronounced yellow colour of the iron(III)–EDTA complex. The effect of various ions on the determination of iron in the pH range 2·0–2·8 is shown in Table 3.

The iron(III)–CPD system, used as an acid–base indicator, has a $pK_1 = 2·8$, and is less stable than the DHP indicator.

The stability constants of complexes formed by CPD with bivalent metals were determined in 50% dioxan medium, the method of Bjerrum and Calvin as modified by Irving and Rossotti[11] being used to obtain values of $\bar{n}$ and pL which were plotted to obtain the formation curves. K_1 and K_2 were calculated by the correction-term method of Irving and Rossotti.[12] Table 4 gives the results, in order of decreasing stability. From the log K_1 values of complexes formed by metal ions having $3d^5$–$3d^9$ configurations, the δH values were calculated (Table 4) according to the method described by George and McClure.[13]

3-*Hydroxypyridine-2-thiol* (*HPT*)

HPT reacts with iron(III), forming three complexes—green (up to pH 3·0), blue (pH 3·0–11·0) and red (pH > 11·0). The green complex contains the reactants in 1:1 molar ratio[14]

Table 3. Effect of various ions on determination of 1·117 mg of iron(III) (≡ 2·00 ml of 0·01*M* EDTA), with CPD as indicator

Foreign ion added	Amount of foreign ion added, *mg*	Vol. of 0·01*M* EDTA soln. used, *ml*	Masking agent
Cl^-, Br^-, $SO_4{}^{2-}$	100	2·00	—
Thiourea	60	2·00	—
Citrate, tartrate, $BO_3{}^{3-}$	20	2·00	—
F^-, IO_3^-	10	2·00 ± 0·01	—
$PO_4{}^{3-}$	7	2·00	—
$S_2O_3{}^{2-}$	5	2·01	—
$C_2O_4{}^{2-}$	4	1·98	—
SCN^-	3	2·01	—
Bi^{3+}	10	2·00	Chloride
Th^{4+}	10	2·00	Citrate
Mo^{6+}, W^{6+}	5	2·00	Tartrate
ZrO^{2+}	5	2·01	Tartrate
Al^{3+}	5	2·00	Acetate
Cd^{2+}, Hg^{2+}	5	2·00	Citrate
Ti^{4+}	4	2·01	Tartrate and fluoride
Cu^{2+}	4	2·01	Thiourea
Sb^{3+}	3	2·01	Tartrate
Zn^{2+}	2	2·02	Tartrate
Pb^{2+}, Co^{2+}, Mn^{2+}	2	2·00 ± 0·01	Acetate

Iodide and Ni^{2+} interfere at all concentration levels.

up to pH 1·0, and 1:2 (iron:HPT) at higher pH. The characteristics of the complexes and their use in spectrophotometric and chelatometric determination of iron(III) have been described.[14,15] The complexation of Pd^{2+} with the ligand is now reported.

HPT forms a yellow 1:1 complex with Pd^{2+} (λ_{max} 410 nm; $4{\cdot}5 \times 10^3$ l.mole^{-1}.cm^{-1}) in acid medium. The complex was studied in 50% aqueous methanol medium. The absorbance is maximal and constant in 0·25–2·0*M* hydrochloric acid medium. A 5-fold molar excess of the reagent is sufficient for full colour development; larger ratios do not affect the colour. Between 4·2 and 12·6 μg of Pd^{2+} per ml can be accurately determined. The procedure is as follows. To a suitable aliquot of Pd^{2+} solution in a 10-ml volumetric flask, add 2·5 ml of 0·01*M* HPT (in methanol), followed by sufficient hydrochloric acid to make its final concentration about 1*M*. Dilute with methanol and water to make the solution 50% (v/v) methanol. Measure the absorbance at 410 nm against a reagent blank. The standard deviation of the method is 0·002 (mean absorbance 0·435 for Pd concentration 10·6 μg/ml).

The tolerance limits for various ions (μg/ml) in determination of 5·0 μg of Pd^{2+} per ml are: Cl^-, NO_3^-, $SO_3{}^{2-}$, $SO_4{}^{2-}$ (750); F^-, Br^-, tartrate, $BO_3{}^{3-}$, $PO_4{}^{3-}$ (650); Zn^{2+}, Cd^{2+}, Al^{3+}, Pb^{2+} (500); citrate, As^{3+}, Sn^{2+} (300); SCN^-, $C_2O_4{}^{2-}$, Ag^+ (250); $UO_2{}^{2+}$, Th^{4+}, Ce^{4+} (125); Hg^{2+}, Zr^{4+}, Mn^{2+}, Ni^{2+} (50); Cu^{2+}, Co^{2+} (35); IO_3^- (20); Rh^{3+}, Ir^{3+} (7). Thiourea, $S_2O_3^{2-}$, EDTA, Bi^{3+}, Cr^{3+}, Mo^{6+}, Ru^{3+}, Os^{8+} and Pt^{4+} interfere.

The method compares favourably with others using thiols, *e.g.*, Bismuthiol I and Bismuthiol II.[16] The Pd^{2+}–HPT complex is stable. The Sandell sensitivity is fairly good (0·024 μg/cm^2 for 0·001 absorbance).

Stability constants and δH values for some bivalent metal complexes of HPT were determined potentiometrically in 50% aqueous dioxan (Table 4).

Table 4. Stability constants of bivalent metal complexes and thermodynamic stabilization energy (δH) of the transition metal complexes with pyridinols

	CPD			HPT			MPC	HPC		
Cation	log K_1	log K_2	δH	log K_1	log K_2	δH	δH	log K_1	log K_2	δH
$UO_2{}^{2+}$	7·94	7·32	—	—	—	—	—	—	—	—
Cu^{2+}	7·62	7·01	26	8·42	7·84	27	25	5·25	5·02	25
Zn^{2+}	6·65	6·02	—	8·06	7·66	—	—	5·08	4·88	—
Fe^{2+}	6·52	5·89	18	7·80	7·28	19	17	5·02	4·46	18
Ni^{2+}	6·01	4·98	33	7·66	6·98	35	32	4·60	3·82	33
Co^{2+}	5·82	4·66	24	7·01	6·31	25	23	4·40	3·32	24
Cd^{2+}	5·62	4·58	—	6·86	5·98	—	—	—	—	—
Mn^{2+}	5·32	—	—	5·60	—	—	—	3·91	2·84	—
Mg^{2+}	4·52	—	—	5·32	—	—	—	—	—	—

6-*Methyl-2-hydroxypyridine-3-carboxylic acid* (*MPC*)

The spectrophotometric study of iron(III) complexation with MPC and stability constants of bivalent metal complexes with the ligand have already been reported.[17] From reported log K_1 values the δH values have been calculated (Table 4).

3-*Hydroxypyridine-2-carboxylic acid* (*HPC*)

The characteristics of the iron(III) complex with HPC in aqueous medium are summarized in Table 2. The procedure for iron(III) determination is as follows.

To an iron(III) solution containing 16–77 μg of the metal add 5·0 ml of 0·01*M* HPC (in water). Adjust the pH to ~ 4·0 with perchloric acid and sodium hydroxide solution and dilute to 10·0 ml in a standard flask. Measure the absorbance at 400 nm against a reagent blank.

The tolerances for other ions (μg/ml) in determination of 2·8 μg of iron per ml are: Cl^-, Br^-, NO_2^-, NO_3^-, CH_3COO^-, $SO_4{}^{2-}$, citrate, tartrate, $BO_3{}^{3-}$, Pb^{2+} (500); $PO_4{}^{3-}$, Ag^+, Cd^{2+}, As^{3+} (400); Zn^{2+} (350); thiourea (300); Al^{3+}, Sn^{4+} (250); Bi^{3+}, Ni^{2+} (200); Co^{2+} (150); Th^{4+}, Ce^{4+} (125); I^-, Hg^{2+}, $UO_2{}^{2+}$ (100); F^-, Mn^{2+} (50); Mo^{6+} (40); $S_2O_3{}^{2-}$, Ga^{3+} (35); Pd^{2+} (4, after masking with citrate). Ag^+, Ga^{3+}, Sn^{4+} and Bi^{3+} give a precipitate which can be separated by centrifuging before measurement of the absorbance. SCN^-, EDTA, Cu^{2+} and Cr^{3+} interfere seriously.

Some stability constants and δH values are given in Table 4.

3-*Hydroxy-2-picolinamide* (*HPA*)

The characteristics of the iron(III)–HPA complex are given in Table 2. The procedure for the determination of iron is as follows. To a suitable aliquot containing between 20 and 100 μg of iron(III), add 2·5 ml of 0·02*M* HPA (in ethanol). Adjust the pH to ~ 2·0 with dilute perchloric acid and sodium hydroxide solution, dilute to 10·0 ml in a standard flask, making the ethanol concentration 50% v/v. Read the absorbance at 480–500 nm against a reagent blank.

In determination of 5·6 μg of iron per ml, the tolerance limits for various ions are: Cl^-, Br^-, NO_2^-, NO_3^-, CH_3COO^-, SO_4^{2-}, BO_3^{3-}, Pb^{2+} (500); Zn^{2+}, Al^{3+}, Th^{4+} (400); Hg^{2+} (250); thiourea (200); Ce^{4+}, $UO_2{}^{2+}$ (130); Mo^{6+} (100); tartrate, Ag^+, Cd^{2+}, Ga^{3+}, Sn^{4+}, Mn^{2+}, Pd^{2+} (50); Co^{2+}, Ni^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}, Pt^{4+} (25–30).

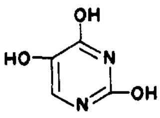
DISCUSSION

In the iron(III)-HPA complex (involving an amide group and a hydroxy group in positions 2 and 3 respectively), a six-membered ring is formed and the molar absorptivity is lower than that of the iron(III) complexes with DHP, AHP, CPD or HPT (all forming five-membered chelates).

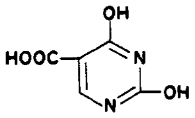
When the hydroxy group is in the 2-position the ligand behaves as a lactam tautomer at low pH and the resulting iron(III)-complex is yellow, as seen in the case of MPC. On the other hand, although the hydroxy group is in the 3-position in HPC, the iron(III)-complex is yellow because the chelation involves co-ordination of the heterocyclic nitrogen atom and the carboxyl group in the 2-position.

Thus to develop heterocyclic phenolic compounds as sensitive reagents giving intense colours with iron(III), it is essential to have the hydroxy group in the 3-position along with a suitable co-ordinating group in the 2-position which would form a five-membered chelate rather than a six-membered one. These observations were later applied in developing the use of pyrimidinols[18] as selective and sensitive reagents for iron(III). The pyridine molecule (I) contains two ring nitrogen atoms separated by one carbon atom. Each nitrogen atom reinforces the electronic effect of the other on the 2- and 4-positions. As the hydroxy group at the 5-position is affected only by the inductive effect of the two nitrogen atoms, it will resemble the 3-hydroxy group in the pyridine molecule. Thus the mode of reactivity of 2,4,5-trihydroxypyrimidine (II) towards iron(III)[18] was found to be similar to that of DHP. Also, the compound

(I)



(II)



(III)

2,4-dihydroxypyrimidine-5-carboxylic acid (III) gives a yellow colour with iron(III), as expected from the complexation of the analogous pyridine compound, MPC.

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Zusammenfassung—Die Komplexbildung von Eisen(III) mit mehreren Hydroxypyridinen wurde untersucht und beim selektivenNachweis und der Bestimmung (spektrophotometrisch und chelatometrisch) des Metalls verwendet. Eisen(III)-Hydroxypyridin-Komplexe werden auch als Indikatoren bei Säure-Basen-Titrationen gebraucht. Eine zu einer Phenolgruppe in einem Pyridinmolekül benachbarte Thiolgruppe liefert einen zur Bestimmung von Pd(II) geeigeten Liganden. Die Stabilitätskonstanten zweiwertiger Metallkomplexe mit Hydroxypyridinen wurden potentiometrisch bestimmt.

Résumé La complexation du fer (III) avec plusieurs pyridinols a été étudiée et utilisée dans la detection et le dosage selectifs (spectrophotometrique et chélatométrique) du métal. Les complexes fer (III) pyridinol sont aussi utilisés comme indicateurs dans les titrages acide-base. Un groupement thiol vicinal d'un groupement phenolique dans une molecule pyridinique fournit un réactif qui est un coordinat convenable pour le dosage de Pd (II). On a déterminé potentiométriquement les constantes de stabilité de complexes de metaux bivalents avec les pyridinols

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SHORT COMMUNICATIONS

DETERMINATION OF MICROGRAM QUANTITIES OF GADOLINIUM BY CATHODE-RAY POLAROGRAPHY

(*Received* 18 *October* 1973. *Accepted* 27 *February* 1974)

Gadolinium has been used as a target material for producing dysprosium-157 by bombardment with alpha-particles from a medical cyclotron.[1] After separation of the radioactive dysprosium in a carrier-free state from the bulk of the gadolinium, the product must be checked for gadolinium contamination before it can be administered for clinical use. A reliable method for the determination of microgram quantities of gadolinium was therefore needed.

Rare earths have been determined by classical d.c. polarography[2,3] in 0·1*M* potassium chloride as supporting electrolyte. It has been shown,[3] however, that of the two waves reported,[2] the first ($E_{1/2}$ – 1·5 V) is due to reduction of hydrogen ions arising from hydrolysis of the rare-earth aquo-ion and the second ($E_{1/2}$ – 1·8 V) is due to the three-electron reduction of the rare-earth ion. The work was done with acidic solutions of gadolinium.

In the present studies, attempts were made to reproduce these results, but by using a cathode-ray polarograph in the derivative mode. A standard gadolinium solution (1 mg/ml) was made up in 0·3*M* nitric acid. To 5 ml of 0·1*M* potassium chloride, in an electrolytic cell containing a mercury pool electrode, were added 5–35 μl of the gadolinium stock solution to obtain a final gadolinium concentration of 1–7 μg/ml (the nitric acid concentration varied from $3 \times 10^{-4}M$ to $2{\cdot}1 \times 10^{-3}M$).

Two well-separated polarographic peaks were obtained at about – 1·55 and – 1·75 V, the amplitude of which increased with increasing gadolinium concentration. A typical set of polarograms is shown in Fig. 1A.

However, it was noticed that identical polarograms of increasing amplitude were also obtained when 0·3*M* nitric acid (which contained no gadolinium) was added to a fresh lot of electrolyte, so that the final strength of the acid in the potassium chloride electrolyte still lay in the range $3 \times 10^{-4}M$–$2{\cdot}1 \times 10^{-3}M$. For a qualitative comparison a set of such polarograms is shown in Fig. 1B. Similar observations were also made after the addition of hydrochloric, sulphuric or acetic acid. Under these conditions, therefore, the peaks observed did not seem to be due to the gadolinium at all but only due to the acid solutions.

Non-aqueous solutions have also been studied with a view to facilitating the determination of rare-earths. Peychal-Heiling and Gutmann[4] used 1,2-propanediol carbonate as solvent and tetraethylammonium perchlorate as supporting electrolyte with some success. The limits of detection were around 0·03 μg/ml, but the $E_{1/2}$ values, and the diffusion currents were markedly affected by varying contamination by water. Moreover, it would not be very convenient to obtain our dysprosium samples in the non-aqueous solvent.

Azo-dyes which form complexes with metal ions have been used for the polarographic determination of aluminium[5] and several other ions including lanthanum.[6] As the waves were not very distinct, Palmer and Reynolds[6] preferred to use derivative polarography, and found limits of detection of around 0·5–10 μg/ml in a pH 13 buffer containing piperidine, with Solochrome Violet RS as azo-dye. It was decided to test the applicability of this method to the determination of gadolinium.

EXPERIMENTAL

Reagents

Standard gadolinium solution, 1 mg/ml. Gadolinium foil (Koch–Light Laboratories) was dissolved in concentrated nitric acid, the solution evaporated to dryness and the residue redissolved in 0·3*M* nitric acid.

Solochrome Violet RS, 0·05% solution in water.

Dimethylamine, 30% w/v solution (DMA). Used without further purification.

Hydrochloric acid, 3M, and sodium hydroxide, 3M

Procedure

To each of five 50-ml standard flasks were added, in the following order, 20 ml of Solochrome Violet solution, an aliquot of the standard gadolinium solution (0, 0·25, 0·5, 0·75, 1·00 ml), 1·5 ml of 30% DMA solution, 3·4 ml of 3*M* hydrochloric acid, and 5 ml of 3*M* sodium hydroxide. Water was added to dilute the mixture to about

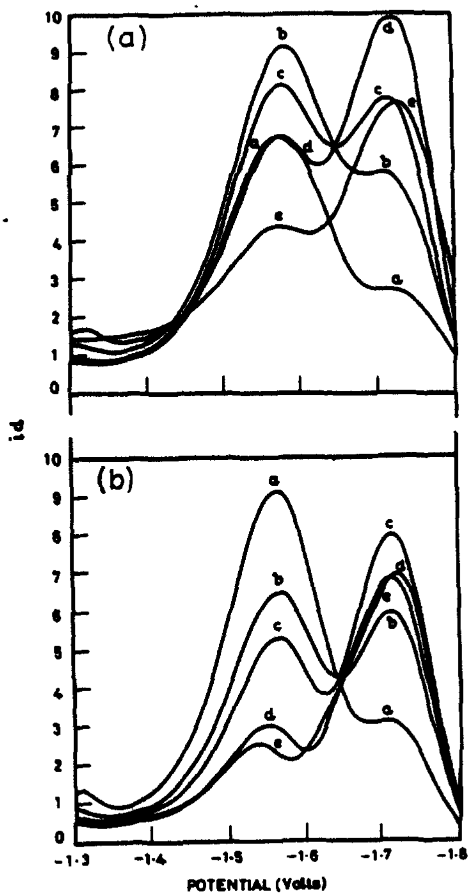

Fig. 1. Polarograms of nitric acid in 0·1*M* KCl medium (*A*) with and (*B*) without gadolinium. (*A*) [Gd]: (*a*) 1, (*b*) 2, (c) 3, (*d*) 5, (*e*) 7 μg/ml: [HNO_3] (*a*) 3 × 10^{-4}, (*b*) 6 × 10^{-4}, (*c*) 9 × 10^{-4}, (*d*) 15 × 10^{-4}, (*e*) 21 × 10^{-4}*M*: sensitivity (*a*) 25, (*b*) 40, (*c*) 60, (*d*) 100, (*e*) 250 μA full-scale deflection. (*B*) [HNO_3] as for (*A*): sensitivity (*a*) 25, (*b*) 60, (c) 100, (*d*) 250, (*e*) 400 μA full-scale deflection.

45 ml and the flasks were heated in the water-bath at 70° for 15 min. After cooling, the solutions were made up to the mark and the derivative polarograms were recorded.

The dye alone gives a peak at −0·75 V, which has been ascribed to a four-electron reduction step.[7] In the presence of gadolinium a second peak appears at −0·95 V (Fig. 2). Upon addition of an increasing amount of gadolinium the second peak increases and the first decreases.

Effect of pH

The heights of both peaks depend on the pH of the solution (Fig. 3). Although at pH 9–10 the first peak remains fairly constant, it was decided to work at pH 12·5 which gives a slightly higher sensitivity for gadolinium.

Effect of ligand concentration

Increased amounts of gadolinium were added to the same amount of Solochrome Violet as described under *Procedure*, and the peaks recorded. The results are shown in Fig. 4. A final dye concentration of 0·02% is adequate for up to about 600 μg of gadolinium in 50 ml (12 μg/ml).

Effect of heating time on complex formation and limits of detection

Most of the metal ions which react with Solochrome Violet do so only slowly at room temperature. This also applies to gadolinium. In a series of experiments the peak-height was found to increase with length of heating up to 15 min and thereafter to remain constant.

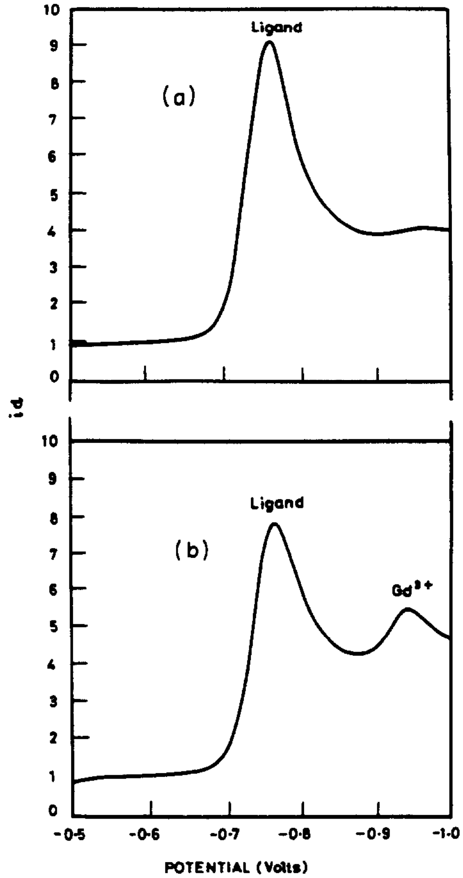

Fig. 2. Polarograms of 0·02% ligand (*a*) without and (b) with gadolinium (0·1 μg/ml).

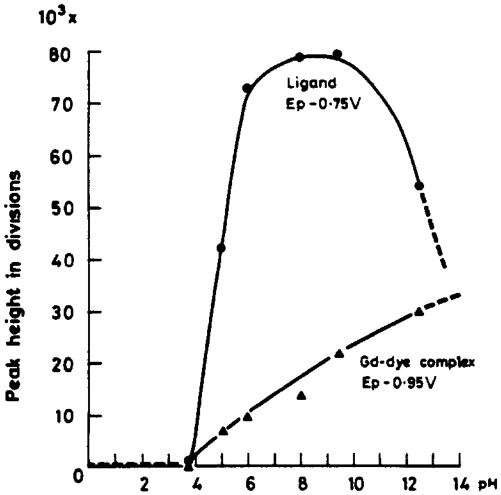

Fig 3 Influence of pH on complex formation.

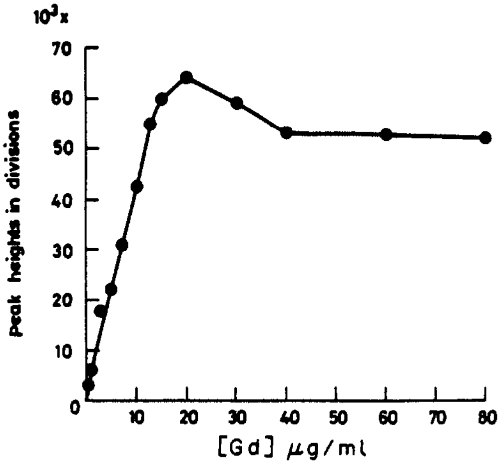

Fig. 4. Calibration graph.

The response is linear for the determination of 0·5–12 µg/ml gadolinium concentrations (coefficient of variation = ±16·7%). Above this concentration the peak height falls rapidly. This is in agreement with the observation made by Palmer and Reynolds.[6]

Interference from other metals

A number of other metal ions were added, in the absence of gadolinium, at concentrations of 5 µg/ml and polarograms were recorded. The results are summarized in Table 1.

Table 1. Interference from other metal ions

Element	E_p, *V*	Remarks
Fe^{3+}	0·83	W.D. irreversible
Cu^{2+}	0·83	Small, irreversible
Zn^{2+}	0·79	W.D., irreversible
Cd^{2+}	0·8	Small, irreversible
Al^{3+}	—	No wave
As^{3+}	0·96	Very small, irreversible
Rh^{3+}	0·96	Very small, irreversible
Ho^{3+}	0·8	W.D. irreversible
Y^{3+}	0·75	W.D. irreversible
La^{3+}	0·85	Small, irreversible
U(VI)	0·73	W.D. irreversible

W.D. = Well defined.

It is perhaps noteworthy that aluminium does not interfere. Arsenic and rhodium interfere even at low concentrations, while moderate concentrations of the other ions could be tolerated, as long as the peaks do not overlap, and the ions do not preferentially complex the Solochrome Violet.

Purity of reagent and stability of the complex

Some solutions were prepared with Solochrome Violet twice recrystallized from 50 % methanol,[7] but no difference in the peak heights or potentials was noticed. Solutions stored for five days before measurement also gave unchanged polarograms.

DISCUSSION

Although the use of 0·1*M* potassium chloride as electrolyte is well established for rare-earth analysis by classical d.c. polarography, its use with fast sweep cathode-ray polarography is impracticable. The second peak observed here, which can easily be mistaken for the metal peak, may either be due to the discharge of potassium and overlap the feeble gadolinium peak or due to the different behaviour of the catalytic reaction under the conditions of cathode-ray polarography.

For the determination of microgram quantities of gadolinium with the cathode-ray polarograph the method investigated is satisfactory. However it is linear only in the range 0·5–12 μg/ml. This is attributed to the limited solubility of the ligand.

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Summary—A cathode-ray polarographic method has been developed for the determination of microgram quantities of gadolinium with the use of an azo-dye, Solochrome Violet RS. Disadvantages in the use of 0·1*M* potassium chloride, commonly recommended as electrolyte for the polarographic determination of rare earths, have been demonstrated. The influence of pH, temperature, ligand concentration and purity, and the stability of the complex, have been investigated for the optimum performance of the method. The linear range is 0·5–12 μg/ml of gadolinium. Interferences by some lanthanides and other cations have been examined.

Zusammenfassung—Zur Bestimmung von Mikrogrammengen Gadolinium mit Hilfe eines Azofarbstoffs, Solochromviolett RS, wurde eine kathodenstrahlpolarographische Methode entwickelt. Die Nachteile der Verwendung von 0.1*M* Kaliumchlorid, das gewöhnlich als Elecktrolyt zur polarographischen Bestimmung seltener Erden empfohlen wird, wurden sichtbar gemacht. Der Einfluß von pH, Temperatur, Konzentration und Reinheit des Liganden und die Stabilität des Komplexes wurden untersucht, um die optimale Arbeitsweise des Verfahrens au erreichen. Der lineare Bereich ist 0,5–12 μg Gadolinium pro ml Störungen durch einige Lanthaniden und andere Kationen wurden untersucht.

Résumé—On a développé une méthode polarographique à rayon cathodique pour le dosage du gadolinium en quantités de l'ordre du microgramme avec l'emploi d'un colorant azoïque, le Solochrome Violet RS. On a démontré les désavantages de l'emploi du chlorure de potassium 0,1*M*, habituellement recommandé comme électrolyte pour le dosage polarographique des terres rares. On a étudié l'influence du pH, de la température, de la concentration et de la pureté du coordinat, et la stabilité du complexe, pour la marche optimale de la méthode. Le domaine linéaire est 0,5–12 μg/ml de gadolinium. On a examiné les interférences de quelques lanthanides et autres cations.

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THIOMERCURIMETRIC DETERMINATION OF SULPHUR, ALIPHATIC AND AROMATIC THIOLS AND DISULPHIDES IN HYDROCARBON SOLVENTS, USING REDUCTION WITH SODIUM ALUMINIUM bis(2-METHOXYETHOXY)DIHYDRIDE

(*Received* 22 *November* 1973. *Accepted* 27 *January* 1974)

Although numerous reagents have been proposed for reduction of a disulphide bond,[1] none can be unreservedly accepted for general use in determination of organic disulphides and sulphur in hydrocarbon solvents. The best results have been obtained by using lithium aluminium hydride in tetrahydrofuran solution,[2] but this reagent is inconvenient and even dangerous in daily analytical application. It may be expected that lithium trialkoxyaluminium hydrides[3] would be more suitable.

In this work a new reagent, sodium aluminium bis(2-methoxyethoxy) dihydride, $NaAlH_2(OCH_2CH_2OCH_3)_2$, (proposed abreviation SAMD), supplied by EGA Chemie KG* as a 70% solution in benzene, has been investigated as a reducing agent for the disulphide bond and proved to be active, convenient in use, and stable when kept under dry hexane.

In earlier work, titration of thiols with sodium *o*-hydroxymercuribenzoate (HMB), in the presence of dithiofluorescein or dithizone as indicator, was recommended.[4,5] A new approach suggested in this work is based on the observation that aromatic thiols in strongly alkaline aqueous solution consume only about 3% of the equivalent amount of HMB in the presence of dithizone, whereas in aqueous alcoholic solution with dithiofluorescein as indicator the consumption of HMB is equivalent to total thiol and hydrogen sulphide. Moreover, according to previous work,[6,7] thiols react with acrylonitrile, whereas hydrogen sulphide does not. In this way hydrogen sulphide and aliphatic and aromatic thiols can be determined in the presence of each other and the same procedure can be applied to sulphur, aliphatic and aromatic disulphides after reduction with SAMD.

EXPERIMENTAL

Reagents

HMB solution, ca. 0·05*N*. Prepared by dissolving 16 g of *o*-hydroxymercuribenzoic acid anhydride in 100 ml of 1*M* sodium hydroxide and diluting to 1 litre. For standardization weigh 20–80 mg of pure diphenylthiourea (equivalent weight 114·15), dissolve it in 20 ml of ethanol, add 2 ml of *M* sodium hydroxide, heat for 1 min in boiling water and titrate with HMB in the presence of dithiofluorescein as indicator. Dilute the standardized solution of HMB with 0·01*M* sodium hydroxide to 10^{-2}, 10^{-3} and $10^{-4}N$, in water and in 50% v/v aqueous n-propanol.

Dithiofluorescein solution. Dissolve 5 mg of dithiofluorescein in 5 ml of 0·3*M* potassium hydroxide containing 0·1% of EDTA, and dilute with 96% v/v ethanol to 50 ml. Keep the solution in a brown bottle in the dark. Use 0·2 ml per titration.

Dithizone solution. Dissolve 5 mg of dithizone in 50 ml of 96% v/v ethanol and keep the solution in the dark. Use 0·2 ml for titrations with $10^{-3}N$ HMB, and 0·1 ml with $10^{-4}N$. When the colour of the solution becomes yellow-green, prepare a new one.

SAMD. Place 5–10 ml of the reagent in a 25-ml brown bottle fitted with a Teflon stopper and fill up with hexane dried with sodium. The reagent forms a viscous layer on the bottom.

Benzene solutions of thiols and disulphides are prepared as follows. To 5 ml of 1*M* sodium hydroxide in a 50-ml separatory funnel add *ca.* 0·5 mmole of *S*-alkylthiuronium salt and 40 ml of benzene, shake, add 5 ml of 2*N* sulphuric acid, shake again, wash the benzene solution with water, then with sodium bicarbonate solution and finally water again. Standardize by titration with HMB. For preparation of a disulphide place 20 ml of this solution and 5 ml of aqueous 0·2*N* iodine in a separatory funnel, shake for 5–10 min, wash the benzene layer first with water, then with *ca.* 0·01*M* sodium thiosulphate, and if the benzene solution is still coloured, with dilute sodium sulphite solution and finally with water. Filter the solution through paper and dry it with sodium sulphate. The concentration of disulphide is assumed equal to the original concentration of thiol.

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Procedure 1

This applies to determination of hydrogen sulphide, aliphatic and aromatic thiols in the presence of each other in aqueous $2M$ potassium hydroxide and of thiols in hydrocarbons

(*a*) *Thiols and hydrogen sulphide*. Dilute 1·5 ml of sample with 5 ml of n-propanol and titrate with *a* ml of $10^{-3}N$ HMB in 50% v/v propanol in the presence of dithiofluorescein. The end-point is indicated by the disappearance of the blue colour

(*b*) *Aliphatic thiols and hydrogen sulphide*. Dilute 1·5 ml of sample with 5 ml of water and titrate with *b* ml of aqueous $10^{-3}N$ HMB, using dithizone as indicator, to the change of colour from yellow to red (in the presence of aromatic thiols) or to purple

(*c*) *Hydrogen sulphide* Dilute 1·5 ml of sample with 5 ml of water, add 0·5 ml of 10% v/v acrylonitrile solution in methanol and titrate with *c* ml of aqueous $10^{-3}N$ HMB, using dithizone as indicator.

(*d*) *Thiols in hydrocarbons*. Dilute 2–5 ml of a hydrocarbon sample with 5 ml of propanol and titrate with HMB in 50% v/v propanol, using dithiofluorescein as indicator.

Calculations. The aliphatic thiols content could be calculated on the basis of the difference $b - 0{\cdot}03(a - b) - c$, and that of aromatic thiols from $a - b + 0{\cdot}03(a - b)$. The results obtained for hydrogen sulphide, n-propanethiol and benzenethiol are demonstrated in Table 1.

Table 1. Determination of hydrogen sulphide, n-propanethiol and benzenethiol in the presence of each other in 5 ml of $2M$ potassium hydroxide

Taken, μeq*			Found, μeq		
Hydrogen sulphide	Propanethiol	Benzenethiol	Hydrogen sulphide	Propanethiol	Benzenethiol
7·00	8·68	10·8	6·85	9·30	10·5
14·00	0	10·8	13·7	0·50	11·0
0	16·7	10·8	0·06	16·5	11·3
7·00	0	21·6	7·03	0·33	21·7
5·66	6·70	15·3	5·30	6·84	15·7
8·50	10·0	6·50	7·96	10·7	6·32
2·83	3·34	24·0	3·03	3·23	23·7

* For H_2S 1 μeq = 0·5 μmole: for thiols 1 μeq = 1 μmole.

Procedure 2

This applies to determination of sulphur and total disulphides. Place 2 ml of hydrocarbon sample (aliphatic samples should be diluted in 1:1 ratio with benzene) in a 15-mm dia. test-tube, and add one drop, *ca.* 0·05 ml, of 70% SAMD by using a small, 4-mm thick, glass stick, which is dipped to a depth of 1 cm in the reagent and rapidly transferred to the test-tube A small glass tube may also be used. On shaking, the reagent should dissolve. To complete the reduction the sample is heated for 30 sec on the water-bath, then is cooled in water and the excess of reagent is decomposed by addition of 2 ml of n-propanol. When no or only weak evolution of hydrogen is observed, the analysis should be repeated with more reagent or the sample should be dried with anhydrous sodium sulphate Compounds containing active hydrogen interfere in the reduction by decomposing the SAMD. The sample is finally titrated with 10^{-2}–10^{-3} N HMB in 50% v/v propanol, with dithiofluorescein as indicator. During the titration ethanol is added in amounts just enough to dissolve the emulsion produced.

The results obtained for sulphur and some disulphides are summarized in Table 2.

The reactions of SAMD with disulphides and sulphur can be expressed as follows:

$$NaAlH_2(OCH_2CH_2OCH_3)_2 + RSSR \rightarrow NaAl(SR)_2(OCH_2CH_2OCH_3)_2 + H_2$$
$$NaAlH_2(OCH_2CH_2OCH_3)_2 + S \rightarrow NaAlS(OCH_2CH_2OCH_3)_2 + H_2.$$

The decomposition with water produces thiols, hydrogen sulphide, sodium and aluminium hydroxide and methoxyethanol The excess of SAMD produces additional hydrogen. Thiophene and thioethers are stable to SAMD under the conditions suggested. However, the sulphur–benzyl bond is not stable enough, and the reduction of dibenzyl disulphide should be carried out at room temperature. On the other hand, di-t-butyl disulphide after 10 min reduction in boiling benzene gives only 75% of the calculated value Any thiols present should be removed by extraction or be determined before the reduction by titration with HMB and the disulphide content calculated by difference Carbon disulphide should be removed as dithiocarbamate after reaction with amines

Table 2. Determination of sulphur and disulphides in benzene solution

Disulphide	Taken, μeq	Rel. std. devn, %	Mean recovery (6 titrations), %
Sulphur	2·1	0·75	94·0
	4·2	0·87	94·5
	57·5	0·33	98·3
Dimethyl	3·0	1·3	99·5
	6·0	0·85	100·2
	45·3	0·44	100·0
Di-n-propyl	4·1	1·2	101·5
	8·3	0·64	100·6
	30·6	0·57	100·0
Di-isoamyl	4·5	1·5	100·3
	8·9	1·0	99·6
Diallyl	5·9	1·0	102·0
	11·8	1·4	99·2
Di-n-dodecyl	4·4	1·2	102·3
	8·7	0·88	98·5
	87·2	1·1	99·8
Diphenyl	3·4	2·2	102·1
	6·9	1·3	99·5
Dibenzyl*	2·7	3·7	101·5
	5·4	1·8	100·4
Tetramethylene	2·5	1·2	99·5
	5·1	1·0	98·3
	50·8	0·94	100·2

* Reduced for 3 min at 18°C

Procedure 3

This applies to determination of aliphatic and aromatic disulphides and sulphur in the presence of each other. To 10 ml of hydrocarbon sample in a test-tube add *ca.* 0·05 ml of SAMD, shake, keep for 1 min on the hot water-bath, cool, add 5 ml of 2*M* potassium hydroxide, and shake after decomposition of the SAMD. Analyse the aqueous phase according to Procedures 1(*a*), (*b*), (*c*). The hydrogen sulphide content is then equal to the original sulphur content. Typical results for dimethyl disulphide, sulphur and diphenyl disulphide are shown in Table 3.

CONCLUSIONS

In view of the results given in Table 2 and the simplicity of the analytical procedure, the proposed method can be recommended for general use. The relative standard deviation, apart from a few values, is in the range 0·5–1·5%. The recovery is near to 100% and only for small amounts of sulphur should a correction be necessary. By reduction, extraction, and titration with $10^{-4}N$ HMB, sulphur at the 0·1-ppm level in hydrocarbons can be determined. By application of the photometric method using dithiofluorescein–HMB complex[8] or the titration with tetramercurated fluorescein[9] the estimation of even lower sulphur contents may be possible.

Table 3. Determination of sulphur, dimethyl disulphide and diphenyl disulphide in 10 ml of benzene in the presence of each other

Taken, μeq			Found, μeq		
Sulphur	Dimethyl disulphide	Diphenyl disulphide	Sulphur	Dimethyl disulphide	Diphenyl disulphide
8·44	6·04	13·8	7·87	6·00	14·1
8·44	12·08	13·8	8·35	12·1	14·2
4·22	12·08	6·90	4·37	11·6	7·21
16·88	3·02	13·8	15·4	3·30	13·3
2·11	9·06	3·45	2·33	8·55	4·07
0·118	0	0	0·114	—	—

The determination of hydrogen sulphide aliphatic and aromatic thiols, or sulphur, aliphatic and aromatic disulphides in the presence of each other, as suggested in Procedures 1 and 3, can be very useful for rapid determination of sulphur compounds in hydrocarbon solvents, although the accuracy is not better than ±5% at a level of *ca.* 0·01% of total sulphur.

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Summary—A method is proposed for determination of hydrogen sulphide and aliphatic and aromatic thiols in hydrocarbon solvents by extraction with 2*M* potassium hydroxide and titration with *o*-hydroxymercuribenzoic acid in the presence of dithiofluorescein and dithizone, with selective masking with acrylonitrile. Sulphur and organic disulphides are readily converted by sodium aluminium bis(2-methoxyethoxy)dihydride in benzene solution into hydrogen sulphide and thiols, which can either be directly titrated after dilution with alcohol or separated by extraction and determined in the presence of each other.

Zusammenfassung—Ein Verfahren zur Bestimmung von Schwefelwasserstoff und aliphatischen und aromatischen Thiolen in Kohlenwasserstoff-Lösungsmitteln durch Extraktion mit 2*M* Kaliumhydroxid und Titration mit *o*-Hydroxymercuribenzoesäure in Gegenwart von Dithiofluorescein und Dithizon wird vorgeschlagen. Dabei wird mit Acrylnitril selektiv maskiert. Schwefel und organische Disulfide werden durch Natriumaluminiumbis(2-methoxyäthoxy)dihydrid in Benzollösung zu Schwefelwasserstoff und Thiolen umgesetzt; diese konnen entweder nach Verdünnung mit Alkohol direkt titriert oder durch Extraktion abgetrennt und nebeneinander bestimmt werden.

Résumé—On propose une méthode pour le dosage de l'hydrogène sulfuré et des thiols aliphatiques et aromatiques dans les solvants hydrocarbures par extraction avec la potasse 2 *N* et titrage à l'acide *o*-hydroxymercuribenzoique en la présence de dithiofluorescéine et de dithizone, avec dissimulation sélective à l'acrylonitrile. Le soufre et les disulfures organiques sont aisément convertis par le dihydrure de bis(2-méthoxyéthoxy) aluminium et sodium en solution benzénique en hydrogène sulfuré et thiols qui peuvent être, soit titrés directement après dilution à l'alcool, soit séparés par extraction et dosés en la présence l'un de l'autre.

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A RADIOCHEMICAL STUDY OF THE FIRE ASSAY OF RHODIUM WITH COPPER AND THE SUBSEQUENT RHODIUM–COPPER SEPARATION

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The determination of the precious metals in ores, rocks, alloys, *etc.* generally requires a prior concentration of the noble metals, which is usually accomplished by means of the fire assay. Practical procedures are described in detail by Beamish[1,2] and by Beamish and Van Loon.[3] Lead is most widely used for extracting the noble metals, but procedures have also been proposed using iron–copper–nickel,[4–8] tin,[9,10] and nickel sulphide.[11–13] More recently, procedures for the recovery of platinum, palladium, iridium, and rhodium by means of copper have been described.[14–16] Copper can be removed from these metals by cation-exchange in hydrochloric acid, adjusted to pH 1·0.

In the present paper, ^{102,102m}Rh tracer has been used to investigate the distribution of rhodium after the fire assay with copper. Rhodium and copper were separated on a Dowex 50 cation-exchanger in hydrochloric acid adjusted to pH 1·5 In that medium, copper is strongly retained by the resin, while rhodium is not adsorbed.

EXPERIMENTAL

Apparatus

The ^{102,102m}Rh activity (^{102}Rh, $t_{1/2}$ = 206 d; ^{102m}Rh, $t_{1/2}$ = 2·9 yr) was measured by gamma-spectroscopy with a 3 × 3 in. NaI(Tl) crystal (Nuclear Enterprises), coupled to an EMI 9531 A photomultiplier and placed in a low-background lead castle. The pulses were analysed with a multichannel spectrometer (SA 40, Intertechnique).

Méker gas–air furnace.

Fire-assay crucibles, Battersea, England.

Glass and saturated calomel electrodes (Radiometer).

The e.m.f. was measured with a Radiometer 22 instrument.

Ion-exchange column (length 51 cm, diameter 5·4 cm).

^{102,102m}Rh tracer solution

^{102,102m}Rh carrier-free tracer was produced by 18-MeV deuteron bombardment of natural ruthenium. The tracer solution also contained ^{101}Rh ($t_{1/2}$ = 3·0 yr). Details concerning the isolation and the yields of the carrier-free ^{102,102m}Rh radionuclides are described elsewhere.[17,18]

Reagents

Nitric acid, reagent grade.

Hydrochloric acid, reagent grade.

Hydrochloric acid of pH 1·5, prepared by diluting 25 ml of 6*M* hydrochloric acid to 5 l. in a volumetric flask with distilled water. The pH was checkes with the glass electrode.

The ion-exchange resins (Dowex 50 W-X8, 50–100 mesh, Fluka and Dowex 50 W-X8, 100–200 mesh, Baker "Analyzed Reagent") were thoroughly washed with 6*M* hydrochloric acid, then with water and finally with hydrochloric acid of pH 1·5.

Copper oxide, borax, sodium carbonate, silica and graphite were all technical grade. The composition of the charge was copper oxide 65·0 g, borax 25·0 g, sodium carbonate 60·0 g, silica 10·0 g and graphite 3·5 g.

Distribution of rhodium after the fire assay with copper

Small aliquots of rhodium tracer were pipetted into a fire-assay crucible onto the mixed charge (70·0 g), which was added in layers so that the tracer was divided over the flux. After addition of about 10 g of silica, the crucible was placed in a gas-heated furnace, and the mixture heated at 1300° for about one hour. About 10 g of flux were added and the mixture further heated for about 30 min

Table 1 Rhodium-copper separation

Experiment	Copper button weight, *g*	Conditions	Rhodium eluted, %	Rhodium in copper eluate, %	Rhodium adsorbed on the resin, %
1	29·3	Resin, Dowex 50W-X8 (50–100 mesh), Fluka Length of the ion-exchange column 41 cm (in HCl of pH 1.5); diameter 5·4 cm Rhodium eluent: 1 l. of HCl (pH 1·5); elution time *ca.* 30 min Copper eluent: 2 l. of 12*M* HCl; elution time *ca.* 90 min.	99·6$_0$	0·22	0 184 (*a*) 0·043 (*b*) 0·047 (*c*) 0·041 (*d*) 0·052
2	27·0	Resin, Dowex 50W-X8 (50–100 mesh), Fluka Length of the column 40 cm (in HCl of pH 1·5); diameter 5·4 cm Rhodium eluent 2 l. of HCl (pH 1·5) Copper eluent: 2 l. of 12*M* HCl Total elution time *ca.* 3 h	99·7$_8$	0·12	0·10 (*a*) 0·026 (*b*) 0·023 (*c*) 0·025 (*d*) 0·026
3	30·0	Resin, Dowex 50W-X8 (100–200 mesh) Baker Analyzed Reagent Length of the column 33 cm (in HCl of pH 1·5); diameter 5·4 cm Other conditions as for experiment 2	99·9$_7$	0·022	0·0057 (*a*) 0·0013 (*b*) 0·00099 (*c*) 0·0011 (*d*) 0·0024

(*a*), (*b*), (*c*), (*d*): Top, second, third and bottom quarters of the resin.

A rhodium standard was prepared as follows: 1 ml of rhodium tracer was pipetted in small aliquots onto 45 g of mixed charge without the copper oxide. The crucible was placed in the furnace and treated in the same way as the others.

After cooling, the crucibles were broken to free the copper button, if present; slag adhering to the button was removed by gentle tapping with a rod and by means of a steel-wire brush. The slags were collected in 250 ml beakers. The crucible walls, together with some adhering glassy layer, were broken and pulverized, and a suitable fraction also placed in 250 ml beakers.

The rhodium activities of the slags and the pulverized crucibles were measured at a large source–detector distance, so that errors due to geometry differences were minimized.

In order to check the presence of metallic copper, the pulverized slags were treated with concentrated nitric acid. After careful washing with distilled water and drying, the rhodium activities of the slags were measured, together with that of the standard.

The rhodium–copper separation

The copper buttons were dissolved in concentrated nitric acid. The nitrate was converted into chloride by repeatedly evaporating to dryness with concentrated hydrochloric acid under an infrared lamp. The salts were dissolved in hydrochloric acid (pH = 1·5) and transferred to a Dowex 50 W-X8 cation-exchange column, previously washed with hydrochloric acid at the same pH. Rhodium was eluted with 2 l. of hydrochloric acid (pH = 1·5). The effluent was concentrated and transferred to a 250 ml conical flask. Copper was removed from the resin with 2 l. of 12*M* hydrochloric acid. The copper effluent was evaporated and also transferred to a 250 ml conical flask. The eluent was removed from the column and the resin extruded. The ion-exchange column was divided into four parts and the resin transferred to 250 ml conical flasks. Distilled water was added to the rhodium and copper solutions as well as to the resin, so that the flasks were filled up to the same height. The rhodium activities of the samples were measured at a large source-detector distance to reduce geometry errors.

The experimental conditions for the copper–rhodium separation are summarized in Table 1. The copper button in the second experiment resulted from a fire assay on a 5·0 g sample. This sample originated from a silver chloride reduction process and contained 94 ppm silver, 1·15 ppm gold, 2·65 ppm platinum, 2·99 ppm palladium and 3·01 ppm rhodium.

RESULTS AND DISCUSSION

The activities due to ^{101,102,102m}Rh were determined from the areas of the 127, 198 and 475 keV (complex) photo-peaks. On the average, *ca.* 0·05% of rhodium remained in the slag. After the nitric acid treatment, the percentage slightly decreased to *ca.* 0·04%. Up to 0·05% of rhodium was present in the crucible walls or in the glassy layer adhering to the walls. This means that rhodium is very effectively collected in copper (*ca.* 99·9%), which confirms the findings of Banbury and Beamish.[14–16]

The results of the copper–rhodium separation are given in Table 1. It appears that with 2 l. of hydrochloric acid at pH 1·5 at least 99·6% of the rhodium could be eluted. Between 50 and 70% of the rhodium left on the resin could be eluted, together with copper, with 2 l. of 12*M* hydrochloric acid. The residual amount of rhodium on the resin varied finally from 0·18 to 0·006% of the initial loading. The variation was due to changes in the experimental conditions, such as different physical properties of the resin. The rhodium–copper separation may also be influenced by the presence of rhodium–nitrite complexes. Indeed, such complexes can be formed during the dissolution of the copper button and are not completely converted into the chloride by repeated evaporations with hydrochloric acid. The conclusion is that with a single fire assay at least 99·8% of the rhodium present can be collected in copper; more than 99·6% can be eluted from the cation exchanger.

The findings with radioactive rhodium tracer are also applicable to "normal" rhodium, possibly present in a sample, since the high-temperature fire-assay ensures isotopic exchange.

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Zusammenfassung—^{102,102m}Rh wurde als Tracer verwendet, um die Anreicherung von Rhodium in Kupfer bei der Schemelzprobe zu untersuchen. Rhodium und Kupfer werden an einem Dowex 50-Kationenaustauscher in Salzsäure von pH 1,5 voneinander getrennt.

Résumé—On a utilisé le ^{102,102m}Rh comme traceur pour étudier la récupération par essai par voie sèche du rhodium dans le cuivre. Le rhodium et le cuivre sont séparés sur un échangeur de cations Dowex 50 en acide chlorhydrique de pH 1,5.

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DETERMINATION OF SULPHUR SPECIES ARISING FROM THE REACTION OF SULPHUR AND SULPHIDE IN A (K, Na)SCN EUTECTIC MELT

(*Received* 15 *June* 1973. *Accepted* 14 *December* 1973)

Sulphur and sulphide react at a temperature higher than 200° in molten potassium thiocyanate and in molten lithium and potassium chloride mixture to give a blue colour[1-4] We have previously observed that at a temperature less than 200° the reaction takes place with polysulphide formation and the appearance of a yellow colour[5,6] Knowledge of the nature of the electrogenerated sulphur and of the occurrence of the reaction with sulphide in molten thiocyanate at low temperature is important for the understanding of the nature of the polysulphide species because under these experimental conditions thermal decomposition of the

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Sulphur and sulphide react at a temperature higher than 200° in molten potassium thiocyanate and in molten lithium and potassium chloride mixture to give a blue colour[1-4] We have previously observed that at a temperature less than 200° the reaction takes place with polysulphide formation and the appearance of a yellow colour[5,6] Knowledge of the nature of the electrogenerated sulphur and of the occurrence of the reaction with sulphide in molten thiocyanate at low temperature is important for the understanding of the nature of the polysulphide species because under these experimental conditions thermal decomposition of the thiocyanate melt is avoided and sulphurous products from the solvent do not interfere with the reaction between sulphide and sulphur.

Voltammetric and spectrophotometric measurements have therefore been made on solutions of sulphur species in (K,Na)SCN eutectic mixture at 155 and 165°. The influence of light on the formation of sulphur has also been studied.

EXPERIMENTAL

The general apparatus and experimental procedure were similar to those described elsewhere.

Apparatus

Voltammetry. A three-electrode Amel model 557/SU polarograph, Graphispot type GRVAM galvanometric recorder, Ag/Ag(I)(0·1*M*) glass reference electrode and platinum vertical alternate movement electrode (VAME)[7,8] were used.

Spectrophotometry. A Unicam SP 700 spectrophotometer with a furnace[9] which holds both sample and reference cells was used.

Irradiation. A Beckman Xe 1045 apparatus equipped with a high-pressure 450-W Osram xenon lamp was used. The light was filtered by the Pyrex glass of the apparatus vessels and a 2-cm cell containing saturated copper sulphate solution was used to remove heating effects.

Reagents

Solvent. The solvent was prepared as previously described.[5]

Sulphur and sulphide. The sulphur was obtained by anodic generation from molten alkali metal thiocyanate by means of a split cylindrical platinum gauze electrode. The current density was 10 μA/mm^2. Sulphide was introduced as pellets of (K,Na)SCN eutectic mixture containing a known quantity of sodium sulphide.

RESULTS AND DISCUSSION

We have found in agreement with Eluard and Trémillon,[10] that the anodic oxidation of SCN$^-$ proceeds quantitatively by the reaction

$$2SCN^- \rightarrow 2S + (CN)_2 + 2e$$

A small amount of elemental carbon and nitrogen arises because of thiocyanate ions being adsorbed at the electrode surface between sulphur atoms or occluded in the bulk of the sulphur phase. The sulphur which is electrolytically produced has a well-defined reduction wave with $E_{1/2} \sim -0{\cdot}5$ V. The i_d/C ratio is constant up to a concentration of 1 meq/kg.

The viscous sulphur electrogenerated on the platinum surface was yellow-orange, and fairly stable in air. The reflectance spectrum in air at room temperature showed a minimum at 400 nm. When the molten (K,Na)SCN mixture was irradiated in the region 350–650 nm, no light was absorbed.

Voltammetric measurements were carried out after each addition of sulphide ion to the melt containing electrolytically generated sulphur. As the sulphide concentration increased the diffusion current of sulphur decreased and an oxidation wave appeared at the potential range corresponding to discharge of sulphide. The plot of diffusion current of this wave *vs.* sulphide ion concentration gave a straight line.

The appearance of this wave and the change in colour from yellow-orange to yellow suggested there was a reaction between sulphur and the sulphide ion, leading to the formation of a polysulphide which underwent anodic oxidation, with a consequent decrease in the sulphur-reduction diffusion current.

The plot of i_d *vs.* $[S^{2-}]$ was a typical amperometric titration curve, with equivalence point at $2{\cdot}5 \times 10^{-4}$ mole kg ($\pm 2{\cdot}3\%$). The initial concentration of electrogenerated sulphur was 1 meq/kg so the result is consistent with a reaction ratio of 1 : 4. Thus, the production of sulphur chains at the electrode surface is indicated, because viscous sulphur consists primarily of S_8 rings at temperatures less than 169°.[11] This could imply that the average number of sulphur atoms in the chain is 4, but we think it more likely that all the chains are S_4. From these results it is possible to calculate an equilibrium constant:

$$K = \frac{[S_5^{2-}]}{[S_4][S^{2-}]}$$

Results for 155° are shown in Table 1.

In order to study the polysulphide formation reaction at a higher temperature, measurements were also carried out at 165°. The upper limit is set by the decomposition of the solvent, which begins at about 170°.

The plot of sulphur diffusion current *vs.* the sulphide ion concentration at this temperature gave an equivalence point at 5×10^{-4} mole/kg ($\pm 0{\cdot}6\%$) of sulphide for an initial sulphur concentration of 1 meq/kg, corresponding to 1 : 2 reaction ratio of sulphide to sulphur. It is thus possible to determine the equilibrium constant of the reaction $S_2 + S^{2-} = S_3^{2-}$.

Table 1. Reaction constants with standard deviations

K, *kg/mole*		
155°C	165°C	155°C*
$1{\cdot}7 \times 10^4 \pm 0{\cdot}3 \times 10^4$	$4{\cdot}5 \times 10^3 \pm 0{\cdot}7 \times 10^3$	$4{\cdot}2 \times 10^3 \pm 0{\cdot}2 \times 10^3$
$1{\cdot}1 \times 10^4 \pm 0{\cdot}2 \times 10^4$	$5{\cdot}0 \times 10^3 \pm 0{\cdot}9 \times 10^3$	$4{\cdot}7 \times 10^3 \pm 0{\cdot}8 \times 10^3$
$1{\cdot}1 \times 10^4 \pm 0{\cdot}1 \times 10^4$	$3{\cdot}9 \times 10^3 \pm 0{\cdot}5 \times 10^3$	$4{\cdot}3 \times 10^3 \pm 0{\cdot}6 \times 10^3$
$1{\cdot}2 \times 10^4 \pm 0{\cdot}3 \times 10^4$	$3{\cdot}8 \times 10^3 \pm 0{\cdot}4 \times 10^3$	$4{\cdot}2 \times 10^3 \pm 0{\cdot}6 \times 10^3$
Mean value		
$1{\cdot}3 \times 10^4 \pm 0{\cdot}2 \times 10^4$	$4{\cdot}3 \times 10^3 \pm 0{\cdot}5 \times 10^3$	$4{\cdot}3 \times 10^3 \pm 0{\cdot}2 \times 10^3$

* With irradiation

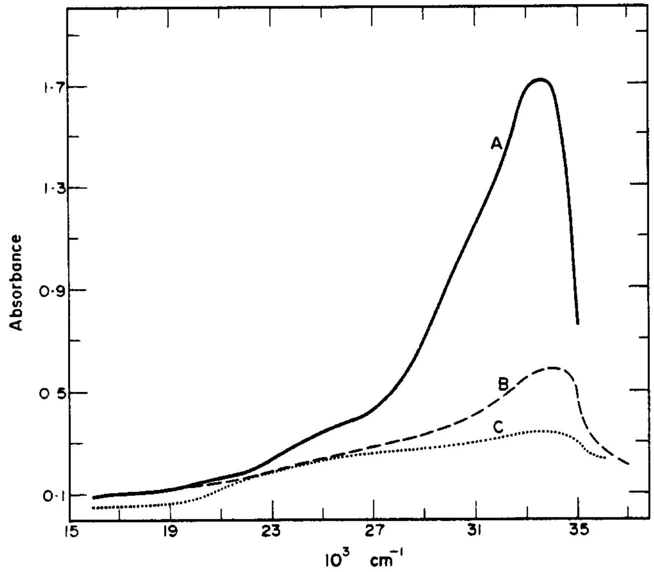

Fig. 1. Absorption spectra of sulphur species in (K,Na)SCN eutectic at 165°C. (*A*) $[S^{2-}] = 8 \times 10^{-4}$ mole/kg and $[S] = 10^{-3}$ eq/kg; (*B*) $[S] = 10^{-3}$ eq/kg; (*C*) $[S^{2-}] = 5{\cdot}1 \times 10^{-4}$ mole/kg.

The reproducibility of end-point detection ($\pm 0{\cdot}6\%$) suggests that there are distinct reactions at the two different temperatures investigated, and that at the higher temperature there is cleavage of the sulphur chains.

We have also carried out the titration at 155° with simultaneous irradiation of the cell. The equivalence point ($\pm 1\%$) and the values of the equilibrium constant are the same as those at 165°.

Visible light is known to break the S–S bond homolytically.[12] The energy of 400-nm radiation is 72 kcal mole, which is higher than that required to cleave a long sulphur chain (34 kcal/mole)[13] and to open an S_8 ring (64 kcal/mole). Therefore the photolysis reaction is presumably $S_4 + h\nu \rightarrow 2S_2$. It is interesting to observe that the sulphur so obtained reacts in the same way with sulphide as that produced electrolytically at 165°.

We have also carried out spectrophotometric measurements to confirm the polysulphide formation. The absorption spectra of sulphur, sulphide, and a mixture of the two in a eutectic melt at 165° are shown in Fig. 1 Comparison of the spectra indicates that the absorption peak at $33{\cdot}5 \times 10^3$ cm^{-1} (298 nm) is attributable to polysulphide The band at 25×10^3 cm^{-1} (400 nm) is also due to polysulphide.[1]

Because no difference between the spectra at 155 and 165° has been observed, it is not possible to distinguish the polysulphides, S_5^{2-} and S_3^{2-}, obtained at the two experimental temperatures

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Summary—Sulphur and sulphide ions react in (K,Na)SCN eutectic melt with the formation of polysulphide. The electrolytic oxidation of SCN^- at 155° forms S_4 which gives S_5^{2-} with S^{2-}; at 165° the sulphur electrogenerated is S_2 that reacts according to $S_2 + S^{2-} = S_3^{2-}$. The equilibrium constants of these reactions have been obtained by voltammetric measurements. The formation of S_2 at 155° by irradiation from a xenon lamp was confirmed. The S_2 reacts with S^{2-} to give S_3^{2-}, and the equilibrium constant for this reaction is the same as that found for the reaction at 165°.

Zusammenfassung—Schwefel und Sulfidionen reagieren in der eutektischen Schmelze (K,Na)SCN zu Polysulfid. Die elektrolytische Oxidation von SCN^- bei 155° liefert S_4 der mit S^{2-} S_5^{2-} bildet. Bei 165° ist der anodisch erzeugte Schwefel S_2, der nach $S_2 + S^{2-} = S_3^{2-}$ reagiert. Die Gleichgewichtskonstanten dieser Reaktionen wurden durch voltammetrische Messungen bestimmt. Die Bildung von S_2 bei 155° durch Bestrahlung mit einer Xenonlampe wurde bestätigt. Dieser S_2 reagiert mit S^{2-} zu S_3^{2-}; die Gleichgewichtskonstante dieser Reaktion ist dieselbe wie die der Reaktion bei 165°.

Résumé—Le soufre et les ions sulfure réagissent dans l'eutectique fondu (K, Na)SCN avec la formation de polysulfure. L'oxydation électrolytique de SCN^- à 155° forme S_4 qui donne S_5^{2-} avec S^{2-}; à 165°, le soufre électrogénéré est S_2 qui réagit selon $S_2 + S^{2-} = S_3^{2-}$. Les constantes d'équilibre de ces réactions ont été obtenues par des mesures voltammétriques. La formation de S_2 à 155° par irradiation avec une lampe au xénon a été confirmée. Le S_2 réagit avec S^{2-} pour donner S_3^{2-}, et la constante d'equilibre pour cette réaction est la même que celle trouvée pour la réaction à 165°.

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DETERMINATION OF IODINE BY ATOMIC-ABSORPTION SPECTROMETRY USING THE PLATINUM-LOOP TECHNIQUE

(*Received* 10 *July* 1973. *Revised* 31 *December* 1973. *Accepted* 20 *January* 1974)

We have previously described the quantitative measurement of the atomic absorption of mercury at 184·9 nm by use of a platinum-loop nebulizer/atomizer and a nitrogen-purged monochromator.[1] The determination of iodine by conventional flame atomic-absorption presents the same difficulties as that of mercury, the most serious being the absorption by oxygen entrained in the flame gases, which is appreciable in the far ultraviolet region, near to the iodine resonance line at 183·0 nm. Previous studies have mainly utilized the 206·2-nm non-resonance line, with correspondingly reduced sensitivity More recently, Kirkbright *et al.*[2] carried out atomic-absorption studies at 183·0 nm, using an inert-gas-separated nitrous oxide/acetylene flame and a nitrogen-purged monochromator. This communication describes the application of the platinum-loop technique to the atomic-absorption determination of iodine, using the 183·0-nm resonance line, with apparatus slightly modified from that used to determine mercury. The apparatus is simpler than that used for the flame determination and requires smaller sample volumes. Cationic and anionic interferences have been studied, and their removal, where possible, is also described.

EXPERIMENTAL

The primary source of resonance radiation was a Tesla-initiated iodine electrodeless discharge lamp (EDL), (fused quartz, 8-mm internal diameter, 5 cm long, filled with argon at 5 mmHg pressure) operated at a power of 15 W in a foreshortened $\frac{3}{4}$-wave resonant cavity (Electro–Medical Supplies Ltd.). Both the stability and intensity of the resonance line at 183·0 nm were increased and the degree of self-reversal greatly reduced by cooling the lamp with a flow of nitrogen.

The experimental arrangement is shown in Fig. 1. Radiation from the EDL source was passed through the absorption tube (length 12·5 cm, internal diameter 7 mm) before entering the grating monochromator (Rank Precision Industries Ltd. Type D 330, linear dispersion 26 Å/mm). The monochromator was flushed with argon at a flow-rate of 1·5 l/min. to remove atmospheric oxygen, which absorbs strongly at wavelengths shorter than 200 nm (similar results could have been obtained by using nitrogen).

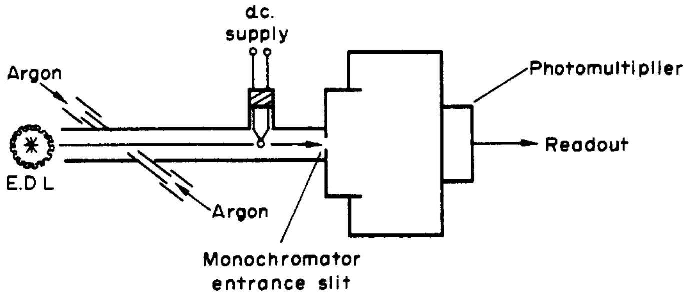

Fig. 1.

The photomultiplier (E.M.I. Ltd. Type 6256S) was loaded with 20 kΩ and its output measured on a Servoscribe potentiometric chart recorder fitted with a 20 nF capacitor across its input terminals to reduce short-term noise. A platinum loop (made from 1·0 cm of 0·1-mm dia. wire; elliptical with major axis 0·86 mm and minor axis 0·62 mm) was used as the atomizing device; this was suspended directly in the absorption path just in front of the monochromator entrance slit. On dipping the loop into the sample solution, a surface-tension film of about 0·1 μl volume was picked up The water in the sample was evaporated by passing a small d.c. current (~0·1 A) through the loop; the dried sample was then atomized by passing sufficient current (~1·9 A) to heat the loop rapidly to just below its melting point of about 1500 K). Argon was used as carrier gas.

RESULTS AND DISCUSSION

Measurements were made both at the 206·2 nm resonance line and the 183·0 nm resonance line When scanned by the monochromator, (bandpass 0·1 nm, scan-rate 1·98 nm/min, chart-speed 30 cm/min) the emission line from the source appeared as a strong, well-resolved peak (Fig. 2). Various concentrations of potassium iodide (40–5000 ppm) gave rise to atomic-absorption signals at 183·0 nm and a scatter signal at 206·2 nm. At concentrations of iodine higher than 500 ppm, some scatter also contributed to the signal at 183·0 nm. At lower concentrations the signal was entirely due to atomic absorption, as verified by the absence of a signal at the 184·9 nm Hg resonance line from a mercury EDL.

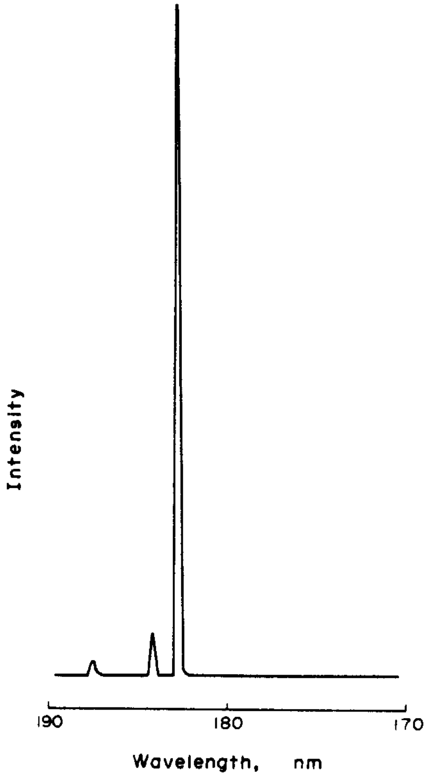

Fig. 2.

The sensitivity was found to be 9 ppm of iodine for 1% absorption, the relative standard deviation of the measurements being 4% at the 100 ppm level (20 variates); the limit of detection was 18 ppm for a signal:noise ratio of 2:1, or, in absolute terms, 1·8 ng of iodine. This compares favourably with the results obtained by using an inert-gas-separated nitrous oxide/acetylene flame,[2] which gave a sensitivity of 12 ppm and a detection limit of 25 ppm (*i.e.*, absolute detection limit of 12·5 μg, the minimum sample required in that method being ~0·5 ml).

Interference studies were done with solutions containing 200 ppm of iodine (as potassium iodide) and 200 ppm of the extraneous cation (as the chloride). The following results were obtained.

Cation	*Interference*, %	*Cation*	*Interference*, %
Cu^{2+}	+20	Mn^{2+}	+25
Na^{+}	−14	Zn^{2+}	−8
Cd^{2+}	−23	Cr^{3+}	+51
Co^{2+}	+15	Al^{3+}	−30

In the case of Cr, Cd, Na and Co, the interference was removed by passing the solutions through a cation-exchange column. Zeo-Karb 225 (H^+-form), and adding a 10-fold molar ratio of potassium hydroxide to the eluate to regenerate potassium iodide. For Zn, Cu, Mn and Al, however, the solution was more acid (pH 1–2) and neutralizing this with potassium hydroxide (the optimum pH for the cation-exchange being about 7), produced a large scatter signal. Therefore the Zeo-Karb was used in the K^+-form, obtained by passing 2 *M* potassium chloride through the column. On passage of the sample solutions through the column, Zn^{2+}, Cu^{2+}, Mn^{2+} and Al^{3+} were preferentially adsorbed, K^+ ions were liberated and the eluate contained the iodine as potassium iodide.

Anionic interferences were investigated in a similar manner by using solutions containing 200 ppm of iodine as potassium iodide and 200 ppm of the extraneous anion, present as the potassium salt. The following results were obtained

Anion	*Interference*, %	*Anion*	*Interference*, %
$C_2O_4^{2-}$	−77	SO_4^{2-}	+12
F^-	−53	BrO_3^-	+7
Br^-	+20	MnO_4^-	+9
ClO_4^-	−14	Cl^-	0
$Cr_2O_7^{2-}$	+20		

Removal of some of these interferences is possible *via* oxidation of the iodide to iodine and extraction into chloroform followed by reduction of the iodine to yield potassium iodide. The oxidizing agent used was ferric chloride, which is too mild an oxidant to oxidize anions other than iodide which may be present. Accordingly, 10 ml of sample solution were mixed with excess of ferric chloride solution and allowed to stand for 1 hr to ensure complete oxidation The iodine formed was extracted into 10 ml of chloroform and then back-extracted by shaking with potassium hydroxide solution (two washings with 5 ml portions of 0·2% solution gave complete stripping, *i.e.*, no detectable colour in the organic layer). This procedure removed interference due to $C_2O_4^{2-}$, F^-, Br^-, ClO_4^-, $Cr_2O_7^{2-}$ and SO_4^{2-} (The dichromate would itself oxidize iodide to iodine.) However interference by BrO_3^- and MnO_4^- was not removed by this method, probably they oxidize I^- to IO_3^- or I^+, which are not extracted into chloroform. No suitable method was devised for removing these interferences.

CONCLUSIONS

The technique has the advantages over flame methods of being both simple and fast. It also demonstrates that an EDL may be used as a satisfactory source of excitation in this region of the spectrum, provided that adequate care is taken to remove oxygen from the light-path. Although most of the interferences examined may be removed, this method cannot be regarded as a technique for general application; however, with fairly simple pretreatments it could be used for specific analytical problems

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2. G. F Kirkbright, T. S. West and P. J. Wilson, *At. Abs Newsletter*, 1972, **11**, 53.

Summary—The use of a platinum-loop atomizer and an electrodeless discharge lamp has been applied to the atomic-absorption determination of mercury at the 183·0-nm resonance line. Oxygen was flushed from the light-path with argon, giving adequate radiation transmission characteristics and a sensitivity of 9 ppm of iodine for 1% absorption. The method is prone to both cationic and anionic interferences, but the use of cation-exchange and solvent-extraction procedures overcomes some of the problems

Zusammenfassung—Eine Platinschleifen-Atomquelle und eine elektrodenlose Entladungslampe wurden zur Atomabsorptionsbestimmung von Quecksilber an der Resonanzline bei 183,0 nm verwendet. Durch Argonspülung wurde Sauerstoff aus dem Lichtweg entgernt; dadurch wurde eine ausreichende Strahlungsdurchlässigkeit erzielt und eine Empfindlichkeit, die 9 ppm Jod für 1% Absorption entspricht. Die Methode ist störungsanfallig gegenüber Kationen und Anionen, jedoch kann man mit Kationenaustausch- und Extraktionsverfahren einige der Probleme überwinden.

Résumé—On a appliqué l'emploi d'un atomiseur à boucle de platine et d'une lampe à décharge sans électrode pour le dosage par absorption atomique du mercure à la raie de résonance 183.0 nm. L'oxygène a été balaye rapidement de la trajectoire de la lumière par l'argon, donnant des caractéristiques de transmission de radiation convenables et une sensibilité de 9 ppm d'iode pour 1% d'absorption. La méthode présente une tendance aux interférences tant cationiques qu'anioniques, mais l'emploi de techniques d'échange de cations et d'extraction par solvant surmonte quelques-uns de ces problèmes

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MICROANALYSIS OF ALL SIX PLATINUM METALS PRESENT IN A DROP BY RING-COLORIMETRY IN CONJUNCTION WITH SOLVENT EXTRACTION

(*Received* 11 *July* 1973. *Revised* 26 *December* 1973. *Accepted* 27 *January* 1974)

There are comparatively few acceptable methods for separation and determination of noble metals in trace amounts, and these usually involve ion-exchange, liquid-liquid extraction, and chromatographic procedures,[1,2] and generally the prior separation of ruthenium and osmium *via* the extraction or distillation of their tetroxides. These methods also relate to the separation and identification of the metal ions rather than to their evaluation.

The present investigation deals not only with the efficient separation of all six platinum metals in a drop of solution but also their evaluation by ring-colorimetry and solvent extraction.

EXPERIMENTAL

Reagents

Standard metal solutions. Standard solutions of ruthenium, rhodium, palladium and iridium were prepared by dissolving ruthenium(III), rhodium(III), palladium(II) and iridium(III) chlorides in dilute hydrochloric acid, and standardized by determining ruthenium, rhodium and iridium by the hydrolytic precipitation method[1] and palladium by the dimethylglyoxime method. Osmium solution was prepared by dissolving 1 g of pure osmium tetroxide in 250 ml of 0·2*M* sodium hydroxide. Platinum solution was made by dissolving chloroplatinic acid in distilled water and standardized by precipitation of the metal with formic acid.

Developing agents

(*i*) Aqueous potassium thiocarbonate (PTC) solution, 0·5*M*.
(*ii*) α-Nitroso-β-naphthol solution in acetic acid, 1% w/v.
(*iii*) Rubeanic acid solution in acetic acid, 1% w/v.
(*iv*) Aqueous sodium diethyldithiocarbamate solution, 8% w/v.

Procedure

Separation. Test solution (5 μl) is spotted on the centre of a filter paper placed on a Weisz ring-oven. It is dried, then fumed with ammonia, and 2 drops (1·5 μl) of α-nitroso-β-naphthol solution are added. The brownish-red complex formed is brought into the ring zone (ring 1, palladium) by washing several times with chloroform. The centre of the disc is punched out and placed on another filter paper, and 1·5 μl of 2*M* hydrochloric acid is applied, followed by 5 μl of 0·05*M* PTC. The olive-green osmium complex is washed into the ring zone (ring 2) with ethyl acetate, the ring-oven being kept at 50–60°. The disc is fumed with bromine and then with ammonia, put on another filter paper, spotted with a drop of 3*M* hydrochloric acid and then with 3 μl of rubeanic acid solution. The blue ruthenium complex is washed into ring 3 with isopropyl alcohol.[2] The disc is put on another filter, then spotted with 3 μl of sodium diethyldithiocarbamate solution followed by 5 μl of 2*M* ammonium acetate solution. The yellow rhodium complex is washed into ring 4 with methyl isobutyl ketone. Ring 4 is treated with PTC and dilute hydrochloric acid to give brown Rh_2S_3. The disc is transferred to another filter, and spotted with 1·5 μl of 3*M* hydrochloric acid followed by 3 μl of rubeanic acid solution. The iridium is washed into ring 5 with distilled water. Ring 5 is treated with PTC and dilute hydrochloric acid to yield brown Ir_2S_3. The disc carrying the platinum-rubeanic acid complex is put on a fresh filter and washed 5 times with 5-μl drops of 0·5*M* PTC and then with distilled water, and finally with 1*M* hydrochloric acid on the hot ring-oven, and dried. Ring 6 is then brown PtS_2 and the disc is discarded.

Determination. The separated ions are determined semi-quantitatively by visual ring colorimetry,[3] a standard scale for each metal being prepared with the chromogenic reagents given above.

RESULTS AND DISCUSSION

Palladium forms an insoluble brown complex with α-nitroso-β-naphthol, which can be extracted with chloroform, resulting in the separation of palladium from the other platinum metals.

Table 1 Results of determinations

Metal ion taken, *mg/ml*		Metal ion found, *mg/ml*	Error, %	Metal ion taken, *mg/ml*		Metal ion found, *mg/ml*	Error, %
Ru(III)	0·48	0·46	−3·1	Os(VIII)	0·75	0·70	−6·6
	0·80	0·76	−5·0		1·00	1·05	+5·0
	1·34	1·26	−5·9		1·50	1·55	+3·3
Rh(III)	0·30	0·32	+6·6	Ir(III)	0·60	0·65	+8·3
	0·45	0·50	+11·1		0·85	0·90	+5·8
	0·90	0·85	−5·5		1·00	1·05	+5·0
Pd(II)	0·54	0·52	−3·7	Pt(IV)	0·64	0·60	−6·2
	0·90	0·85	−5·5		0·96	0·90	−4·1
	1·08	1·02	−5·5		1·28	1·32	+3·1

Osmium yields an olive-green complex with potassium thiocarbonate in acid medium. The complex is extractable with ethyl acetate; Rh, Ir, Ru and Pt do not form complexes under these conditions.

Fuming with bromine oxidizes any free thiocarbonate and any sulphides of platinum and ruthenium (to sulphate). In strongly acidic medium ruthenium and platinum form complexes with rubeanic acid. The ruthenium complex is soluble in isopropyl alcohol, but the platinum complex is not

Rhodium(III) forms a complex with diethyldithiocarbamate, but platinum and iridium do not, under the conditions specified. The rhodium complex is soluble in methyl isobutyl ketone. As the colour of the ring is very faint, it is developed with PTC and hydrochloric acid, which yield Rh_2S_3 with the rhodium.

Iridium(III) is separated from the platinum rubeanic acid complex by washing with distilled water and developed with PTC to give iridium sulphide. The platinum rubeanic acid complex is converted into a soluble PTC complex which is washed into the ring zone and converted into the sulphide by heating.

Interferences

Metal ions which form complexes with the reagents used will interfere, but many of them can be removed beforehand, or may not be associated with the platinum metals in the kind of sample usually analysed

The six platinum metals generally occur together in the form of alloys, and the common metals usually found with them are iron, titanium and chromium in the form of their oxide ores. The analysis of different alloys of platinum metals requires the separation of gold, silver, nickel *etc.* which are generally also present.

Before the solution of the platinum metals is applied to the ring oven, the following procedure can be used for removal of Ag, Pb, Au, Hg, Ni, Co, Zn, Fe, Ti, Cr, Th, Zr, Pd.

Ag, Pb, Au, Hg and Pd can be separated by precipitation as the sulphides from cold solution (pH 0·7–1·0) with potassium thiocarbonate. The other platinum metals (Ru, Rh, Os, Ir, Pt) are then obtained as sulphides by heating the filtrate and adding more PTC to ensure their complete precipitation. The ions of Ni, Co, Zn, Fe, Ti, Cr, Th and Zr will remain in solution. The platinum metals sulphides thus obtained are then dissolved in excess of potassium thiocarbonate reagent.

The palladium is recovered by adding excess of PTC reagent to the sulphides of Ag, Pb, Au, Hg and Pd. Au and Pd will form soluble thiocarbonate complexes, leaving Ag, Hg and Pb in the residue. Then a 5-μl drop of the Au and Pd complex solution is spotted on a filter on the ring oven, and fumed with bromine, followed by the application of 3 μl of γ-nitroso-β-naphthol solution. The palladium complex is washed into the ring zone with chloroform, and the disc is punched out, put on a fresh filter and washed several times with 2*M* hydrochloric acid and then with ferrous sulphate solution to reduce the gold to the metal (brown).

Ru, Rh, Os, Ir and Pt are then separated by applying 5 μl of the solution of their thiocarbonate complexes to a filter paper on the ring oven, fuming with bromine and ammonia, and then applying the normal procedure.

Results of a few determinations are given in Table 1. The errors are within the permissible limits for semiquantitative analysis.

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Summary—The ring-oven method, combined with solvent extraction, has been used for the separation of all six platinum metals when present in μg-amounts in a drop of solution. The separated constituents are determined by ring-colorimetry.

Zusammenfassung—Die Ringofen-Methode wurde zusammen mit der flüssig-flüssig-Extraktion zur Trennung aller sechs Platinmetalle verwendet, wenn in einem Tropfen Lösung μg-Mengen vorlagen. Die getrennten Bestandteile werden durch Ring-Colorimetrie bestimmt.

Résumé—La méthode du four annulaire, combinée avec l'extraction par solvant, a été utilisée pour la séparation des six métaux de la mine du platine quand ils sont présents en quantités de l'ordre du μg dans une goutte de solution. Les constituants séparés sont dosés par colorimétrie annulaire.

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THE OXYGEN-SHIELDED AIR-ACETYLENE FLAME IN EMISSION ANALYSIS

(*Received 7 June 1973. Revised 9 January 1974. Accepted 19 January 1974*)

Recent studies have shown flame-emission spectroscopy (FES) to be a useful complementary technique to atomic-absorption and fluorescence spectroscopy,[1-7] with good analytical sensitivity[8] and ready applicability to multi-element analysis.[9,10] The present work examines FES with an oxygen-shielded air–acetylene flame. The low burning velocity of the shielded flame permits it to be supported on a wide burner slot, to give a low background inner zone similar to that observed with a multi-slot burner.[11] A simultaneous enhancement of the flame temperature occurs on shielding, because of oxygen-supported combustion in the outer diffusion zone.[12] This creates a high-temperature low-background system, found to be very suitable for FES.

EXPERIMENTAL

A Varian AA5 spectrometer was used, with the standard Ebert 0·5-m monochromator and 638 line/mm grating, giving a reciprocal dispersion of 3·3 nm/mm at the exit slit for the first order. A 285 Hz chopper was used to modulate flame emission signals. The spectrometer output was recorded on a Phillips PR 4069M/OO recorder, with a 3 sec time constant.

The oxygen-shielded burner was similar to that described earlier,[12] but with a slot reduced to 2·5 cm in length and increased to 1·25 mm in width, to give the low-background inner zone mentioned above, and with the water cooling omitted. The burner was mounted directly in the AA5 burner assembly. This emission burner was unable to support a C_2H_2–N_2O flame, because of the higher burning velocity, and emission measurements on C_2H_2–N_2O flames were therefore made by using the standard Varian nitrous oxide head. Detection limits in this flame were obtained at a constant N_2O flow of 8·2 l./min, with fuel flow, burner position, monochromator slit and photomultiplier voltage optimized for each element.

FES results for all flames used were obtained by using analytical-reagent grade chemicals dissolved in either demineralized distilled water or 1*M* hydrochloric acid. A 1000 μg/ml potassium solution was used as an ionization suppressant where necessary, except for calcium, for which potassium salts of sufficient purity were not available, and for barium in the shielded flame. Owing to the low background of the shielded flame, signal-enhancement due to ionization suppression was found to be more than offset by increased flame noise from the potassium ionization continuum in the spectral region observed

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EXPERIMENTAL

A Varian AA5 spectrometer was used, with the standard Ebert 0·5-m monochromator and 638 line/mm grating, giving a reciprocal dispersion of 3·3 nm/mm at the exit slit for the first order. A 285 Hz chopper was used to modulate flame emission signals. The spectrometer output was recorded on a Phillips PR 4069M/OO recorder, with a 3 sec time constant.

The oxygen-shielded burner was similar to that described earlier,[12] but with a slot reduced to 2·5 cm in length and increased to 1·25 mm in width, to give the low-background inner zone mentioned above, and with the water cooling omitted. The burner was mounted directly in the AA5 burner assembly. This emission burner was unable to support a C_2H_2–N_2O flame, because of the higher burning velocity, and emission measurements on C_2H_2–N_2O flames were therefore made by using the standard Varian nitrous oxide head. Detection limits in this flame were obtained at a constant N_2O flow of 8·2 l./min, with fuel flow, burner position, monochromator slit and photomultiplier voltage optimized for each element.

FES results for all flames used were obtained by using analytical-reagent grade chemicals dissolved in either demineralized distilled water or 1*M* hydrochloric acid. A 1000 μg/ml potassium solution was used as an ionization suppressant where necessary, except for calcium, for which potassium salts of sufficient purity were not available, and for barium in the shielded flame. Owing to the low background of the shielded flame, signal-enhancement due to ionization suppression was found to be more than offset by increased flame noise from the potassium ionization continuum in the spectral region observed

RESULTS

Noise levels in the shielded flame

All studies on the shielded flame were made at a constant air flow-rate of 6·2 l./min and constant oxygen flow-rate of 4·0 l./min, corresponding to the shielding "plateau" for this particular flame.[12] For most of the elements examined, emission signals were observed to increase with fuel flows higher than those corresponding to the luminous limit of the flame. However, a simultaneous and severe increase of flame noise also occurred at this point, and accordingly a flame stoichiometry just below that of the luminous limit was adopted for optimum sensitivity.

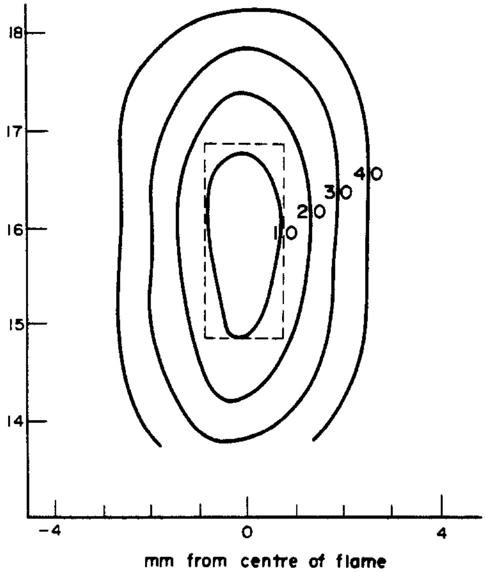

Fig. 1. Background emission profiles of the shielded flame. Contours give the % intensity increase relative to the minimum intensity at the centre of the flame. Contours were measured at 240·0 nm and a slit-width of 25 μm.

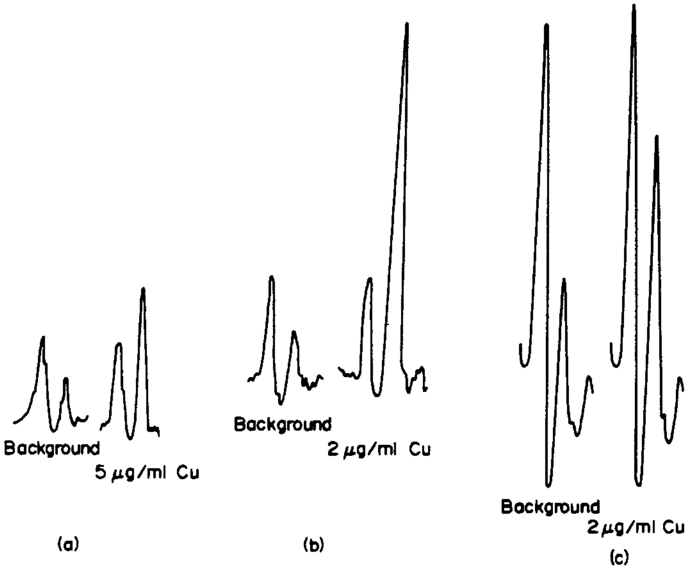

Fig. 2. Cu emission at 324·8 nm (a): Air–acetylene flame, monochromator slit 25 μm, photomultiplier voltage 850 (b): Shielded air–acetylene flame, same instrumental settings as for (a). (c): Nitrous oxide–acetylene flame, monochromator slit 25 μm, photomultiplier voltage 450 V.

Figure 1 shows the background noise contours of the shielded flame, measured for the luminous-limit flame. The results of Fig. 1 were obtained by using a 0·5 mm dia. circular collimator; subsequent results were obtained by replacing this with a larger collimator, approximately matching the 10% contour, shown by the dotted outline in Fig. 1. The low flame background given by this system is illustrated by the results in Fig. 2, showing the flame emission signals of Cu at the optimum 324·8 nm line. These results show the shielded flame to give a background intensity little different from that of an air–acetylene flame alone, but an emission signal for Cu of similar magnitude to that from the C_2H_2–N_2O flame at the instrument settings used.

Analytical sensitivity

The work of Koirtyohann and Pickett[4–6] among others has shown the C_2H_2–N_2O flame to be probably the most sensitive and versatile system currently available for flame emission work. Accordingly the emission sensitivities given by the shielded burner were compared with the corresponding results given with the same instrument, by the C_2H_2–N_2O flame, and with those determined elsewhere (Table 1). Although difficulties arise in giving any exact comparison of analytical data between different laboratories,[4,9] it is felt that the AA5 spectrometer used here is sufficiently similar to many other units in current use for the comparative data in Table 1 to offer some indication of the level of analytical sensitivity which may be expected from FES with the shielded flame.

Spectral interferences; calibration curves

Spectral interferences were generally found to be of comparable magnitude in the shielded flame and in the C_2H_2–N_2O flame. The latter flame, however, did show a clear advantage in reducing interferences due to band emission from the alkaline-earth metal oxides and hydroxides, presumably because of its enhanced chemical

Table 1. Detection limits at a signal to root-mean-square noise ratio of 2:1, *μg ml*

Species	*λ, nm*	Shielded flame*	C_2H_2–N_2O*	C_2H_2–N_2O[14]	C_2H_2–N_2O[4]	Separated C_2H_2–N_2O[15]
Al	396·2	0·5	0·05	0·05	0·01§	0·03
Ba	553·6	0·001†	0·002	0.002	0·002§	0·1†
Be	234·9	20	40	1·0	40	—
BeO	470·9	0·4	0·4		0·2	—
Ca	422·7	0·0002†	0·0001	0·0002	0·0001	0·003†
Co	345·4	0·07	0·05	0·03	0·05	—
	352·7	—	—	—	—	0·2
Cr	425·4	0·01	0·006	0·004	0·005	0·001
Cu	324·8	0·006	0·05	0·01	—	—
	327·4	0·01	0·03	—	0·01	0·03
Fe	372·0	0·05	0·06	0·03	0·05	0·05
Li	670·8	0·0001	0·0002	0·00002	0·00003	—
Mg	285·2	0·005	0·01	0·07	0·005	0·001
Mn	403·1	0·008	0·006	—	0·005	—
	403·3	—	—	0·008	—	0·005
Ni	341·5	—	—	—	0·03	—
	352·4	0·03	0·04	0·02	—	0·05
Sc	391·2	2·5	0·4	—	—	—
	402·0	—	—	—	0·03	—
	402·4	—	—	0·8	—	—
Sr	460·7	0·0001	0·0001	0·0005	0·0002§	0·02†
Ti	334·9	—	—	0·2	—	—
	399·9	>20	0·2	—	0·2	—
Tl	377·6	0·01	0·08	0·1	—	0·08†
	535·1	0·03	0·05	0·02	0·02	—
V	318·5	—	—	—	—	0·2
	437·9	1·5	0·1	0·1	0·01	—
Zr	360·1	>20	10	5	3	—

* This study: 100 *μm* and 25 *μm* monochromator slits were used with the shielded and C_2H_2–N_2O flames respectively.

† No ionization suppressant used with these elements.

§ Detection limits for Al, Ba and Sr given as 0·005, 0·001 and 0·0001 respectively, in later publications.[5,6]

reducing properties.[5] The calibration curves obtained with both flames, both in the presence and absence of spectral interferences, were also similar. In all cases examined, calibration curves were linear over a range of more than two orders of magnitude from the detection limit

The results obtained show that FES with the oxygen-shielded flame is capable of giving a very similar performance to the C_2H_2–N_2O flame for many elements. The major advantage of the former appears to be its low background, which permits good sensitivity to be obtained, in particular for Cu and Tl, with a comparatively low-resolution monochrochromator. This contrasts with the rather stringent optical requirements for FES in the C_2H_2–N_2O flame,[4] a conclusion which is emphasized by the experimental conditions used, where resolution was further reduced by the use of large slit-widths to compensate for inadequate photomultiplier sensitivity.

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Summary—Flame-emission studies have been made on 18 elements in the inner zone of an oxygen-shielded air-acetylene flame. The shielded flame gave higher emission sensitivity that that of the C_2H_2–N_2O flame for Cu and Tl, and comparable sensitivity for a number of other elements, but poorer sensitivity for elements forming stable refractory oxides in flames. The inner zone of the shielded flame has low emission-background and high flame-temperature, permitting good analytical sensitivity to be obtained with relatively low-resolution optical equipment.

Zusammenfassung—Die Flammenemission von 18 Elementen wurde in der inneren Zone einer mit Sauerstoff abgeschirmten Luft–Acetylen Flamme untersucht. Die abgeschirmte Flamme ergab bei Cu und Tl eine höhere Emissionsepfindlichkeit als die C_2H_2–N_2O-Flamme, bei einer Anzahl anderer Elemente vergleichbare Empfindlichkeit, geringere Empfindlichkeit jedoch bei Elementen, die in Flammen stabile feuerfeste Oxide bilden. Die innere Zone der abgeschirmten Flamme weist einen geringen Emissions-Untergrund und eine hohe Flammentemperatur auf; daher erlaubt sie gute analytische Empfindlichkeit bei relativ gering auflösender optischer Ausrüstung.

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* Present address: Department of Chemistry, Memphis State University, Memphis, Tennessee, U.S.A.

Résumé—On a effectué des études d'émission de flamme sur 18 éléments dans la zone interne d'une flamme air-acétylène protégée de l'oxygène. La flamme protégée a donné une sensibilité d'émission plus élevée que celle de la flamme C_2H_2–N_2O pour Cu et Tl, et une sensibilité comparable pour un certain nombre d'autres éléments, mais une sensibilité plus faible pour les éléments formant des oxydes réfractaires stables dans les flammes. La zone interne de la flamme protégée an un found d'émission bas et une haute température de flamme, permettant d'obtenir une bonne sensibilité analytique avec un équipement optique de résolution relativement faible.

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ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG–V*

SORPTION VON FLIESSMITTELDÄMPFEN AN CELLULOSE

(*Eingegangen am* 27. *März* 1972. *Angenommen am* 19. *Januar* 1974)

In einer früheren Veröffentlichung[1] wurde gezeigt, daß bei der Sorption von Alkohol–Wasser-Gemischen an Cellulose deren Massezunahme nicht allein auf eine Erhöhung des Wassergehalts zurückgeführt werden kann, sondern, daß neben Wasser auch Alkohole an der Cellulose gebunden werden. Nun war es interessant, noch die Zeitabhängigkeit der Massezunahme der Sorption zu prüfen und festzustellen, wie sich Cellulosepulver verhält, das Lösungsmitteldämpfen mit steigendem Wassergehalt ausgesetzt worden ist.

EXPERIMENTELLER TEIL

Die benutzten Lösungsmittel wurden durch mehrfache Destillation gereinigt. Die Sorption der Lösungsmittel an der Cellulose wurde in einer zylindrischen chromatographischen Kammer von 10 cm Durchmesser und 25 cm Höhe durchgeführt. Das Cellulosepulver wurde in einem Wägeglas 55 × 35 mm untergebracht, während das Lösungsmittel den Boden der Kammer bedeckte.

Cellulose: Whatman Cellulose Powder, Standard Grade. Der Wassergehalt wurde durch biamperometrische Titration mit Karl-Fischer-Lösung bestimmt.

ERGEBNISSE UND DISKUSSION

Um die Verhältnisse bei der Sorption des Fließmittels am Träger noch von einer anderen Seite her zu erfassen, wurde die Sorption aus der Gasphase untersucht.

Zeitabhängigkeit der Sorption

Um die Zeitabhängigkeit der Massezunahme zu erfassen, wurden 1,0000 g des getrockneten Cellulosepulvers 1 bis 10 Tage in der gesättigten Atmosphäre der möglichst wasserfreien niederen aliphatischen Alkohole aufbewahrt. Die Resultate sind in Abb. 1 dargestellt. Das Diagramm zeigt, daß die Massezunahme in erster Näherung mit der Dielektrizitätskonstanten der Solventien abfällt. Der schwankende Wassergehalt der Gemische scheint dabei die Meßwerte nur in untergeordnetem Maße zu beeinflussen.

Einfluß des Lösungsmittel-Wasser-Verhältnisses

Zur Untersuchung des Einflusses des Wassergehalts auf die Sorption der Lösungsmitteldämpfe durch lufttrockene Cellulose wurden weitere Proben eine Woche über dem Gemisch Lösungsmittel/Wasser aufbewahrt und danach wieder die Massezunahme bestimmt. Die erhaltenen Meßwerte sind leider ohne größeren experimentellen Aufwand nur qualitativ reproduzierbar. Die Ergebnisse sind in Abb. 2 dargestellt. Trotz der unbefriedigenden Reproduzierbarkeit kann man aus diesen Versuchsreihen wesentliche Informationen über die Massezunahme, über den Einfluß des Alkohol–Wasser-Verhältnisses, über die Zusammensetzung des Sorbats usw. bekommen.

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* Mitteilung IV: *Talanta*, 1974, **21**, 641.

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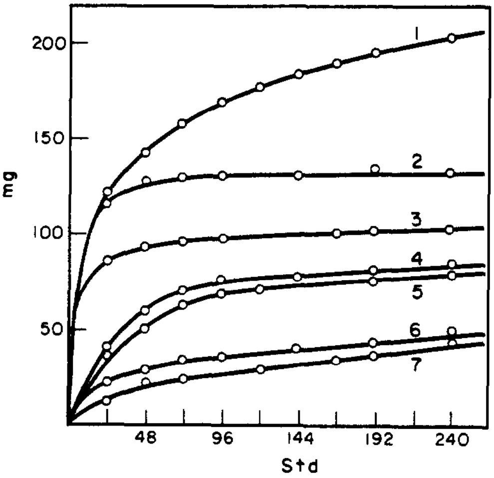

Abb. 1. Zeitabhängigkeit der Massezunahme der Cellulose bei der Sorption von Lösungsmitteldämpfen: (1) Wasser; (2) Methanol (99,56%); (3) Äthanol (95,07%); (4) 1-Propanol (99,30%); (5) 2-Propanol (98,25%); (6) 1-Butanol (99,55%); (7) 2-Butanol (98,83%).

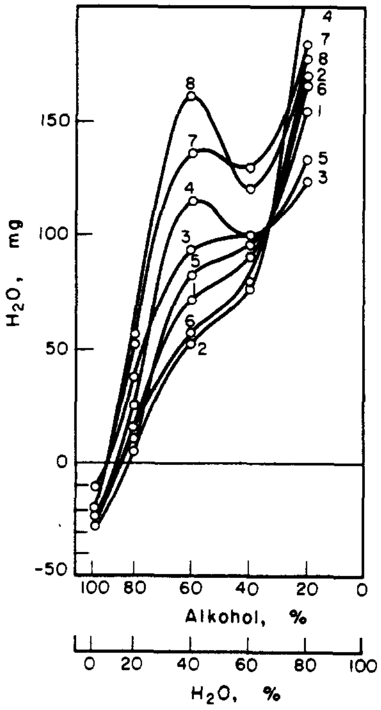

Abb. 2. Reproduzierbarkeit der Meßwerte bei der Sättigung der lufttrockenen Cellulose mit Dämpfen wäßriger Alkohole. Abhängigkeit der Wasserzunahme vom Wassergehalt des ursprünglichen Alkohols

Kurven 1, 2, 3, 4: Versuchsreihe *a* Kurven 5, 6, 7, 8: Versuchsreihe *b*. Methanol (1, 5), Äthanol (2, 6), 1-Propanol (3, 7), tert-Butanol (4, 8)

Die einzelnen Meßwerte dieser Versuchsreihe sind in Tabelle 1 zusammengestellt. Bei der Berechnung der Zusammensetzung des sorbierten Fließmittels wurde auf die Summe aus aufgenommenem organischen Lösungsmittel und aufgenommenem Wasser plus dem bereits in der lufttrockenen Cellulose vorhandenen Wasser bezogen. Wegen der starken Streuungen auch innerhalb der Reihen wurde auf eine graphische Darstellung verzichtet.

Auch die Ergebnisse dieser Untersuchungen lassen wieder interessante Schlüsse im Hinblick auf das verfolgte Ziel zu. Mit steigendem Wassergehalt der Alkohole steigen sowohl die Massezunahme, wie auch der Wassergehalt der Cellulose. Die Art des Alkohols spielt zwar eine erkennbare und systematische Rolle, doch sind die Unterschiede zwischen den einzelnen Kurven unwesentlich und gegenüber dem Einfluß der Versuchsbedingungen

Tabelle 1. Sättigung lufttrockener Cellulose mit Dämpfen wasserhaltiger Lösungsmittel. Einwaage an Cellulose 1,0000 g, Wassergehalt 48,3 g/l g Cellulose.

Fließmittel	Gehalt an org. Lösungsmittel, %	Massezunahme, *mg*	Wassermenge gefunden, *mg*	Wasseraufnahme, *mg*	Sorbiertes H_2O, %	Org. Lösungsmittel in Fließmittel, %
Methanol	95	97,4	22,4	−25,9	15,4	84,6
	90	100,6	47,1	−1,2	31,6	68,4
	85	104,6	43,8	−4,5	28,6	71,4
	80	135,9	64,9	16,6	35,2	64.8
	60	103,7	99,9	51,6	65,7	34,3
	40	109,6	127,6	79,3	80,8	19,2
	20	149.2	185.4	137.1	93,9	6.1
Äthanol	95	56,5	24.3	−24,0	23,2	76,8
	90	60,0	63,8	15,5	58,9	41,1
	85	33,2	46,2	−2,1	56,7	43.3
	80	69,7	62,5	14,2	53,0	47,0
	60	140,9	130,6	82,3	69.0	31,0
	40	146,1	147,1	98,8	75,7	24,3
	20	148.5	214,0	165,7	—	—
2-Propanol	95	40,5	29,8	−18,5	33.5	66.5
	90	66,9	62,9	14,6	54,7	45.3
	85	109,7	81,1	32,8	51,3	48,7
	80	83,3	87,4	39,1	66,4	33.6
	60	171,2	191,0	142.7	87.0	13.0
	40	116,9	140,1	91.8	84.8	15.2
	20	120.7	175,0	126.7	—	—
tert,-Butanol	95	24,4	38,2	−10,1	52.5	47.5
	90	59,7	71,5	23,2	66.2	33.8
	85	55,7	62,8	14,5	60,4	39,6
	80	76,9	84,7	36,4	67,6	32,4
	60	110,7	162,3	114,0	—	—
	40	121,4	145,2	96,9	85.6	14,4
	20	151.5	226.3	178.0	—	—
Aceton	95	51,3	46,0	−2,3	46,2	53,8
	90	79,6	94,3	46,0	73,7	26.3
	85	114,7	125,6	77,3	77,0	23,0
	80	76,2	83,9	35,6	67.4	32,6
	60	105,5	114,3	66,0	74,3	25,7
	40	155,6	169,7	121,4	83,2	16,8
	20	162,9	205.6	157,3	97.3	2,7
Pyridin	95	167,2	27,4	−20,9	12,7	87,3
	90	—	—	—	—	—
	85	188,2	44,5	−3,8	18,8	81,2
	80	133,3	66,1	17,8	36,4	63,6
	60	145,6	99,1	50,8	51,1	48,9
	40	140.9	141,8	93,5	74,9	25,1
	20	145.2	209,7	161.4	—	—

gering. Der Wassergehalt der Cellulose nimmt zwar erwartungsgemäß mit steigendem Wassergehalt der Lösungen zu, diese Abhängigkeit ist aber nicht linear und verläuft in charakteristischer Weise (Abb 2).

Ein bemerkenswertes Ergebnis dieser Messungen ist die Tatsache, daß im Verlauf der Sorption sogar ein bereits fixiertes Solvens durch ein anderes ersetzt werden kann Das geht aus den Kurven in Abb. 2 hervor Aus der lufttrockenen Cellulose, die schon vor der Sättigung 48,3 mg Wasser pro 1 g Cellulose enthielt, wurde bei der Sättigung mit den Dämpfen der hochprozentigen Alkohole ganz eindeutig das Wasser verdrängt und dessen Platz an der Trägerphase durch den Alkohol eingenommen.

Aus den Versuchen dieser Reihe geht hervor, daß es auch bei der Einwirkung von Lösungsmitteldämpfen auf die Cellulose zur Bildung einer Phase kommt, die aus allen Lösungsmittelkomponenten aufgebaut ist. Der Anteil des Wassers ist gewöhnlich größer als im ursprünglichen Gemisch und wird durch das benutzte organische Lösungsmittel bestimmt. Eine praktische Folgerung daraus ist, daß es bei der Sättigung der Cellulose mit den Dämpfen des reinen Lösungsmittels kaum eine Schicht geben kann, die nur aus dem reinen Solvens besteht.

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1. J. Michal und G. Ackermann, *Talanta*, 1965, **12**, 171.

Summary—The sorption of solvent vapours onto dried cellulose has been investigated. The time-dependence and the effect of the solvent–water ratio is discussed. The studies concerned the properties of methanol, ethanol, propanol and butanol.

Zusammenfassung—Es wird die Sorption von Lösungsmitteldämpfen an getrockneter Cellulose untersucht und dabei die Zeitabhängigkeit, sowie der Einfluß des Verhältnisses Lösungsmittel zu Wasser diskutiert. Die Untersuchungen erstrecken sich auf das Verhalten von Methanol, Äthanol, Propanol und Butanol.

Résumé—On a étudié la sorption de vapeurs de solvants sur la cellulose desséchée. On discute de la dépendance par rapport au temps et de l'influence du rapport solvant-eau. Les études ont concerné les propriétés des méthanol, éthanol, propanol et butanol.

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ERRATA

In the May issue on page 357 the name M. K. Kumaran as an author of the paper was printed by mistake and should be deleted.

On page 254 in the March 1974 issue, line 25 should be replaced by the following:

($J_{4,5'}$), and that at 8·56 ppm to $H_{3'}$ because of the $J_{3',4'}$ coupling constant of 7·5 Hz. The remaining pyridyl proton,

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SPECTROCHEMICAL DETERMINATION OF TRACE BISMUTH AND LEAD IN IRON–BASE AND HIGH-TEMPERATURE SUPERALLOYS*

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Summary—A method is presented for determination of lead and bismuth in steels and superalloys, based on co-precipitation with manganese dioxide followed by optical-emission or atomic-absorption measurements. The limit of determination is about 0·0001% and the relative standard deviation is 4% at the 0·002% level.

A chemical spectrographic method is proposed for determining trace amounts of bismuth and lead in iron–base and high temperature superalloys. The method utilizes the separation of the elements from the matrix by co-precipitation with manganese dioxide before their determination by optical emission or atomic absorption. Manganese dioxide is produced by the reaction of potassium permanganate with a manganese salt such as manganese sulphate. Elements such as bismuth and lead have been found to be effectively absorbed on the manganese dioxide surface. The use of manganese dioxide as a collector was first reported by Blumenthal[1] in 1928. Several investigators have used the technique since. Pyburn and Reynolds[2] published a comprehensive study of the separation of trace metals by the manganese dioxide collection method. Their study shows poor collection for copper and negligible collection for zinc, but better results are reported for lead and tin. A detailed study of manganese dioxide as a collection agent for lead and bismuth in nickel (before atomic-absorption analysis) was published by Burke[3] in 1970. We have also used manganese dioxide in the past few years as a means of concentrating traces of bismuth and lead in ferrous and high-temperature superalloys in an effort to improve sensitivities and detection limits for both elements. The complex composition of superalloys (Chromium–cobalt–niobium–tantalum–molybdenum–tungsten–titanium–aluminium–nickel) necessitated the development of a method whereby lead and bismuth could be separated and concentrated with minimum interferences from the multi-element matrix. The manganese dioxide precipitate can be arced in an optical-emission spectrograph or may be dissolved in a small volume of hydrogen peroxide and hydrochloric acid for atomic-absorption analysis as reported by other investigators.[3,4] The proposed method gave us a useful means of determining bismuth and lead at the 0–200 ppm level without cumbersome separations and with no involved sample preparation. A few experiments showed that antimony and tin can also be concentrated in the same way, thus offering possibilities for trace

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determination of these elements. X-Ray fluorescence examination of the manganese dioxide precipitate for bismuth and lead showed the sensitivity to be too low and the background too high for use of X-ray fluorescence for the final determination.

EXPERIMENTAL

Apparatus

A JACO 3·4 m Ebert optical-emission spectrograph, JACO console microphotometer, photographic processing equipment, and a JACO 82-500 absorption spectrograph with a Sargent recorder were used.

Materials

Electrodes. The upper counter-electrode (ASTMC5) and lower sample electrode (ASTMS-11) were both of high-purity graphite.

Bismuth solution 1 mg/ml.

Lead solution 1 mg/ml.

Manganous sulphate monohydrate, 5% *solution.*

Potassium permanganate, 0·25*M*.

Procedure

Two procedures, one for low-alloy iron–base and high-temperature superalloys and the other for stainless-steel matrices were developed.

Low-alloy iron–base and high-temperature superalloys. Dissolve up to 5 g of sample in 10 ml of conc. sulphuric acid and 30 ml of water. Treat this solution with sufficient 1·2*M* nitric acid (200 ml) and adjust the final volume to 200 ml by boiling off the excess. Add 5 ml of 5% manganous sulphate solution and heat to boiling. Add 10 ml of 0·25*M* potassium permanganate solution slowly and continue boiling for 2 min. Allow the solution to stand at a temperature of about 70° for 30 min and then filter through a micropore membrane (5 μm). Wash the precipitate three times with 1·2*M* nitric acid, using the first two washings to transfer the last traces of precipitate from the beaker to the membrane.

Stainless-steel matrices. Dissolve up to 5 g of sample in 90 ml of 4*M* hydrochloric acid and 30 ml of conc. nitric acid added in that order. The nitric acid is added with caution to avoid any violent reaction. Then add 20 ml of (70%) perchloric acid and evaporate to dense fumes of perchloric acid. This step is necessary to oxidize chromium to the 6+ state, since chromium(III) reacts with the added potassium permanganate, and prevents complete formation of the manganese dioxide. The manganese dioxide is then precipitated and treated as for the other alloys (starting from addition of 1·2*M* nitric acid).

The dried manganese dioxide residue can be either directly arced in the optical-emission spectrograph or dissolved in a definite volume of a suitable solvent and the resulting solution used for atomic-absorption analysis. A suitable solvent is 10 ml of a mixture of conc. hydrochloric acid, hydrogen peroxide and water (2 : 1 : 1 v/v), used in a 150 ml beaker with gentle heating.

The following optical-emission conditions are used for bismuth and lead.

Discharge	d.c. arc
Voltage (open-circuit)	220 ± 20V
Current (short-circuit)	6–12 A
Spectral region	2250–3450 Å
Slit-width	30 μm
Preburn period	nil
Exposure period	5, 10, 30 sec (moving plate)
Sample polarity	positive
Analytical-line pairs	Bi 3067·72 Å Pb 2833·07 Å Mn 3035·0 Å Mn 2842 Å

The 3067·72 Å bismuth line is a doublet with the second peak at 3067·64 Å. The latter is interfered with by a molybdenum line at 3067·64 Å. The Pb 2833·07 Å line is interfered with by Zr 2833·3 Å and Mn 2833·3 Å, the latter being the more serious. The interference, however, appears negligible at the 5 and 10 sec exposures and becomes serious only for longer exposures. This was confirmed by moving-plate results whereby it was found that lead substantially separates from the less volatile manganese during the 5 and 10 sec exposures.

The dissolved manganese dioxide residue is analysed by atomic absorption according to the following conditions.

Lamps	bismuth and lead, single-element
Resonance lines	2231Å Bi, 2170 Å Pb
Entrance slit	100 μm
Exit slit	150 μm
Air-flow	5·7 l./min
Acetylene-flow	2·4 l./min

RESULTS AND DISCUSSION

Bismuth can be determined very satisfactorily by the proposed method over the range 0–100 ppm. Optical emission is the best method for the 0–5 ppm range, and atomic-absorption for higher levels.

As no superalloy standards with ultralow bismuth contents are available, the standard-addition technique was used, four 1-g samples of High Temperature Superalloy 494-100 being spiked with 0·0001, 0·0003 and 0·0005% bismuth and a log–log plot of intensity ratio *vs.* concentration being made. Inspection of the Bi/Mn intensity ratios given in Table 1 clearly indicates that the unspiked samples 494-100, 494-102 and 494-122 contain levels of bismuth lower than or equal to 0·0001%. A cross-check with Ledoux's Chemical Laboratory* confirmed our optical-emission bismuth values.

Table 1. Bismuth, optical-emission spectroscopic results for 1-g samples of high-temperature superalloys

Sample	Bismuth added, %	Bi/Mn intensity ratio	Bismuth, %*	Bismuth %†
494-100		0·40	≤ 0·0001	≤ 0·0001
494-100	0·0001	0·45	0·00011	
494-100	0·0003	0·60	0·00025	
494-100	0·0005	0·85	0·00055	
494-102		0·40	≤ 0·0001	≤ 0·00005
494-122		0·40	≤ 0·0001	≤ 0·00005

* Our results.
† Ledoux's results.

For the maximum of 0·0001% bismuth specified in our superalloy programme the proposed optical-emission method is operating at its limit of detection if a 1 g sample is taken. For better reliability a larger sample should be taken, preferably 5 g, but may present dissolution problems, as is the case with the superalloys.

A 5-g sample was found to be the minimum weight suitable for the atomic-absorption analysis. Calibration graphs constructed by use of low-allow steels and stainless steels spiked with bismuth are linear but the slope for stainless steels is almost twice that for low-alloy steels. What is significant however, is that both graphs are linear, indicating constant bismuth recoveries during co-precipitation with manganese dioxide. As no certified standards with 0·0001–0·01% bismuth were available at the time the method was developed, the inclusion of at least one reagent blank and five synthetic standards was necessary and is still recommended. From Table 2 it can be seen that the proposed atomic-absorption method provides a new analytical capability for accurately determining bismuth at trace levels never before possible by direct methods. Recently the NBS (361–365) series of low-alloy steels was also analysed for bismuth by atomic absorption. The results given in Table 3 show the bismuth values obtained by our method, in comparison with NBS values.

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* Independent Referee Laboratory, New Jersey, U.S.A.

Table 2. Bismuth results obtained by atomic absorption (5 g samples)

Sample	Bismuth, % Assumed	Found
Low alloy	0·0005	0·0005
Low alloy	0·001	0·0014
Low alloy	0·002	0·0019
Low alloy	0·004	0·0033
Low alloy	0·006	0·0044
Low alloy	0·008	0·0090
Low alloy	0·010	0·0110
16 Cr-10 Ni Stainless	0·0004	0·00047
18·5 Cr-9·5 Ni Stainless	0·0016	0·0014
20·5 Cr-10 Ni Stainless	0·0032	0·0032

Agreement between our values and the NBS values is very satisfactory. A 1–5 g sample was found suitable for lead analysis by optical emission for levels ranging from 1 to 200 ppm.

The standard-addition technique was used for the high-temperature superalloy 494-150 to compensate for the lack of certified standards. Table 4 shows that the detection limit for lead by optical emission is 3 ppm when a 1 g sample is used. A wet chemical determination of lead in 494-150 by the dithizone method gave a value of $\leq 0{\cdot}0002$ which is in good agreement with the optical-emission value. Optical-emission sensitivity for lead was considerably improved by using a 5 g sample; however, no lead was detected in NBS 361 and 365. Excellent agreement was obtained between the optical emission and the dithizone methods for 18–8 stainless-steel samples 73-729 and 73-730.

Lead determination by the manganese dioxide and atomic-absorption method has been found successful for low-alloy and stainless steels at levels ranging from 0·0005 to 0·02%. The proposed method offers a new, rapid approach for determining lead at critical 0·001–0·002% levels with excellent accuracy and precision.

Results for low-alloy and stainless-steel samples and certified standards, interpreted from a calibration graph constructed with synthetic samples, are exhibited in Table 5 along with values obtained by the dithizone method.

Table 3. Bismuth in NBS Series 361–365 by atomic absorption (5g samples)

Sample	Bismuth, % Found	NBS values
NBS 361	0·0003	(0·0004)*
NBS 362	0·0054	(0·006)⁺
NBS 363	0·0007	(0·0008)*
NBS 364	0·0024	(0·002)⁺
NBS 365	Not detected	< 0·00001

* NBS value from a single laboratory.

⁺ NBS approximate value from heat analysis Spark-source mass spectrometry.

Table 4. Optical-emission determination of lead

Sample	Pb found, %	Pb present, %
494-150	≤0·0003	0·000*
494-150	≤0·0003	0·0001
494-150	≤0·0003	0·0003
494-150	0·0006	0·0006
494-150	0·0009	0·0010
494-150	0·002	0·0020
NBS 361	Not detected	<0·0001†
NBS 362	0·0006	0·0006
NBS 363	0·0016	0·0018
NBS 364	0·010	0·019
NBS 365	Not detected	<0·00005
73-729-1	0·0006	0·0006‡
73-729-2	0·0006	
73-730-1	0·0006	0·0006
73-730-2	0·0006	

* Lead added.

† Lead reported by NBS (361 value from single laboratory, 362 value from heat analysis, 363 value from single laboratory, 364 provisional value, 365 polarographic).

‡ Lead analysed by dithizone method at Crucible Materials Research Center.

Table 5. Lead results by atomic absorption

Sample	Type	Weight, g	Lead, %		
			Atomic absorption	Dithizone	NBS certificate
NBS 130a	Low alloy	0·20	0·217		0·23
BC 328	Low alloy	2·0	0·0148		0·015
BC 273	Low Alloy	5·0	0·003		0·003
NBS 442	16 Cr-10 Ni	5·0	0·0021		0·0017
NBS 443	18·5 Cr-9·5 Ni	5·0	0·0024		0·0025
NBS 444	20·5 Cr-10 Ni	5·0	0·0037		0·0037
72-1553	18 Cr-8 Ni	5·0	0·0030	0·0027	
72-1554	18 Cr-8 Ni	5·0	0·0033	0·0039	
72-1558	18 Cr-8 Ni	5·0	0·0049	0·0048	
72-1562	18 Cr-8 Ni	5·0	0·0130	0·0140	
72-1831	18 Cr-8 Ni	5·0	0·0009	0·0008	
72-1929	18 Cr-8 Ni	5·0	0·0008	0·0007	
72-1930	18 Cr-8 Ni	5·0	0·0006	0·0005	
72-1564	18 Cr-8 Ni	5·0	0·0065	0·0061	

Inspection of Table 5 reveals that the method determines lead as accurately as does the dithizone method. It is also more rapid and has the advantage that bismuth can be determined on the same sample. The coefficient of variation was found to be 4% for both elements (10 variates) at the 0·002% level.

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Zusammenfassung—Ein Verfahren zur Bestimmung von Blei und Wismut in Stählen und Superlegierungen wird angegeben, das auf der Mitfällung mit Mangandioxid und nachfolgender Messung der optischen Emission oder der Atomabsorption beruht. Die Grenze der Bestimmung ist etwa 0,0001%, die relative Standardabweichung 4% bei etwa 0,002%.

Résumé—On présente une méthode pour la détermination du plomb et du bismuth dans les aciers et superalliages, basée sur la coprécipitation avec le bioxyde de manganèse suivie de mesures d'émission optique ou d'absorption atomique. La limite de dosage est d'environ 0.0001% et l'écart type relativ est de 4% au niveau de 0,002%.

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DESIGN AND PUBLICATION OF WORK ON STABILITY CONSTANTS

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Summary—Methods for determining stability constants are reviewed critically. Recommendations are made about the choice of technique, the detailed design of experiments, the calculation of the constants and the presentation of the results for publication.

Many discussions of stability constants start by an exhortation to consider either "the formation of N complexes BA_n (where $n \leq N$ and charges are omitted for clarity) by the addition of n ligands A to a central group B" or, even more depressingly, "the formation of complexes of general composition $B_qA_pH_jM_mX_x(H_2O)_w$ in an aqueous solution containing the bulk electrolyte MX." This latter formula is usually simplified by assuming that, since the concentrations of M, X and water hardly vary, the (average) values of m, x and w are fixed for a particular set of values of q, p and j. The contributions of those species which make up the medium are then thankfully ignored, and the complexes are written as $B_qA_pH_j$, where q and p may have values of zero, or of any positive whole number. The value of j is also integral, and is positive for species which act as Brønsted acids, but negative for those which contain one or more hydroxyl groups.

The discussions usually continue by defining an overall stability constant, which is merely the equilibrium constant for the formation of each particular complex from the appropriate components B, A and H (or OH). Obviously, the concentration of each complex in a given solution depends on the value of this constant, expressed as a concentration quotient, and on the equilibrium concentrations of B, A and H, and if it were possible to measure the concentrations of the complex, and of the components in equilibrium with it, the value of the stability constant could be obtained.

The very large literature on the determination of stability constants (see, *e.g.* ref. 1) has grown up because it is seldom, if ever, possible to obtain direct measurements of the equilibrium concentrations of all species which are present in a solution in which complexes are formed. The equilibrium concentrations of the components B, A and H depend not only on the fractions of these species which are consumed in the course of complex formation, but also on the *total* concentrations of these components. An increase in the total concentration of a ligand will, by the law of mass action, always increase the concentration of free ligand, albeit sometimes by a very small amount. The equilibrium concentration of one of the components can therefore be related to the stability constants of the complexes and to the analytical composition of the system. Conversely, measurement of the variation of the free concentration of but one species with the overall composition of the solution can, in principle, lead to values of the stability constants.

Any change in the extent of complex formation in a solution is reflected by changes in several aspects of its behaviour. Variation of suitable properties with the composition of the solution may therefore be exploited to give information about the complexes which are formed. It is sometimes possible to study a property which depends only on the concentration of one species, and so provides a method of measuring the equilibrium concentration of that species. For example, a potentiometric cell can sometimes be designed so that its e.m.f. can give a measure of the concentration of uncomplexed metal ion, and the total concentration of a metal ion in an organic solvent which has been equilibrated with an aqueous solution is often proportional to the concentration of uncharged metal complex in the aqueous phase.

Interpretation is much more difficult when several species contribute to the property which is being measured. Thus the distribution of a metal ion between a cation-exchange resin and a solution depends on the concentration of the free metal ion and of any cationic complex, together with the various partition coefficients of the cations between the two phases.

Spectrophotometric measurements may also be difficult to interpret, since the absorbance of the solution depends on the concentrations, and molar absorptivities, of all species which absorb radiation of the wavelength used. However, if addition of the ligand to a metal ion results in a marked change in absorbance, because of the formation of a single complex, the concentration of this species may be determined spectrophotometrically. Methods in which the concentration of a single species can be followed are deservedly more popular than those in which several species contribute to the quantity being measured. The latter are, indeed, best restricted to those situations in which the former cannot be used, but some studies seem to have been motivated by a desire to show that a particular technique can be used to measure stability constants, rather than by a resolve to obtain "good" experimental results in the most efficient possible manner.

Although the general formula $B_qA_pH_j$ embraces conventional polybasic acids ($q = 0$, $p = 1$, $j \geq 0$) and molecular complexes of organic species ($j = 0$), the term "stability constant" normally refers to the formation of a complex in which the central group, B, is a metal ion. The ligand, A, may be a simple anion or neutral molecule (*e.g.*, Cl^-, NH_3, C_2H_2) or a multidentate organic anion or molecule of considerable complexity (*e.g.*, polyamines and aminopolycarboxylate ions). With the exception of the method-hunters, the majority of workers have measured stability constants by means of some form of potentiometry, and it is with this method that the present paper is mainly, but not exclusively, concerned. An attempt will be made to answer such questions as: "on what assumptions is the experimental method based?"; "how can we tell if they are justified?"; "what should we do if it emerges that they are not?"; "which method is appropriate for which system?"; "how can experimental results best be processed?"; "what do the stability constants mean?"; how may the results best be reported?"; and, of course, "why should one want to measure stability constants anyway?"

SURVEY OF EXPERIMENTAL METHODS

Methods for measuring stability constants may be classified according to whether or not any of the species $B_qA_pH_j$ exists in more than one phase. Within each group of techniques, further classification may be based on the way in which the measured property varies with the concentrations of the species being studied. The techniques most commonly used[2] are shown in Table 1.

Table 1. Some methods for measuring stability constants

	All species $B_qA_pH_j$ in homogeneous solution	At least one species $B_qA_pH_j$ distributed between two phases
Experimental output (fairly) directly related to concentrations of individual species.	Classical analysis **Potentiometry** Polarography Amperometry	**Solvent extraction** Solubility Vapour pressure
Output depends in general on concentrations of more than one species; but in favourable cases method can give single concentrations.	**Spectrophotometry** Kinetics	**Ion-exchange**
Output always depends on the concentrations of two or more species	Colligative properties Conductivity	

Many of the methods listed are of very restricted application. Classical chemical analysis, for example, can only be used on very inert systems; most complexes are so labile that addition of an analytical reagent displaces the equilibrium before, say, a precipitate can be separated or an absorbance measured. Determination of concentration by measuring distribution between solution and vapour is restricted to systems where only one species is volatile, but it has been used to study complexes of metal ions with small, uncharged ligands such as ammonia and acetylene. Ebullioscopy and cryoscopy are, of course, restricted to a single temperature for any particular system. Changes in the colligative properties of a solution, and in the electrical conductivity, are usually swamped by the presence of a bulk electrolyte. If the solubility of a sparingly soluble solid, *e.g.*, BA_c, is measured, the constancy of the solubility product $[B][A]^c$ precludes independent variation of the concentrations of free metal ion and free ligand. The use of amperometry and polarography is restricted to those systems in which the metal ion can be reversibly reduced at a dropping mercury electrode; but these systems can better be studied potentiometrically by using amalgam electrodes.

Measurements which depend on the concentrations of several species are often difficult to interpret. Colligative properties, which depend only on the total number of solute species, can only be interpreted unambiguously in simple systems. On the other hand, techniques such as spectrophotometry and ion-exchange may lead to ambiguous (or, at least, imprecise) results just because each species contributes to the property to a different extent, and so increases the number of parameters needed to describe the system. Thus the expression for the absorbance of a solution involves the molar absorptivities of all absorbing species in addition to stability constants and concentration variables. The interpretation of kinetic measurements is often particularly complicated. The rate of exchange between, say, Fe(II) and Fe(III) in a solution of their complexes, can be described only by introducing a rate constant for each pair of species between which exchange is possible. Techniques of this class are most useful for systems in which it can be firmly established that only one species contributes to the property measured.

The rest of this paper will deal only with the four techniques printed in boldface in Table 1. The general principles of careful equilibrium work will be illustrated with references to potentiometry, since it is the method most commonly used; and potentially the best. An analyst might however, complain that since potentiometry can only be used for complexes which are appreciably soluble in the medium, the technique involves the use of just those solvents which he tries to avoid. Solvent extraction will also be considered in some detail, since it can often be used when potentiometry is inapplicable. Spectrophotometry and ion-exchange will be discussed in the light of how to use apparently unpromising techniques to the best advantage.

Systems of simple, mononuclear complexes

The simplest systems of complexes are those in which only one series of complexes is formed and only one of the integers q, p and j varies. Examples are:

(*i*) Oligomers B_q ($p = 0, j = 0$) formed by self-association of such species as S_2 in the vapour phase, or phenol in organic solvents. (*ii*) Acids H_jA ($q = 0, p = 1$) in solutions which contain no complexing metal ions. (iii) Complexes BA_n ($q = 1, j = 0$; p is variable, conventionally written as $p = n$ when $q = 1$). These species are formed by combination of non-basic ligands, such as halide ions, with simple metal ions such as Hg^{2+} and Fe^{3+}: similar complexes are formed by combination between these ligands and composite, but infinitely stable, central groups such as

$$Hg_2^{2+}(q = 2, j = 0),\ VO^{2+}(q = 1, j = -2)^* \text{ or } UO_2^{2+}(q = 1, j = -4)^*$$

The great majority of those species which act as ligands for metal ions can also act as Brønsted bases and combine with at least one proton; and so it is usually necessary to deal with systems in which at least the two series of species BA_n and H_jA coexist. In many studies it is assumed that no further complexes are formed (*i.e.*, that q can have values of only 0 and 1, such that, when $q = 0, p = 1$; and when $q = 1, j = 0$).

Considering, for the moment, only the series BA_n and H_jA, we may express the total (analytical) concentrations B, A and H as

$$B = \sum [BA_n] \tag{1}$$

$$A = \sum [H_jA] + \sum n[BA_n] \tag{2}$$

$$H = \sum j[H_jA] + [H^+] - [OH^-] \tag{3}$$

(For alkaline solutions, H may be negative.) The summations run from zero to the maximal values $n = N$ and $j = J$, inclusive.

The equilibrium concentrations $[BA_n]$ and $[H_jA]$ may be expressed in terms of the equilibrium concentrations, b, a and h of B. A and H, together with $(N + J)$† overall stability constants

$$\beta_n = [BA_n]/ba^n \tag{4}$$

$$^{H}\beta_j = [H_jA]/h^ja \tag{5}$$

The quantities β_n and $^{H}\beta_j$ are concentration quotients, and may be treated as parameters only if the activity coefficients of the species involved remain constant over the whole range of concentrations used. Introduction of the stability constants into the mass-balance expressions (1–3) gives

$$B = \sum \beta_n b a^n \tag{6}$$

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* VO^{2+} cannot be distinguished from $V(OH)_2^{2+}$, nor UO_2^{2+} from $U(OH)_4^{2+}$ by *equilibrium* studies in *aqueous* solution.

† For $n = 0$ or $j = 0$ the constants β_n and $^{H}\beta_j$ become unity.

$$A = \sum {}^{\mathrm{H}}\beta_j h^j a + \sum n\beta_n b a^n \tag{7}$$

$$H = \sum j^{\mathrm{H}}\beta_j h^j a + h - K_w h^{-1} \tag{8}$$

where $K_w = h[\mathrm{OH}^-]$ is the stoichiometric ionic product of water.

Values of ${}^{\mathrm{H}}\beta_j$ for the formation of the acids $\mathrm{H}_j\mathrm{A}$ are usually determined in solutions which contain no B. Measurement of h leads to the average number, $\bar{j}$, of protons bound to each A. For $B = 0$, we may write

$$\bar{j} = \frac{\sum j[\mathrm{H}_j\mathrm{A}]}{\sum [\mathrm{H}_j\mathrm{A}]} = \frac{H - (h - K_w h^{-1})}{A} \tag{9}$$

Thus $\bar{j}$ can easily be obtained from measurements of h, H and A (provided that $h \gg K_w h^{-1}$, or that K_w has been determined under the exact conditions used). By combining equations (7)–(9) we can also express $\bar{j}$ as

$$\bar{j} = \frac{\sum j^{\mathrm{H}}\beta_j h^j}{\sum {}^{\mathrm{H}}\beta_j h^j} \tag{10}$$

which is a polynomial in the single variable h. Since the coefficients of equation (10) are the required values of ${}^{\mathrm{H}}\beta_j$, these may be obtained from the experimental function $\bar{j}(h)$, and hence from measurements of h, H and A. The most suitable way of solving equations derived from equation (10) depends on how many acids are formed, and to what extent they coexist.

The average number, $\bar{n}$, of ligands A bound to B can be analogously defined as

$$\bar{n} = \frac{\sum n[\mathrm{BA}_n]}{\sum [\mathrm{BA}_n]} \tag{11}$$

Again, this average degree of complex formation may be related to experimental quantities. Thus, from equations (2), (3) and (9)

$$\bar{n} = \frac{A - [H - (h - K_w h^{-1})]/\bar{j}}{B} \tag{12}$$

If values of ${}^{\mathrm{H}}\beta_j$ (and K_w) have been determined *under exactly the same conditions*, the value of $\bar{j}$ can be calculated for any value of h. Combination of the values of h and $\bar{j}$ with the analytical concentrations B, A and H then gives the value of $\bar{n}$.

The variation of $\bar{n}$ with a, like the function $\bar{j}(h)$, can be expressed as a simple polynomial, in which the coefficients are the required stability constants. Thus, from equations (4) and (11) we obtain

$$\bar{n} = \frac{\sum n\beta_n a^n}{\sum \beta_n a^n} \tag{13}$$

where the sole variable is the concentration, a, of free ligand. The value of a may also be obtained by measuring h in a solution of known B, A and H. Since, from equation (2)

$$\sum [\mathrm{H}_j\mathrm{A}] = A - \sum n[\mathrm{BA}_n] \tag{14}$$

no further information is needed to enable us to calculate a from the expression

$$a = \frac{A - \bar{n}B}{\sum {}^{\mathrm{H}}\beta_j h^j} \tag{15}$$

which follows from equations (6), (7), (11) and (14). If the ligand A does not combine with protons, ${}^{\mathrm{H}}\beta_j = 0$ for all values of j above zero. The denominator of equation (15) then becomes unity, and equation (12) takes the simple form

$$\bar{n} = \frac{A - a}{B} \tag{16}$$

The experimental function $\bar{n}$ (a) can then be obtained from measurements of a, A and B.

Equations (15) and (16) become trivial unless the value of $(A - \bar{n}B)$ differs appreciably from A: and this condition may be unfulfilled if the metal ion is present only in low concentration. It may, however, be possible to measure an alternative concentration variable, such as the fraction, α_c, of B which is present in the form of a particular species BA_c. (The concentrations most commonly measured are those of the uncomplexed metal ion, and of the electrically neutral complex.) From equation (2)

$$\alpha_c = \frac{[\mathrm{BA}_c]}{B} = \frac{[\mathrm{BA}_c]}{\sum [\mathrm{BA}_n]} = \frac{\beta_c a^c}{\sum \beta_n a^n} \tag{17}$$

the quantity α_c, like $\bar{n}$, is a function of a only, and the stability constants are calculable from the measurements of α_c and a. If $A \gg \bar{n}B$, approximate values of

$$a \approx \frac{A}{\sum {}^{\mathrm{H}}\beta_j h^j} \tag{18}$$

may be combined with measurements of α_c and h to give preliminary values of β_n which may then be refined. The values of a from equation (18) are combined with the rough values of β_n to give values of $\bar{n}$ (A, h), which are fed into equation (15) to give better values of a. Refined values of β_n are obtained from the experimental values of α_c together with the improved values of a, and so on, until convergent values of the stability constants are obtained.

The procedure outlined above requires that: (*a*) precise values of B, A and H are known for all the solutions used; (*b*) values of the concentration quotients ${}^{\mathrm{H}}\beta_j$ and β_n are constant: (*c*) the *concentration* of H^+ (or, as appropriate, of A, or BA_c) can be measured: (*d*) no complexes other than $\mathrm{H}_j\mathrm{A}$ or BA_n can be detected; (*e*) the stability constants calculated from the experimental functions $\bar{j}$ (h), $\bar{n}$ (a) or α_c (a) are compatible with the primary measurements.

These points will now be considered in more detail.

Total analytical concentrations

Solutions are normally prepared by dilution of standard stock solutions, which have been made up from highly purified components. Stock, and diluted, solutions should be stored at the constant temperature at which measurements will be made. The stock solutions (including those prepared by weighing-out of reagent grade materials) should always be analysed, preferably by two widely differing methods. The analysis of stock solutions is often considered to be one of the most tedious aspects of the determination of stability constants. But since the values of B, A and H form the basis of all subsequent calculations, the utmost care should be taken with the initial analyses. Failure to obtain "good" stability constants is often traceable, after much elapsed time, to inadequate analysis of stock solutions.

Dilute solutions should be prepared by using Grade A volumetric glassware. (Some workers may feel that the effort involved in recalibration of Grade A glassware is amply repaid by their resulting sense of virtue: but it is questionable whether it leads to any significant improvement in the values of the stability constants.) In order to allow for any temperature change which may occur during dilution, slightly less than the required volume of diluent should be added in the first instance, and the dilution completed by topping up to the mark only when the bulk of the diluted solution has returned to the constant temperature of the surroundings.

In addition to conventional methods of analysis, there are a number of useful tricks of the equilibrium chemist's trade. One is Gran's method for determining end-points of a variety of potentiometric titrations.[3–5] It can be used to determine concentrations of weak acids, strong acids, and even of strong acids in the presence of a readily hydrolysable metal ion such as Fe^{3+}. Solutions which contain both hydrogen ions and metal ions M^{z+} may also be analysed by running an aliquot (v l.) through a cation-exchange resin in the hydrogen form. Since $v(H + zB)$ moles of hydrogen ion emerge from the resin, separate determination of the initial concentration B of metal gives the required value of H.

Occasionally, the analysis of a solution of an organic base, such as a carboxylate ion, can be carried out potentiometrically[5,6] in the same operation as the measurement of $\bar{j}$. A volume V of a solution of say NaA, of initial concentration A_i is titrated with a volume v of strong acid of concentration H_i, and the free hydrogen ion concentration is measured potentiometrically. From equations (8) and (9), the value of $\bar{j}$ is given by

$$\bar{j} = \frac{H - h}{A} = \frac{H_i v - h(V + v)}{A_i V} \tag{19}$$

Since, for a monobasic acid, $\bar{j}$ tends to a value of $\bar{j}_{max} = 1$ at high acidities, the required value of A_i is obtained as

$$A_i = \lim_{h \to \infty} [H_i v - h(V + v)]V^{-1} \tag{20}$$

Constancy of stability constants

The stoichiometric stability constant β_n may be related to the standard free energy change $\Delta G°$ for the formation of BA_n from its components by the expression

$$-RT \ln \beta_n = \Delta G° + RT \ln \frac{\gamma_n}{\gamma_0 \gamma_A^n} \tag{21}$$

The activity coefficients γ_n and γ_A of the species BA_n and A refer to the same (usually molar) concentration scale as do the values of β_n. An exactly analogous expression can be written for ${}^H\beta_j$. So the concentration quotients β_n and ${}^H\beta_j$ only behave as parameters if both the temperature and the activity coefficient term $\gamma_n \gamma_0^{-1} \gamma_A^{-n}$ are held constant.

Temperature control is little problem. For work at "room" temperature the whole laboratory can often be thermostatically controlled at, say, 25° ± 1°. The temperature of the thermostat tank in which the measurements are done can then usually be kept steady to ±0·1°.

Control of activity coefficients is less easy. Only at exceedingly low ionic strengths are activity coefficients independent of the ion-size parameter, even for ions of the same charge-type. It is usually preferable to use solutions in which there is a high, almost constant, concentration of a bulk electrolyte which plays the smallest possible part in the equilibria which are being studied and has little, if any, additional effect on the measurements. The perchlorate ion is a popular bulk anion on account of its very low tendency to form complexes. The background cation is usually sodium, which complexes only weakly with most ligands and forms a very soluble perchlorate, but lithium perchlorate, although less soluble, has advantages in potentiometric studies of protonic equilibria, on account of the similarity between the H^+ and Li^+ ions.

The concentration of bulk electrolyte can be held "constant" in a number of slightly different ways. Let us suppose that the background electrolyte is $3M$ sodium perchlorate and that we wish to study complex formation between a metal ion M^{z+} and an anionic ligand A^{y-}. In order to keep the number of types of species as low as possible, it is best to add the metal ion in the form of $M(ClO_4)_z$ and the ligand as Na_yA. There is then the choice of designing the solutions so that, for example, $[Na^+] = 3M$, or $[ClO_4^-] = 3M$ or that ($[Na^+] \nless 3M$ and $[ClO_4^-] \nless 3M$). Table 2 gives details of the concentrations of metal ion solution $[M^{z+}] = B_i$ and ligand solution $[A^{y-}] = A_i$ in the three cases mentioned, and shows how the concentrations change when the solutions are mixed.

It is convenient to define the standard state as the hypothetical molar state in the appropriate ionic medium. Thus as B_i and A_i decrease to zero, the activity coefficients of metal ion, ligand and complexes tend to unity. In moderately concentrated solutions of metal ion and ligand, the activity coefficients may differ appreciably from unity, to an extent which depends on the exact composition of the solution. For studies of weak complexes, fairly high concentrations of ligand will be needed. Care should therefore be taken to see that solutions are always prepared so that the concentrations are consistent with the (explicit) conditions which have been chosen for the ionic medium.

At the beginning of an investigation, belief in the constancy of the activity coefficient quotient must be an act of faith. But the faith can sometimes be put to the test. If no more than two complexes are formed in any concentration range, the formation curve, $\bar{j}$ (log h) or $\bar{n}$ (log a) is symmetrical about its mid-point; and if a single complex is formed, the formation curve is of unique shape. It is most unlikely that a formation curve would be fortuitously symmetrical, let alone of the required shape. Such theoretical behaviour is strongly indicative of the constancy of the activity coefficient quotients, and hence also of the stability constants.

When three or more complexes coexist, interpretation of experimental results may be ambiguous. It is possible that measurements made up to a high free ligand concentration are equally compatible with, say, the formation of complexes BA–BA_4, with constant activity coefficient quotients, or with the existence of only three complexes, with variable activity coefficient quotients. Particular care must therefore be taken when interpreting measurements made in media which differ markedly from that referring to standard state.

Further complications arise if the system is heterogeneous; means of supposedly controlling activity coefficients in aqueous solutions cannot be applied to ion-exchange resins, or to solutions in organic solvents (see p. 821). However, we shall optimistically assume that, at least in aqueous solutions, the law of mass action is valid in terms of concentrations. The next problem is that of determining the concentration variables experimentally.

Potentiometric determination of concentrations

Potentiometric studies of chemical equilibria are usually carried out by means of the cell

$$\overset{-}{\text{reference half-cell}} \;\Big\Vert\; \begin{matrix}\text{solution in which}\\ \text{equilibria take place}\end{matrix} \;\Big|\; \overset{+}{\begin{matrix}\text{probe for metal, ligand, or}\\ \text{hydrogen ions}\end{matrix}}$$

(I)

although cells without liquid junction have occasionally been used. Metal, and amalgam, electrodes can act as probes for a variety of metal ions. In skilled hands, the latter electrodes are usually the more satisfactory; they are more readily reversible provided that all traces of oxygen have been excluded. The concentrations of a few simple anionic ligands, such as halides and sulphate, can be measured with "electrodes of the second kind" such as $Ag/AgCl/Cl^-$. The range of probes for metal ions and simple anions has been greatly extended by the introduction of a variety of specific-ion electrodes.[7] Although some of these function satisfactorily, even in the presence of a high concentration of background electrolyte, considerable development is needed before they can be widely used for very precise work.

Further extension of the range of probes for metal and ligand ions can be achieved by introducing additional species. The ratio of $[Fe^{3+}]$ to $[Fe^{2+}]$ can be determined by means of a redox electrode, and if the Fe(II) is known to be uncomplexed, the value of $[Fe^{3+}]$ can be obtained. This redox system has been used to determine the concentration of free fluoride ions in a solution containing Al(III) fluoride complexes; the stability constants of the Fe(III)–F^- complexes were known and those of the Fe(II)–F^- complexes were negligible. The use of auxiliary species, added only to facilitate measurement, greatly extends the scope of potentiometry, but each reagent added carries with it additional parameters, or assumptions, or both, and thereby decreases the precision of the final stability constants.

Electrodes which respond to hydrogen ions are used much more frequently than those which respond to metal ions or ligands. The hydrogen gas electrode is, however, unpopular except for extremely rigorous work. It comes to equilibrium inconveniently slowly, and cannot be used in the presence of substances which oxidize hydrogen or poison the catalytic surface of the electrode. On the other hand, the quinhydrone electrode is a quick and convenient probe for hydrogen ions, but quinhydrone is no exception to the general caveat about auxiliary species. At values of $pH > 7$ or of $pH < 1$, it acts as an acid or base respectively, and so displaces the very equilibria it was introduced to probe. Quinhydrone may be an added nuisance in studies of metal complexes, since it combines with some metal ions, such as Cu(II). An overwhelming majority of studies of protonic equilibria in systems A, H and A, B, H have been carried out with a glass electrode, thereby avoiding the introduction of any auxiliary species. The e.m.f. of cell (I), which contains a glass electrode in the right-hand half-cell, is given by

$$E = E^{\circ\prime} + RTF^{-1}\ln h + E_j \qquad (22)$$

The term $E^{\circ\prime}$ (which includes the half-cell potential of the reference electrode, the standard potential and asymmetry potential of the glass electrode, and the supposedly constant term $RTF^{-1}\ln\gamma_H$) should be constant over a period of at least several hours. The term E_j represents the overall diffusion potential generated at any liquid–liquid junction within the cell; its value should be kept as low as possible by avoiding gross concentration gradients. The same ionic medium should therefore be used for the two half-cell solutions and the salt-bridge, as in the cell:

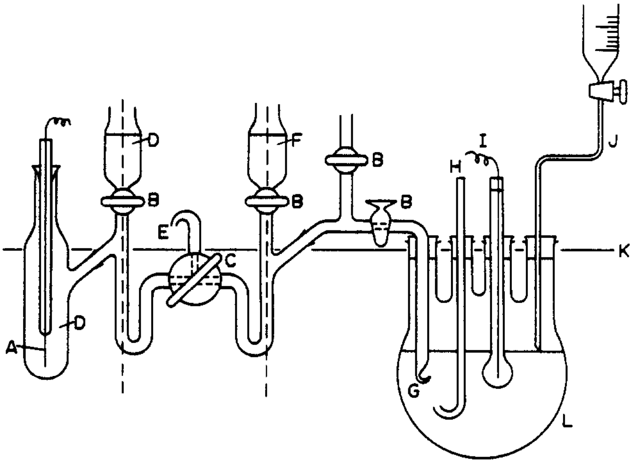

Fig. 1. Apparatus using cell (II) and Wilhelm-type liquid junction. The parts outside the dotted lines may conveniently be bent perpendicular to the plane of the paper. *A*, silver electrode; *B*, two-way stop-cocks; *C*, three-way stop-cock; *D*, reference solution; *E*, to waste; *F*, bridge solution; *G*, J-shaped liquid junction; *H*, inlet for nitrogen stirring; *I*, glass electrode; *J*, burette; *K*, level of thermostat liquid; *L*, vessel containing test solution. (Reproduced with permission, from ref. 5.)

	reference solution			test solution		
−						+
Ag(s)	Ag^+	0·01*M*	$NaClO_4$ 3·00*M*	H^+	*hM*	GE
	ClO_4^-	3·00*M*		Na^+	(3 − *h*)*M*	
	Na^+	2·99*M*		ClO_4^-	3·00*M*	

(II)

A convenient cell incorporates a "Wilhelm" salt-bridge, see Fig. 1. The ubiquitous "calomel electrode" which incorporates both the reference half-cell and the salt-bridge, is much less satisfactory. There will be large non-reproducible concentration gradients across the junction (*a*) in the cell

			(a)		
−					+
Hg(l)	$Hg_2Cl_2(s)$	satd. KCl		test solution	GE

(III)

Moreover, equilibria involving metal ions may be disturbed by interaction between these ions and chloride ions which have leaked across the junction.

Determination of *h* by measurement of the e.m.f. of cell (II) requires values of $E^{\circ\prime}$ and E_j for substitution into equation (22); and since $E^{\circ\prime}$ includes the variable asymmetry potential of the glass electrode, its value must be determined afresh for each set of measurements. At the start of an investigation the value of $(E^{\circ\prime} + E_j)$ must be determined for a set of solutions in which *h* is known, as in the titration of strong acid with strong base. (Only one of these need be of known concentration, since Gran's procedure[3–5] may be used to give a precise location of the end-point). When only a small fraction of the background cation is replaced by H^+, the value of $(E^{\circ\prime} + E_j)$ is often a constant, indicating that E_j is negligible. For a larger degree of replacement, however, $(E^{\circ\prime} + E_j)$ varies with *h*. Very fortunately, the variation is linear, so that values of $E^{\circ\prime}$ and $x + E_j h^{-1}$ may be obtained as the intercept and slope respectively. The value of x depends only on the ionic medium (*i.e.*, on the solvent, and on the nature and concentration of the bulk electrolyte): it is unaffected by the presence of metal ion and ligand provided that the background salt is indeed present in large excess. Once the value of x for a particular medium has been obtained the constant value of

$$E^{\circ\prime} = E - RTF^{-1}\ln h - xh \tag{23}$$

may readily be determined as a prelude to each set of measurements. Titration of strong acid with strong base, or of ionic medium with strong acid is convenient. Although $E^{\circ\prime}$ may vary by a few tenths of a millivolt from day to day, larger variations may indicate deterioration in the health of the glass electrode and should be viewed with suspicion.

The value of h in the test solution can be obtained from the measured e.m.f. and the known values of $E^{\circ\prime}$ and x by means of equation (23); but in solutions which are so acidic that E_j is not negligible, an approximate value of h must first be obtained by setting $x = 0$, and then refined by successive approximation.

A glass electrode can be analogously used as a probe for hydroxyl ions, provided that it has a negligible "sodium error", *i.e.*, that the value of $(E + RTF^{-1}\ln[\mathrm{OH}^-])$ is a linear function of $[\mathrm{OH}^-]$. The intercept of such a plot gives $E_{\mathrm{OH}}^{\circ\prime}$ while the slope gives $y = E_j[\mathrm{OH}^-]$. For a given medium, the difference $(E_{\mathrm{OH}}^{\circ\prime} - E_{\mathrm{H}}^{\circ\prime})$ gives $RTF^{-1}\ln K_w$, and the value of y is numerically smaller than that of x, and of opposite sign.

Half-cells which respond to metal ions or to simple ligands may be calibrated as concentration probes in the same way as glass electrodes, but the values of E°, as defined by *e.g.*, $(E - RTF^{-1}\ln[\mathrm{M}^{z+}]^{1/z})$ or $(E + RTF^{-1}\ln[\mathrm{Cl}^-])$ are acceptable parameters; they neither change with time, nor need to be "corrected" by a term attributable to junction effects.

Although measurements with glass electrodes normally involve the use of pH-meters, the assembly should always be calibrated as a concentration probe, as described above, rather than "standardized" with a buffer of conventionally agreed pH. Since the pH of the test solution is operationally defined as

$$\mathrm{pH} - \mathrm{pH}_s = \frac{E - E_s}{RTF^{-1}\ln 10}$$

where E_s is the e.m.f. of cell (III) when the test solution consists of a standard buffer of pH_s, the difference $(\mathrm{pH}-\mathrm{pH}_s)$ can only give the log of the ratio, h_s/h, of the hydrogen ion concentrations in the two solutions if (*a*) the values of E_j for the two cells are either negligible or identical, and (*b*) the values of γ_{H} in the two solutions are identical or calculable. If the test solution contains a high concentration of background electrolyte, and if the standard buffer is prepared as recommended, it is most unlikely that either condition referred to in (*b*) is fulfilled. Standardization of a pH-meter with a buffer of fixed pH becomes even more difficult if the glass electrode is to be used in a mixed aqueous–organic solvent; but the electrode can be calibrated as a concentration probe in any medium which contains H^+ ions.

The titration procedure may be made more convenient if various tricks-of-the-trade are employed. Stirring, for example, can be carried out with a stream of nitrogen, which has been freed from oxygen and presaturated with solvent by being bubbled through a sample of the ionic medium. It is often elegant, and sometimes essential, to keep either A or B constant during a titration, so that functions $\bar{j}(h)_A$ and $\bar{n}(a)_B$ may be obtained. This is readily accomplished by having more than one titrant. For example, a solution of initial concentrations B_i, A_i, H_i may be titrated with equal volumes of a solution of sodium hydroxide and of metal ion solution of concentration $2B_i$. In this way, the value of H can be varied over a wide range, while that of B is kept at a constant value of B_i.

Ingenious procedures can be devised so that as much information as possible can be obtained from one set of measurements, based on a single determination of $E^{\circ\prime}$ with no subsequent transfer of the glass electrode between one solution and another. For example, one composite titration in a study of the system B, A, H might consist of the following stages.

(*a*) Titration of an aliquot of standard strong acid with a solution of sodium bicarbonate. The concentration of the base is obtained by Gran's method, and the value of $E^{\circ\prime}$ from equation (22).

(*b*) Addition of an aliquot of a solution of B and H, and titration with the bicarbonate solution. This gives the concentration of acid in the metal ion solution, together with the pH at which the metal ion undergoes appreciable hydrolysis or precipitation. (The bicarbonate ion is often preferable to the hydroxyl ion as a titrant for solutions containing metal ions, since it is less likely to give local hydrolytic precipitation.)

(*c*) Addition of an aliquot of either (i) ligand in acid, followed by titration with base, or (ii) ligand in neutral solution, followed by titration with acid. Alternatively, the metal ion solution from (*b*) may be titrated with a solution of ligand, often in the form of an HA–A buffer.

Potentiometry can yield values of $\bar{n}$ for many systems in which $0{\cdot}05M > B > 0{\cdot}0001M$ and, for some metal ions, values of α_0 within the concentration range $0{\cdot}05M > B > 0{\cdot}001M$. Before we discuss the processing of the measurements, we shall look briefly at some other experimental methods.

Liquid-liquid extraction

Determination of stability constants by this technique normally involves distribution of an uncharged metal complex BA_c between an aqueous solution (containing bulk electrolyte) and an organic solvent which is almost immiscible with it. The uncharged complexing reagent H_gA may also be distributed between the two phases, but charged species BA_n and H_jA are usually confined to the aqueous phase. Since the metal is often present only in tracer quantities, the total metal concentration in each phase is usually measured radiometrically. The total concentrations, B_0 and A_0, of B and A in the organic phase are related to the partition coefficients P_c and P_g of BA_c and H_gA by the expressions

$$B_0 = [BA_c]_0 = P_c[BA_c] \tag{25}$$

$$A_0 = [H_gA]_0 + c[BA_c]_0 = P_g[H_gA] + cP_c[BA_c] \tag{26}$$

where $[\,]_0$ and $[\,]$ refer to concentrations in the organic and the aqueous phase respectively. The distribution ratio, q, of metal is then

$$q = \frac{B_0}{B} = \frac{P_c[BA_c]}{B} = P_c\alpha_c \tag{27}$$

The value of a can be obtained from a knowledge of the total quantity of A in the system, the volumes of the two phases, the values of P_g, β_j, and the measured hydrogen ion concentration of the aqueous phase at equilibrium. Thus the function $P_c\alpha_c(a)$ can be obtained from measurements of q and h, after equilibrium has been established.

Determination of q involves measuring B_0 and B in uncontaminated samples of each phase. Direct radiometric liquid-counting of such samples of a β-emitter does not, however, lead to a value of q, because the two phases have slightly different self-absorption characteristics. The value of B_0 is best obtained from the difference between the initial and final counts of the aqueous phase, assuming 100% mass balance. Values of B_0 obtained in this way should then be plotted against those obtained by direct counting of the organic phase. A linear plot, of slope slightly different from unity, should be obtained; and any points which lie markedly off the line should be discarded. Alternatively, the radioactive solutes may be precipitated from aliquots of the various solutions, and redissolved in a fixed volume of a particular solvent. Since all counts then refer to the same medium, the mass balance may readily be checked, provided that the equilibrium volumes of two phases are known. This method is especially suited to the determination of very high, or very low, values of q by use of unequal volumes of the two phases.

The value of h may be determined by using the equilibrated aqueous phase as test solution in cell (II). The value of $E^{\circ\prime}$ for the cell must previously have been established by using a solution of standard acid in the appropriate ionic medium, and checked with a second standard acid solution. Since the electrode must be washed and dried before being immersed in the test solution it is essential to check, by means of one of the standard solutions, that the value of E° has not changed during this transfer.

Although q and h can be obtained with less precision than is afforded by potentiometric titrations, the results are acceptable if sufficient care is taken. The assumption of constant partition coefficients (tantamount to supposing activity coefficients to be constant in both phases) should not overtax credulity, provided that concentrations of solutes in the organic phase are low and that these solutes are uncharged species (rather than ion-pairs). The assumption is vindicated by the fact that a good description of distribution data can usually be obtained by introducing only one parameter in addition to the stability constants.

Ion exchange

The distribution ratio of a metal ion between a cation-exchange resin and an aqueous solution is given by

$$q = \sum P_n \alpha_n \tag{28}$$

where the summation includes terms for all cationic species. Interpretation is much more difficult than for distribution between two liquids, except in the special case where the free metal ion is the only cation formed; but even then, there are considerable difficulties inherent in the technique. Since it is impossible to wash the resin free from aqueous solution without displacing the partition equilibria, the quantity of metal ion adsorbed on the resin can only be obtained from the difference between the initial and final aqueous solutions. Activity coefficients in the resin are highly sensitive to the nature of the cations. Values of q can only be compared if they refer to constant load (of B) on the resin and so for each required point q, a set of values $q(B)_a$ must be measured, and interpolated to give q at one value of B. The method therefore demands a much greater expenditure of time and effort than does solvent extraction; and the results obtained are probably less precise and more difficult to interpret. The technique is therefore not recommended.

Spectrophotometry

This might seem to be an unpromising technique, because the apparent molar absorptivity ε of B in a solution containing complexes BA_n gives $\sum \varepsilon_n \alpha_n$ where ε_n is the individual molar absorptivity of BA_n. If, as often happens, the values of ε_n are appreciable for all species BA_n at the wavelength used, computation of the $(2N + 1)$ parameters ε_n and β_n is difficult, and the results obtained are of low precision. Nonetheless, the technique has marked advantages over, say, ion-exchange. The value of ε can be measured easily and reliably, and the values of ε_n are true parameters and are unchanged by minor variations in the composition of the solution. So in the special situation where only one absorbing species (BA_c) exists, spectrophotometry provides a convenient and precise method for measuring α_c, and forms a useful complement to potentiometry. Moreover, if the complex has a high absorptivity only trace concentrations of B are needed. So spectrophotometry can be used to study some systems in which low solubilities preclude the use of potentiometry.

A value of a is, of course, also needed and is usually obtained by combining the experimental value of h with the known value of A. (The approximation $A \sim a$ is valid only for non-basic ligands in the presence of tracer concentrations of metal ions, a situation seldom encountered in spectrophotometric work.) Unless the metal is present in tracer concentrations, measurements of B, A, a or B, A, h are needed to give values of $\bar{n}$, a, and these measurements can yield values of β_n without recourse to spectrophotometry.

Much early, and regrettably, some recent spectrophotometric work has made use of the "method of continuous variations" in which absorbance is measured as a function of AB^{-1} in solutions of constant $(A + B)$. If a single complex is formed, its composition and sometimes its stability constant can be obtained from the position of the extremum on the graph. But the interpretation is ambiguous unless a single 1:1 complex is formed, and the method is not to be recommended.

A forthcoming review paper deals with spectrophotometric methods *in extenso*.[9]

TREATMENT OF RESULTS

Checking the general formula

The measured quantities $\bar{n}$, α_c, q and ε are all unique functions of a if, and only if, complex formation between B and A is restricted to the simple, mononuclear species BA_n. If, however, polynuclear species B_qA_p $(q > 1)$ are present the value of

$$\frac{A - a}{B} = \frac{\sum p\beta_{qp} b^q a^p}{\sum q\beta_{qp} b^q a^p} \tag{29}$$

will depend on both b and a; and an experimental plot of $(A - a)B^{-1}$ against log a will produce separate curves for different values of B. If, on the other hand, the complexes are mononuclear, but include hydrolysed or protonated complexes BA_nH_j $(j \neq 0)$ the value of $(A - a)B^{-1}$ will be independent of b, but will be a function of both a and h. (Dependence on both a and h will be observed even in the absence of mixed species if the two series of complexes $B(OH)_{-j}$ and BA_n are formed.)

Before attempting to calculate stability constants it is therefore essential to obtain measurements for solutions with at least two, widely spaced, values of B in order to check whether or not polynuclear species are formed. It is advisable to plot all experimental values of $(A - a)B^{-1}$ (or α_c, q or ε, as appropriate) as a function of log a so that the results may be easily surveyed. The possibility of combination of H^+ or OH^- with any species containing B must be similarly checked by plotting $(A - a)B^{-1}$ against log a for systems of widely differing h or A. [Since, for basic ligands, a varies with both A and h, coincidence of functions $\bar{n}$ (log $a)_A$ demonstrates the absence of protonated or hydroxo-complexes as effectively as does coincidence of the functions $\bar{n}$ (log $a)_h$.]

Computation of stability constants

"If at least N sets of values of $\bar{n}$, a or $\alpha_{c,a}$ are available, equations (13) or (17) may be solved for the required stability constants β_n'' is a typical conclusion to a brief account of experimental aspects of stability constant work. It assumes, of course, that only species BA_n are present; but questions arise as to the best way of handling the experimental data when, as is usually the case, more than N sets of measurements are available.

Large numbers of methods, good and bad, have been described[1,10] for obtaining stability constants, not only from measurements of $\bar{n}$, a and α_c, a, but also from functions q, a and ε, a which contain one or more unknown parameters in addition to the stability constants. One criterion of a "good" method is that it makes full use of the data. There is little point in carefully determining a whole titration curve and then calculating values of β_1 and β_2 from only two points on it. Conversely, the constants obtained can never be more precise than the primary data, however elegant the method used for calculating them. Satisfactory stability constants can be obtained only be combining careful, well-designed experiments with rigorous computational technique.

Whatever the complexity of the system, the problem is one of fitting experimental values of $\bar{n}(a)_{B,h}$ or $\alpha_c(a)_{B,h}$ with parameters which give as good a description as possible of the measurements. If the only complexes formed are BA_n, the data can be represented in two dimensions, since $\bar{n}$ and α_c are functions only of a. If mixed, or polynuclear, complexes are formed, the data must represent a surface in three, or more, dimensions.

Data of high precision are probably best processed by electronic computation, regardless of the type of complexes which are formed; and the advantages of such methods increase with the complexity of the system. Available programs,[10] include those for treating errors (systematic, correlated and random). Systems containing complexes BA_n, even in the presence of BHA, can be treated by linear least-squares techniques. If polynuclear complexes, or two or more mixed complexes, are present, more elaborate search techniques, such as "pit-mapping" must be used. LETAGROP VRID, the most sophisticated of these programs, is of very wide applicability, but it would be foolish to use so sledge-hammer a procedure unless the system were fairly complicated.

If the system can be described by only one, or two, parameters, electronic computers offer little advantage over graph paper, unless the measurements are exceedingly precise. Graphical methods are of two main types.

(*i*) *Linear, non-logarithmic plots.* Up to two parameters may be obtained from a single plot. Further parameters can be squeezed (with decreasing precision) from the measurements by successive extrapolations.

(*ii*) *Curve-fitting methods*, usually based on a semi-logarithmic plot involving one normalized variable. If a single complex BA is formed, the curves $\bar{n}$ (log a) and α_c (log a) are of unique shape. The value of β_1 can be obtained by matching the experimental points with the theoretical curves $\bar{n}$ (log $\mathbf{a}$) and α_c (log $\mathbf{a}$) where $\mathbf{a} = \beta_1 a$ is the normalized value of a.

For systems of two or more complexes, the curves are not of unique shape; but when $N = 2$, the parameter $\beta_1^2\beta_2^{-1}$ can be obtained from the shape of the experimental curve, and that of β_2 from its position on the log $\mathbf{a}$ axis. The "projection strip" method[1,10] is particularly convenient.

Curve-fitting procedures are of little use when more than three species (*e.g.*, B, BA and BA_2) coexist, but if the formation curve shows a plateau at an integral value of $\bar{n}$, measurements of $\bar{n}$ above this value may be treated separately from those below it. In many systems H_jA (*e.g.*, H^+–PO_4^{3-}) the formation of each species occurs in widely separated steps, each of which may be treated as for a monobasic acid. Similarly, since mercury(II) halides HgX_2 exist as the sole complex over a very wide range of free halide ion concentration, sets of data in the regions $\bar{n} < 2$ and $\bar{n} > 2$ may be treated independently of each other.

Graphical methods have been much criticized by the purists on account of their subjectivity, both in the values of the parameters and in their limits of error. But the judgment of an experienced worker may be but little inferior to the machinations of a computer; and when waiting-time is taken into account, graphical methods may well be quicker (as well as cheaper). It is often easier to tell from a graph, rather than from tabulated print-out, when all is not well. Dud points, and systematic errors, obtrude like sore thumbs. A glance at the formation curve may suggest that it starts, improbably, at $\bar{n} = 0{\cdot}0005$ rather than at $\bar{n} = 0$; or that it is not symmetrical about $\bar{n} = 1$, as it should be, if the only complexes present are BA and BA_2. A good fit between experimental points and a theoretical curve is an effective way of demonstrating that the calculated parameters give a satisfactory description of the system; curve-fitting procedures provide an automatic comparison of the two functions.

Data should, ideally, be processed by two different procedures, and whatever the method used to calculate stability constants, the values obtained should *always* be checked* by substitution into equations (13) and (17) to ensure that they represent the experimental data satisfactorily (see Figs. 2–4). Nevertheless, however good the experimental and theoretical techniques, and the compatibility between them, stability constants can never be unequivocally "right", but only "compatible with the data" within certain limits. This distinction may seem ludicrously pedantic for precise work on, say, a monobasic acid

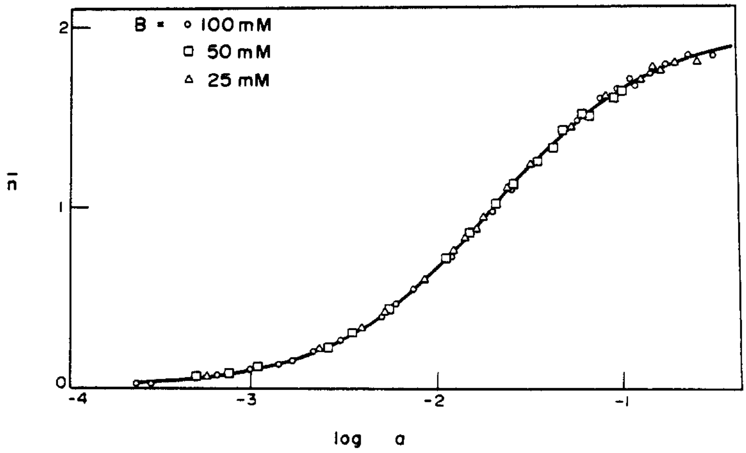

Fig. 2. Formation curve $\bar{n}$ (log a) for the mononuclear copper(II) methoxyacetate system at 25°C in 3M $NaClO_4$.[12] The points represent experimental values, and the curve is calculated for $\log \beta_1 = 2{\cdot}01$ and $\log \beta_2/\beta_1 = 1{\cdot}33$. (Reproduced with permission, from ref. 5.)

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* Not only by the author, but also by the referee.

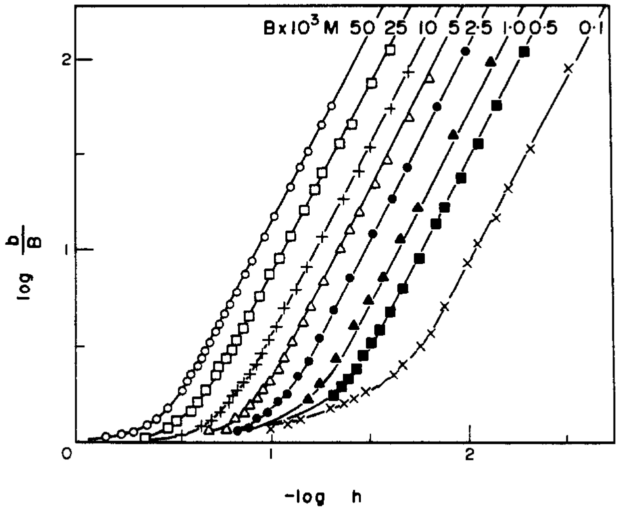

Fig. 3. Values of log b/B as a function of log h for hydrolysed bismuth(III) perchlorate solutions in $3M$ $NaClO_4$ at 25°C. The curves are calculated by using only two parameters β_{qpj} for the species $B_qA_pH_j$, *viz.* $\log \beta_{1,0,-1} = 1{\cdot}58$ and $\log \beta_{6,0,-12} = 0{\cdot}33$. (Reproduced with permission from ref. 13.)

over the whole range $0 \leq \bar{j} \leq 1$, but the distinction increases in importance with the complexity of the system. It is an essential corrective to complacency about interpretation of measurements on systems containing mixed, or polynuclear, complexes, or even about stability constants of simple mononuclear complexes obtained by techniques such as spectrophotometry, which involve several additional parameters.

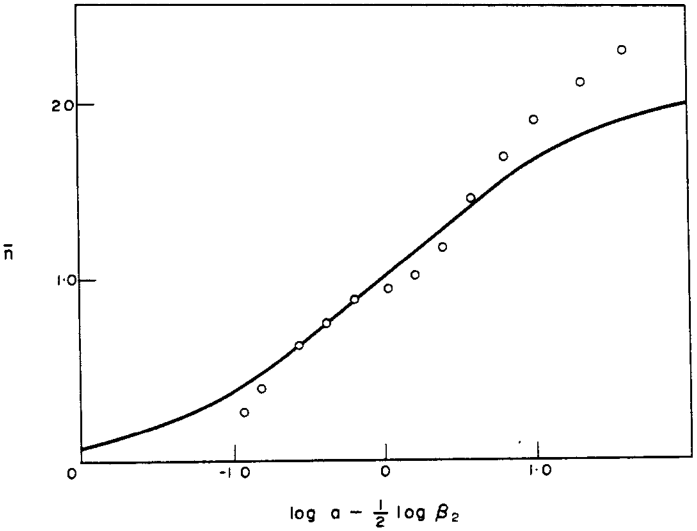

Fig. 4. Illustration of a type of formation curve encountered all too frequently, even in the 1970's. Points: experimental values submitted for publication. Curve: calculated from authors' constants "obtained by least-squares method".

Table 2. Molarities of some differently prepared ionic media

	Solution 1. Metal ion			Solution 2. Ligand			Mixture of v_1 ml of solution 1 and v_2 ml of solution 2			
	B	$[\mathrm{Na}^+]$	$[\mathrm{ClO}_4^-]$	A	$[\mathrm{Na}^+]$	$[\mathrm{ClO}_4^-]$	B	A	$[\mathrm{Na}^+]$	$[\mathrm{ClO}_4^-]$
$[\mathrm{Na}^+] = 3$	B_i	3	$3 + zB_i$	A_i	3	$3 - yA_i$	$\frac{v_1 B_i}{v_1 + v_2}$	$\frac{v_2 A_i}{v_1 + v_2}$	3	$3 + \frac{zB_i v_1 - yA_i v_2}{v_1 + v_2}$
$[\mathrm{ClO}_4^-] = 3$	B_i	$3 - zB_i$	3	A_i	$3 + yA_i$	3	$\frac{v_1 B_i}{v_1 + v_2}$	$\frac{v_2 A_i}{v_2 + v_2}$	$\frac{yA_i v_2 - zB_i v_1}{v_1 + v_2}$	3
$[\mathrm{Na}^+] \nless 3$ $[\mathrm{ClO}_4^-] \nless 3$	B_i	3	$3 + zB_i$	A_i	$3 + yA_i$	3	$\frac{v_1 B_i}{v_1 + v_2}$	$\frac{v_2 A_i}{v_1 + v_2}$	$3 + \frac{yA_i v_2}{v_1 + v_2}$	$3 + \frac{zB_i v_1}{v_1 + v_2}$

Display of results

Values of stability constants, represented as numbers in a table, may not seem very interesting; graphs[14] have greater impact.

We have seen that a combined plot of experimental points $\bar{n}$, log a and the calculated formation curve is useful for convincing the researcher and others that the values obtained for the stability constants are respectable. But a value of $\bar{n} = 1$ may, of course, mean that $\alpha_1 = 1$; or that $\alpha_0 = 0{\cdot}5$, $\alpha_1 = 0$ and $\alpha_2 = 0{\cdot}5$. A better feel for the system may be obtained if the stability constants are used to construct distribution plots for the various species present.

In simple, mononuclear systems, the distribution of species can be represented by two-dimensional diagrams (see Fig. 5). Plots of α_n (log a) for values of $0 \leq n \leq N$ probably provide the best insight into the system, but distribution diagrams in the form of a set of plots of $\sum_0^n \alpha_n$ against log a have also been used.

If mixed or polynuclear complexes are formed, values of α_n depend on two or more variables. The distributions of species in such systems can be represented as surfaces in three or more dimensions. Two-dimensional graphs can be constructed by cutting sections through the surface at constant values of one, or more, of the variables. A system which contains species BA_nH_j may, for example, be represented as a series of plots of α_n against log a at a number of values of pH.

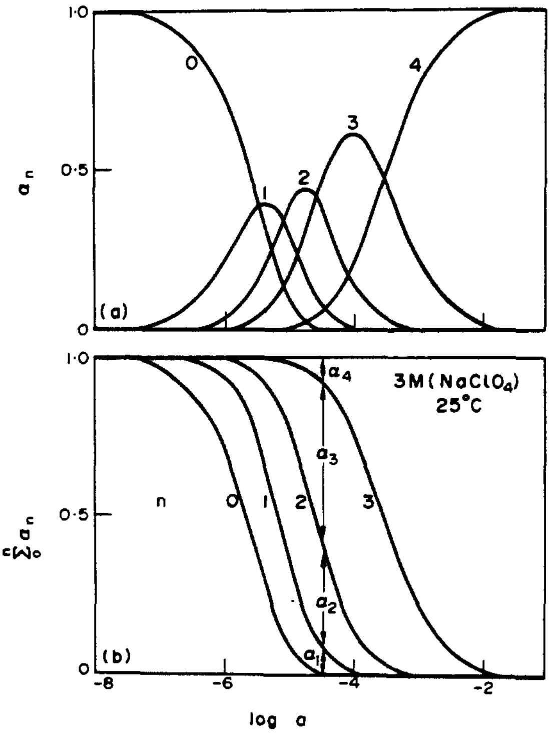

Fig. 5. Distribution diagrams for the mononuclear system[15] Cd^{2+}–CN^-, (a) α_n and (b) $\sum_0^n \alpha_n$, for values of $0 \leq n \leq 4$ as functions of log [CN^-]. (Reproduced, with permission, from ref. 16.)

Publication

Plots providing comparisons of theoretical and experimental functions and those showing the distribution of the various complexes, should always be drawn, if only for the edification of the research group. Presentation of the work to a wider audience (whether of examiners or journal-readers) requires, in addition, a clear statement of the following points.

1. The temperature of the measurements.
2. The ionic medium (including a statement as to which species, if any, is held at constant concentration).
3. The credentials of any stock solutions. This should include the source and purity of starting materials (especially of any synthesized) and a report on the analysis of the solutions.
4. The apparatus.
5. The design and execution of the experiments.
6. Methods of converting measurements, e.g. of E, A, B, H or of q, E, A, B, H into secondary functions such as $\bar{n}$, a or α_c, a. The values of any necessary parameters, such as β_j and P_c should be quoted, together with a report of how they were obtained. (These values must, of course, refer to conditions identical to those used for the measurements.)
7. The methods used for obtaining values of stability constants together with (defined) limits of error, from the secondary functions.
8. The numerical values of stability constants, and of the limits of error, together with the concentration scale to which they apply.
9. A critical comparison of these values with any which have been previously reported for the same system.

The object of the work

Determination of good stability constants clearly involves a great deal of painstaking work. Why should people take all this trouble? (Some, of course, don't, to the obvious detriment of their results.)

Equilibrium constants are measured for two main types of reason, to which the over-simplified labels "applied" and "pure" may be attached. Although the two categories overlap, the "applied" situations are basically those in which values of equilibrium constants are needed to calculate the distribution of species in a particular solution. Thus values of ${}^{H}\beta_j$ are needed in order to calculate the concentration of A in equilibrium with protonated species at a particular pH. Values of β_n may be needed in order to design satisfactory separative, or other analytical, procedures. Observed values of ΔH or ε for a solution containing several complexes can yield values of ΔH_n and ε_n for the individual species if the concentration of each species can be calculated.

For "applied" purposes of this type, the most useful quantities are probably the concentrations $[B_qA_pH_j]$ as a function of log h at fixed values of B and A. Calculation involves solving equations (6), (7) and (8) for b and a and, except for very simple systems, is best performed by an electronic computer.

"Pure" problems are those designed to increase insight into the nature of chemical behaviour, rather than into the properties of one particular set of solutions. The values obtained have provided evidence for the existence of a strange collection of polynuclear hydroxo-complexes of metal ions, and have led to many attempts to correlate the stability of complexes with the properties of the metal ion, the ligand and, occasionally, the solvent.

The usefulness of work on stability constants is not restricted to studies of chemical behaviour *in vitro*. Interactions between metal ions and a wide variety of ligands, ranging in complexity from cyanide to haem, have long been of interest to biochemists. More recently, stability constants have extended their domain to become the concern of soil scientists and oceanographers.

Since the stability constants give a measure of ΔG for the formation of a complex, the variation of β_n with temperature, leads in principle to values of ΔH_n and ΔS_n for the formation of the separate complexes, but over the narrow range of temperatures which can be used, changes in β_n may be little larger than experimental error. Moreover, the method is based on the assumption that ΔH is independent of temperature. Values of ΔH_n are better obtained by combining calorimetric values of ΔH with the appropriate values of α_n, which are calculated from the stability constants. These values of ΔH_n may then be combined with the stability constants to give values of ΔS_n. This type of work is only successful if all the measurements are of the highest precision.

Acknowledgement—The author is very grateful to St. Anne's College, Oxford for financial support.

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Zusammenfassung—Es wird eine kritische Übersicht über die Methoden zur Bestimmung von Stabilitätskonstanten gegeben. Es werden Empfehlungen zur Wahl der Arbeitsweise, zur genauen Planung der Experimente, zur Berechnung der Konstanten und zur Wiedergabe der Ergebnisse in der Veröffentlichung ausgesprochen.

Résumé—On passe en revue de manière critique les méthodes de détermination des constantes de stabilité. On fait des recommandations sur le choix de la technique, l'étude détaillée des expériences, le calcul des constantes et la présentation des résultats pour publication.

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NEW CHROMOGENS OF THE FERROIN TYPE—VII

SOME 3-SUBSTITUTED-1,2,4-TRIAZINES, 3,5-DISUBSTITUTED-1,2,4-TRIAZOLINES AND TRIAZOLES, AND 2,4- AND 2,6-BIS TRIAZINYL AND TRIAZOLINYL SUBSTITUTED PYRIDINES

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Summary—Chelation and chromogenic properties of 39 new ferroin compounds in reactions with iron(II), copper(I), and cobalt(II) have been investigated spectrophotometrically. The results demonstrate that the chromogenic properties of triazole and triazoline heterocycles are inferior to triazine and pyridine when incorporated into the ferroin chromophore grouping. The triazole and triazoline compounds also undergo hydrolytic decomposition, strongly catalysed by iron(II), making them unsuitable as colorimetric reagents. An outstanding chromogen was found from among the triazine derivatives which is superior in sensitivity to all ferroin-type chromogens previously studied.

Among the extensive array of ferroin-type compounds synthesized by F. H. Case, certain triazine derivatives have proved particularly interesting for their sensitivity and usefulness as iron and copper chromogens. Previous papers in this series have included results and discussion of their chelation properties.[1–3] New synthetic approaches have been devised by Case to prepare additional and more varied triazine derivatives in hopes of finding even more superior chromogenic reagents. This note reports our findings on the iron(II), copper(I), and cobalt(II) chelation properties of these recently synthesized triazines.[4] In addition, the chromogenic properties of some new triazolines and triazoles, also synthesized recently by Case,[5] are reported.

The new compounds, listed below by name, will be referred to by Roman numeral. Structures of the compounds are shown in the papers by Case describing their syntheses.[4,5]

3-*Substituted*-1,2,4-*triazines*

I	3-(2-Pyridyl)-1,2,4-triazine
II	3-(2-Pyridyl)-5,6-dimethyl-1,2,4-triazine
III	3-(4-Methyl-2-pyridyl)-1,2,4-triazine
IV	3-(4-Methyl-2-pyridyl)-5,6-dimethyl-1,2,4-triazine
V	3-(4-Phenyl-2-pyridyl)-5,6-dimethyl-1,2,4-triazine
VI	3-(2-Thiazolyl)-1,2,4-triazine
VII	3-(2-Thiazolyl)-5,6-dimethyl-1,2,4-triazine
VIII	3-[2-(1,10-Phenanthrolyl)]-5,6-dimethyl-1,2,4-triazine

3,5-*Disubstituted*-1,2,4-*triazolines*

IX	3-(2-Pyridyl)-5-methyl-1,2,4-triazolines

X	3-(2-Pyridyl)-5-phenyl-1,2,4-triazoline
XI	3-(2-Pyridyl)-5-(2-phenol)-1,2,4-triazoline
XII	3,5-bis(2-Pyridyl)-1,2,4-triazoline
XIII	3-(4-Methyl-2-pyridyl)-5-phenyl-1,2,4-triazoline
XIV	3-(4-Methyl-2-pyridyl)-5-(2-pyridyl)-1,2,4-triazoline
XV	3-(4-Phenyl-2-pyridyl)-5-phenyl-1,2,4-triazoline
XVI	3-(4-Phenyl-2-pyridyl)-5-(2-pyridyl)-1,2,4-triazoline
XVII	3-(2-Thiazolyl)-5-phenyl-1,2,4-triazoline
XVIII	3-(2-Thiazolyl)-5-(2-pyridyl)-1,2,4-triazoline
XIX	3-[2-(1,10-Phenanthrolyl)]-5-phenyl-1,2,4-triazoline
XX	3-[2-(1,10-Phenanthrolyl)]-5-(2-pyridyl)-1,2,4-triazoline

3,5-*Disubstituted*-1,2,4-*triazoles*

XXI	3-(2-Pyridyl)-5-phenyl-1,2,4-triazole
XXII	3-(2-Pyridyl)-5-(2-pyridyl)-1,2,4-triazole
XXIII	3-(4-Methyl-2-pyridyl)-5-phenyl-1,2,4-triazole
XXIV	3-(4-Phenyl-2-pyridyl)-5-phenyl-1,2,4-triazole
XXV	3-(2-Pyridyl)-5-methyl-1,2,4-triazole

Bis-substituted pyridines

XXVI	2,4-bis(5,6-Dimethyl-1,2,4-triazin-3-yl)pyridine
XXVII	2,4-bis(5,6-Diphenyl-1,2,4-triazin-3-yl)pyridine
XXVIII	2,4-bis[5,6-bis(2-Pyridyl)-1,2,4-triazin-3-yl)]pyridine
XXIX	2,6-bis(5,6-Dimethyl-1,2,4-triazin-3-yl)pyridine
XXX	2,6-bis(5,6-Diphenyl-1,2,4-triazin-3-yl)pyridine
XXXI	2,6-bis[5,6-bis(2-Pyridyl)-1,2,4-triazin-3-yl]pyridine
XXXII	2,4-bis(5-Phenyl-1,2,4-triazolin-3-yl)pyridine
XXXIII	2,4-bis[5-(2-Pyridyl)-1,2,4-triazolin-3-yl]pyridine
XXXIV	2,6-bis(5-Phenyl-1,2,4-triazolin-3-yl)pyridine
XXXV	2,6-bis[5-(2-Pyridyl)-1,2,4-triazolin-3-yl]pyridine
XXXVI	2,6-bis[3-(2-Pyridyl-1,2,4-triazolin-5-yl]pyridine
XXXVII	2,6-bis[3-(4-Methyl-2-pyridyl)-1,2,4-triazolin-5-yl]pyridine
XXXVIII	2,6-bis[3-(4-Phenyl-2-pyridyl)-1,2,4-triazolin-5-yl]pyridine
XXXIX	2,6-bis[3-(2,2-bipyrid-6-yl)-1,2,4-triazolin-5-yl]pyridine

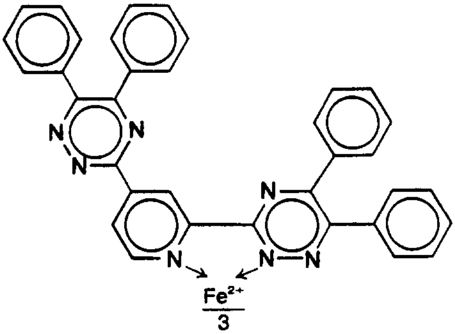
EXPERIMENTAL

Preparative details and elemental analyses of the new compounds, samples of which were furnished by Case for the present study, are published elsewhere.[4,5]

The various standard solutions, pH buffers, reagents, and procedures used in this investigation are described in an earlier communication of this series.[1] Spectra were recorded with a Cary Model 14 spectrophotometer and corrected for absorbance due to reagent blanks. Ligand: metal ratios of the chelates were determined spectrophotometrically by the mole-ratio method.[6]

RESULTS AND DISCUSSION

Spectral properties, solvents and conditions used for preparing solutions of the chelates, and other distinctive aspects of the iron(II) chelates are summarized in Table 1. The most sensitive iron chromogen of the group is **XXVII**. It is also the most sensitive found to date of all the known ferroin-type chromogens, at least on the basis of molar absorptivities. Its structure is shown below, with co-ordination site for iron(II) indicated.



Chromogen **XXVII** acts as a bidentate ligand to form a tris-chelate with iron(II), as indicated by the 1:3 ratio of iron to ligand found by the mole-ratio method. As expected from empirically based predictions,[7,8] phenyl or aryl substituents in the heterocyclic rings *para* to the co-ordinating nitrogen atoms greatly enhance absorptivity of the iron(II) chelate. All of the most sensitive ferroin chromogens have this feature, as for example **XXVII** (the most sensitive) and the two next most sensitive: 2,6-bis(4-phenyl-2-pyridyl)-pyridine (ϵ = 3·02 × 10^4 at 583 nm for its iron chelate)[8] and 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (ϵ = 2·87 × 10^4 at 561 nm for its iron chelate).[9]

Compound **XXVII** has great promise as a colorimetric reagent for iron. It is relatively simple to synthesize compared to the two next most sensitive ferroin reagents mentioned above, and its intensely absorbing iron(II) chelate is highly extractable, permitting preconcentration before measurement. One disadvantage is its insolubility in water and other common solvents. Its practical use is limited to chloroform extraction procedures, and it is not readily adapted to automation. However, chemical modification of **XXVII** by sulphonation to produce water-soluble sulphonated derivatives should be relatively easy. Sulphonation has provided very useful water-soluble derivatives of other phenyl-substituted ferroin chromogens.[10–12]

The triazoline and triazole derivatives **IX–XXV** and **XXXII–XXXIX** are noteworthy for their adverse behaviour, lack of stability in solution, and relatively poor chromogenic properties. Colours and spectra of the iron(II) chelates change drastically with time, the changes being catalysed by heat, and influenced by pH as well as hydroxylamine concentration. Our studies indicate that these compounds undergo hydrolytic decomposition, reverting back to the aldehyde (or ketone) and the carboxamide from which they were originally synthesized by condensation. In some cases the unmistakable odour of the aldehyde could be detected over aged solutions of the iron(II) chelates. On storage of the solutions, the spectra change, approaching those of the iron(II) chelates of the pyridylcarboxamide hydrazones (the hydrazidines) in question.[9] If hydroxylamine is present as reductant in sufficient excess, the spectra of aged solutions of the iron(II) complexes of **IX** and **X** resemble that of pyridine-2-amidoxime,[9] suggesting that hydrolysis has occurred followed by replacement of hydrazine with hydroxylamine to convert the hydrazidine into the amidoxime. An important observation in this regard is that **XXXVI**, **XXXVII**, and **XXXVIII** do not give coloured iron(II) complexes unless hydroxylamine is added, and only after prolonged standing or brief heating are the typical ferroin red colours then produced. The spectroscopic data reported in Table 1 for these three compounds are for solutions prepared with hydroxylamine and heated before measurement. Another result, pertinent as evidence of hydrolytic decomposition, is that the iron(II) complex of XXXIX has an apparent ligand:iron ratio of 1:1. This surprising result can be explained on the basis that the original ligand decomposes to yield three separate bidentate ligands or two separate terdentate ligands. Either is theoretically possible, but further study is necessary for substantiation. Finally, it is interesting that decomposition of the triazoline and triazole com-

Table 1. Properties of the iron(II) chelates

Chromogen	Colour	λ, nm	ϵ, l.mole^{-1}.cm^{-1}	Solvent*	Fe:L ratio	Remarks†
I	Red	525	$1{\cdot}13 \times 10^4$	*a*	1:3	5
II	Red	525	$1{\cdot}45 \times 10^4$	*a*	1:3	5
III	Red	531	$1{\cdot}21 \times 10^4$	*a*	1:3	5
IV	Red	527	$1{\cdot}53 \times 10^4$	*b*	1:3	5
V	Red	533	$1{\cdot}99 \times 10^4$	*b*	1:3	5
VI	Red	522	$1{\cdot}34 \times 10^4$	*b*	1:3	1
VII	Red	530	$1{\cdot}00 \times 10^4$	*b*	1:3	1
VIII	Magenta	588	$1{\cdot}04 \times 10^4$	*b*	1:2	5
IX	Red	506	$7{\cdot}3 \times 10^3$	*a*	1:3	2,3,4
X	Red	500	$9{\cdot}2 \times 10^3$	*b*	1:3	2,3,4
XI	Red	520	$5{\cdot}0 \times 10^3$	*a*	1:3	2,3,4
XII	Magenta	520	$9{\cdot}4 \times 10^3$	*a*	1:2	2,4
XIII	Red	490	$1{\cdot}5 \times 10^4$	*b*	1:3	2,4
XIV	Magenta	520	$9{\cdot}9 \times 10^3$	*a*	1:2	2,4
XV	Purple	525	$1{\cdot}62 \times 10^4$	*b*	1:3	2,4
XVI	Magenta	531	$7{\cdot}7 \times 10^3$	*b*	1:2	2,4
XVII	Colourless	—	—	—	—	—
XVIII	Green	635	$4{\cdot}8 \times 10^3$	*b*	—	1,2,4
XIX	Purple	550	$1{\cdot}34 \times 10^4$	*b*	1:2	1,5
XX	Purple	552	$1{\cdot}26 \times 10^4$	*b*	—	5
XXI	Orange	470	$4{\cdot}0 \times 10^3$	*b*	—	1,3,4
XXII	Yellow	455	$3{\cdot}6 \times 10^3$	*b*	—	1,3,4
XXIII	Orange	470	$2{\cdot}6 \times 10^3$	*b*	—	1,3,4
XXIV	Red	515	$6{\cdot}4 \times 10^3$	*b*	—	1,3,4
XXV	Orange	480	$3{\cdot}1 \times 10^3$	*b*	—	1,4
XXVI	Red	540	$2{\cdot}06 \times 10^4$	*b*	1:3	5
XXVII	Violet	563	$3{\cdot}20 \times 10^4$	*c*	1:3	5
XXVIII	Violet	565	$1{\cdot}60 \times 10^4$	*b*	1:3	5
XXIX	Red-brown	448	$1{\cdot}08 \times 10^4$	*b*	1:2	5
		552	$1{\cdot}11 \times 10^4$			
XXX	Green-black	468	$1{\cdot}80 \times 10^4$	*b*	1:2	5
		580	$1{\cdot}40 \times 10^4$			
XXXI	Blue-black	470	$1{\cdot}69 \times 10^4$	*b*	1:2	5
		580	$1{\cdot}40 \times 10^4$			
XXXII	Red	535	$1{\cdot}15 \times 10^4$	*b*	—	2,4
XXXIII	Magenta	515	$6{\cdot}4 \times 10^3$	*b*	—	2,4
XXXIV	Red	560	$1{\cdot}5 \times 10^3$	*b*	—	1,2,3
XXXV	Red	580	$5{\cdot}0 \times 10^3$	*b*	—	1,2,3
XXXVI	Red	625	$5{\cdot}0 \times 10^2$	*b*	—	1,2,3
XXXVII	Red	630	$3{\cdot}0 \times 10^3$	*b*	1:2	1,2,3
XXXVIII	Yellow	—	—	—	—	Ppte
XXXIX	Magenta	550	$9{\cdot}6 \times 10^3$	*b*	1:1	3,4

* *a*, Water (pH 7). *b*, Ethanol and water (pH 7). *c*, Chloroform and ethanol (extracted from water, pH 7).

† 1, Beer's law not followed unless very large excess of chromogen is added. 2, Slow colour formation (5–30 min necessary for completeness). 3, Ligand undergoes hydrolytic decomposition. 4, Poor colour stability on aging. 5, Colour stability good.

Table 2. Spectroscopic properties of copper(I) and cobalt(II) chelates

	Copper(I)			Cobalt(II)		
Chromogen	λ, nm	ε, l.mole^{-1}.cm^{-1}	Remarks†	λ, nm	ε, l.mole^{-1}.cm^{-1}	Remarks†
I	462	$5\cdot1 \times 10^3$	*a*	437	710	*b*
II	450	$7\cdot4 \times 10^3$	*b*	437	380	*b*
III	460	$5\cdot2 \times 10^3$	*a*	450	330	*b*
IV	454	$7\cdot4 \times 10^3$	*b*	450*	700	*b,d*
V	460	$6\cdot4 \times 10^3$	*b*	450*	280	*b,d*
VI	425*	$5\cdot0 \times 10^2$	*b,d,e*	450*	320	*b,d*
VII	425*	$4\cdot8 \times 10^2$	*b,d,e*		0	*b,d*
VIII	450	$2\cdot6 \times 10^3$	*b*	545	1110	*b*
XXVI	468	$9\cdot2 \times 10^3$	*b*	475*	400	*b,d*
XXVII	510	$1\cdot52 \times 10^4$	*c*	475*	170	*c,d*
XXVIII	503	$6\cdot8 \times 10^3$	*b*	475*	3100	*b,d*

* Wavelength not a maximum but a shoulder or at side of band just before reagent blank absorbance becomes appreciable.

† *a*, Water (pH 7). *b*, Ethanol and water (pH 7) as solvent. *c*, Chloroform and ethanol as solvent (complex extracted from water, pH 7). *d*, Colours and spectra of chelate and chromogen are very similar. *e*, Poor stability; absorbance not linear with concentration.

pounds in aqueous solutions is strongly catalysed by the presence of iron(II). This is taken as evidence that the co-ordinated ligands are more susceptible to hydrolysis than the free ligands, a conclusion consistent with the known electron-withdrawing effect of the metal cation, which could promote bond-weakening in remote but conjugated groups.

The ligand: iron ratios found for most of the iron(II) chelates are consistent with predictions based on structures of the ligands. There are, however, a number of notable exceptions, namely for compounds **XII**, **XIV**, and **XVI** (also for **XXXIX**, as discussed above). From structural considerations each of these three should be capable of only bidentate action, yet the mole ratio results indicate terdentate behaviour. Apparently these compounds also undergo hydrolysis; in this case to yield terdentate ligands.

Chromogens **XXIX**, **XXX**, and **XXXI** are substituted triazine analogues of 2,6-bis(2-pyridyl)pyridine, a well-known terdentate chromogenic ligand for iron(II).[7] As expected, the iron(II) complexes of these were found to be bis-chelates (iron:ligand ratio 1:2). The spectra of the chelates exhibit two well-resolved intense bands in the visible region, with the same general appearance as that for the terpyridine iron(II) complex.

Listed in Table 2 are the results obtained for the copper(I) and cobalt(II) complexes of some of the chromogens. The triazole and triazoline derivatives are omitted because of their poor behaviour and instability in solution and the relatively weak colour intensities observed for their reactions with copper and cobalt. The most promising copper chromogen is **XXVII**. On the basis of its molar absorptivity it is slightly more sensitive than bathocuproine, which forms an intense yellow copper(I) chelate ($\epsilon = 1\cdot42 \times 10^4$ at 479 nm), popularly employed for determination of trace amounts of copper.[13,14] Although chromogen **XXVII** lacks suitable water-solubility, it is soluble in chloroform and can be employed effectively as a colorimetric–extraction reagent for simultaneous determination of both copper and iron in aqueous solution after extraction into chloroform.

None of the new compounds is particularly noteworthy as a cobalt chromogen. Their use as colorimetric reagents for cobalt is not advocated, particularly since more sensitive reagents are available.

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Zusammenfassung—Die Chelat- und Farbbildungseigenschaften von 39 neuen Ferroinverbindungen in Reaktionen mit Eisen(II), Kupfer(I) und Kobalt(II) wurden spektrophotometrisch untersucht. Die Ergebnisse zeigen, daß die farbbildenden Eigenschaften von Triazol- und Triazolin-Heterocyclen dem Triazin und Pyridin unterlegen sind, wenn man sie in den Ferroin-Chromophor einbaut. Die Triazol- und Triazolinverbindungen zersetzen sich auch hydrolytisch, wobei Eisen(II) ein starker Katalysator ist; daher sind sie als colorimetrische Reagentien ungeeignet. Unter den Triazinderivaten wurde ein hervorragender Farbbildner gefunden, der allen bisher untersuchten Chromogenen vom Ferrointyp an Empfindlichkeit überlegen ist.

Résumé—On a étudié spectrophotométriquement la chélation et les propriétés chromogènes de 39 nouveaux composés de la ferroïne dans des réactions avec les fer(II), cuivre(I) et cobalt(II). Les résultats démontrent que les propriétés chromogènes des hétérocycles triazole et triazoline sont inférieurs à la triazine et à la pyridine quand ils sont incorporés au groupement chromophore ferroïne. Les composés du triazole et de la triazoline subissent aussi une décomposition hydrolytique, fortement catalysée par le fer(II), les rendant impropres comme réactifs colorimétriques. On a trouvé un chromogène remarquable parmi les dérivés de la triazine, qui est supérieur à tous les chromogènes de type ferroïne étudiés auparavant.

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ATOM-FORMATION PROCESSES IN CARBON-FURNACE ATOMIZERS USED IN ATOMIC-ABSORPTION SPECTROMETRY

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Summary—A mechanism for the production of atoms during carbon-furnace atomization is presented, based on the reaction

$$MO(s) + C(s) \rightarrow CO(g) + M(g)$$

The lowest temperature at which this reaction is thermodynamically feasible has been calculated for 27 elements and is shown to be consistent, for the majority of elements, with the lowest temperatures at which a substantial population of the atoms appears in the carbon-furnace atomizer. The theory has been developed further to explain qualitatively the losses of elements that occur during heating cycles before the atomization.

High-temperature flames such as air–acetylene and nitrous oxide–acetylene remain the most popular method for the atomization of sample solutions in analytical atomic-absorption spectrometry. Whilst it is relatively easy to calculate the degree of atomization of solutions in the highest zones of flames where the assumption of thermal equilibrium is reasonably valid,[1,2] it is much more difficult to (*a*) determine degrees of atomization in primary reaction zones or (*b*) predict with any degree of certainty the nature of reactions leading to the formation of atoms in the primary reaction zone. Such information as is available on atomization reactions suggests that radicals present in high concentration in primary reaction zones play an important role in the chemical reduction of particles and/or molecules formed during the rapid evaporation of the sample solution.[3–7]

Although carbon-furnace atomization was first demonstrated many years ago,[8] the wide application of the technique in routine analysis is much more recent and coincides with the introduction of commercially available equipment. The physical design (*e.g.*, dimensions, method of addition of sample) varies from instrument to instrument,[8–10] but in all cases an aliquot (up to about 100 μl) of the sample solution is placed in contact with the inner wall of a cylindrical graphite tube. The tube is then heated to temperatures as high as 3000° in an inert atmosphere to bring about atomization of the sample in order that atomic-absorption measurements can be made. When the operation of a carbon furnace is compared to that of a flame, it is logical to suggest that the carbon itself plays a role in the chemical reduction of the sample solution to produce atoms.[11] To take an example, Halls and Townshend[12] pointed out that the thermal chemistry of magnesium sulphate would predict that on heating a solution of this salt, $MgSO_4(s)$ would be formed on evaporation of the solvent and hydrated water molecules. This would be converted into $MgO(s)$ at 890° and this oxide is known to sublime to give magnesium oxide gas molecules without decomposition at 2770°. If this occurred in a carbon furnace little if any atomic absorption would be observed. In fact very sensitive determinations of magnesium can be made by using this method at temperatures as low as 1550°. Whilst this and other indirect evidence points to the conclusion that the carbon tube plays a role in atom production, no strong evidence has yet been put forward to support this mechanism.

For most elements, metal solutions of oxy-anion salts such as sulphate and nitrate are preferred in the furnace atomizer rather than the chloride solutions normally used in flame atomization. Chloride solutions give a higher degree of molecular volatilization, which decreases the degree of atomization in the furnace. Most oxy-anion salts of metals decompose to the corresponding metal oxide on heating. A possible model for the formation of metal atoms would therefore be the reduction of the metal oxide by the graphite, yielding carbon monoxide and free metal atoms as in reaction (1):

$$MO(s) + C(s) \rightarrow CO(g) + M(g) \quad (1)$$

where M is the metal being atomized. This model assumes that sufficient energy is released on the formation of carbon monoxide to produce metal atoms directly in the gaseous state rather than in intermediate solid or liquid states. If it is assumed that reaction (1) exists in thermodynamic equilibrium near the surface of the graphite tube then it is possible to use free-energy data to calculate the overall free-energy change of the reaction. The overall free-energy change will vary with temperature but will become negative at some particular temperature above which the reaction is thermodynamically feasible. If the model is valid this temperature should be related to the lowest temperature at which a substantial population of atoms is observed in the carbon furnace. The free energy calculations can therefore be tested against experimental observation of atomic absorption. This approach takes no account of reaction rates but it is generally assumed that at high temperatures reaction rates for carbon reduction of oxides are reasonably fast if the reaction has a negative free-energy change.[13] Long-term equilibrium cannot be assumed, as the metal vapour is carried away in a stream of argon.

Thermodynamic data obtained from various sources[13–19] allowed the calculation of reduction temperatures for 27 elements and measurements of the "appearance" temperatures of all these elements have been attempted and the results are reported in this paper.

EXPERIMENTAL

Measurements of atom populations were carried out by atomic-absorption analysis with a Perkin–Elmer H.G.A. 70 Heated Graphite Atomizer mounted in a Perkin–Elmer 306 Atomic Absorption Spectrophotometer. The H.G.A. 70 consists essentially of a graphite tube which can be heated electrically by currents of up to 400 A at 10 V and can attain maximum atomization temperatures of 2600°. The instrument and its operation have been described in detail elsewhere.[10] Perkin–Elmer Intensitron hollow-cathode lamps were used for most elements and were operated at the manufacturer's recommended currents. For a few elements, hollow-cathode lamps from other manufacturers (Hilger, Pye Unicam and ASL) were used. A deuterium arc background-corrector was used to remove any non-specific absorption. The atomization temperature of the graphite tube depends on the applied voltage and temperatures were obtained from the temperature–voltage calibration supplied by the manufacturer. The temperature attained shows small variations from instrument to instrument (dependent in part on the mains supply voltage) and from tube to tube, particularly with respect to the age of the tube. Much more serious temperature variations have been reported to occur along the length of the tube[20] and the sample solutions must be placed reproducibly in the centre of the tube. We have used thermocouples to check the temperatures attained at the position of sample addition and find them in agreement over a wide range of temperatures with the calibration graph supplied by the manufacturer.

Experimental appearance temperature measurements were carried out on solutions of the sulphate salts of the metals or of the nitrates when the sulphates could not be used for solubility reasons.

RESULTS AND DISCUSSION

Mechanism of atomization

In the production of aluminium atoms from a solution of aluminium sulphate, solid aluminium sulphate and then aluminium oxide will be formed as the temperature is raised. The carbon reduction model then predicts that aluminium atoms will be released through the reaction

$$Al_2O_3(s) + 3C(s) \rightarrow 3CO(g) + 2Al(g)$$

The overall free-energy change, ΔG°, for this reaction will be given by the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants, i.e.,

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G^\circ_f Al(g) + 3\Delta G^\circ_f CO(g) - \Delta G^\circ_f Al_2O_3(s) - 3\Delta G^\circ_f C(s)$$

In Table 1 are given the free energies of formation of all these species at temperatures between 2300 and 2600 K, obtained from the Janaf tables,[14] and the calculated values of $\Delta G^\circ_{\text{reaction}}$. For purposes of comparison the values are rounded off. The values predict that the release of aluminium atoms becomes thermodynamically feasible between 2400 and 2500 K. Values for the free energy of reaction for the reduction of TiO_2, Cu_2O, PbO and ZnO together with those for Al_2O_3 are given in Table 2 and show that the temperature at which the reduction of the oxide becomes thermodynamically feasible varies considerably with the oxide.

The temperature at which the free energy change becomes negative for each oxide should correspond to the lowest temperature at which a substantial population of the atoms of the element appears in the carbon furnace. This temperature is referred to as the

Table 1. Calculation of free energy of reaction of aluminium oxide with graphite

Temp., *K*	ΔG°_f Al(g), *kcal/mole*	ΔG°_f CO(g), *kcal/mole*	ΔG°_f Al_2O_3(s), *kcal/mole*	ΔG°_f C(s), *kcal/mole*	$\Delta G^\circ_{\text{reaction}}$*, *kcal/mole*
2300	11·34	−74·31	−224·87	0	+24·62
2400	8·72	−76·28	−218·36	0	+ 6·97
2500	6·12	−78·25	−212·09	0	−10·42
2600	3·52	−80·20	−205·83	0	−27·73

* For the purposes of the calculation of appearance temperature these values can be further rounded off to whole numbers (cf. Table 2) because the temperatures cannot be measured sufficiently accurately to warrant better accuracy in $\Delta G^\circ_{\text{reaction}}$

Table 2. Calculation of free energies of reaction of oxides of Al, Ti, Cu, Pb and Zn with graphite. All values in *kcal/mole*

Temp., *K*	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600
$\Delta G^\circ_{\text{react}}$ for Al_2O_3	+138	+119	+100	+81	+62	+43	+25	+7	−10	−28
$\Delta G^\circ_{\text{react}}$ for TiO_2	+83	+71	+60	+49	+37	+27	+16	+6	−5	−15
$\Delta G^\circ_{\text{react}}$ for Cu_2O	+10	+1	−7	−15	−23	−31	−39	−47	−55	−63
Temp., *K*	800	900	1000	1100	1200	1300	1400	1500	1600	1700
$\Delta G^\circ_{\text{react}}$ for PbO	+16	+9	+2	−4	−11	−17	−23	−29	−35	−40
$\Delta G^\circ_{\text{react}}$ for ZnO	+45	+35	+25	+15	+3	−10	−20	−35	−45	−60

appearance temperature and was obtained as follows. The instrument was set to give full-scale deflection at the optimum atomization temperature for a particular element. The temperature of atomization was then reduced until this signal just disappeared completely. The atomization voltage was then increased in 0·25 V increments until a small signal (3–5% of full-scale deflection) appeared, and the corresponding temperature under these conditions was taken as the appearance temperature. This technique gave results to the nearest 50° over most of the working range.

The thermodynamic data[13–19] allowed the calculation of reduction temperatures for 27 elements, and these temperatures, the experimentally observed appearance temperatures, and the melting and boiling points of the elements are given in Table 3. Good agreement between the temperature at which $\Delta G^\circ_{\text{reaction}}$ becomes negative and the appearance temperature was obtained for the first 18 elements in Table 3. Agreement to ± 100° is considered acceptable when the uncertainties in the measured temperatures and in the thermodynamic data are taken into account, and the values for SrO may be considered only just outside the range of good agreement. It was interesting that if calculations were done for production of copper from CuO, the agreement with the appearance temperature was destroyed. The oxide Cu_2O is known[21] to be the most stable oxide above 800° in a non-oxi-

Table 3. Thermodynamic reduction temperatures and appearance temperatures for 27 elements undergoing carbon-furnace atomization. The melting and boiling points of the elements are included for comparison

Oxide	Element m.p., *K*	Element b.p., *K*	Temperature at which $\Delta G^\circ_{\text{react}}$ becomes negative, *K*	Appearance temperature of element, *K*
PbO	600	2042	1000–1100	1000
Al_2O_3	932	2720	2400–2500	2300
Cu_2O	1356	2855	1800–1900	1730
Fe_3O_4	1812	3160	1700–1800	1750
Na_2O	371	1163	1200–1300	1230
NiO	1728	3110	1700–1800	1800
Cr_2O_3	2176	2915	1800–1900	1800
ZnO	693	1181	1200	1100
CoO	1768	3150	1800	1720
Sc_2O_3	1673	2750	2400–2500	2450
CdO	594	1038	> 800	850
V_2O_3	2190	3650	2400–2500	2350
SiO_2	1683	2950	2300	2300
BaO	983	1910	2300	2200
TiO_2	1950	3550	2400–2500	2420
LiO_2	454	1604	1900–2000	2100
Mn_3O_4	1517	2314	1600–1700	1600
Ag_2O	1234	2450	1200–1300	1150
SrO	1043	1640	2300	2100
HgO	234	629	Below room temperature	—
B_2O_3	2300	4200	$\Delta G^\circ_{\text{react}}$ still + ve at b.p.	—
NbO	2770	5200	> 3000	—
SnO_2	505	2960	1350	1800
K_2O	336	1039	1100	1550
Sb_2O_3	903	1910	1100–1200	1550
CaO	1123	1765	2400–2500	1800
MgO	923	1390	2100–2200	1550

dizing atmosphere and in the presence of carbon and the results suggest that it is formed as an intermediate from $CuSO_4$ in the carbon furnace.

Agreement with the theory could also be said to occur with three other elements, Hg, B and Nb. The free-energy change for the reduction of mercuric oxide is negative below room temperature and in fact an absorption signal for mercury was observed on simply evaporating a solution of mercuric nitrate to dryness at 60°. On these grounds alone, the heated graphite atomizer does not appear to be as suitable for the determination of mercury as the cold vapour techniques. The free-energy change for the reduction of B_2O_3 is still positive at the boiling point of the oxide, which should therefore leave the tube without being reduced. As expected, no atomic-absorption signal could be observed for boron, or for niobium, for which the free energy change for the reduction of the oxide is still positive at the maximum temperature 3000 K available in the atomizer.

Agreement with the theory appears to be poor for only the last five elements in Table 3. Of these the metal vapour appears at higher temperatures than predicted for Sn, K and Sb. An explanation for this may be that although the reduction of the oxides of the metals is thermodynamically feasible at a lower temperature, the rate of reduction may be too slow to produce a substantial population of free atoms until much higher temperatures are reached. However, both potassium and antimony are well known to exist in associated forms at high temperatures.[22] For example antimony exists as Sb_2 and Sb_4 units in the gas phase up to temperatures above 2000 K.[22] Thus the reduction reaction for K_2O and Sb_2O_3 may give rise to associated vapour at low temperatures, which could not give an atomic absorption signal. It is not so easy to give a plausible explanation for the lack of agreement for calcium and magnesium, which appear at temperatures much lower than predicted.

Reaction (1) predicts that metal atoms are formed directly in the gaseous state following reduction of oxide, without the intermediate formation of solid and/or liquid metal. The good agreement between the predictions of reaction (1) and the experimental observations supports the theory. If intermediate solid or liquid metal was formed much closer agreement of the experimental observations with the boiling points of the metals would be expected. Table 3 shows that such agreement is hardly ever obtained, the majority of elements appearing at temperatures well below their boiling points and the alkali and alkaline earth metals appearing either close to or above their boiling points.

An interesting conclusion of practical importance can be drawn from these results. It can be predicted that the direct atomization of metals or alloys such as ferrous or copper-based alloys in carbon furnaces would be very difficult as under these conditions signals would not be expected until a substantial vapour pressure had been built up and this would require a high temperature (see b.p. values in Table 3). The use of a nitric or sulphuric acid solution of the metal alloy would provide signals at much lower temperatures *via* the reduction of oxides. Chloride solutions would also be disadvantageous owing to molecular volatilization problems, except for those elements, such as iron and chromium, where chloride solutions are known to decompose to yield the oxide.

Losses of metals during preheating steps

The carbon–furnace atomizers available for atomic-absorption spectrometry include a facility for preheating samples at temperatures up to 1100° before high-temperature atomization. This is particularly useful for dry-ashing organic materials before trace metal determinations are carried out, and the usual procedure involves drying at 100° followed by ashing at 490°, 750° or 1100° and atomization. Unfortunately the atomization signals of the more volatile elements are reduced by pre-ashing at these temperatures and the reduction in signal increases with temperature and the ashing time. This is now well known, and Fuller[11] has attributed the reductions in signal to carbon reduction of the oxides of the elements to solid or liquid metal during ashing, and removal of the metal by vaporization, depending on the vapour pressure of the metal. The vapour will then be removed by the stream of inert gas.

Figure 1 illustrates the loss of the signal due to Cu, Ni, Co and Fe, as a function of time of ashing at 1100° and shows that losses are substantial at even very short ashing times and that losses for these four elements decrease in the order Cu > Ni > Co > Fe. The free-energy change for reaction (1) is still positive at this temperature so that it is unlikely that this could account for the observed loss of signal. However, the free-energy changes for the conversion of metal oxides into solid metals, referred to as ΔG_2°, *e.g.*,

$$NiO(s) + C(s) \rightarrow CO(g) + Ni(s) \qquad (2)$$

become negative at much lower temperatures and this reaction probably occurs as postulated by Fuller.[11] We selected nine elements for study and the temperatures at which $\Delta G_2^\circ = 0$ are shown in Table 4, together with the loss of atomization signal after preheating for 300 sec at 750° and 1100°, and the appropriate vapour pressures of the elements.

If reaction (2) occurs, then the amount of an element lost during ashing will depend on (*a*) whether ΔG_2° is negative at the ashing temperature, (*b*) the value of ΔG_2° at the ashing temperature, which will determine the equilibrium constant of reaction (2) (this will be a

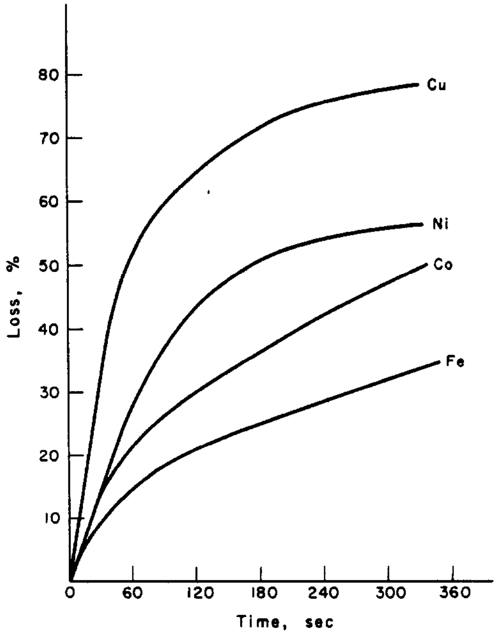

Fig. 1. Variation of the loss of atomization signal for Cu, Fe, Co and Ni with time during preheating at 1100°C.

Table 4. Loss of atomization signal on preheating of samples for 300 sec at 750° or 1100°C

Element	Temperature at which $\Delta G_2^\circ = 0$, °C	Loss on preheating at 750°C for 300 sec, %	Vapour pressure at 750°C, *mmHg*	Loss on preheating at 1100°C for 300 sec, %	Vapour pressure at 1100°C, *mmHg*
V	1600	0	—	0	$3{\cdot}88 \times 10^{-9}$
Cr	1200	0	—	0	$8{\cdot}05 \times 10^{-5}$
Fe	700	0	$3{\cdot}10 \times 10^{-9}$	31·8	$2{\cdot}95 \times 10^{-5}$
Co	500	5	$2{\cdot}77 \times 10^{-8}$	47·8	$3{\cdot}44 \times 10^{-3}$
Ni	450	11·8	$9{\cdot}36 \times 10^{-8}$	55·0	$8{\cdot}73 \times 10^{-3}$
		25·8	$1{\cdot}03 \times 10^{-8}$	78·0	$9{\cdot}11 \times 10^{-4}$
Pb	300	100	$1{\cdot}11 \times 10^{-2}$	100	6·18
Sn	600	−10*	5×10^{-8}	74	$1{\cdot}33 \times 10^{-3}$
Zn	900	100	85·6	100	308

* −10% indicates an increase of 10% in the signal.

function of the difference in temperature between that at which $\Delta G_2^\circ = 0$ and the ashing temperature), (*c*) the rate of reaction (2) which is after all a solid/solid reaction, and (*d*) the vapour pressure of the metal.[22]

The results in Table 4 are in acceptable agreement with (*a*), (*b*) and (*d*). No losses occur for vanadium and chromium, where the value of ΔG_2° is still positive at the ashing temperatures used. For the next four elements, the difference in temperature between that at which $\Delta G_2^\circ = 0$ and the ashing temperature is in the order Cu > Ni > Co > Fe which is in agreement with the observed losses shown in Fig. 1 and Table 4. Losses of iron at 750° may have been too small to be observable and would be in agreement with the fact that this temperature is only 50° above that at which $\Delta G_2^\circ = 0$, and that the vapour pressure is very low. Losses for lead and zinc are very high, in line with the very high vapour pressures of these elements and rapid removal of these metals once formed. An anomalous situation occurs for zinc at 750° since ΔG_2° is still positive at this temperature, which may be due to the necessity of using unsatisfactory thermodynamic data for this element.[16] Tin actually shows an increase in signal after preheating at 750° and a 74% loss at 1100° and is anomalous for other reasons and is under further detailed study.

It may be concluded from this study that carbon plays an important role in the production of atoms in carbon furnace atomization and that during rapid atomization at high temperatures carbon reduction leads to the direct liberation of gaseous metal atoms. Prior heating at lower temperatures leads to the formation of solid or liquid metals and a relatively slower liberation of metal vapour for the more volatile elements. This paper has discussed one model for atomization processes based on carbon reduction. Although one or two other reaction models could be postulated, the agreement of experimental data with the reduction model lends support to this theory. This paper has been concerned with carbon–furnace atomization but other devices, including tungsten and tantalum strips, are used for atomization purposes. One of the advantages of carbon in this context is that it has a high affinity for oxygen, which is removed as a gaseous species, giving efficient atomization of oxides and leaving the surface clean for subsequent samples. The other materials also have a high affinity for oxygen and should give efficient atomization but may suffer from the disadvantage that the corresponding oxides are much less volatile.

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Zusammenfassung—Ein Mechanismus der Bildung von Atomen im Graphitofen wird angegeben, der auf der Reaktion

$$MO(s) + C(s) \rightarrow CO(g) + M(g)$$

beruht. Die niedrigste Temperatur, bei der diese Reaktion thermodynamisch möglich ist, wurde für 27 Elemente berechnet; es zeigt sich, daß sie bei den meisten Elementen mit der niedrigsten Temperatur zusammenfällt, bei der eine merkliche Menge von Atomen in der Graphitofen-Atomquelle auftaucht. Die Theorie wurde weiterentwickelt, um qualitative den Verlust an Elementen zu erklären, der bei Heizzyklen vor der Atombildung eintritt.

Résumé—On présente un mécanisme pour la production d'atomes pendant l'atomisation au four de carbone, basée sur la réaction:

$$MO(s) + C(s) \rightarrow CO(g) + M(g).$$

La température la plus basse à laquelle cette réaction est thermodynamiquement réalisable a été calculée pour 27 éléments et est reconnue être en accord, pour la majorité des éléments, avec les plus basses températures auxquelles une population importante des atomes apparaît dans l'atomiseur à four de carbone. On a développé davantage la théorie pour expliquer qualitativement les pertes d'éléments qui se produisent durant les cycles de chauffage avant l'atomisation.

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QUANTITATIVE DETERMINATION OF HYDROXYLAMINE

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Summary—This paper is a survey of 66 studies from the literature and presents a review of the quantitative methods most widely used for the determination of hydroxylamine and its salts. Volumetric, electrochemical and spectrophotometric methods are discussed, compared and evaluated.

The quantitative determination of hydroxylamine is very important both in studies of biological processes, and for industrial purposes. It has been confirmed, *e.g.*, that hydroxylamine is produced during the reduction of nitrates by *E. coli* and *Torula* yeast.[1] It has also been detected in bacterial media and in the tissues of a number of organisms. Ammonia is reported to have been produced *in vivo* from hydroxylamine by various micro-organisms.[2] Hydroxylamine is also formed as an intermediate during oxidation of ammonia to nitrate by *Nitrosomonas*.[3]

Moreover, hydroxylamine is often found in biological materials in combined forms, *e.g.*, as hydroxamic acids or oximes. Both types of compound, which are often important industrial raw materials, can be determined as hydroxylamine after a preliminary hydrolysis.[4–7]

Another important problem is posed by the difficulty of determining hydroxylamine when present together with other nitrogen compounds such as nitrates, nitrites, ammonia, hydroxamic acids and oximes which often accompany hydroxylamine in the process of the nitrogen cycle and in a number of industrial processes.

There exists only a short review[7(a)] of the methods for the quantitative determination of hydroxylamine, but there is no comprehensive review of all the methods. The purpose of this paper is to compare the quantitative methods for the determination of hydroxylamine described in the literature.

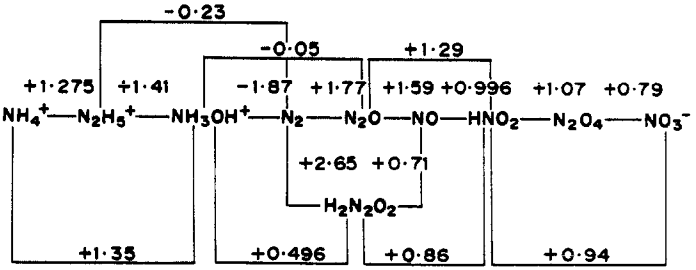
Hydroxylamine and its salts are usually determined by methods based on oxidation or reduction either in acid or in basic solution. Those most frequently employed are volumetric, electrochemical and spectrophotometric methods.

VOLUMETRIC METHODS

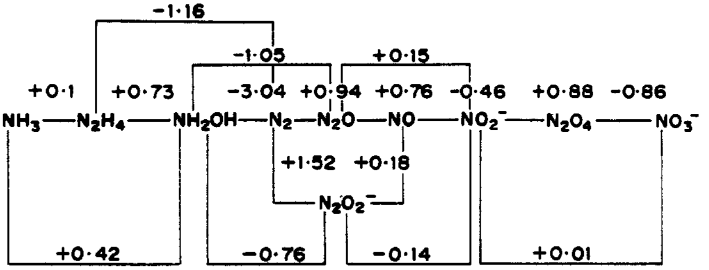
The most widely used of the classical titrimetric procedures for the determination of hydroxylamine and its salts are those based on redox reactions, generally involving the oxidation of hydroxylamine.[8–28] The products depend on the oxidizing agent used, but can include nitrogen,[15–17,19,20] nitrous oxide[8,10–14,18,28] and nitric acid.[21–24] Oxidation has also been made the basis of a complexometric method.

Reducing methods have seldom been used.[10] Reduction potentials for nitrogen species in aqueous solutions[8a] are illustrated in the following diagram.

Acidic solution



Basic solution



The volumetric methods are laborious but provide relatively accurate results if the analytical procedures are rigidly adhered to; the relative error is usually within ± 1–2%. They are particularly useful for fairly large (milligram) amounts of hydroxylamine.

Oxidation with ferric salts

Raschig[8] is regarded as the originator of this frequently used approach, although Meyeringh[9] was perhaps the first to propose it. It has been discussed in detail by Bray, Simpson and MacKenzie,[10] and later by Milligan.[11] The method is simple and gives good accuracy if the prescribed conditions are rigorously maintained. It consists in oxidizing hydroxylamine with an excess of a ferric salt in acid medium in accordance with the reaction

$$2NH_2OH + 4Fe^{3+} \longrightarrow 4Fe^{2+} + 4H^+ + N_2O + H_2O$$

The mixture is boiled, and the ferrous iron produced is titrated with standard potassium permanganate solution. Another possibility is to use a mercuric salt in the presence of thiocyanate as titrant for unreacted iron(III).[11(a)]

Raschig[8] pointed out that this method gives satisfactory results if a large excess of ferric salt (about three-fold) is used and the sulphuric acid is kept at a suitable concentration.

Bray *et al.*[10] also emphasized the accuracy of the method. Two errors may, however, occur: a positive error caused by interaction of potassium permanganate with hydroxylamine or the intermediate product hyponitrous acid still present in the solution, or a negative error due to the presence of oxygen. Both errors can easily be avoided. The precision of the method is better than ±0·2%. In the modified Raschig method, a ceric salt can be used for the titration of the ferrous ion. This reagent is stable to boiling and the accuracy and precision are the same as in the Raschig method. Rao and Rao[12] improved this method by the addition of copper sulphate as catalyst. They found that ferric alum oxidizes hydroxylamine quantitatively and rapidly to N_2O even at room temperature if 1 ml of a 5% copper sulphate solution is added per 50 ml of reaction solution. The reaction rate is sufficiently rapid only when the concentration of ferric alum is at least twice as high as that of hydroxylamine. The ferrous salt produced is titrated with standard sodium vanadate solution.

Oxidation with ceric salts

Benrath and Ruland[13] were the first to investigate the oxidation of hydroxylammonium sulphate with ceric sulphate and found that nitrous oxide and nitrogen were produced, of which 69–73% was nitrous oxide. They gave neither data nor a precise description of their experiments.

Cooper and Morris[14] gave an accurate procedure for the determination of hydroxylamine by this method. They investigated the effect of pH, volume of solution, temperature, presence of chloride ion and concentration of the oxidant on the reaction

$$2NH_2OH + 4Ce^{4+} \longrightarrow N_2O + 4Ce^{3+} + 4H^+ + H_2O.$$

The excess of Ce^{4+} was titrated with standard arsenious acid solution. The accuracy of the method is similar to that of the ferric salt method. An advantage of this method is the good stability and high oxidation potential of ceric sulphate solution.

Oxidation with vanadate

Hoffmann and Kuspert[15] oxidized hydroxylamine with an acidic vanadate solution and measured the liberated nitrogen volumetrically. Alternatively, the vanadyl salt produced could be titrated with a standard solution of potassium permanganate. Kurtenacker and Neusser[16,17] found that ammonium metavanadate acts on an alkaline solution of hydroxylamine to give a mixture of NH_3, NO, N_2O and N_2. In neutral solution the reaction is slower and N_2O and NH_3 are produced. In acid solution, hydroxylamine is oxidized to N_2O and N_2 nearly quantitatively. The course of the reaction depends on the pH. Gowda, Rao and Rao[18] described the conditions for the determination of hydroxylamine by this method. They found that sodium vanadate oxidizes hydroxylamine quantitatively and rapidly to N_2O even at room temperature if the reaction is carried out in hydrochloric acid solution with copper sulphate as catalyst. By this procedure, the authors determined 0·1–0·3 mmole of hydroxylamine hydrochloride; the relative error did not exceed 0·4%.

Oxidation with potassium ferricyanide

Sant[19] reported a method in which hydroxylamine could be determined by oxidizing it to nitrogen with an excess of potassium ferricyanide in a weakly alkaline solution (pH 8–9) and titrating the resultant ferrocyanide with standard ceric sulphate solution. He proposed using this method also for the determination of oximes and their metal chelates. The dark brown colour obtained when too much ferricyanide is used makes it difficult to perceive the end-point. These difficulties can be avoided by employing an improved method suggested by Sant.[20] This also involves oxidation of the hydroxylamine with an excess of potassium ferricyanide in a borate buffer and subsequent iodometric titration of the excess of oxidant with a standard thiosulphate or arsenious acid solution. The sequence of reactions occurring in this method is as follows:

$$2NH_2OH + 2[Fe(CN)_6]^{3-} + 2OH^- \longrightarrow N_2 + 2[Fe(CN)_6]^{4-} + 4H_2O$$

$$2[Fe(CN)_6]^{3-} + 2I^- \xrightarrow{Zn^{2+}} 2[Fe(CN)_6]^{4-} + I_2$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

$$2H_3AsO_3 + 2I_2 + 2H_2O \longrightarrow 2H_3AsO_4 + 4I^- + 4H^+$$

In a strongly alkaline solution the reaction is non-stoichiometric. Sant[21] also developed a method for determining milligram amounts of hydroxylamine by direct titration with hydroxylamine of the alkaline ferricyanide solution in the presence of zinc sulphate to raise the oxidation potential of the ferricyanide by precipitation of zinc potassium ferrocyanide. This procedure also permits rapid determination of hydroxylamine and hydrazine in solutions containing both these components. The relative error rarely exceeds 2%. Hydroxylamine is in this case titrated with ferricyanide in the presence of zinc sulphate to form nitric acid. The end-point of the titration is shown by precipitation of a clear white residue of zinc potassium ferrocyanide. The following reactions occur during determination of hydroxylamine:

$$2[Fe(CN)_6]^{3-} + 2e^- \longrightarrow 2[Fe(CN)_6]^{4-} \xrightarrow{Zn^{2+}} Zn_3K_2[Fe(CN)_6]_2$$

$$NH_2OH + 7OH^- \longrightarrow NO_3^- + 5H_2O + 6e^-$$

In the absence of zinc sulphate and in a weakly alkaline solution, hydrazine and hydroxylamine are oxidized to nitrogen, whereas in its presence only hydrazine is converted into nitrogen. The determination of hydrazine and hydroxylamine is conducted in two stages. The determination time does not exceed 45 min.

Oxidation with bromine, bromate and bromine monochloride

Rupp and Mader[22] were the first to utilize bromine for the determination of hydroxylamine. The oxidation product is nitric acid. According to Kurtenacker *et al.*[17,23] this method is applicable only to small amounts of hydroxylamine, because nitrogen oxide is also evolved from larger quantities. Kurtenacker and Wagner[23] obtained better results by using potassium bromate in hydrochloric acid medium to oxidize the hydroxylamine.

The most meticulous method seems to have been proposed by Burger, Gaizer and Schulek[24] who have shown that bromine monochloride is useful for determining hydroxylamine, which is oxidized quantitatively to nitric acid by an excess of that reagent according to the equation:

$$NH_2OH + 3BrCl + 2H_2O \longrightarrow HNO_3 + 3HBr + 3HCl$$

Bromine monochloride is produced by acidification of a potassium bromate and potassium bromide solution with hydrochloric acid according to the reaction:

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \longrightarrow 3BrCl + 3H_2O$$

The excess of bromine monochloride is determined iodometrically. It is essential in this method to use an adequate excess of bromine monochloride, as this is reduced to bromide which subsequently reduces more BrCl to elementary bromine. This causes a decrease in the reaction rate because elementary bromine oxidizes hydroxylamine more slowly. This procedure was employed to determine about 3–12 mg of hydroxylamine hydrochloride with an error of ±0·5%. The authors mentioned have demonstrated that elementary chlorine can also be used to oxidize hydroxylamine with an error not exceeding 1–2%.

Oxidation with iodine

The reaction between iodine and hydroxylamine has been studied by a number of investigators.[10,25-27] It was found to be extremely slow in acidic medium, but more rapid in basic medium containing such salts as $NaHCO_3$, CH_3COONa or Na_2HPO_4. Even in these cases the reaction rate decreases at the end of titration, with the result that the determination has a considerable positive error[10] and is irreproducible.[25] Another source of error is the fact that hydroxylamine is oxidized in these cases not only to N_2O but also to nitrite.

Bartoušek[28] developed a direct method for the determination of hydroxylamine by titration with iodine. He found that in the presence of magnesium oxide there occurs the stoichiometric reaction

$$2NH_2OH + 2I_2 \longrightarrow N_2O + 4HI + H_2O$$

Decomposition of hydroxylamine, which is unstable in strongly alkaline medium, is minimized by magnesium oxide, which gives only a weak alkaline reaction. The titration must, however, be carried out immediately after addition of the magnesium oxide in order to prevent decomposition of hydroxylamine in basic medium. Too slow a titration leads to negative errors due to spontaneous decomposition, while too rapid a titration causes positive errors, probably owing to the formation of nitrate.

The method is rapid and the results are fairly accurate and reproducible if the prescribed conditions are used. It can be used for determining 5–30 mg of hydroxylamine hydrochloride, but for more than 30 mg the titration becomes too slow and high results are obtained.

Reduction with titanous salts

The most widely used reductant for hydroxylamine is titanium(III) in acid solution,[10] with exclusion of air, according to the reaction

$$NH_2OH + 2Ti^{3+} + H_2O \longrightarrow NH_4^+ + 2TiO^{2+} + H^+$$

The excess is titrated with standard permanganate solution. The results from this method are comparable with those obtained by oxidation with ferric salts. It is, however, somewhat laborious, as the reaction has to be carried out under an inert atmosphere, and the solution of titanium(III) must be prepared by prior reduction of a titanium(IV) solution.

Determination of hydroxylamine by the complexometric method

Buděšínský[29] developed a method based on oxidation of hydroxylamine by the mercury(II)-EDTA complex in basic medium according to the reaction:

$$2NH_2OH + 2HgY^2 + 4OH^- \longrightarrow N_2O + 2Y^{4-} + 2Hg + 5H_2O$$

The EDTA released is titrated with standard lead solution, Methylthymol Blue being used as indicator. This method can also be used for determining hydrazine and phenylhydrazine. Amounts of 10–30 mg may be determined with a relative error within ±1%.

Investigation of the hydroxylamine reaction with arsenic, antimony and bismuth salts has shown[30] that these reagents cannot be utilized for the quantitative determination of hydroxylamine.

ELECTROCHEMICAL METHODS

The electrochemical methods utilize the oxidizing and reducing properties of hydroxylamine. Some are based on reactions exploited in classical volumetric methods. The most widely used of these methods are chronopotentiometry, coulometry, potentiometry and polarography.

Coulometry

Szebelledy and Somogyi[30(a)] oxidized hydroxylamine with coulometrically generated bromine. The determination was conducted in a silver coulometer, with potassium bromide solution as electrolyte. Bromine, which oxidizes hydroxylamine to nitric acid, is formed at the anode. The end-point of the reaction is indicated by the brown tint of free bromine, which can then be determined iodometrically.

This method is suitable for the determination of less than 8 mg of hydroxylamine, since larger amounts give rise to significant side-reactions. The reaction rate depends on the temperature, being slow below 60°, particularly near the end-point, which is then difficult to perceive. When the conditions above are adhered to, the relative error does not exceed ± 1%.

Takahashi and Sakurai[31] also described a coulometric method for the determination of hydroxylamine. It is based on the quantitative reduction of Fe^{3+} to Fe^{2+} by hydroxylamine:

$$2NH_2OH + 4Fe^{3+} \longrightarrow 4Fe^{2+} + 4H^+ + H_2O + N_2O$$

The ferrous ions produced are titrated with electrogenerated ceric ion. The use of an electrolyte solution of ceric sulphate, ferric sulphate and hydrochloric acid at a constant current of suitable magnitude gives results within ± 1%. Platinum generating and indicating electrodes were used, and a calomel reference electrode.

This method was used to analyse 2–10 ml of solutions containing 0·04–0·20 mole of hydroxylamine, with an error of ± 1%. Repeated use of the same solution is however not advisable, as large errors are obtained.

Chronopotentiometry

Davis[32] determined hydroxylamine in acidic medium at a platinum anode. He observed a single anodic wave when 1*M* sulphuric acid was used as the medium, and the transition time corresponded to a six-electron oxidation to nitrate. As the pH of the solution was increased, multiple waves appeared and the total transition time became shorter. This implies oxidation to some lower oxidation state, but the oxidation mechanism and the nature of the products are uncertain. In any medium the oxidation is inhibited by an oxidized electrode. This method was employed to determine hydroxylamine with a precision of ± 1% at concentrations over 1·4m*M*. At lower concentrations, the error increased progressively owing to the fact that the electrode surface became oxidized and charged.

Morris and Lingane[33] described a chronopotentiometric method for the simultaneous determination of hydroxylamine and hydrazine, satisfactory for as little as 2% of hydrazine in the presence of 98% of hydroxylamine, and 2% of hydroxylamine in the presence of 98% of hydrazine. In 0·1N sulphuric acid, when a platinum electrode is used, hydrazine produces a four-electron wave ($E_{1/4} = +0{\cdot}36$V *vs.* S.C.E.) resulting from oxidation to nitrogen. Hydroxylamine produces a six-electron wave ($E_{1/4} = +0{\cdot}83$V *vs.* S.C.E.) resulting from oxidation to nitrate. The errors are within ±5% for most cases. At high hydrazine concentrations nitrogen bubbles form on the electrode surface and block the access of hydroxylamine, thus leading to low results. In this method chloride ion interferes and must be removed.

Potentiometric methods

Britton and Königstein[34] developed an accurate potentiometric method for the determination of hydroxylamine and hydrazine in basic medium. Fehling's solution is titrated with hydrazine and hydroxylamine salts at 90°. The platinum foil used as an indicating electrode acts after the end-point as a copper electrode in equilibrium with cuprous ions. The potential break amounts to 200–300 mV. In order to obtain correct results, the titration must be carried out under nitrogen to prevent oxidation of the cuprous ion by air.

Buděšinský[35] determined hydroxylamine in pyridine–ethyl alcohol medium (1 : 1), using cupric actate as titrant at room temp. However, the break at the end-point is not very large, and very accurate results cannot be obtained. The mean relative error for 4–18 mg of hydroxylamine hydrochloride is ±0·5%. Moreover, the determination is inhibited by cyanide, thiocyanate and iodide.

Hydroxylamine can also be determined potentiometrically with potassium ferricyanide in 10–25% potassium hydroxide medium, as proposed by Vulterin and Zýka.[36] A potential break of about 500 mV is obtained at the end-point. For 14–26 mg of hydroxylamine, the error does not exceed 1·4%.

Attempts have been made to use iodine monochloride[37,38] for a potentiometric titration of hydroxylamine. However, the direct titration is non-quantitative as the point of inflection does not coincide with the equivalence point (±3%), probably because of side-reactions. Better results were obtained with an indirect titration of hydroxylamine in which the excess of iodine monochloride was titrated with standard hydrazine sulphate solution.

Attempts to use manganese(III) salts[39] or permanganate[40] have not been successful.

Polarographic methods

The fast reaction between hydroxylamine and titanium(III) has been the basis of an amperometric method for determining hydroxylamine.[41] The reaction occurs according to the equation:[42]

$$Ti^{3+} + HONH_3^+ \longrightarrow Ti^{4+} + NH_2 + (OH^- + H^+)$$

In the presence of oxalic acid as a radical-capture agent, titanium(III) and hydroxylamine react in a 1:1 ratio. Also in oxalic acid solution, titanium(III)/(IV) shows a wave with $E_{1/2} = -0{\cdot}25$ V *vs.* S.C.E., which is pH-dependent. The titration end-point was best when a temperature of 50° was used, whereas when hydroxylamine was titrated with potassium bromate, the best temperature lay in the range 60–70°. In contrast to the previous method where measurements were made by oscillographic polarography because of the large diffusion current of the titanium wave, in the bromate titration a rotating platinum electrode was used, and the absolute error did not exceed 1%.

The reduction waves of the *N*-alkylhydroxylamines and hydroxylamine[43] cannot be distinguished from each other, but hydroxylamine can be determined in the presence of nitroethane,[43] the reduction wave of which does not interfere.

During hydroxylamine reduction in an aqueous alcohol solution of tetraethylammonium iodide, hydroxylamine was found[44] to give three distinct waves, one with a half-wave potential of $E_{1/2} = -1{\cdot}44$ V *vs.* S.C.E., which disappears at higher pH values, and two waves which may be observed in the pH range 5·6–13·3. One of these waves, which has $E_{1/2} = -2{\cdot}1$ V, decreases with increase in pH, and at pH about 14 merges with the second wave which has $E_{1/2} = -2{\cdot}35$ V. Because of the instability of hydroxylamine in alkaline medium, and in order to increase the reaction rate at 60 and 100°, the investigations were conducted at pH 11·7–12·3 instead of at pH 14. This made it possible to determine hydroxylamine concentrations of the order of 10^{-3} *M*.

Iversen and Lund[45,46] based their method on the anodic waves of hydroxylamine. They demonstrated that hydroxylamine and *N*-alkylhydroxylamines could be determined simultaneously, provided the respective concentrations were of the same order. For hydroxylamine $E_{1/2} = -0{\cdot}32$ V whereas for the *N*-alkylhydroxylamines the absolute values are higher.

Iversen and Lund used an alkaline solution containing 2% of potassium sulphite to remove the oxygen. Deaeration with nitrogen was not satisfactory, as two poorly reproducible waves were then obtained. Addition of sulphite resulted in a single well-formed wave being recorded. The wave-height was proportional to the hydroxylamine concentration in the range 10^{-4}–10^{-3}*M*.

Turian and Smekałova[47] developed an indirect procedure for the polarographic determination of hydroxylamine, making use of the reaction

$$NH_2OH + CH_2O \longrightarrow H_2C{=}NOH + H_2O$$

and the fact that the compound formed is polarographically active. In acidic medium, formaldoxime gives two waves, the second of which lies too near the electrolyte discharge potential, so only the first wave with $E_{1/2} = -0{\cdot}45$ V is made use of, for hydroxylamine concentration 10^{-5}–10^{-2}*M*.

SPECTROPHOTOMETRIC METHODS

These methods are based on coloured derivatives either of hydroxylamine itself, or of compounds obtained from it quantitatively, and can be classified into three groups.

1. Methods for the determination of nitrites previously obtained by quantitative oxidation of hydroxylamine.[1,6,7,48–54]
2. Methods based on direct reaction with hydroxylamine.[52,55–60(a)]
3. Other methods.[5,61]

The methods in the first group are based on the Griess reaction[1,7,48–51] or a modification, the Shinn reaction.[6,54] The Griess reaction[48] involves reaction between nitrite and sulphanilic acid in acid solution, and subsequent coupling of the diazo-compound with α-naphthylamine to yield an intensely coloured dyestuff.

Blom[49] made use of this reaction for the quantitative determination of hydroxylamine after prior oxidation with iodine to nitrite:

$$NH_2OH + 2I_2 + H_2O \longrightarrow HNO_2 + 4HI$$

The accuracy of the determination depends on complete removal of nitrite from the sample, and on restriction of the concentration range to that where the Lambert–Beer law is obeyed.

Enders and Kaufmann[50] converted the nitrite into diazosulphanilic acid, which was then decomposed by heating with sodium azide. Drozdov and Iskandaryan[51] showed that this procedure was not very satisfactory and could cause an error of the order of 10% in the determination of hydroxylamine. Nitrite was therefore removed[51] by conversion into diazosulphanilic acid and heating until this compound had completely decomposed.

Csáky[7] has also shown that the thiosulphate used in the Blom method to remove excess of iodine, causes opacity of the solution, and thus impairs the accuracy of the determination. He therefore proposed using sodium arsenite instead of thiosulphate.

It has indeed been demonstrated[50] that the error in the determination of hydroxylamine at concentrations of 10^{-8}–$10^{-5}M$ does not exceed 2–3%, and that the inaccuracies at higher concentrations result from poor solubility of the dyestuff. Drozdov and Iskandaryan[51] have shown that the linear dependence between absorbance and concentration holds at concentrations even lower than $5 \times 10^{-7}M$, *i.e.*, at lower concentrations than in the study of Enders and Kaufmann.

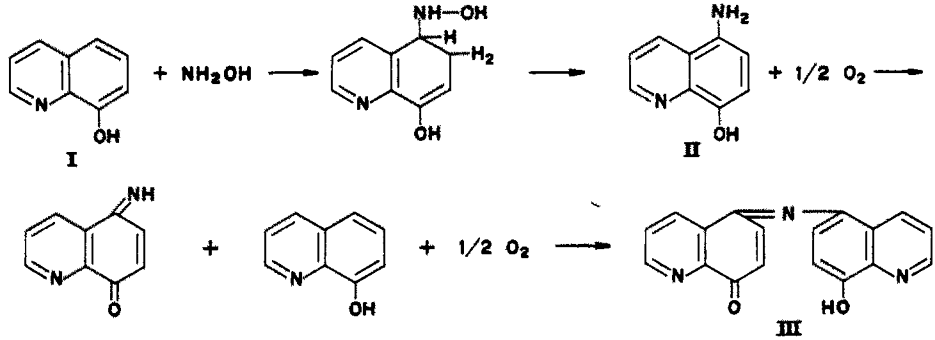
Ferrari[52] has demonstrated that when the sample contains organic substances reacting with the Nessler reagent, *e.g.*, aldehydes, it becomes impossible to determine hydroxylamine and hyponitrous acid separately, and only a simultaneous determination of these two substances is possible.

The Blon–Griess method has many attractive features, including high sensitivity and rapidity of determination—the total determination time does not exceed 0·5 hr—but its versatility is impaired by some disadvantages, such as (*a*) the diazo dyestuff produced is an indicator, and consequently the absorbance is pH-dependent,[53] remaining constant only in the pH range 2·2–5·0, (*b*) the reaction rate depends on the temperature[53] and rapidly decreases below 10°, (*c*) various ions such as chloride interfere, affecting accuracy of the hydroxylamine determination, for which reason acetic acid solution is preferred to mineral acid[51] as reaction medium, and (*d*) low solubility of the coloured product, necessitating working within a restricted concentration range to ensure that the Lambert–Beer law is obeyed.

Some of the disadvantages mentioned above have been overcome by using the Shinn reagent,[6,54] *N*-(1-naphthyl)-ethylenediamine instead of the Griess reagent α-naphthylamine. The method is improved[6] in that the reaction time is decreased from 10–30 min to 2 min or less, the dye formed is stable for at least 3 hr, the sensitivity of the reaction and the solubility of the dye are increased (hence the use of acetic acid as solvent is no longer necessary and aqueous solution can be used), and there is no interference from iron in concentrations less than 5000 ppm, whereas in the Griess reaction the presence of 40 ppm of iron(II) causes a 4% error.

The effect of temperature on the molar absorptivity, which decreases at above 10°, is also observed in the Shinn reaction. The molar absorptivity is also decreased by excess of acetic acid, as a result of the decreased pH; the maximum molar absorptivity is observed at pH 3·05. Nitrites and sulphites[54] must be removed from the solution, as in the Griess method.

The methods based on direct reaction with hydroxylamine involve a variety of reactions, and are not easily summarized. Prodinger and Svoboda[56] based their method on the Berg and Becker reaction:[55] hydroxylamine reacts with 8-hydroxyquinoline (I) in alkaline medium to yield 5-amino-8-hydroxyquinoline (II) which in the pressence of aerial oxygen reacts with a second molecule of 8-hydroxyquinoline to produce an intensely green compound commonly called "indo-oxine" (III).



The concentration range for which Beer's law is valid is somewhat restricted,[55,56] and is also dependent on the reaction time:[56] the law is obeyed for the range 2–10 μg/ml, after 4 hr reaction time, and for 100–200 μg/ml after 1 hr. Deviations from linearity are observed both below 1 μg/ml and above 100 μg/ml (indo-oxine precipitates from the solution).

This reaction is also pH-dependent. Maximum colour development is observed at pH 11·5, and below pH 10 the indo-oxine does not form at all. Carbon dioxide must be absent, since it otherwise buffers the solution and affects colour development, and most metal ions other than those of the alkali metals must also be removed since they form chelates with 8-hydroxyquinoline. A 1000-fold excess of ammonium salts can be tolerated,[56] but the determination is affected by organic substances, particularly by diethyl ether, and by sulphuric acid.

Hydroxylamine gives a colour reaction with ninhydrin,[57] but in this case the molar absorptivities of the products from ammonia and hydroxylamine are identical, so the explanation that hydroxylamine is reduced to ammonia by stannous chloride present in the ninhydrin solution seems to be well-founded.

During investigations of the hydrolysis of *N*-hydroxyurea ($H_2N{-}CO{-}NHOH$) by urease,[4] hydroxylamine was found to form a coloured complex with the Nessler reagent, the molar absorptivity of which is some five times that of the corresponding ammonia product.[58] Despite the fact that the absorption spectrum in both reactions is the same, it seems reasonable to assume that hydroxylamine is oxidized to nitrite, and that the Nessler reagent is reduced just as it is in its reaction with aldehydes. It has been demonstrated by Csáky[7] that one half of the hydroxylamine is recovered as nitrate after reaction with the Nessler reagent, the remaining part being probably strongly linked to the mercuric iodide complex and responsible for considerable absorbance even at lower concentrations of hydroxylamine. Organic substances reacting with Nessler's reagent interfere,[52] though ammonia itself does not interfere seriously, partly because the molar absorptivity of the coloured product is much less than that of the hydroxylamine product, and partly because ammonia tends to be lost from alkaline solution by volatilization.

The qualitative Jaffe test in which α-hydroxylamines react with alkaline picrate to give an orange product, has been adapted by Knobler and Weiss[59] for the quantitative determination of hydroxylamine, canaline and α-amino-oxy acids. The advantages of this method are simplicity and rapidity, and its insensitivity to chloride ions and light. Another advantage is that the spectra of the coloured products remain the same for several days. A good linear dependence of the absorbance on the hydroxylamine concentration was observed for the range 0·5–3 μM.

The reactions of hydroxylamine and oximes with *p*-nitrobenzaldehyde to form *p*-nitrobenzaldoxime have been investigated.[60] The Lambert–Beer law holds for less than 5×10^{-7} equivalents, when the absorbance is measured at 368 nm. The author suggests, however, that hydroxylamine and oximes can be determined simultaneously if care is taken to control the pH and other reaction conditions, but he does not give detailed procedures.

Making use of the fact that hydroxamic acids form a red complex with ferric chloride, Brune and Rieger[60a] developed a quantitative determination of hydroxylamine. They reacted ethyl acetate and hydroxylamine in alkaline medium, and obtained sodium acetylhydroxamate. The free acid forms a red complex with ferric chloride. It was found that the Lambert–Beer law was complied with for 0·2–1·0 g of $^{+}NH_3OH.HSO_4^{-}$/l.

In the third group are included the methods based on the reducing properties of hydroxylamine, and which are therefore indirect methods.

One of these[5] is a modification of Raschig's method in which hydroxylamine reduces iron(III) to iron(II), which in turn is estimated photometrically as the 1,10-phenanthroline complex. The absolute error does not exceed 2%, but it must be added that this method is not yet fully developed.

In another method, potassium chromate is the oxidant, and the excess of chromate is determined photometrically as the red oxidation product of *o*-dianisidine.[61] In the optimum pH range 1–2 the absorbance at 470 nm is constant from 10 to 25 min after mixing. However, this method would not seem very suitable for the determination of hydroxylamine as the oxidation of hydroxylamine is not stoichiometric.

Summing up the spectrophotometric methods, it must be emphasized that they are sensitive and rapid but not one is universally applicable. They can also be used for determining hydroxylamine derivatives such as oximes,[5,6,7,56] after quantitative hydrolysis.

CONCLUSIONS

It must be said that none of the instrumental methods discussed here is suitable for determining milligram or larger amounts of hydroxylamine. They are, however, successful in determining small quantities of hydroxylamine when and where these must be determined quickly, as there is no need to prepare standardized titration solution.

On the other hand, electrochemical and spectrophotometric methods are very sensitive to interferences, temperature changes and pH, hence the need for standardization before the measurements. The properties of the solutions were found to have less influence on the volumetric methods.

It seems best to use all of these techniques; in biological determinations, however, where the amounts of hydroxylamine are very small, the use of spectrophotometric methods seems advisable.

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Zusammenfassung—Es wird eine Übersicht über 66 Arbeiten aus der Literatur gegeben, die sich mit den zur Bestimmung von Hydroxylamin und seinen Salzen am meisten gebrauchten quantitativen Methoden befaßt. Die volumetrischen, elektrochemischen und spektrophotometrischen Methoden werden diskutiert, verglichen und bewertet.

Résumé—Ce mémoire est un examen de 66 études de la littérature et présente une revue des méthodes quantitatives les plus largement utilisées pour le dosage de l'hydroxylamine et de ses sels. Les méthodes volumétriques, électrochimiques et spectrophotométriques sont discutées, comparées et évaluées.

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A CRITICAL EVALUATION OF FLUOROMETRIC METHODS FOR DETERMINATION OF SELENIUM IN PLANT MATERIALS WITH 2,3-DIAMINONAPHTHALENE

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Summary—The published methods for fluorometric determination of Se in plants are reviewed, with particular attention to those using 2,3-diaminonaphthalene as the fluorometric reagent. Two steps in the analysis are shown to be critical: the final stages of the digestion and the complete conversion of the Se to Se(IV). A modified experimental procedure is given.

It has been shown[1,2] that selenium, though an essential nutrient, is also toxic even in trace concentration. Passwater[3] states that the permissible level for selenium intake for mammals lies between 0·5 and 3·5 μg/g of diet, with the optimum at 2·0 μg/g. The distribution of selenium over a particular geographic region can vary widely.[4]

For control analysis of animal feeds and for assessing natural distributions of selenium a rapid, reliable and inexpensive trace method is required. The methods available have been reviewed by Passwater.[3] Those with acceptably low detection limits include fluorometry, atomic-fluorescence spectrophotometry and neutron-activation, and of these the cheapest and most widely used is fluorometry.

The aim of this work was to evaluate the published methods for the fluorometric determination of selenium in plants in order to produce a reliable procedure for general use.

EXPERIMENTAL

Apparatus

All fluorescence measurements were made with a Hitachi–Perkin–Elmer MPF 2A spectrofluorometer. The experimentally determined optimal excitation and emission wavelengths were 380 and 520 nm respectively. Since uncorrected spectra were used, these wavelengths should be checked by each operator for his own particular instrument.

Reagents

Standard Se solution. Prepared by dissolving 50 mg of pure selenium in 5 ml of concentrated nitric acid and 2 ml of concentrated hydrochloric acid and diluting to 100 ml with water. Regular gravimetric analysis of this solution by the hydroxylamine method[5] showed that the concentration remained unchanged for at least 2 months.

2,3-Diaminonaphthalene (DAN) Recrystallized twice by the procedure of Watkinson.[6] Before each analysis a fresh 0·1% solution of 0·1*M* hydrochloric acid was prepared and shaken twice with 10 ml portions of decalin to remove fluorescent impurities. The aqueous layer was then filtered through a fine-porosity filter paper saturated with water

EDTA–hydroxylamine solution. The masking–reducing solution (0·02*M* in EDTA and 0·3*M* in hydroxylamine) was prepared by the method of Olson.[7]

Zinc–dithiol reagent. A 1% suspension of the zinc complex of toluene-3,4-dithiol in redistilled 95% ethanol was prepared according to Koval'skii and Eermakov.[8]

Nitric acid. Analytical-grade reagent doubly distilled.

Decalin. Analytical-grade reagent doubly distilled.

Procedure

Samples were ground and heated at 100° for 24 hr in an air-oven before analysis. A 1 g sample was placed in a 100 ml Kjeldahl flask and 10 ml of concentrated nitric acid were added (a reagent blank was also run). If practicable, this mixture was allowed to stand overnight in order to achieve gradual dissolution without loss of selenium, otherwise it was heated on an electric hot-plate until the organic matter had dissolved, the flask being rotated regularly to ensure that the refluxing acid washed all traces of sample from the neck of the flask. In either case, 2 ml of 72% perchloric acid were then added and the mixture heated, without boiling, until the appearance of perchloric acid fumes (about 40 min), after which 1 ml of water was added, and the solution reheated to fuming, which was continued for a further 15 min. After cooling, 2 ml of 1*M* hydrochloric acid were added and the flask was placed on a boiling water-bath for 15 min to convert all the selenium into Se(IV). If separation of selenium with zinc–dithiol complex was considered necessary, the procedure of Koval'skii and Eermakov[8] was followed and the addition of EDTA omitted in the steps described below. Alternatively, if EDTA masking was to be employed, the solution was transferred to a suitable vessel (such as a 25 × 200 mm culture tube fitted with a screw top), 5 ml of EDTA–hydroxylamine soln were added and the pH was adjusted to 2·0 with 7*M* ammonia. The volume was approx. 40 ml at this stage. The DAN solution was prepared. 5 ml were added to the sample and the tube was placed in a water-bath at 50° for 30 min, then cooled, and 10·0 ml of decalin were added and the tube was shaken on a mechanical shaker for 6 min. The organic layer was placed in a centrifuge tube containing a little anhydrous calcium chloride and centrifuged for 1 min. With a clean dry teat-pipette, some of the extract was transferred to a 1 cm quartz cell and the fluorescence read under the experimentally determined optimal conditions. The fluorescence of the sample was compared with that of a suitable range of standards treated according to the procedure after the heating period on the boiling water-bath.

RESULTS AND DISCUSSION

Drying and digestion of sample

The drying of samples at temperatures up to 100° does not result in any appreciable volatilization of selenium,[9] but prolonged heating at elevated temperature should be avoided.[6] The normal method of drying the sample is simply to store it in a desiccator for an extended period or to dry it in an air-oven at 100°.

The first step is quantitative dissolution of the selenium and complete destruction of organic matter. The two main methods of dissolution are acid digestion and combustion in oxygen in closed systems, and the complete recovery of selenium in these two methods has been demonstrated with ^{75}Se tracer.[10]

Combustion in oxygen has included bomb,[11] flask[6,9,11–13] and flow[14] techniques, the Schöniger flask method being used most, but this procedure is unsuitable for samples with a high inorganic content because of retention of selenium in the ash.[15]

Acid digestion is more widely applicable but can lead to high blank values because of the large volume of reagents used. A recently developed digestion procedure[16] using nitric acid vapour gives very low blank values and could be used where blank levels are a problem. Charring of the sample must be avoided since this usually leads to losses of selenium through volatilization.[17] Mixed acids are generally used for digestion, usually nitric and perchloric. Such a mixture readily oxidizes plant material without charring and has a high oxidation potential which is maintained throughout the digestion. The maximum temperature attained during digestion is 200° and this is sufficiently low to prevent volatilization of selenium. Sulphuric acid is generally considered unsuitable because it causes charring, but it has been employed in a mixture with molybdic and perchloric acids;[18] this mixture however, has the disadvantages of being applicable only to small samples and of difficulty in purifying the sulphuric and molybdic acids.

Table 1. Recovery of Se for various times of fuming

Fuming time, *min*	Wt. Se found, *μg*	Recovery, %
3	0·01	10
5	0·80	80
10	0·95	95
15	1·00	100
20	1·01	101
50	1·00	100

There is ample evidence[6,11,12,19] that no significant differences exist between the results obtained by acid digestion and combustion in oxygen. Acid digestion was chosen for this work because of the less specialized apparatus required and its wider use. Of the available acid mixtures, nitric–perchloric was selected after consideration of ease of purification and general applicability. The conditions for successful use of this mixture are critical although this fact does not appear to have been widely recognized. Most workers have noted the need to prevent charring of the sample and to remove traces of nitric acid completely from the final solution in order to prevent side-reactions with the fluorometric reagent. These conditions are achieved by slow heating, delayed addition of perchloric acid, and heating to fuming several times. Olson[7] reported that the precision of the fluorometric procedure was improved if heating was continued for 15 min beyond the appearance of perchloric acid fumes. Shorter heating times led to low recoveries. We have confirmed Olson's results, using 1 μg of selenium (Table 1). For reproducible results, it is essential to fume the solutions for 15–20 min.

Fluorescence interference caused by the presence of undigested plant material has been observed by many workers and is attributed to lipoidal plant material by Dye *et al.*[11] It is likely that extraneous fluorescence is caused by unoxidized chlorophyll or xanthophyll, both of which are known to fluoresce strongly. The presence of unoxidized pigments can be detected by comparison of emission spectra of standard selenium and digested plant soln. Any difference between the spectra indicates the presence of fluorescent impurities and that the digestion system is inefficient. The extended fuming process described above was found sufficient to remove such fluorescent interferences from the plant materials analysed.

The next step involves conversion of all the selenium into the +4 oxidation state (which is required for reaction with DAN). The oxidation potential of the acid digestion mixture is such that most of the selenium in the sample is in the +4 state after digestion. There may be some selenate however,[19] and this is usually reduced with hydrochloric acid:

$$H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2$$

Levesque and Vendette[20] have noted that the correct reducing conditions are highly critical and, again this does not appear to be widely recognized. They found that the correct conditions obviate stringent subsequent pH adjustments and can also lessen certain interferences. The critical nature of the reductant was attributed to the effects of heat and excess of acid on the equilibrium between selenic and selenous acids in the solution. Variations in the amount of 1*M* hydrochloric acid added and the heating conditions used gave rise to recoveries of added ^{75}Se of between 8·0 and 95·0%. The optimum conditions were 2 ml of 1*M* hydrochloric and heating on a boiling water-bath for 15 min.

Separation of selenium

Separation of selenium from the matrix is only necessary when a high concentration of interfering elements is present. Extensive studies of interferences[11,13,21,22] show that oxidizing agents (*e.g.*, hypochlorite, nitrite) which can react with DAN and reducing agents [*e.g.*, tin(II)] which react with selenite, are the chief interferents. Enhancement of fluorescence by antimony(III) and chromium(III)[13] and catalysis of oxidation of DAN by copper(II)[21] have also been observed.

Selenium can be separated from the digest or the interferences can be masked with EDTA. Separation methods include co-precipitation with arsenic[23] or solvent extraction of the complex of selenium with toluene-3,4-dithiol into carbon tetrachloride.[8,19,24] Co-precipitation from perchloric acid media is unsuitable[12,23] and the additional manipulations required can lead to losses. The extraction method is more convenient. The masking method with EDTA effectively removes interference from copper, iron(II) and vanadium, but traces of nitrous acid still interfere and must therefore be absent.[24]

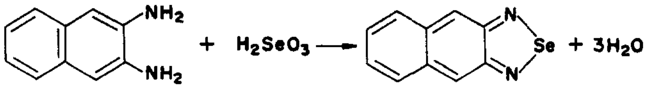
The dithiol extraction method was examined experimentally and we encountered no difficulties. However it took 1·5–2 hr to complete because of the necessity to evaporate the extract on a water-bath. Because of the time factor, this method should be used only for samples containing a high concentration of inorganic ions. Otherwise, it is enough to mask the interferences with EDTA. Also the dithiol method is unsuitable for samples digested with the molybdic–sulphuric–perchloric acid mixture, because of interference from molybdenum which forms a strong, green complex with dithiol, competing with selenium.

In general, whether EDTA masking is sufficient must be tested experimentally. The grass samples analysed in this laboratory required only the use of EDTA.

Formation and extraction of the fluorescent complex

Several aromatic diamines have been investigated[25] for use as fluorometric reagents for selenium, the most successful being 3,3′-diaminobenzidine (DAB) and 2,3-diaminonaphthalene (DAN). DAN has the greater fluorescence sensitivity[25] and has almost entirely replaced DAB in recent years. A further advantage is that DAN can be more readily purified.

DAN reacts with Se(IV) according to



This reaction is confined to the +4 oxidation state of Se.

DAN, like many aromatic diamines, undergoes rapid decomposition in light, to give highly fluorescent products which must be removed before the reagent is of analytical value. For this reason, purification of DAN assumes particular importance. It has been found satisfactory to recrystallize the reagent from water and to extract the freshly prepared 0·1% DAN soln (in 0·1*M* hydrochloric acid) twice with decalin or cyclohexane to remove fluorescent impurities.[6,7,25] All operations must be performed either under a

Table 2. Rate of piazselenol formation at 15° and 50° (Conditions used: pH 2·0, 1 μg Se)

Development time, *min*	Fluorescence reading	
	15°	50°
5	10	57
10	22	75
15	30	78
20	37	80
30	54	83
50	70	83
100	81	83
120	83	83

yellow safe-light or in diffuse daylight, and the recrystallized reagent kept in a light-proof container. Preparation of a fresh DAN solution immediately before use is essential. Wilkie and Young[26] have suggested that a more stable DAN solution results when 10% hydrochloric acid is used as solvent and have emphasized the need for short extraction times in order to reduce fluorescent interferences from the reagent.

The reaction of DAN with selenium(IV) is pH-sensitive, although less so at elevated temp.[25] The kinetics and possible mechanism of this reaction have been studied in detail by Cukor and Lott[27] who conclude that the reacting species are the monoprotonated diamine and undissociated selenous acid. The rate of formation of the piazselenol at the optimum pH of 2·0 was investigated in this laboratory at room temperature (15°) and at 50°. After various times, the piazselenol was extracted with decalin and the fluorescence measured. The results appear in Table 2. Optimum development times were 120 min at 15° and 30 min at 50°.

Because of the lower sensitivity to pH at higher temperatures and the short time at 50°, this temperature was subsequently used for piazselenol formation.

The reaction is usually done under weakly reducing conditions to prevent the interference of oxidizing agents (hypochlorite, nitrite and traces of nitric acid). Hydroxylamine is suitable and is frequently added to the EDTA solution, thereby producing a combined masking–reducing solution. The rate of piazselenol formation is not affected by hydroxylamine, which may therefore safely be used to prevent oxidation of DAN.[27]

The solvents used to extract the piazselenol include cyclohexane,[6,13,20] decalin,[7,12,18,25] toluene[21] and n-hexane,[26] cyclohexane and decalin being the most popular. Levesque and Vendette[20] found that for selenium up to 0·012 μg/ml, decalin solution gave about 1·5 times the emission from cyclohexane solution. Despite this, they chose cyclohexane because it was easier to handle and gave less variability. We compared toluene and decalin

Table 3. Comparison of toluene and decalin as extractants for the piazselenol

Solution	Solvent	Fluorometer reading
Blank	Decalin	0, 0, 0
Blank	Toluene	13,12,12
1 ppm Se	Decalin	100,100,100
1 ppm Se	Toluene	92,90,91

Table 4. Comparison of results obtained by various laboratories for samples. Values are expressed as μg of Se/g of dry material

	Previous analyses			
	Analyst 1	Analyst 2	Analyst 3	University of N.S.W.
Lucerne Chaff	0·135–0·149	0·134–0·145	0·130–0·135	0·143, 0·143, 0·143, 0·145, 0·147
No. of analyses	5	7	2	5
Mean	0·14	0·14	0·13	0·144
Wheat and Hay Chaff	0·018–0·030	0·016–0·021	0·020–0·025	0·018, 0·019, 0·020, 0·021, 0·024
No. of analyses	5	9	2	5
Mean	0·02	0·02	0·02	0·021
Liver	1·184–1·408	1·150–1·150	1·36–1·39	1·149, 1·150, 1·150, 1·150, 1·150
No. of analyses	9	3	2	5
Mean	1·28	1·15	1·38	1·150

(Table 3) and found decalin superior, consistently giving higher fluorescence intensities and lower blank values without any evidence of the variability experienced by Levesque and Vendette. We therefore chose decalin as the best solvent.

Analysis of samples

Powdered and dried samples were obtained from CSIRO Division of Nutritional Biochemistry (Adelaide) and analysed by the proposed procedure. These samples had previously been analysed fluorometrically with DAN by three Government departments. A liver sample containing a relatively high concentration of inorganic ions was included as an example of a matrix requiring dithiol separation. Our results, together with those of previous analyses, appear in Table 4.

The variation of results between different analysts is evident, especially for the liver sample, which proved more difficult to digest than the grass samples. The precision of our results was as good as or better than that obtained by other analysts. These results indicate that the described procedure is suitable for accurate determination of selenium in plants in the range 0·02–1·5 μg.

CONCLUSION

The fluorometric procedure with DAN for selenium has two critical steps: the final stages of the digestion and the complete conversion of selenium into oxidation state +4. Particular attention must be paid to the details of these two steps if precise and accurate results are to be obtained.

Acknowledgement—The authors wish to thank the CSIRO Division of Nutritional Biochemistry for kindly supplying analysed samples.

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Zusammenfassung—Es wird eine Übersicht über die bekannten Methoden der fluorimetrischen Bestimmung von Selen in Pflanzen gegeben, wobei besonderer Wert auf die Methoden mit 2,3-Diaminonaphthalin als fluorometrisches Reagens gelegt wird. Es wird gezeigt, daß zwei Arbeitsgänge bei der Aanlyse kritisch sind: die Endstufen des Aufschlusses und die vollständige Überführung von Se in Se(IV). Es wird eine geänderte Arbeitsvorschrift angegeben.

Résumé—On passe en revue les méthodes publiées pour le dosage fluorimétrique de Se dans les plantes, en portant une attention particulière à celles utilisant le 2,3-diaminonaphtalène comme réactif fluorimétrique. On montre que deux phases de l'analyse sont essentielles: les stades finaux de la digestion et al conversion complète de Se en Se(IV). On donne une technique expérimentale modifiée.

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ANALYSIS OF HIGH-BOILING PETROLEUM STREAMS BY HIGH-RESOLUTION MASS SPECTROMETRY

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Summary—The major group types in petroleum streams may be analysed by high-resolution mass spectrometry. The method described here relies on a calibration matrix derived from the high-resolution spectra both of pure compounds and of cuts separated from petroleum. The analytical results have been assessed statistically for precision.

Mass spectrometry has been a valuable analytical tool in the petroleum industry for the quantitative analysis of the hydrocarbon group types present in refinery streams. Low-resolution mass spectrometry (LRMS) has, traditionally, been the most widely documented. Typically, in an LRMS analysis, a petroleum stream would be separated into a saturated and an aromatic fraction. Both fractions would be analysed separately by using characteristic integral m/e values and their intensities. Such LRMS methods have become increasingly sophisticated to the extent that Robinson[1] has reported recently a comprehensive procedure which does not require that the oil be separated.

By contrast, high-resolution mass spectrometry (HRMS) has not been widely reported as a technique for the quantitative analysis of petroleum. An exception is the application of HRMS to the analysis of the aromatic portions of oils and similar samples.[2] The sparse use of HRMS in petroleum analysis has been caused mainly by lack of the dedicated and versatile data-acquisition systems so essential for routine petroleum analyses. A less important drawback has been the comparatively low sensitivity of HRMS. The advantages of HRMS have been outlined by Gallegos *et al.*,[3] who published the only HRMS approach to the group type analysis of petroleum streams. The recent availability of dedicated computer systems and the increasing use of electrical recording at high resolution have been added incentives to the development of HRMS for the routine analysis of oils.

The work reported here is a continuation of an earlier paper[4] which described one approach to optimizing a high-resolution instrument for quantitative studies. We adopted an approach similar to but more precise than that described earlier.[3] The atomic compositions of all the characteristic ions are computed for the sample spectrum. Additionally, the calibration matrix reported here is derived from high-resolution spectra of calibrants. This is in contrast to a low resolution matrix modified to be compatible with the output from a high resolution mass spectrometer.[3]

The scope of this method covers samples boiling in the range of about 240–550°. Distillate streams and some process streams may be routinely analysed providing the sulphur content is not too high. Quantitative results are reported for three saturated, thirteen aromatic, five aromatic sulphur and one aromatic oxygenated group types.

EXPERIMENTAL

The high-resolution mass spectrometer used was an MS-902 made by Associated Electrical Industries Ltd. The procedures described earlier[4] were adopted to ensure quantitative operation of the instrument. In summary, the dynamic resolution was 10^4, scan speed 4·6 min/decade and the ion-source temperature set to a nominal value of 250·0 ± 0·1°. This temperature was adjusted to give, for the standard paraffin blend,[4] $\Sigma 71/TI = 0{\cdot}56 \pm 0{\cdot}02$.* Under these conditions the fragmentation of n-hexadecane was 1·2 for $(m/e = 127)/(m/e = 226)$. This ratio is higher than that quoted by ASTM[5] for low-resolution procedures. The temperature of the all-glass heated inlet system was about 310°. The sample size was 1 μl with 0·7 μl of perfluorokerosine being run concurrently to establish the reference masses. A mass range from 617 to 60 was scanned for the standard runs.

A schematic diagram of the system is shown in Fig. 1. The storage scope was used to monitor the optimization of the peak profile during the dynamic run at 10^4 resolving power. To obtain the highest accuracy of mass measurement over the entire mass range it was necessary to adjust the instrument operating parameters to give uniform peak widths at both high and low values of m/e.

The MSDS-30 data system automatically calculates the atomic composition of all the ions in the sample spectrum. Error limits of 10 ppm were routinely set for the error of the mass measurements which, for most samples, were large enough to identify more than 90% of all the ions. The intensities and compositions of all the ions were stored on the 256K disc associated with the PDP8I computer. These data were subsequently transferred, off-line, to an IBM 1800 computer, which produced the intermediate and final reports. If some ions were not unequivocally identified during the mass identification step with the MSDS-30 system an extra program was used to process the transferred data. The preliminary IBM 1800 output reported only those ions identified unequivocally. The additional program used criteria based on minimum mass deviations and smooth carbon number distributions of the constituent hydrocarbon and sulphur group types.

The intensity, Z-number, atomic composition and accuracy of measurement for each ion were listed in the intermediate output from the IBM 1800. The final step summed the characteristic ion intensities and processed these by matrix inversion to give matrix solutions in units of total ionization. These matrix solutions were multiplied by weight sensitivity factors and finally normalized to give weight percentages.

Although not all the ion intensities are used in the method the sum of the characteristic ion intensities should be about 90% of the total ionization. Similarly, the preliminary output which lists the summations of characteristic ion intensities should not include ions which are not accounted for by the method. These conditions, together with certain resolution requirements, necessarily restrict the applicability of the method.

Calibration

Table 1 shows the calibration matrix covering 22 group types. This matrix was constructed from standard high-resolution analyses on a variety of pure chemicals and blends of pure chemicals. These were obtained from API project 42 and from syntheses in our own laboratories. A selection of benzthiophenes was obtained from the Bureau of Mines, U.S.A. Several cuts composed of condensed-ring saturated compound types were isolated by "Sephadex" separations in our own laboratories.

Blends of pure compounds belonging to one Z-number class were made up to reflect, where possible, current views about the composition and structure of petroleum.[6] Weight sensitivities were determined from high-resolution analyses of mixtures synthesized from two or more Z-number class blends.

The paraffin ($Z = +2$) blend was composed of normal and isoparaffins with the carbon number ranging from 10 to 36. The ratio of iso to normal paraffins was about 0·4 and the average carbon number was 20. The matrix in Table 1 contains the calibration coefficients expressed as the ratio of the sum of the intensities of the ions characteristic of each group type to the sum of all the ion intensities from mass 65 upwards. For the paraffin group the characteristic ions were $C_5H_{11}^+$, $C_6H_{13}^+$, $C_7H_{15}^+$ and $C_8H_{17}^+$.

The characteristic ionic compositions for the two remaining saturated groups corresponded to the integral masses selected by Clerc, Hood and O'Neal.[7] The blend of mono + non-condensed cycloparaffins was composed mainly of trisubstituted monocycloparaffins with average carbon number 18. No analytically significant trends were observed relating molecular weight to the matrix coefficient for this group type. It was not possible, with the compounds and narrow cuts which were available, to resolve two-, three- or four-ring and higher condensed ring cycloparaffins. Consequently the matrix will resolve only condensed from mono + non-condensed ring saturated compounds. The pattern coefficient for condensed ring saturated compounds, although not a function of molecular weight, did change with degree of condensation. The matrix value finally selected for this composite group was calculated from the high-resolution spectrum of a mixture of tri- and tetra-condensed ($\simeq$ 80/20 w/w) cycloparaffins separated from a Western Canadian crude oil by "Sephadex" liquid chromatography.

The choice of calibration material for the aromatic groups was severely limited, particularly for the more highly condensed ring groups. Wherever possible, trisubstituted aromatic compounds were predominant in the blends. As an example, the average carbon number of the alkyl benzene blend was 21, the average degree of substitution was three and the average carbon numbers of the three substituents was 2, 2 and 11 respectively. For all the

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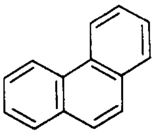
* $\Sigma 71$ is the sum of the C_nH_{2n+1} series, *i.e.*, 71, 85, 99, 113; TI is the sum of all ion intensities in the spectrum.

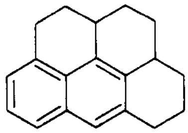
Table 1. Calibration matrix and sensitivities based on total ionization

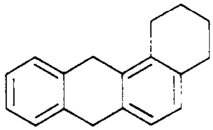
Z No / Summation																						
+2	0·5198	0·1040	0·0182	0·0104	0·0018	—	—		-	—	—	—	—	—	—	—	—	—	—	—	—	—
0	0·0613	0·4594	0·1070	0·0061	0·0004	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
−2,4,6 etc	0·0221	0·1500	0·3563	0·0883	0·0111	0·0023	—		—	—	—	—	—	—	—	—	—	—	-	—	-	—
−6	0·0156	0·0160	0·0090	0·7435	0·0612	0·0310	0·0071	—	0·0024	—	—	—	—	—	—	—	—	—	—	—	—	—
−8	0·0077	0·0102	0·0160	0·0796	0·5782	0·1185	0·0362	0·0131	0·0043	0·0009	—	—	—	—	—		—	—	—	—	- -	—
−10	0·0043	0·0837	0·0392	0·0373	0·0860	0·4718	0·0911	0·0369	0·0197	0·0066	—	—	—	—	—	-	—	—	—	—	—	—
−12	0·0028	0·0101	0·0072	0·0214	0·0214	0·0497	0·6271	0·0897	0·0411	0·0055	—	-	- -	—	- -	—	—	—	—	—	—	—
−14		0·0005	-	0·1384	0·0516	0·0207	0·0109	0·4630	0·0500	0·0264	0·0032	—	—	—	—	—	—	—	—	—	—	—
−16	0·0016	0·0086	0·0034	0·0500	0·0500	0·0200	0·0060	0·0170	0·4577	0·1000	0·0339	0·0063	0·0007	—	—	—	—	—	—	—	-	—
−18	-	0·0050	0·0005	0·0010	0·0100	0·0100	0·0100	0·0060	0·0250	0·4590	0·1000	0·0240	0·0036	0·0010	—	—	—	—	—	—	—	—
−20	—	—	—	0·0100	0·0100	0·0150	0·0050	0·0050	0·0170	0·0200	0·4500	0·0432	0·0020	0·0020	—	—	—	—	—	—	—	—
−22	—	—	—	0·0050	0·0050	0·0300	0·0200	0·0200	0·0546	0·0134	0·0466	0·4522	0·0996	0·0274	0·0020	0·0020	—	—	—	—	—	—
−24	0·0028	0·0110	0·0049	0·0084	—	0·0018	0·0061	0·0105	0·0010	—	—	0·0142	0·4914	0·1657	0·0350	0·0040	—	—	—	—	—	—
−26	0·0010	0·0100	0·0050	0·0050	—	—	0·0500	0·0050	0·0400	0·0050	0·0400	0·0200	0·0200	0·4500	0·1500	0·0200	—	—	—	—	—	—
−28	0·0010	0·0100	0·0050	0·0050	—	—	0·0050	0·0050	0·0400	0·0100	0·0050	0·0100	0·0200	0·0200	0·4500	0·1000	—	—	—	—	—	—
−30	0·0010	0·0100	0·0050	0·0050	—	—	0·0500	0·0050	0·0400	0·0100	0·0050	0·0100	0·0200	0·0200	0·0200	0·4500	0·0100	—	—	—	—	—
−10S	—	—	—	0·0247	0·0360	0·0542	0·0268	0·0008	—	—	—	—	—	—	—	—	0·5899	—	—	—	—	—
−16S	—	0·0013	—	0·0046	0·0197	0·0142	0·0114	0·0393	0·0638	0·0163	0·0100	0·0100	—	—	—	—	0·0013	0·5040	0·0118	—	—	—
−18S	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·4900	0·0100	—	—
−20S	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·4800	0·0100	—
−22S	—	0·0100	0·0100	0·0050	0·0050	0·0010	0·0010	0·0500	0·0550	0·0200	—	—	—	—	—	—	0·0010	0·0020	—	—	0·4700	—
−16O	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·5000
Wt/T I	1·0	0·70	0·75	0·82	0·70	0·70	0·71	0·70	0·76	0·70	0·70	0·70	0·70	0·70	0·70	0·70	0·65	0·75	0·75	0·75	0·90	0·75

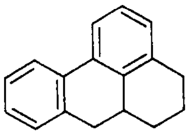
aromatic and sulphur types the characteristic ions were C_nH_{2n-Z} and $C_nH_{2n-(Z+1)}$. These correspond to the most intense ions in the spectra of petroleum aromatics, namely the parent and parent-H series. In practice, the preliminary listing obtained from an HRMS analysis of a calibration blend produced an element map, which, after division of the characteristic intensities by the sum of all the ion intensities, gave the matrix coefficients.

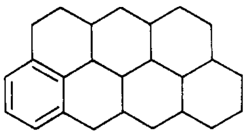
In selecting the blending components for di and more highly condensed aromatics some discussion about the structure of petroleum is essential. Mass spectrometry provides an analysis of petroleum by group types which are defined by the Z-number. For decreasing Z-numbers the choice of available structural types which may be included in the blends becomes increasingly more complex (in practice the choice is limited by the availability of such compounds). It is not firmly established which of these structures predominate in petroleum streams. Consider the group types of Z-number − 18. Several skeletal structures (I–VI) represent a few of the choices made available by the number of rings plus double bonds allowed by a Z-number of − 18.

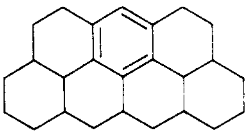

(I)


(II)


(III)


(IV)


(V)


(VI)

Two structural extremes, I and VI, are readily apparent and the former may be postulated to predominate in catalytically cracked streams and the latter in severely hydrogenated streams. Indications are that intermediate hybrid structures such as **II**, **III** or **IV** occur in virgin streams[8] and their concentrations will depend on the crude source. Unfortunately few such hybrid compounds and their homologues are readily available for mass spectral studies. It is probable that structures such as V or VI will give rise to significant fragment ions which are characteristic of cycloalkyl groups. In order to achieve satisfactory percentages for aromatic and saturated compounds for straight-run materials, several experimental matrices were generated from aromatic blends composed of different percentages of hybrid molecules. The final matrix shown in Table 1 was derived after critical appraisal of a variety of test results over a 2-yr period. However, in most cases, the blends contained significant proportions of structures similar to I.

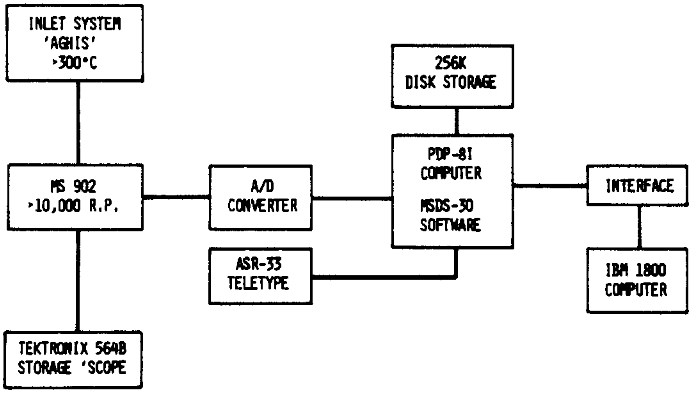


FIG. 1. Schematic diagram of HRMS system.

RESULTS AND DISCUSSION

The ratio of saturated compounds to aromatics in an oil is an important property in petroleum processing. A variety of different types of oils was analysed and the saturated and aromatic contents were determined. The saturated content was obtained by adding the

Table 2. Weight percentages of saturated and aromatic compounds by HRMS and liquid chromatography

Stream type		HRMS	Liq. chrom.
Light distillate	sat.	76·8	80·8
	arom.	23·2	19·2
Heavy distillate	sat.	74·8	76·1
	arom.	25·2	23·9
Light lube feed	sat.	67·2	69·4
	arom.	32·8	30·6
Cat. cracker feed	sat.	68·3	68·5
	arom.	31·7	31·5
Heavy lube feed	sat.	61·3	59·5
	arom.	38·7	40·5
Heavy lube basestock	sat.	81·4	78·9
	arom.	18·6	21·1
Aromatic basestock	sat.	47·6	45·7
	arom.	52·4	54·3
Decant oil (ex. F.C.C.U.)	sat.	7·9	9·7
	arom.	92·1	90·3
Light cycle oil (ex. F.C.C.U.)	sat.	20·0	21·7 (includes ≃5% olefins)
	arom.	79·8	78·3
Aromatic extract	sat.	35·1	27·7
	arom.	64·9	72·3

amounts of the three individual saturated groups. The aromatic content was obtained, similarly, by addition of the nineteen remaining groups. The results were compared with those from the separation of the oils by ASTM D2007 procedures. The results are shown in Table 2. An example is shown where there was often a poor agreement for aromatic extracts from lube-oil processing. The reason for this is that extracts often contain significant concentrations of both sulphur and nitrogen types and of aromatic types below $Z = -30$. The agreement between the two techniques for catalytically cracked stocks is, at first sight, surprising. However, it must be remembered that decant oils contain large percentages of three- and four-ring aromatic compounds. The only compounds available for calibration at low Z-numbers were mainly condensed aromatic molecules. Nevertheless it would seem from these results that the method is relatively insensitive to the microstructure of the stream components providing all the ionic compositions are accounted for by the matrix. The saturated–aromatic ratio was strongly dependent on source temperature and to achieve agreement between the two techniques required strict adherence to the criteria established earlier.[4]

Error analyses were carried out on a standard aromatic oil. This oil was analysed under standardized conditions over a two-month period. A total of 18 analytical runs was made and these formed the basis for the statistical analyses. Reproducibility may be defined as the quantitative expression of the random error associated with a single operator in a given laboratory obtaining successive results with the same apparatus under constant operating conditions on the identical test material. The 95% confidence limit is given by

$$L_{95} = \frac{ts}{\sqrt{n}}$$

where L_{95} is the 95% confidence limit, t is the value of *Student's* t function, s is the estimated standard deviation and n is the number of experiments.

Table 3. Statistical analysis of a standard aromatic oil

Group type	Z-number	$\bar{X}$, % w/w Mean of 18 analyses	s, % w/w		L_{95}, % w/w	
Paraffins	+2	12·5	0·95		0·48	
Cycloparaffins	0	19·1	0·75	1·77	0·38	0·91
Condensed cycloparaffins	−2	30·4	1·80		0·92	
Benzenes	−6	5·5	0·81		0·41	
Indanes	−8	4·9	0·33		0·17	
Dinaphthene benzenes	−10	5·2	0·34		0·16	
Naphthalenes	−12	4·4	0·16		0·08	
Acenaphthenes	−14	3·7	0·33		0·17	
Fluorenes	−16	3·6	0·35		0·18	
Phenanthrenes	−18	3·4	0·51		0·26	
Naphthenephenanthrenes	−20	1·1	0·62			
Dinaphthenephenanthrenes	−22	0·6	0·25			
Chrysenes	−24	0·3				
Dinaphthenepyrenes	−26	0·1				
Dibenzofluorenes	−28	—				
Dibenzanthracenes	−30	—				
Benzothiophenes	−10S	1·6	0·31			
Dibenzothiophenes	−16S	2·7	0·36			
	−18S	0·2				
	−20S	0·2				
	−22S	—				
Dibenzofurans	−16O	0·5				

Table 3 shows these data. The different *Z*-number classes have been assigned names corresponding to a single group type. This is for convenience only and the predominance of the specific group type within any *Z*-number class will depend on many factors, as discussed briefly in the section on calibration material. The arithmetical averages ($\bar{X}$) for 18 runs are shown with the associated standard deviations and limits at the 95% confidence level. Also shown are the errors for the total saturated content. The mean (μ) for this set of runs is given by

$$\mu = \bar{X} \pm \frac{ts}{\sqrt{n}}$$

In practice, however, the error associated with any analytical number resulting from a single analysis is realistically associated with $\bar{X} \pm ts$ and here t is 2·145. The error of an analytical result is thus about twice the standard deviation for the mean of this set of runs.

Applications of most analytical methods involve mathematical manipulation of individual group type concentrations. To assess the additivity of the present method an example is shown where 46·3% by weight of the extracted aromatics is added to the standard oil. A comparison between the calculated and observed compositions may be made from the data in Table 4. The difference between these two compositions approximates to the reproducibility for the analysis.

The resolution and sensitivity available routinely for this procedure limit the scope of the analysis to the predominant group types found in petroleum. A primary resolution requirement for the separation of the $^{12}C_1$–H_{12} doublet is $<5 \times 10^3$ at mass 300. Equally important is the separation of the C_2H_8–$^{32}S_1$ doublet, requiring again $<5 \times 10^3$ resolving power at mass 300. Examples of these important doublets are the overlapping of paraffins (C_nH_{2n+2}) and naphthalenes (C_nH_{2n-12}) and of the latter with dibenzothiophenes

Table 4. Analysis of standard oil blended with 46·3% w/w aromatic fraction

Group type	Z-number	Calculated, % w/w	Observed, % w/w
Paraffins	+2	7·2	8·4
Cycloparaffins	⩽ 0	10·3	11·9
Condensed cycloparaffins	⩽ −2	19·1	19·1
Benzenes	−6	6·7	6·6
Indanes	−8	6·6	6·9
Dinaphthene benzenes	−10	8·1	7·4
Naphthalenes	−12	6·8	6·7
Acenaphthenes	−14	6·6	5·9
Fluorenes	−16	6·1	6·2
Phenanthrenes	−18	6·8	6·3
Naphthenephenanthrenes	−20	3·1	2·7
Dinaphthenephenanthrenes	−22	1·7	1·7
Chrysenes	−24	0·6	0·9
Dinaphthenepyrenes	−26	0·9	0·4
Dibenzofluorenes	−28	—	—
Dibenzanthracenes	−30	—	—
Benzothiophenes	−10S	2·0	2·3
Dibenzothiophenes	−16S	4·5	4·6
	−18S	0·9	0·7
	−20S	0·7	0·4
	−22S	—	—
Dibenzofurans	−16O	1·1	0·9

($C_nH_{2n-16}S$). The doublet, C_3–SH_4, requiring $>8 \times 10^4$ resolving power, did not appear to limit the precision of the method. In most instances the characteristic ions corresponding to groups in these two series (*e.g.*, $C_nH_{2n-16}S$ and C_nH_{2n-26}) occurred in separate and fairly distinct regions of the spectrum. It is also probable that the distribution of sulphur compound types reflects the distribution of the hydrocarbons found in the oil. Consequently, to determine only five of the sulphur group types may be misleading. However these five specific classes of sulphur types were found to encompass the majority of aromatic sulphur compounds, provided the total sulphur content did not exceed 10%. Thus the analysis of aromatic lubricating oil extracts showed not only inaccurate total aromatic contents but also summations of sulphur and aromatic types not accounted for in this matrix.

In the petroleum industry it is usual to classify an oil for virtually any purpose by different functions of the density and mid boiling point. The Bureau of Mines Correlation Index (BMCI), one such complex function, assesses an oil as a feedstock for carbon black production. If the matrix developed here has any validity in analysing highly aromatic streams then the BMCI should correlate, over a limited boiling range, with some function of the analytical results. The data in Fig. 2 show the results of plotting BMCI against a linear function of the weight percentages of two-, three- and four-ring aromatics (MSCI). The correlation is reasonably precise for predictive purposes but would be improved by introduction of some molecular weight function in the mass spectrometric terms. These data indicate that the aromaticity of an oil may be usefully assessed by the present matrix.

This procedure may also be used to observe gross changes in the hydrocarbon composition of an oil such as occur during moderately severe hydrogenation (>1000 scf/bbl*).

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* scf bbl = Standard cubic feet per band.

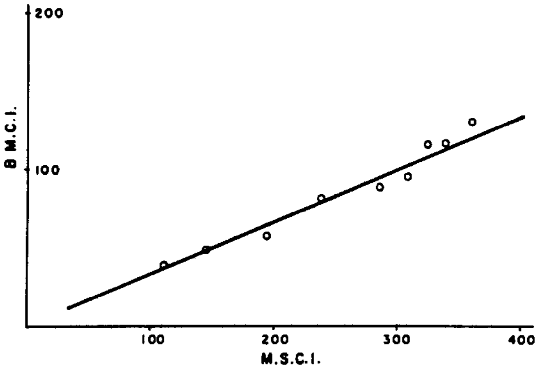

FIG. 2. Correlation of coking properties of different oils, MSCI with BMCI.

Table 5 shows results of compositional changes accompanying hydrogenation of an FCCU light cycle oil. From the composition it can be seen that reduction of two- and three-ring aromatic compounds and sulphur compounds is quite extensive. The hydrogen consumption calculated from the change in composition agreed with the consumption observed at the plant level.

In conclusion, the matrix method presented here represents a useful addition to the analytical skills of the petroleum chemist. Whilst the method is restricted to the major hydrocarbon and sulphur types the principles outlined here allow for much modification and extension of its scope. As with many approaches to the analyses of high-boiling petroleum streams the major limitations lie in our relative ignorance of their detailed composition. Thus the method described here does not increase our knowledge of this composition but rather reflects our *a priori* assumptions concerning the microstructure of petroleum. As research is continued into composition, processing and evolution of the heavy ends of petroleum, the calibration data will be more meaningful and realistic.

Table 5. Analysis of a light cycle oil feed and the hydrogenated product

Group type	Feed, % w/w	Hydrogenated product, % w/w
Paraffins	17·6	23·3
Monocycloparaffins	7·9	9·6
Condensed cycloparaffins	10·8	18·5
Benzenes	9·0	10·8
Indanes	6·4	22·9
Dinaphthene benzenes	2·9	9·8
Naphthalenes	25·1	2·2
Acenaphthenes	6·4	2·1
Fluorenes	6·3	0·7
Phenanthrenes	5·2	0·1
Benzothiophenes	3·1	—
Dibenzothiophenes	1·4	—
H_2 consumption observed		1095 scf/bbl
H_2 consumption calculated		1045 scf/bbl

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Zusammenfassung—Petroleumdämpfe können durch hochauflösende Massenspektrometrie auf gröbere Gruppentypen analysiert werden. Das hier beschriebene Verfahren ist aufgebaut auf einer Eichmatrix, die aus hochaufgelösten Spektren sowohl reiner Verbindungen als auch aus Petroleum abgetrennter Schnitte abgeleitet ist. Die Analysenergebnisse wurden statistisch auf ihre Genauigkeit hin ausgewertet.

Résumé—Les types de groupes principaux dans les vapeurs de pétrole peuvent être analysés par spectrométrie de masse à haute résolution. La méthode décrite ici s'appuie sur une matrice d'étalonnage dérivée des spectres de haute résolution à la fois des composés purs et des fractions séparées du pétrole. Les résultats analytiques ont été appréciés statistiquement pour la précision.

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REDOX INDICATOR PROPERTIES OF SOME SUBSTITUTED CHRYSOIDINS

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Summary—Indicator properties of eleven substituted chrysoidins have been studied. Conditional reduction potentials of the three appreciably reversible indicators in this group were obtained by classical approaches and by use of a potentiopoised standard solution procedure. Chemical and electrochemical observations lead to the conclusion that the other eight indicators act irreversibly in their oxidation. Hence, only transition potential ranges can be reported for these. Substitution in other than the 4-position induces greater irreversibility, while the hydroxy group in the 4-position produces a greater degree of reversibility than does either the methoxy or ethoxy group, 4-Hydroxychrysoidin appears to be the best of the group for bromate titrations.

For some time we have sought further information on the indicator properties of substituted chrysoidins which have been recommended by Schulek and Rosza.[1] A particular goal has been determination of conditional redox potentials of these substances at various levels of hydrogen ion concentration. Previous information about these compounds is unsatisfactory. Pungor and Schulek found a value of 0·76 V relative to the N.H.E. for 4-ethoxychrysoidin, by measuring the potential of a solution assumed to be equimolar in both oxidized and reduced forms.[2] Details of their procedure are incomplete. Another reported value for this substance is 1·0 V.[3]

In preliminary work we carried out classical titration procedures on solutions of reagent grade 4-ethoxychrysoidin in 1·00*M* sulphuric acid, using 0·01–0·1*M* solutions of cerum (IV). End-points were observed potentiometrically with a platinum indicator electrode and calomel reference electrode system. The platinum electrode was treated before use, to remove oxide deposits.

The titration curves were obtained by two methods. In the first only 4-ethoxychrysoidine was present and the formal potential, E', was observed as the potential corresponding to 50% titration. For the second method a small amount of tin (II) was added to the indicator solution and both were then titrated, the tin (II) first, followed by the indicator. Resolution of the two curves was obtained and the E' value was taken as the E value midway between the two inflection points. The indicator solutions employed in both cases were in the range 2×10^{-4}–$4{\cdot}6 \times 10^{-2}M$.

In this work, the electrode system was often found to be poorly poised in spite of oxide-removal treatment and the flushing of air from solutions by nitrogen. The titrations were therefore long and tedious and it was only with great care that several sets of apparently reasonable results could be gathered. These indicated conditional E values in the range

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0·77–0·78 V for sulphuric acid concentrations from 0·5 to 2*M*. Figures 1 and 2 show typical titration curves.

Because of the electrode problems encountered, corroboration of these results was sought by other methods.

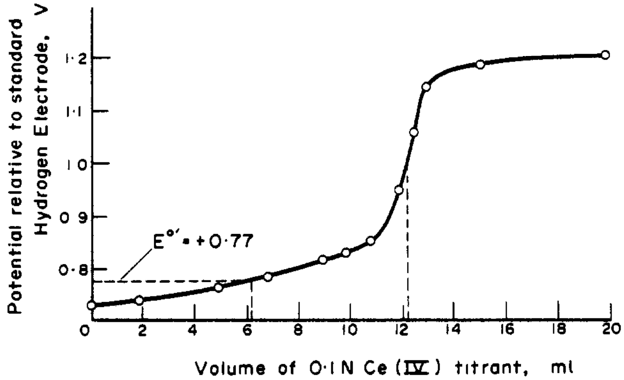

Fig. 1. Potentiometric titration of 4-ethoxychrysoidin in 1*M* sulphuric acid with 0·1*M* cerium (IV) oxidant.

Titration medium: 1*M* H_2SO_4, 75 ml;
Quantity of indicator: 0·0732 g;
Titration condition: titration medium deaerated with nitrogen before and during titration;
Titrant was not deaerated; oxygen scrubbers were not employed in the nitrogen train.

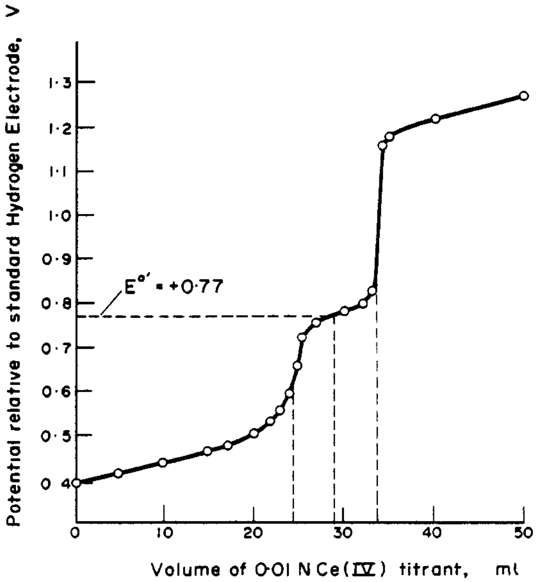

Fig. 2. Simultaneous potentiometric titration of tin (II) and 4-ethoxychrysoidin in 0·5*M* sulphuric acid with 0·01*M* cerium (IV) oxidant.

Titration medium: 0·5*M* H_2SO_4, 125 ml;
Quantity of indicator: 0·005 g;
Quantity of tin (II): 0·0282 g of $SnCl_2 \cdot 2H_2O$;
Deaeration: both the titrant and the titration medium were deaerated with nitrogen gas. An oxygen scrubber was utilized in the gas train.

The potentiopoise method proposed by Smith and Banick appeared to be a possible technique for evaluation of conditional redox constants.[4] In this, equimolar solutions of vanadyl and vanadate compounds are adjusted to various acidities. This causes variation in the ratio of reduced to oxidized species to produce a series of solutions of varying E values which may be measured potentiometrically. An indicator, added to such a series, displays its transition range and an E' value may then be obtained for the middle of the range.

Since the vanadyl–vanadate couple did not have a sufficiently low potential range, other couples were sought. The quinone–hydroquinone couple proved to have too much colour while the U(VI)–U(IV) and arsenite–arsenate couples gave drifting potentials with the platinum indicator electrode. Some reasonably promising results were observed at times with the arsenite–arsenate couple over the range 0·70–0·80 V. Further investigation of the system may be worthwhile, using some other indicator electrode than platinum.

However, a fourth couple proved superior and attention was concentrated on its application. This was the system studied by Kolthoff and Tomicek,[5] namely the ferricyanide–ferrocyanide couple for which the ionization constant of $HFe(CN)_6{}^{3-}$ was reported as much smaller than the first three for $H_4Fe(CN)_6$. The value of K_a for this fourth ionizatiòn step was found to be $5{\cdot}6 \times 10^{-4}$.

Hence, for the Nernst equation of the reaction, $Fe(CN)_6{}^{3-} + e^- \rightleftharpoons Fe(CN)_6{}^{4-}$ we have

$$E = E^\circ - \frac{RT}{nF}\log\frac{K_a[HFe(CN)_6^{3-}]}{\{H^+\}[Fe(CN)_6^{3-}]}$$

Thus this couple should demonstrate a potential which varies with hydrogen ion concentration in such a manner that establishment of potentiopoised solutions in a manner analagous to the vanadyl–vanadate couple should be possible. Experimentation was therefore undertaken to test this. Alternative procedures based on (*a*) microtitration of the indicators with standard oxidant, using another indicator electrode than platinum and (*b*) cyclic voltammetry, were also deemed appropriate for investigation.

It was also desired to investigate the effect of various substituents on the formal potential of the parent compound, chrysoidin. Since only 4-ethoxychrysoidin was found commercially available, synthesis of ten such compounds was undertaken.

EXPERIMENTAL

Apparatus

Spectrophotometer. Beckman DK-2; Beckman Electroscan 30*M*.

Potentiometer. Leeds & Northrup "Student" model with appropriate accessories.

Infrared spectrometer. Perkin–Elmer Infracord 137.

Mass spectrometer. Consolidated Electrodynamics, model 21–103 C.

Aminco motor-driven syringe burette.

Electrodes. Carbon paste indicator electrodes prepared according to Adams;[6] saturated calomel electrodes, either Sargent Model 30080–15 or an electrode prepared according to Adams;[6] platinum indicator electrode; Beckman Planar Disk. No. 39273.

Volumetric pipettes and flasks were all Class A.

Reagents

Substituted chrysoidins. These were prepared, with one exception, by diazotization of appropriate substituted anilines and coupling with *m*-phenylenediamine. The product was purified by extraction into acetone, volatilization of the solvent and recrystallization from either methanol or ethanol.

The substituted anilines used were; *m*-, *o*- and *p*-toluidine, *m*-, *o*- and *p*-anisidine, *p*-nitroaniline, *p*-phenoxyaniline and sulphanilic acid. If these materials were badly discoloured, they were purified by vacuum distillation (two times). The 4-ethoxychrysoidin was a commercial product.

To avoid the undesirable diazotization of aminophenols,[7] 4-hydroxychrysoidin was prepared by a procedure similar to that of Tedder and Theaker.[8] Phenol in acetone–water solution was treated with sodium nitrite, cooled overnight at 0–5° and then reacted successively with sulphamic acid and sodium bicarbonate such that a two-phase system resulted (white solid but red-brown liquid). After addition of *m*-phenylenediamine and stirring for 2 hr the desired red-orange solid product was obtained in crude form, and purified as for the other indicators.

Potassium ferricyanide and ferrocyanide. Recrystallized from water and dried overnight at 120°.

Nitrate-free cerium (IV) solution. Prepared according to Smith and Fly.[9]

Potassium bromate. Recrystallized and dried at 180°.[10]

Characterization of substituted chrysoidins

Purity of recrystallized products. This was ascertained by thin-layer chromatography on Eastman Chromogram TLC plates by conventional ascending elution with the best solvent system found, namely butanol–*n*-hexane (1:3). Properly purified materials exhibited one spot, in contrast to the several spots found with crude materials.

Infrared examination. The IR spectrum of each purified, substituted chrysoidin was obtained over the range 3–15 μm (KBr pellet technique). The principal peaks observed were as expected for the presumed products.

Molecular weight determinations. These were obtained by mass spectrometry for several of the compounds and found to agree with expected values within 0·3 atomic mass units.

Elemental analyses. Analyses of 4-hydroxychrysoidine for C, H and N were in satisfactory agreement with theory.

Procedures

Potentials of potentiopoised ferri- and ferrocyanide solutions. Stock solutions (0·1000*M*) of ferrocyanide and ferricyanide were prepared once a week (although found stable for several weeks). The potentiopoised solutions were then obtained by addition of 1·00-ml of each stock solution to a 100·0 ml volumetric flask. The latter was then filled to the mark with strong acids of appropriate molarity to cover the desired range.

The potential of each solution (0·001*M* total concentration for each of the two species) was then measured with a platinum electrode–saturated calomel reference electrode system and the Electroscan 30*M* to record the values. These readings were confirmed by data obtained with the L & N potentiometer. The results are listed in Table 1, and were found to be reproducible and a plot of *E vs.* acid concentration was essentially linear over the range 1–4*M* sulphuric or hydrochloric acid.

Table 1. Ferrocyanide-ferricyanide potentiopoised potentials as a function of H_2SO_4 concentration

H_2SO_4 concentration, *M*	Potential *vs.* SCE Electroscan, *V*	Potential *vs.* SCE Potentiometer	Potential *vs.* NHE
0·10	0·362	0·362	0·608
0·30	0·412–0·410	0·410	0·656
0·50	0·436	0·437	0·681
0·71	0·458	0·460	0·706
1·01	0·484	0·484	0·730
1·32	0·509	0·508	0·754
1·52	0·524	0·524	0·770
1·72	0·537	0·538	0·784
2·02	0·555	0·555	0·801
2·33	0·576	0·578	0·824
2·54	0·587	0·591	0·837
2·75	0·605	0·606	0·854
3·06	0·624	0·625	0·871
3·29	0·647	0·651	0·897
3·53	0·663	0·663	0·909
3·68	0·681–0·682	0·682	0·928
3·99	0·772–0·775	0·699	0·945
4·52	0·780–0·784	0·787–0·790	1·035
5·03	0·786–0·816	0·828–0·830	1·075

Table 2. Ferrocyanide–ferricyanide formal potentials by the potentiopoise method

Indicator	Observed E *vs.* HNE, V; at first colour change	at final colour change	Formal potential E' as midway value of F, V	Acid concentration, M	$E^{\circ\prime}_{corr}$*, V
Sodium diphenylbenzidine sulphonate	0·840	0·986	0·913	3·67	0·88†
Variamine Blue B	0·608	0·818	0·713	1·07	0·713§
4-Ethoxychrysoidin	0·793	0·890	0·842	2·53	0·82‡
2-Methylchrysoidin	0·784	0·952	0·868	2·86	
3-Methylchrysoidin	0·836	0·974	0·905	3·34	
4-Methylchrysoidin	0·857	0·960	0·909	3·44	
2-Methoxychrysoidin	0·782	0·958	0·870	2·88	
3-Methoxychrysoidin	0·836	0·974	0·905	3·34	
4-Methoxychrysoidin	0·802	0·913	0·858	2·80	0·83‡
4-Phenoxychrysoidin	0·776	0·913	0·845	2·58	
4-Hydroxychrysoidin	0·793	0·915	0·854	2·71	0·83‡

* ($E^{\circ\prime}_{corr}$ was calculated from E' (midway E value) on the basis of correction for hydrogen ion concentration, assuming the reactions involved take the general form $\text{Ind}_{ox} + 2e^- + 2\text{H}^+ \rightarrow \text{Ind}_{red}$.

† Value reported in the literature: 0·87 V.[12] It appears to be generally considered that two electrons and two hydrogen ions are involved for this indicator.

‡ Substituted chrysoidins exhibiting reversibility in oxidation.

§ Value reported in the literature: 0·712 V.[13] The numbers of electrons and hydrogen ions involved for oxidation of the indicator appear unknown However, the correction for 1·07*M* acid is considered negligible.

Transition range of selected indicators by use of potentiopoised solutions. An initial series of potentiopoised solutions was prepared such that the sulphuric acid concentration ranged from 1 to 5*M* at intervals of 1*M*. To 1 ml portions of each, in test-tubes, 5 or 10 drops of indicator solution (0·1%) in ethanol were added. After stirring, the start and end of the colour change were noted. For this range a similar set of potentiopoised solutions was prepared differing in acid concentration in steps of 0·1*M* and used to determine the first and last perceptible colour change and the corresponding potentials for the two solutions in question. The mean of these two values was then taken as E'.

The results obtained in this manner for nine substituted chrysoidins are given in Table 2. If we assume that oxidation of the reduced form of the indicator involves two hydrogen ions and two electrons, a corrected potential E'_{corr} may be calculated for 1*M* hydrogen-ion concentration by subtraction of 0·0295 log $\{\text{H}^+\}$ from E'. Schulek and Somogyi concluded that in the case of 4-ethoxychrysoidin,[11] the two electrons and two hydrogen ions were involved in the oxidation In work described later in this paper, it was observed that only three of the substituted chrysoidins studied were chemically and electrochemically reversible. The correction was therefore applied only to these three and is recorded in Table 2 This was also done in the case of two indicators of other types for which redox potentials are available in the literature, as indicated in the table.

Table 3. Absorbance as a function of equivalents of oxidant added

Equiv Ce mole ind.	Absorbance* 4EC	4OHC	Equiv. KBrO_3/mole ind.	Absorbance* 4EC	4OHC
0·00	1·551	1·229	0·00	1·321	1·333
0 50	1·128	0·880	0·50	1·530	1·602
1·00	0·692	0·611	1·00	1·695	1·815
1·50	0·360	0·348	1·50	1·630	1·804
2·00	0·180	0·168	2·00	1·426	1·529
2·50		0·170	2·50	1·163	1·265
3·00	0·180	0·172	3·00	0·767	0·750
4·00	0·190		3·50	0·232	0·450
			4·00	0·123	0·124
			4·50		0·110

* 4EC = 4-Ethoxychrysoidin; 4OHC = 4-hydroxychrysoidin.

For the seven substituted chrysoidins exhibiting irreversibility, such a correction based on the Nernst equation seems irrelevant. For these indicators the useful information is found in the colour transition interval, the mid-point E' of this range and the pertinent acid concentration for the latter.

Determination of n *in the oxidation of 4-ethoxychrysoidin and 4-hydroxychrysoidin.* This was done spectroscopically since the oxidized and reduced forms of the indicator differ appreciably in colour. Solutions were prepared to be 1·0 mM in the indicator and 1·0M in sulphuric acid. Portions (1 ml) of the solutions were placed in 10-ml volumetric flasks with varying amounts of 0·1M ceric sulphate, diluted to the mark with 1·00M acid and mixed, and the absorbance was observed at the wavelength of maximum absorption (430 nm) for the reduced form. A similar study was carried out with 0·1N potassium bromate, 1 ml of 1M potassium bromide also being added to each solution. The results for both procedures are summarized in Table 3.

The consumption of cerium (IV) as oxidant indicates that $n = 2$, since the absorbance becomes essentially constant after addition of two equivalents of cerium per mole of indicator. The results with bromate are best interpreted in terms of the conclusions of Schulek and Somogyi,[11] that the indicator process first involves a two-step bromination, the bromo products being more intensely coloured than the original indicator and causing a rise in absorbance until 2·5 equivalents of bromate have been added per mole of indicator. Beyond that point, a two-electron oxidation takes place, with Beer's law presumably being obeyed, after addition of 3·0 equivalents of oxidant. Essentially constant absorbance is obtained after addition of 4·0 equivalents per mole of indicator. Presumably there is competition between bromination and oxidation.

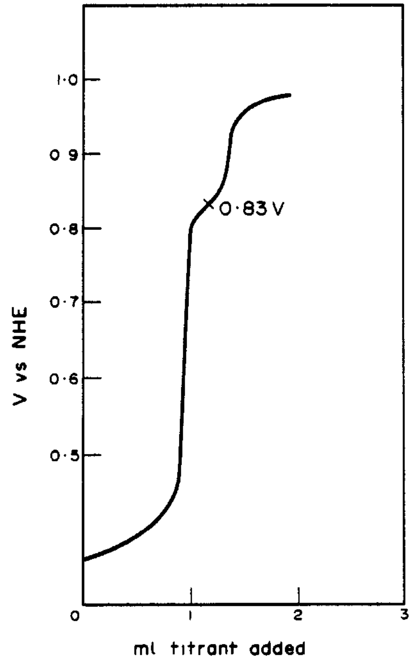

Fig. 3. Titration of 4-hydroxychrysoidin in 1M H_2SO_4. Titrant, 0·1N $KBrO_3$.

Further verification of a two-electron exchange for both indicators was obtained from peak heights observed in cyclic voltammetry. By use of the equations of Adams with the assumption that the diffusion constant of azobenzene may be substituted for that of the indicators,[14] the value of n was found to be 2·1 for 4-hydroxychrysoidin and 2·3 for both 4-ethoxychrysoidin and 4-methoxychrysoidin.

Determination of formal potentials by microtitration. Either 0·1N potassium bromate or cerium (IV) was used as titrant. With the former, 1 g of potassium bromide was also added, the medium being sulphuric acid of known molarity. With cerium (IV) as titrant, 2 drops of osmium tetroxide solution were added as a catalyst. To the solutions containing the indicator was also added 0·1 meq of arsenic (III). The reagent reacted with the latter before oxidizing the ~0·025 mmole of indicator. The reagent was added with a motor-driven syringe, the potential being recorded on the Electroscan 30; the indicator electrode was carbon-paste, the reference electrode a saturated calomel electrode.

The titration curves of arsenic (III) and indicator was resolved and $E^{0'}$ for the latter was observed as the potential halfway between the two inflection points. Preliminary runs were made with a 1·4 V range on the Electroscan.

A second titration was then recorded with a switch to the expanded 0·56 V scale as the arsenic (III) end-point was approached. This permitted greater sensitivity. With either scale the zero of the instrument *vs.* SCE was set so that the chart scale would read directly in V *vs.* NHE. Typical titration curves are found in Figs. 3 and 4.

After the end-point, the syringe was removed and excess of solid ferrous ammonium sulphate was stirred into the solution to see whether the original colour could be obtained. Results in these titrations did not differ whether air was present in the solutions or was removed with nitrogen.

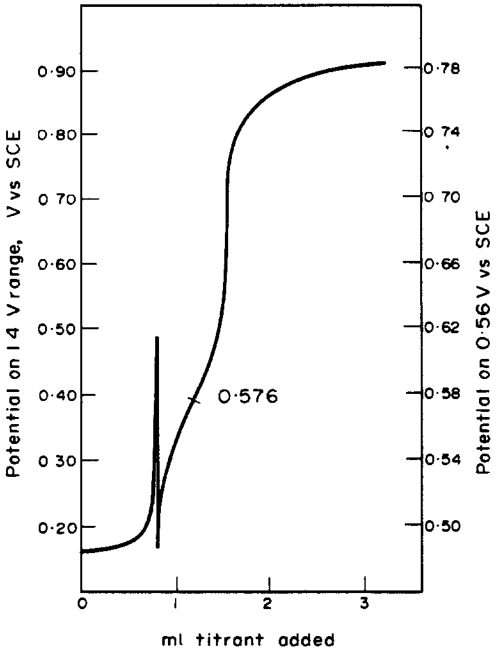

Fig. 4. Titration of 4-hydroxychrysoidin in 1*M* H_2SO_4. Titrant, 0·1*N* $KBrO_3$. Change in scale expansion during titration.

The results obtained with eight of the substituted chrysoidins by bromate titration in 1*M* sulphuric acid are given in Table 4. The effects of variation in sulphuric acid concentration upon the bromate and cerium (IV) titration of 4-ethoxychrysoidin and 4-hydroxychrysoidin are found in Table 5.

The data in Table 4 tends to disagree appreciably with those which might be predicted from the results given in Table 2. Thus the bromate titration results indicate that the ease of oxidation of the irreversible indicators should be in the order 4-methylchrysoidin > 2-methylchrysoidin > 3-methylchrysoidin > 3-methoxychrysoidin > 2-methoxychrysoidin. The potentiopoise data, however, would place the order; 2-methylchrysoidin > 2-methoxychrysoidin > 3-methylchrysoidin = 3-methoxychrysoidin > 4-methylchrysoidin.

The reasons for the variations observed may lie in the difference in mechanism of oxidation which occurs when bromate is involved or to variable electrode effects for the various indicators at the carbon paste electrode.

For the three indicators which exhibited chemical reversibility, the $E^{\circ\prime}$ results from bromate titration and the potentiopoise method agree within 0·008 V or better. This also holds for the cerium (IV) titration results for 4-ethoxychrysoidin.

Agreement between the two procedures is also quite good at higher acid concentrations for two of the reversible indicators, the results for which are given in Table 5. Thus, 4-hydroxychrysoidin is found to have an E' value of 0·844 V in 3*M* sulphuric acid as compared to the potentiopoise value of 0·854 V for 2·72*M* acid. In the case of 4-ethoxychrysoidin, a value of 0·842 V is found by both methods at 2*M* acid concentration.

In three of the four series of results given in Table 5, a variation in E' occurs as the acid concentration changes but the effect is some 25% less than assumed for the correction to $E^{\circ\prime}$ from Table 2. This might be attributed to difference in activity values for the two cases but other factors may be present.

The lack of variation in E' at higher acid concentrations for cerium (IV) oxidation of 4-ethoxychrysoidin is puzzling. In the earlier titration attempts with this reagent at a platinum electrode, a similar constancy of the potential value at higher acidities was also noted The mechanism of oxidation may here involve a side-reaction with products which lead to a potential that nullifies the effect of increasing acid concentration.

Table 4. Formal potentials as determined by titration with bromate (E° for $1M$ H_2SO_4)

Indicator	Potential *V vs.* NHE	Colour reverts with ferrous ion
2-Methylchrysoidin	0·855	No
3-Methylchrysoidin	0·856	No
4-Methylchrysoidin	0·826	No
2-Methoxychrysoidin	0·886	No
3-Methoxychrysoidin	0·878	No
4-Methoxychrysoidin	0·825	Yes
4-Hydroxychrysoidin	0·822	Yes
p-Ethoxychrysoidin	0·826	Yes

Table 5. Potentials at acidity other than $1M$ H_2SO_4 as determined by microtitration

Indicator	Concentration of H_2SO_4, *M*	E' or midway potentials, *V vs.* NHE Cerium	Bromate
4-Hydroxychrysoidin	1·0	0·782	0·822
	2·0	0·786	0·832
	3·0	0·794	0·844
	4·0	0·809	0·849
	6·0	0·830	no break
4-Ethoxychrysoidin	1·0	0·814	0·826
	2·0	0·814	0·842
	3·0	0·814	
	4·0	0·814	

Table 6. Titration of arsenate with bromate, using various substituted chrysoidins as indicators

Indicator, 0·1% in MeOH	Drops of indicator	Volume of As, *ml*	Consumed ave. vol. of BrO_3^-, *ml*	No. of trials	Ave. dev., *ml*	Normality of both solutions
4-Ethoxychrysoidin	4	25·00	25·04	2	0·00	0·1000
4-Hydroxychrysoidin	4	25·00	25·03	3	0·00	0·1000
4-Ethoxychrysoidin	2	39·95	39·97	1		0·1000
4-Hydroxychrysoidin	2	39·95	39·96	2	0·015	0·1000
4-Ethoxychrysoidin	1	25·00	25·04	1		0·01000
	1	25·02	25·02	1		0·01000
4-Hydroxychrysoidin	1	25·00	25·02	3	0·02	0·01000
2-Methoxychrysoidin	4	25·00	25·00	3	0·01	0·1000
3-Methoxychrysoidin	4	25·00	24·97	3	0·03	0·1000
4-Methoxychrysoidin	4	24·95	24·89	3	0·01	0·1000
2-Methylchrysoidin	12	24·95	25·17	1		0·1000
3-Methylchrysoidin	25	24·95	no end-point observed			
4-Methylchrysoidin	4	24·95	25·00	2	0·00	0·1000
4-Phenoxychrysoidin	20	24·95	25·51	1		0·1000
4-Nitrochrysoidin	3	24·95	25·08	1		0·1000
4-Sulphochrysoidin	24	24·95	no end-point observed			

In view of the difference in mechanism for the cerium (IV) and bromate oxidation of the two indicators of Table 5, the E' values obtained may be expected to vary for the two processes. The large differences of 0·04–0·05 V for 4-hydroxychrysoidin are surprising, however, in view of the agreement of the bromate titration values with those of the potentiopoise method.

The important attribute of a redox indicator of course, is its behaviour under actual titration conditions. To investigate this, solutions 0·1000N in arsenic (III) and potassium bromate were prepared by the usual procedures. Aliquots of arsenic (III) were then titrated, different indicators being added in various amounts.

The results are summarized in Table 6. Some indicators found to be chemically irreversible required inordinate amounts of titrant to produce an end-point. In other cases no end-point could be obtained whatever.

The degree of reversibility of the various indicators was investigated by cyclic voltammetry. It was found that only 4-hydroxychrysoidin was highly reversible, 4-ethoxychrysoidin and 4-methoxychrysoidin only quasi-reversible, and the rest of the indicators highly irreversible. This work will be presented in a separate publication.

In the practical work summarized by the data in Table 6, the difference in reversibility between 4-hydroxychrysoidin and 4-ethoxychrysoidin was estimated chemically. After titration to the end-point for each indicator was complete, solid ferrous sulphate was added in small amounts at a time with stirring until colour reversion was noted. Titration was then carried out to a second end-point, ferrous sulphate again added and the process continued as long as successive end-points could be observed.

With 4-hydroxychrysoidin, repeated end-points could be observed for a total of about five cycles, whereas no more than three were possible with 4-ethoxychrysoidin. With the latter the second end-point was much weaker than that for 4-hydroxychrysoidin.

Similar results to those for 4-ethoxychrysoidin were obtained with 4-methoxychrysoidin by this colour reversion technique. The other substituted chrysoidins studied acted in a completely irreversible manner to give a single end-point, or no end-point at all.

CONCLUSIONS

Substitution of chrysoidin in other than the 4-position appears to promote a high degree of irreversibility for oxidation of the product. Substitution of groups in the 4-position tends to increase the degree of reversibility, in some cases to a high degree. The nature of the substituting group is critical. Reversibility decreases as the group varies from hydroxy to ethoxy to methoxy and becomes complete irreversibility in the case of the 4-methyl, 4-phenoxy, 4-nitro and 4-sulpho compounds.

It appears that 2-methoxychrysoidin and 3-methoxychrysoidin may be useful as irreversible indicators for bromate titrations in a colour transition range centred on the values 0·85–0·9 V relative to the NHE.

The other six, irreversible, substituted chrysoidins studied appear to have no utility as irreversible indicators for bromate titrations.

In the case of the three indicators with variable degrees of reversibility, the $E^{\circ\prime}$ value obtained as the average from two methods of measurement (potentiopoising and bromate titration) are very similar, being 4-methoxychrysoidin 0·828 V, 4-ethoxychrysoidin 0·824 V, 4-hydroxychrysoidin 0·828 V. These may represent the best values available for these three indicators but the chemistry of oxidation appears complex and the effect of the oxidant system may be appreciable, as for cerium (IV) with 4-hydroxychrysoidin.

The value of 0·82 V for 4-ethoxychrysoidin is appreciably different from the value reported by Pungor and Schulek and from that obtained in our earlier titration procedures. In the latter case we attribute the differences to greater problems of reversibility at the platinum electrode used then than at the carbon-paste electrode.

In view of its greater reversibility in the redox process, the indicator 4-hydroxychrysoidin seems to be superior for use in titrations involving bromate and related oxidants and should be seriously considered for such work.

Finally, the use of the potentiopoise technique, as developed by Smith and Banick and further extended in its range by the work reported here, should be useful in preliminary screening of proposed redox indicators, particularly where various degrees of irreversibility may be involved. Further study of its applicability, especially in terms of extension of the range of observable potentials, may be worthy of consideration.

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Zusammenfassung—Die Indikatoreigenschaften elf substituierter Chrysoidine wurden untersucht. Die Reduktionspotentiale der drei ziemlich reversiblen Indikatoren dieser Gruppe wurden auf klassischem Wege und mit Hilfe einer Methode mit Standardlösungen und ausbalanciertem Potential erhalten. Die chemischen und elektrochemischen Beobachtungen führen zu dem Schluß, daß die anderen acht Indikatoren sich bei der Oxidation irreversibel verhalten. Daher können für diese nur Übergangspotentialvereiche angegeben werden. Substitution an anderen Stellen als der 4-Stellung führen zu größerer Irreversibilität, während die Hydroxygruppe in 4-Stellung zu einem höheren Grad von Reversibilität führt als die Methody- oder &thoxygruppe. Für Bromat-Titrationen scheint 4-Hydroxychrysoidin der beste Indikator in der Gruppe zu sein.

Résumé—On a étudié les propriétés d'indicateurs de onze chrysoïdines substituées. On a obtenu les potentiels de réduction conditionnels des trois indicateurs assez fortement réversibles dans ce groupe par les voies classiques et par l'emploi d'une technique de solution étalon potentioéquilibrée. Les observations chimiques et électrochimiques mènent à la conclusion que les huit autres indicateurs agissent irréversiblement dans leur oxydation. Par suite, seulement les domaines de potentiel de transition peuvent être rapportés pour ceux-ci. La substitution en une position autre que 4 entraîne une plus grande irréversibilité, tandis que le groupe hydroxy en position 4 produit un plus grand degré de réversibilité que ne le fait le groupe méthoxy ou éthoxy. La 4-hydroxychrysoïdine apparaît être la meilleure du groupe pour les titrages de bromate.

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SHORT COMMUNICATIONS

THE OXIDATION OF ORGANIC COMPOUNDS BY TERVALENT MANGANESE COMPOUNDS—II*

THE DETERMINATION OF MANDELIC ACID WITH A TERVALENT MANGANESE STANDARD SOLUTION IN PERCHLORIC ACID MEDIUM

(*Received* 13 *February* 1974. *Accepted* 6 *March* 1974)

We pointed out earlier the possibility of using tervalent manganese compounds as oxidimetric titrants for organic compounds, in particular mandelic acid.[1] From a kinetic study of the reaction of mandelic acid with the pyrophosphate complex of tervalent manganese[2] it appears that the reaction rate depends on the stability constant of the manganese complex. For this reason, we have attempted to use a solution of hexa-aquomanganese(III) ions in perchloric acid for the determination of mandelic acid. This solution, so far prepared either electrolytically[3] or by oxidation of manganese(II) with permanganate[4] is, from our experience,[5,6] sufficiently stable to be used as a titrant under suitable conditions. The present paper demonstrates that it can be used in perchloric acid medium for determination of small amounts of mandelic acid according to the equation

$$C_6H_5CHOHCOOH + 2Mn^{3+} \rightarrow C_6H_5CHO + CO_2 + 2Mn^{2+} + 2H^+$$

EXPERIMENTAL

Reagents

Mandelic acid. 0·0005, 0·001, 0·00125 *and* 0·0015*M solutions* Prepared by accurate dilution of solutions 10 times as concentrated, made by dissolving accurately weighed amounts of the pure substance and diluting with water to 1 l

Hexa-aquomanganese (*III*) *solution*, 0·005*M in perchloric acid.* The stability of this solution increases with increasing concentration of perchloric acid and of manganese(II);[5] the optimum medium is 6*M* acid and 0·4*M* manganese(II) perchlorate In this medium, a 0·005*M* reagent solution can easily be prepared chemically by slowly adding, with constant stirring, 10 ml of 0·02*M* potassium permanganate to the solution obtained by mixing 150 ml of 8*M* perchloric acid and 40 ml of 2*M* manganese(II) perchlorate. If manganese dioxide separates, it is filtered off on a porosity -4 frit, since its presence affects the reagent stability unfavourably.

Procedure

First the dependence of the reagent consumption on time was determined in 3*M* perchloric acid medium at 20° From preliminary experiments it was found that the reaction proceeds sufficiently rapidly in 3–6*M* perchloric acid medium Since the reagent is most stable in the 6*M* acid, this medium was used for the reagent preparation, giving 3*M* perchloric acid on mixing 10 ml of the reagent solution and 10 ml of an aqueous solution of the test substance To 10·00 ml of 0·005*M* solution of hexa-aquomanganese(III) in 6*M* perchloric acid at 20°, were added 10·00 ml of 0·00125*M* mandelic acid also at 20°, and after time *t* the unreacted manganese(III) was determined potentiometrically, by titration with 0·005*M* ferrous sulphate. A blank determination was run in parallel. The potential (platinum electrode) stabilizes almost instantaneously under the given conditions and the inflection potential lies around 800 mV *vs.* S.C.E., the potential change in the vicinity of the equivalence point being roughly 200 mV/0·02 ml of 0·005*M* ferrous sulphate The results obtained, which were the same for three identical measurements, are given in Table 1, and show that the mandelic acid is oxidized to benzaldehyde and carbon dioxide, that the reaction is completed within 20 min and that further oxidation does not occur on standing with excess of reagent The production of benzaldehyde was verified by the formation of the 2,4-dinitrophenylhydrazone and proof of its identity (m.p and i.r spectrum) The procedure given is satisfactory for 0·0005–0·0015*M* mandelic acid if the mixture is left to react for 30 min at room temperature; 1 ml of 0·005*M* ferrous sulphate

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* Part I: *Talanta* 1974, **21**, 157

Table 1. The rate of the oxidation of mandelic acid with hexa-aquomanganese(III) in $3M$ $HClO_4$ medium at 20

Time, *min*	5	10	20	30	60	120	240
Reagent consumption, *mole/mole*	1·98	1·99	2·00	2·00	2·00	2·00	2·00

Table 2. The determination of mandelic acid with a standard solution of hexa-aquomanganese(III) ions

Mandelic acid taken, *mg*	0·761	1·522	2·282
Mandelic acid found, *mg*	0·764	1·523	2·285
Standard deviation, *mg*	$0{\cdot}008_0$	$0{\cdot}008_5$	$0{\cdot}007_0$

corresponds to 0·3803 mg of mandelic acid. Typical results are given in Table 2. The standard deviations were calculated from 10 determinations.

DISCUSSION

The advantages of determining mandelic acid by oxidation with manganese(III) were discussed in the previous paper,[1] but the reactions proposed were slow [12 hr with the pyrophosphate complex. 2 hr with manganese(III) sulphate]. In perchloric acid medium the reaction is faster (30 min). However, even this reaction cannot be used for the determination of mandelic acid in concentrations below $5 \times 10^{-4}M$ because when a $0{\cdot}001M$ solution of hexa-aquomanganese(III) is used, it is impossible to determine the unreacted manganese(III) by potentiometric titration with $0{\cdot}001M$ ferrous sulphate, since the potential change at the equivalence point is too small to be measured.

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Summary—An indirect titrimetric determination of mandelic acid, based on its oxidation by a standard solution of hexa-aquomanganese(III) in perchloric acid medium, is described.

Zusammenfassung—Ein Verfahren zur indirekten massanalytischen Bestimmung von Mandelsäure wurde beschrieben. Es beruht auf deren Oxidation mittels Masslösung von Hexaquomanganat (III) ionen $[Mn(H_2O_6)^{3+}]$ in Perchlorsäuremedium.

Résumé—Le dosage volumétrique indirect de l'acide mandelique, basé sur l'oxydation par la solution des hexaaquo-manganése(III) ions, dans le milieu de l'acide perchlorique est présenté.

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STRUCTURAL ANALYSIS OF SOME CHLORINATED PESTICIDES BY NUCLEAR QUADRUPOLE RESONANCE SPECTROMETRY

(*Received* 8 *January* 1974. *Accepted* 26 *February* 1974)

Nuclear Quadrupole Resonance (NQR), developed as a branch of radiofrequency spectroscopy, has already contributed significantly in providing information on the molecular and crystalline structure of various compounds. The NQR technique appears to have great potential for development as a physical method of interest to analytical chemistry and especially for elucidating the structure of organic and inorganic compounds.[1] The ^{35}Cl spectrum, like the ^{1}H NMR spectrum of a molecule or its infrared spectrum, is a spectroscopic "fingerprint", which can be used to identify either a particular molecule or a particular type of chlorine atom. By analogy with the magnetic resonance, the term "chemical shift" of NQR frequencies is used, which is an essential parameter in structural analysis. Fitzky,[2] reviewing the analytical aspects of NQR for chlorinated compounds, points out two important pieces of information which the NQR spectra supply in relation to the structural analysis: (*i*) the number of lines in the whole spectrum, which must be equal to the number of chlorine atoms per molecule or in cases where there are several molecules per unit cell of the crystal, the appropriate multiple, and (*ii*) the multiplet grouping, indicating an accumulation of atoms of similar chemical linkage in certain functional groupings of the molecule.

However, for precise structure assignments the use of shift tables[3] and correlation charts[2,4,5] is recommended. Figure 1 illustrates a correlation chart of NQR frequencies for ^{35}Cl resonances in the range 28–43 MHz at 77 K.

Spectra–structure correlation charts have been used for elucidating the structure of several organochlorine compounds commonly used as pesticides, and of a number of cyclodiene chlorinated insecticides.[4,5] However, in the case of 1,2,3,4,10,10-hexahydro-1,4-*endo*-*exo*-5,8-dimethanonaphthalene (Aldrin) one resonance frequency only was observed and in the case of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene (Endrin), five frequencies were observed.[5] The absence of other resonances in the spectrum of Aldrin was considered to be due to the lack of instrumental sensitivity; the spectrum of Endrin was considered complete, with both vinylic chlorine atoms resonating at the same frequency (37·7 MHz).

In the present work we report the complete NQR spectra of Aldrin and Endrin; further we analyse the two isomers of 6,7,8,9,10,10-hexachloro-1,5,5*a*,6,9,9*a*-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide (Endosulfan α and Endosulfan β).

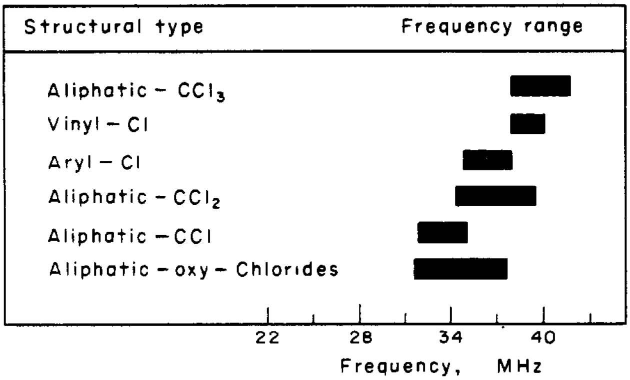
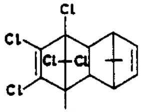
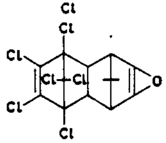
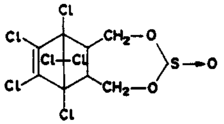


Fig. 1. Spectra–structure correlations of ^{35}Cl resonances at 77 K.

Table 1. ^{35}Cl pure quadrupole resonance (*MHz*) of some chlorinated pesticides at various temperatures

Compound	Structure	Resonance frequency (this work)	Literature value[5]
Aldrin		35·80, 37·90, 38·10 (300)* 36·86, 36·92, 37·22 37·14, 38·38, 38·48 (77)	37·9(295)
Endrin		35·93, 36·14, 36·18 36·43, 37·19, 37·86 (300)	35·9, 36·1, 36·3 37·0, 37·7 (295)
Endosulfan α		36·92, 37·07, 37·30 37·48, 38·37, 38·92 (77)	
Endosulfan β		36·72, 36·91, 37·05 37·15, 37·19, 37·24 37·26, 37·35, 37·69 38·08, 38·79, 39·16 (77)	

* The temperature (*K*) of the measurement is given in parenthesis.

EXPERIMENTAL

The samples of Aldrin and Endrin used in the present work were analytical grade (99% purity) from Shell Chemical Co., New York, and were used without further purification. The samples of the two isomers of Endosulfan were also analytical grade (>99% purity) from Hoechst A. G., Frankfurt, Germany.

The spectra were obtained by using a Decca-Radar nuclear quadrupole resonance spectrometer. Samples (0·5–1 g) were placed in a glass tube (1 cm dia) and positioned in the spectrometer coil. When closely spaced lines were suspected, side-band suppression by slow variation on the quench frequency was used, for better distinction between line and side-band. The spectra were obtained at two temperatures, 77 K (liquid nitrogen bath), and 300 K (water-bath). Frequency measurements were accurate to ± 0·01 MHz and temperature measurements to ±1°.

RESULTS AND DISCUSSION

The NQR spectrum of Aldrin exhibits three resonance signals at room temperature and the expected six signals at lower temperatures. The frequencies are given in Table 1. The assignment of the signals to specific chlorine atoms is discussed elsewhere.[6]

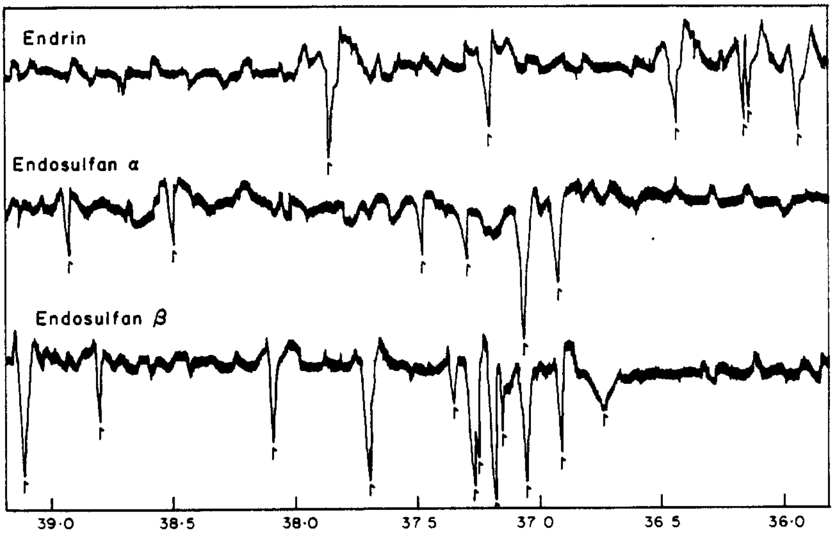


Fig. 2. NQR spectra of Endrin at 300 K and of Endosulfan α and β at 77 K.

Table 2. Assignment of signals (MHz at 77 K) to specific chlorine atoms in Endosulfan α and β

Position of chlorine atoms	Endosulfan α	Endosulfan β
Vinylic chlorine atoms	38·92	39·16
	38·37	38·79
		38·08
		37·69
Chlorine atoms of the dichloromethylene bridge	37·48	(37·35)*
	37·30	37·26
		(37·24)
		37·19
Chlorines on the bridgehead carbon atom	37·07	(37·15)
	36·92	37·05
		36·91
		(36·72)

* The existence of the lines at the frequencies enclosed in brackets is uncertain.

The NQR spectrum of Endrin at 300 K is given in Fig. 2. It is seen that this compound also exhibits the expected six signals. The assignment by Roll and Biros[5] of both the vinylic chlorine atom resonances at 37·7 MHz and the bridge dichloromethylene chlorine atom resonances at 36·3 and 37·0 MHz is therefore probably incorrect. From the spectra–structure corelation chart given in Fig. 1, the resonance signals at 37·86 and 37·19 MHz may be assigned to the two vinylic chlorine atoms, since they give higher frequencies than aliphatic chlorine atoms do.

Increasing accumulation of chlorine nuclei at one carbon atom results in a shift towards higher frequencies, thus the resonances of dichlorosubstituted carbon atoms occur at higher frequencies than those of monochlorosubstituted carbon atoms.[2–5] Therefore the signals of the chlorine atoms on the dichloromethylene bridge carbon are probably those centred at 36·43 and 36·18 MHz. Finally, the remaining resonance frequencies 36·14 and 35·93 MHz are attributed to the bridgehead chlorine atoms.

The NQR spectrum of Endosulfan α at 77 K exhibits the expected six resonances corresponding to the six chlorine atoms found in the molecule. The number of resonance lines found in the case of Endosulfan β at 77 K suggests that there are two molecules per unit cell. The spectra of Endosulfan α and β are also shown in Fig. 2. The data obtained in the present work are summarized in Table 1 and are compared with literature values. The assignments can be made in a fashion similar to that used for Endrin and are summarized in Table 2.

However, these assignments are only tentative, since in some cases, as with the spectra–structure correlation for vinylic ^{35}Cl atoms, insufficient data have been collected for meaningful correlations. Thus, in hexachlorocyclopentadiene[7] the low-frequency lines correspond to vinylic chlorine atoms and the high-frequency group to dichloromethylene chlorine atoms. The present results complete and extend the cyclodiene chlorinated pesticide results previously published.[5]

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Summary—Nuclear Quadrupole Resonance (NQR) spectrometry provides a useful technique for the determination of structure and has been employed to demonstrate the difference in the chemical environment of the ^{35}Cl atoms in several chlorinated organic compounds commonly used as pesticides. A tentative assignment of signals to specific chlorine atoms has been made, by utilizing spectra–structure correlation charts, in 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (Endrin) and in two isomers of 6,7,8,9,10,10-hexachloro-1,5,5*a*,6,9,9*a*-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide (Endosulfan α and β).

Zusammenfassung—Die Kernquadrupolresonanz-(NQR)Spektrometrie ist bei der Strukturermittlung nützlich; sie wurde dazu verwendet, den Unterschied in der chemischen Umgebung von ^{35}Cl-Atomen in mehreren chlorierten organischen Verbindungen zu zeigen, die im allgemeinen als Pestizide verwendet werden. Die Signale wurden bei 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*, *endo*-5,8-dimethanonaphthalin (Endrin) und in zwei Isomeren von 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxid (Endosulfan α und β) mit Hilfe von Specktren-Struktur-Korrelationstabellen versuchsweise den einzelnen Chloratomen zugeordnet.

Résumé—La spectrométrie de résonance quadrupôle nucléaire (RQN) fournit une technique utile pour la détermination de structures et a été employée pour démontrer la différence dans l'environnement chimique d'atoms ^{35}Cl dans plusieurs composés organiques chlorés utilisés communément comme pesticides. On a procédé à une attribution possible des signaux à des atomes de chlore spécifiques, en utilisant des diagrammes de corrélation spectres-structure, dans le 1,2,3,4,10,10-hexachloro 6,7-époxy 1,4,4a,5,6,7,8,8a-octahydro 1,4-*endo*, *endo* 5,8-diméthanonaphtalène (Endrine) et dans deux isomères du 6,7,8,9,10,10-hexachloro 1,5,5a,6,9,91-hexahydro 6,9-méthano 2,4,3-benzodioxathiépine 3-oxyde (Endosulfan α et β).

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FORCED-FLOW CHROMATOGRAPHY OF THE LANTHANIDES WITH CONTINUOUS IN-STREAM DETECTION

(*Received* 16 *November* 1973. *Accepted* 4 *March* 1974)

Recently the application of forced-flow chromatography to the separation and in-stream quantitative analysis of metal ions has been described.[1] Analytical methods based on rapid separation by ion-exchange chromatography and in-stream effluent analysis have been presented for lead,[2] iron,[3] and chromium [4] by anion-exchange and zinc, nickel, and lead by cation-exchange. Many other separations have been shown to be possible.

The work of Spedding *et al.*,[5–7] in achieving the first ion-exchange separation of the rare earths in 1947 perhaps most clearly demonstrated the potentialities of ion-exchange chromatography. Recently the application of pressurized ion-exchange chromatography to the rapid separation of the lanthanides has been described.[8] Although the separation itself took only 2–4 hr, the elution curve was constructed by fraction-collecting and radiochemical techniques. The total separation and analysis required about a week.

This paper describes the application of forced-flow chromatography with simultaneous in-stream colorimetric effluent analysis, to the cation-exchange separation and determination of 13 lanthanides.

EXPERIMENTAL

Apparatus

The liquid-chromatograph used in this work has been described in another paper.[1] The same instrumentation was used. The analytical column was a 1 m × 2·8 mm thick-walled glass tube fitted with type MB-3 "Cheminert" column fittings from Chromatronix Inc. Dowex 50 W X8 (250–325 mesh) was thoroughly washed in acetone,

Summary—Nuclear Quadrupole Resonance (NQR) spectrometry provides a useful technique for the determination of structure and has been employed to demonstrate the difference in the chemical environment of the ^{35}Cl atoms in several chlorinated organic compounds commonly used as pesticides. A tentative assignment of signals to specific chlorine atoms has been made, by utilizing spectra–structure correlation charts, in 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (Endrin) and in two isomers of 6,7,8,9,10,10-hexachloro-1,5,5*a*,6,9,9*a*-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide (Endosulfan α and β).

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Reagents

2-Hydroxyisobutyric acid solution, 0·4*M*, was prepared by stirring 41·6 g of the solid (Aldrich Chemical Co., "98+%") with about 800 ml of water in a 1-l. beaker until the soluble solids appeared to have dissolved and the solution was then filtered into a 1-l. volumetric flask and diluted to volume. All standard metal ion solutions (0·01*M*) were prepared by dissolving sufficient of the rare earth oxide in 10 ml of conc. nitric acid and diluting to 200 ml. Sample solutions were prepared by further dilution.

4-(2-Pyridylazo)resorcinol (PAR), 0·0125% w/v in 5*M* ammonia was used as reagent for the in-stream colorimetric analysis.

Procedure

The flow rate of the CMP-2 metering pump was set at 0·4 ml/min and the column was conditioned for 30 min with the 0·4*M* 2-hydroxyisobutyric acid (HIBA) at pH 2·9. For the gradient elution 2 beakers, *A* and *B*, were placed on a level surface and equal amounts (75 ml) of HIBA were added to each. A connecting glass tube of 4 mm bore was also filled. The pH of the solution in beaker *A* was adjusted to 4·5 The pump inlet was placed in beaker *B*, and the eluting solution, stirred by a magnetic stirrer, was then pumped through the column. As the liquid level in beaker *B* was lowered, the solution of higher pH passed into beaker *B*, raising the pH of the eluent. A mixture of about 5 μg of each of 13 rare earths was injected onto the column immediately after beginning the gradient elution

After sample-injection the entire separation could be left unattended until all ions had been eluted. The order of elution was the same as that usually observed, *i.e.*, in inverse order of atomic number.

RESULTS

Figure 1 shows the separation of 13 lanthanides on the Dowex 50W X8 column. The separation, which was achieved at a flow rate of 0·4 ml/min, required about 4 hr. It is evident that the resolution of the first 2 and last 3 ions is not complete. However, in most cases involving real samples, not all the lanthanides would be present and the gradient can be adjusted to give complete resolution for either light or heavy lanthanides. This separation was performed on a sample solution containing about 5 × 10^{-4} mole of each of the rare-earth oxides per litre.

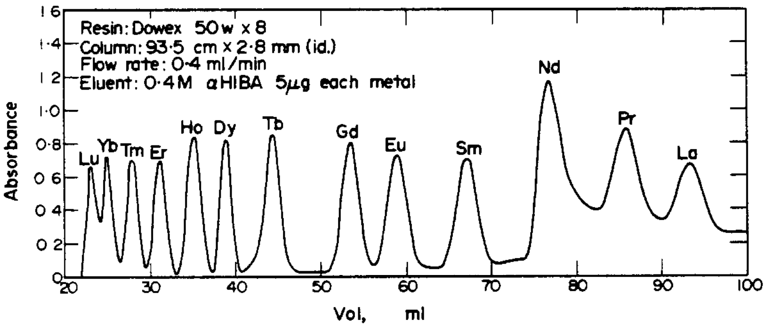

Fig. 1. Chromatographic separation of rare earths.

The primary innovation in this work is the application of in-stream colour reagent addition to achieve continuous detection of sample components, thus eliminating the need for fraction-collecting, radioisotope-handling or continuous attention The colorimetric detection could easily be used to give quantitative results if desired.

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Summary—A method for ion-exchange separation of rare earths is described in which the elements are detected automatically after addition of a colour-forming reagent. A separation of 13 rare-earth elements was accomplished in 4 hr.

Zusammenfassung—Ein Verfahren zur Ionenaustauschtrennung seltener Erden wird beschrieben, bei dem die Elemente nach Zugabe eines farbbildenden Reagens automatisch nachgewiesen werden. Es gelang, die Trennung von 13 seltenen Erden in 4 h durchzuführen.

Résumé—On décrit une méthode pour la séparation des terres rares par échange d'ions, dans laquelle les éléments sont décelés automatiquement après addition d'un réactif générateur de coloration. On a réalisé une séparation de 13 éléments des terres rares en 4 hr.

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SEPARATION OF GOLD FROM LEAD-RICH MINERALS FOR NEUTRON-ACTIVATION ANALYSIS

(*Received* 4 *October* 1973. *Accepted* 29 *November* 1973)

Because of the rarity of gold,[1] very sensitive analytical methods are required in any gold exploration programme. Neutron-activation analysis, destructive or non-destructive, is useful for this purpose.[2,3] In the destructive method a suitable procedure is needed for the separation of traces of gold from the bulk of other materials in the ore.

Gold has been separated from mineral sources by many workers.[4-7] The separation, however, becomes particularly difficult when the mineral contains an appreciable amount of lead, because when the ore solution in *aqua regia* is evaporated to remove nitric acid, lead chloride begins to precipitate and co-precipitates some gold. It therefore poses the problem of whether gold can be separated directly from the *aqua regia* medium.

The aims of the present investigation were (*i*) to find a suitable non-isotopic carrier for gold and (*ii*) to find an easy method of separation of gold from solutions of minerals in *aqua regia*. Gold-198 was used as radioactive tracer.

EXPERIMENTAL

Reagents

Gold-198 in hydrochloric acid was procured from BARC, Trombay, India. Inactive gold solution was prepared by dissolving a known amount of spectroscopically pure gold in *aqua regia*, evaporating the solution almost to dryness to remove nitric acid and diluting with dilute hydrochloric acid. All other reagents were of analytical grade.

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Procedure

Separation of gold by solvent extraction. Thirty ml of an acid solution containing known amounts of radioactive and inactive gold were shaken vigorously (~ 150 shakes/min) for 4–5 min with an equal volume of methyl isobutyl ketone in a 250 ml separating funnel. The two phases were allowed to separate, and then the activity in each was determined. The organic phase was first evaporated and the ^{198}Au was taken up in very dilute hydrochloric acid for counting.

Co-precipitation of gold by lead sulphide. Known amounts of active and inactive gold solution were taken, to which was added the requisite amount of lead nitrate solution. The acidity of the solution was adjusted and lead precipitated with hydrogen sulphide and separated by centrifugation. The activity in both the solid and the solution was determined.

RESULTS AND DISCUSSION

Gold can be extracted in several ways, but for our purposes a solvent such as methyl isobutyl ketone (MIBK) which is not easily affected under strong oxidizing conditions seemed most appropriate. Ichinose[8] has found that extraction of gold with MIBK is greatest from a 1 : 3 mixture of 1*M* nitric and hydrochloric acids. The time of shaking was found to be important, but 4–5 min gave complete extraction in a single step. Loss of gold during concentration by evaporation has been reported,[9] and to avoid this the gold was stripped by evaporating the MIBK in contact with very dilute hydrochloric acid. The process was slow but there was no significant loss of gold. Lead sulphide has been used before as a co-precipitant.[10,11] Since neither lead nor sulphur on neutron capture gives rise to any undesirable radioactivity, we chose lead sulphide to co-precipitate gold.

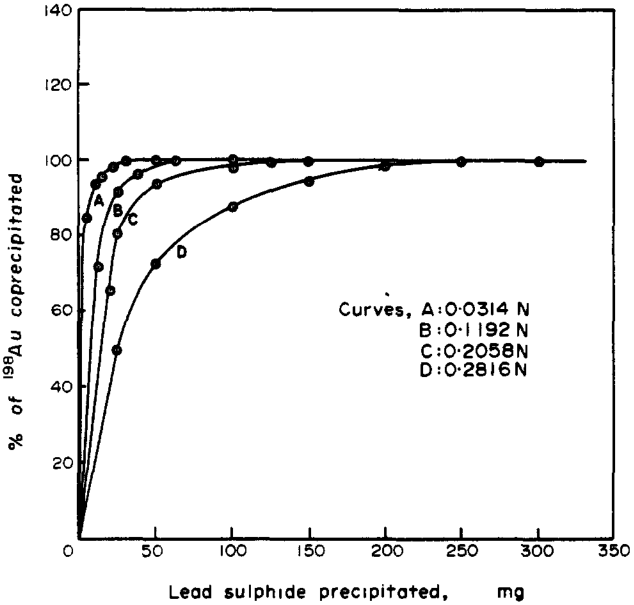

Fig. 1. Uptake of ^{198}Au by different amounts of lead sulphide precipitated at different concentrations of hydrochloric acid.

Figure 1 shows the amount of lead sulphide that is necessary to collect all the gold present in solution at different concentrations of acid. It is evident that about 20 mg of lead sulphide are sufficient when the acidity of the medium is ~0·03*N*, and the gold is present in the range 10^{-7}–10^{-4}*M*. Even when tartaric acid is present in solution to complex antimony, tin, copper, *etc.*, this amount of lead sulphide is sufficient.

The specific activity of ^{198}Au was determined in different amounts of lead sulphide precipitate and found to remain unchanged when up to 30 mg were taken. A slight decrease in specific activity with larger amounts may be due to self-absorption. It may be concluded that the distribution of gold in the lead sulphide was uniform, hence quantitative collection of the precipitate is unnecessary. Recovery of gold was virtually complete (99·8–100%) irrespective of the initial concentration of gold (10^{-7}–$10^{-4}M$). The method is very simple and easily adaptable.

Acknowledgement—Grateful acknowledgement is due to Professor A. K. Saha for his interest and encouragement in this work.

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Summary—An easy method for the recovery of gold from lead-rich minerals has been developed. The gold is extracted with methyl isobutyl ketone from an *aqua regia* solution of the mineral, then stripped into aqueous medium by evaporating the solvent, and finally co-precipitated with lead sulphide. The gold is uniformly distributed in the lead sulphide.

Zusammenfassung—Eine einfache Methode zur Gewinnung von Gold aus bleireichen Mineralien wurde entwickelt. Das Gold wird mit Methylisobutylketon aus einer Lösung des Minerals in Königswasser extrahiert, dann durch Verdampfen des Lösungsmittels wieder ins wäßrige Medium überführt und schließlich zusammen mit Bleisulfid ausgefällt. Das Gold ist gleichmäßig im Bleisulfid verteilt.

Résumé—On a mis au point une méthode facile pour la récupération de l'or de minéraux riches en plomb. L'or est extrait par la méthylisobutylcétone d'une solution du minéral dans l'eau régale, puis réextrait en milieu aqueux par évaporation du solvant et finalement coprécipité avec le sulfure de plomb. L'or est réparti uniformément dans le sulfure de plomb.

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STUDY OF ION-ASSOCIATION COMPLEXES USED IN SPECTROPHOTOMETRIC DETERMINATION OF IRON

(*Received* 10 *July* 1973. *Accepted* 14 *December* 1973)

Spectrophotometric methods based on the formation of the simple chelate complexes of iron(II) with such ligands as 2,2′-bipyridyl (bp), 1,10-phenanthroline (phen) and 4,7-diphenyl-1,10-phenanthroline (bathophen) sulphide was uniform, hence quantitative collection of the precipitate is unnecessary. Recovery of gold was virtually complete (99·8–100%) irrespective of the initial concentration of gold (10^{-7}–$10^{-4}M$). The method is very simple and easily adaptable.

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Knížek and Musilová[2] used Methyl Orange for the extraction of iron(II) complexes. This has been developed for the spectrophotometric determination of iron.[3] The purpose of this study was to investigate the effect of the components of such system on the absorbance of the resulting ion-association complex.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and were not purified additionally. All reagents were in aqueous solution except 4,7-diphenyl-1,10-phenanthroline which was used in ethanolic solution.

RESULTS AND DISCUSSION

The ion-association complexes with the ligands bp, phen and bathopen and the anions of Methyl Orange (MO) and Benzyl Orange (BO) were studied.

In all experiments the chelate was formed in the presence of hydroxylamine hydrochloride and acetate buffer of pH 5·5. Extractions with chloroform did not differ significantly from those with 1,2-dichloroethane, which was used in preliminary experiments.[2] At pH 5·5 the basic forms of the indicators MO and BO are present at maximal concentration.

The continuous variation method for the chloroform extract at constant (10-fold excess relative to iron) concentration of the chelating agent (bp, phen or bathophen) has shown that the complex ion:dye ratio is 1:2. This is similar to other systems of this type.

An excess of reactants is needed for quantitative reaction. It was found that the greatest excess of MO or BO is necessary for the bp complex; with the other systems lower concentrations of the dye suffice (Fig. 1).

The spectra of the reactants and ion-association complexes have been recorded (Figs. 2 and 3). To eliminate the effect of solvation, chloroform was used as the solvent. However, the spectra were almost identical with those of the corresponding complexes in water.

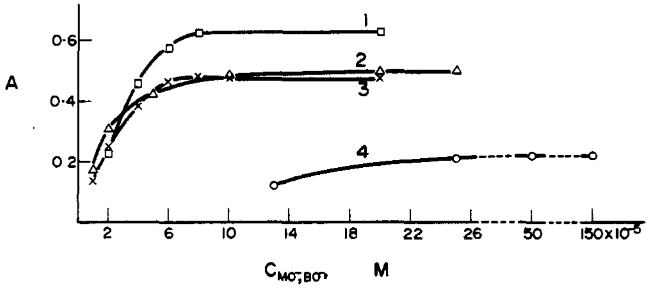

Fig. 1. Effect of excess of dye in aqueous solution on the absorbance of the extract. $\lambda = 420$ nm. $C_{Fe(II)} = 1 \times 10^{-5} M$; $C_{ligand} = 1 \times 10^{-4} M$. *1*—Fe(bathophen)$_3^{2+}$-MO$^-$; 2—Fe(phen)$_3^{2+}$-BO$^-$; *3*—Fe(phen)$_3^{2+}$-MO$^-$; *4*—Fe(bp)$_3^{2+}$-MO$^-$.

Spectra were also recorded for chloroform solution of the dye–tetramethylammonium ion complexes. For BO the spectrum was nearly the same as for aqueous medium but for MO absorption maximum was at 425 nm compared with 440 nm for alkaline aqueous solution.

The degree of extraction was determined by stripping the complex with an acid aqueous solution to decompose both the ion-association complex and the chelate. The absorbance of the dye liberated was taken as the measure of the amount of iron extracted since in the absence of the iron(II) chelate, extraction of the dye is negligible.

The degree of extraction depends on the chelate cation: with bp it is 40%, with phen it is >95% and with bathophen it is close to 100%.

The practical apparent molar absorptivities for the systems studied are: Fe(bp)$_3$(MO)$_2$ = 2·20 × 10^4; Fe(phen)$_3$(MO)$_2$ = 4·83 × 10^4; Fe(bathophen)$_3$(MO)$_2$ = 6·03 × 10^4; Fe(phen)$_3$(BO)$_2$ = 5·27 × 10^4; Fe(bathophen)$_3$(BO)$_2$ = 5·69 × 10^4 l mole^{-1}.cm^{-1}.

These values agree within experimental error with values estimated on the basis of reaction stoichiometry, absorptivities of the reactants and of degree extraction.

For analytical application the most suitable system is Fe(phen)$_3$(MO)$_2$. The bp chelates, because of low extractability, do not offer sufficient sensitivity. For the bathophen chelates, negative errors may occur owing

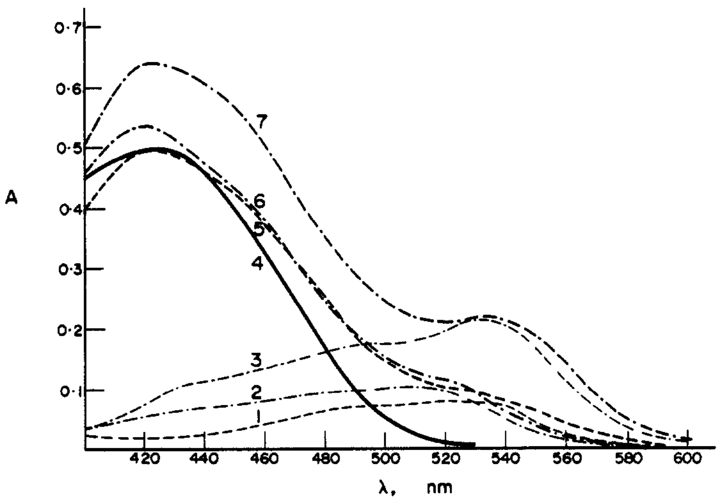

Fig. 2. Absorption spectra in chloroform solution.
1—$Fe(bp)_3(ClO_4)_2$; 2—$Fe(phen)_3(ClO_4)_2$; 3—$Fe(bathophen)_3(ClO_4)_2$; 4—$(CH_3)_4N(MO)$; 5—$Fe(bp)_3(MO)_2$; 6—$Fe(phen)_3(MO)_2$; 7—$Fe(bathophen)_3(MO)_2$. $C_{Fe(II)} = 1 \times 10^{-5}M$; $C_{chelate} = 3 \times 10^{-5}M$; $C_{MO} = 2 \times 10^{-5}M$.

to extraction of their perchlorate or nitrate complexes at high ($10^{-2}M$) concentrations of these ions. BO is equally advantageous but more difficult to obtain in pure form.

These procedures are less selective than the direct phenanthroline method, because Co(II), Ni, Cu(II), Zn and Cd which form colourless chelates of similar structure and stability, interfere, giving high results. Therefore a preliminary separation of iron by extraction as the iron(III) chloride or thiocyanate complex is recommended.

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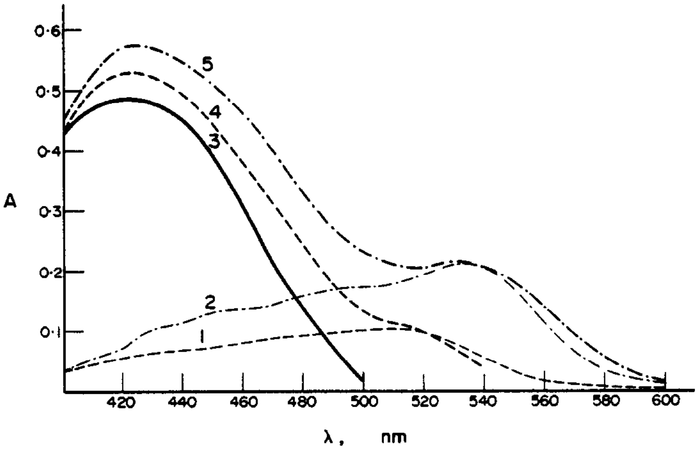

Fig. 3. Absorption spectra in chloroform solution.
1—$Fe(phen)_3(ClO_4)_2$; 2—$Fe(bathophen)_3(ClO_4)_2$; 3—$(CH_3)_4N(BO)$; 4—$Fe(phen)_3(BO)_2$; 5—$Fe(bathophen)_3(BO)_2$. $C_{Fe(II)} = 1 \times 10^{-5}M$; $C_{chelate} = 3 \times 10^{-5}M$, $C_{BO} = 2 \times 10^{-5}M$.

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1. Z. Marczenko, *Kolorymetryczne oznaczanie pierwiastków*, PWN, Warszawa, 1968.
2. M. Knížek and M. Musilová, *Talanta*, 1968, **15**, 479.
3. A. Hulanicki, M. Galus, W. Jędral, R. Karwowska, and M. Trojanowicz, *Chem. Anal.*, (*Warsaw*), 1971, **16**, 1011.

Summary—The following ion-association systems were investigated spectrophotometrically: Fe(2,2′-bipyridyl)$_3$(Methyl Orange)$_2$; Fe(1,10-phenanthroline)$_3$(Methyl Orange)$_2$; Fe(4,7-diphenyl-1,10-phenanthroline)$_3$(Methyl Orange)$_2$; Fe(1,10-phenanthroline)$_3$(Benzyl Orange)$_2$; Fe(4,7-diphenyl-1,10-phenanthroline)$_3$(Benzyl Orange)$_2$. The molar absorptivities may be calculated with good precision on the basis of the spectra of the reacting species (iron chelate and dye anion), their stoichiometry and the degree of extraction. Analytically the most useful is the Fe(1,10-phenanthroline)$_3$(Methyl Orange)$_2$ complex, molar absorptivity $4{\cdot}83 \times 10^4$ l. mole^{-1}.cm^{-1} at 420 nm, but many metals (Co, Cu, Ni, Zn, Cd) form similar extractable complexes and interfere.

Zusammenfassung—Folgende Ionenassoziat-Systeme wurden spektrophotometrisch untersucht: Fe(2,2′-Bipyridyl)$_3$(Methyl-orange)$_2$; Fe(1,10-Phenanthrolin)$_3$(Methyl-orange)$_2$; Fe(4,7-Diphenyl-1, 10-phenanthrolin)$_3$(Methyl-orange)$_2$; Fe(1,10-Phenanthrolin)$_3$(Benzyl-orange)$_2$; Fe(4,7-Diphenyl-1,10-phenanthrolin)$_3$(Benzyl-orange)$_2$. Ihre molaren Extinktionskoeffizienten können recht genau aus den Spektren der reagierendent Spezies (Eisenchelat und Farbstoff-Anion), der Stöchiometrie und dem Extraktionsgrad berechnet werden. Den größten analytischen Nutzen hat der Komplex Fe(1,10-Phenanthrolin)$_3$(Methyl-orange)$_2$ mit dem molaren Extinktionskoeffizienten $4{,}83 \times 10^4$ l.mol^{-1}.cm^{-1} bei 420 nm, aber viele Metalle (Co, Cu, Ni, Zn, Cd) bilden ähnliche extrahierbare Komplexe und stören.

Résumé—Les systèmes d'association ionique suivants ont été étudiés spectrophotométriquement: Fe(2,2′-bipyridyl)$_3$ (Méthylorange)$_2$; Fe(1,10-phénanthroline)$_3$ (Méthylorange)$_2$; Fe(4,7-diphényl 1,10-phénanthroline)$_3$ (Méthylorange)$_2$; Fe(1,10-phénanthroline)$_3$ (Benzylorange)$_2$; Fe(4,7-diphényl 1,10-phénanthroline)$_3$ (Benzylorange)$_2$. Les coefficients d'absorption molaires peuvent être calculés avec une bonne précision sur la base des spectres es espèces réagissantes (chélate de fer et anion du colorant), leur stoechiométrie et le degré d'extraction. Analytiquement, le plus utile est le complexe Fe(1,10-phénanthroline)$_3$ (Méthylorange)$_2$, coefficient d'absorption molaire $4{,}83 \times 10^4$ l. mole^{-1} cm^{-1} à 420 nm, mais de nombreux métaux (Co, Cu, Ni, Zn, Cd) format es complexes extractibles imilaires et interfèrent.

Talanta Vol 21, pp 901–904 Pergamon Press 1974 Printed in Great Britain

NOTICES

AMERICAN VACUUM SOCIETY

SHORT COURSES IN VACUUM SCIENCE AND TECHNOLOGY

A 4 day basic course in "Vacuum Technology" and seven 1 day special subject courses will be offered in conjunction with the 21st National Symposium of the American Vacuum Society, which will be held at the Disneyland Hotel, Anaheim, California, on 8–11 October 1974. The basic course will cover vacuum technology from fundamental theory to state-of-the-art concepts. The 1 day special subject courses will be basic and will cover theory, equipment, and applications. The courses to be offered are: Fundamentals of Sputtering Technology; Partial Pressure Analysis; Fundamentals of Evaporation Methods; Leak Detection; Freeze Drying; Surface Analysis: Microcircuit Thin Film Technology.

Course outlines and application forms can be obtained from Nancy Hammond, American Vacuum Society, 335 East 45th Street, New York, New York 10017.

THE 1975 PITTSBURGH CONFERENCE

The 26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Ohio, U.S.A., 3–7 March 1975. Many aspects of the general fields of Analytical Chemistry and Spectroscopy will be represented. In addition to the general sessions, symposia are being arranged on the following specific topics:

(1) Coblentz Society Award Symposium
(2) Spectroscopy Awards Symposium
(3) Symposium on Surface Chemistry (ASTM E-2)
(4) Panel Forum and Discussion—Computer Laboratory Systems (ASTM E-31)
(5) The Impact of Tunable Lasers on Spectroscopy and Chemistry
(6) Supplemental Fuels from Coal: New Analytical Needs
(7) Liquid Chromatography—Today and Tomorrow; A Symposium, Panel Discussion, and Open Forum
(8) Field Sampling and Analysis of Atmospheric Contaminants
(9) The Role of Standards in Accurate Measurements
(10) Polymer Analysis
(11) The Science of Toxicology

The general papers are *not* to be restricted to the symposium topics, and discussions of all aspects of Analytical Chemistry and Spectroscopy are solicited. It is expected that there will be many contributions in the areas of new instrumentation, new and growing techniques (such as plasma chromatography, laser spectroscopy, etc.), general pollution problems, analytical problems associated with industrial safety, and many other areas of current activity

Those wishing to present papers in the 1975 Pittsburgh Conference Technical Programme should submit three copies of a 150-word abstract to:

Peter M. Castle, Program Chairman
1975 Pittsburgh Conference
Building 401, Room 4A31
Westinghouse Research Laboratories
Beulah Road
Pittsburgh, PA 15235 U.S.A.

1. Correspondence regarding papers should be sent in *duplicate* to:
Peter M. Castle, Program Chairman
at the above address.

2. The final date for receipt of *title* and 150-word *abstract* is 1 October 1974. Abstracts received after this date will not be accepted.
3. A brief abstract, in triplicate, of not more than 150 words for use in categorizing sessions must be submitted. The abstract should state clearly (a) the objective of the research, (b) equipment and procedures used, and (c) typical results and conclusions. Use the attached abstract form for the original copy and include two copies on plain white paper. Enclose a stamped, self-addressed postcard which will be returned to indicate receipt of abstract.
4. The letter transmitting the title and abstract should contain the following:
   (a) the title of the paper;
   (b) the names of the author(s), the company(s), or institution(s) in whose laboratory the work was done, and the address(es). If the present address of any author is different, both addresses should be given;
   (c) in the case of multiple authors, the name of the person who will present the paper should be distinctly indicated by underlining;
   (d) a *statement* that the paper, or all material in it, has *not* been published or presented previously.
5. Presentation time will be limited to 15 min with an additional 5 min allowed for discussion.
6. Papers should be classified according to subject matter as indicated on the abstract form.
7. A 350 word abstract which will be reproduced in booklet form and made available to attendees will be required by 15 December 1974. Forms and details concerning this abstract will be sent to authors after acceptance of papers.
8. Slides must be 3¼ in. × 4 in. (horizontal) or 2 in. × 2 in. and numbered. *Legible and meaningful slides are very important to a paper's success.* Large print and moderation in the use of detail are crucial to a slide's effectiveness.

ANALYTICAL CHEMISTRY DIVISION, IUPAC

Following the elections at the XXVII Conference of IUPAC at Munich, Germany in 1973, the composition of the Division Committee, responsible for the administration of the Division, is as follows:

President: Prof. N. Tanaka (Japan)
Vice-President: Prof. W. Kemula (Poland)
Secretary: Mr. R. W. Fennell, Materials Department, Royal Aircraft Establishment, Farnborough, Hampshire GU14 6TD, U.K.
Members: Prof. D. N. Hume (U.S.A.)
Prof. H. Kaiser (Germany)
Prof. I. M. Kolthoff (U.S.A.)
Prof. O. Samuelson (Sweden)
Prof. B. Trémillon (France)
Prof. T. S. West (U.K.)
Prof. Yu. A. Zolotov (U.S.S.R.)

The main work of the Division is performed by its seven Commissions, and their projects are listed below.

Commission V.1 Analytical Reactions and Reagents

Chairman: Prof. R. Belcher (U.K.)
Secretary: Prof. F. Pellerin, Hôpital Général Emile Roux, F-95600 Eaubonne, France

Projects:
1.1. Methods of analysis of food additives (CEE Contract)
1.2. Methods for determination of carbonyl
1.3. Redox indicators
1.4. Complexmetric indicators
1.5. Acid–base indicators for non-aqueous titration
1.6. Methods for polyphenols
1.7. Primary standards
1.8. Colorimetric and fluorimetric determination of steroids

Commission V.2 Microchemical Techniques and Trace Analysis

Chairman: Dr. O. G. Koch (Germany)
Secretary: Dr. M. Pinta, Office de la Recherche scientifique et technique Outre-Mer, 70–74 route d'Aulnay, F-93140 Bondy, France

Projects:
- 2.1. Study on accuracy and precision of the determination of metals in organic compounds
- 2.2. Determination of C, H and N in organometallic compounds
- 2.3. Standard reference materials for trace analysis
- 2.4. Contamination in trace analysis
- 2.5. Trace analysis of surfaces
- 2.6. Stability of solutions used as trace analytical standards
- 2.7. Volatility losses of trace elements in destruction of organic substances
- 2.8. Applicability of high pressure decomposition in the trace analysis of biological materials
- 2.9. Analysis of organoboron compounds
- 2.10. Determination of minor impurities in analytical reagents
- 2.11. Sensitivities of trace analytical methods

Commission V.3 Analytical Nomenclature

Chairman: Prof. H. M. N. H. Irving (U.K.)
Secretary: Dr. H. Zettler, Norddeutsche Affinerie, Postfach 67, Alsterterrasse 2, D-2000 Hamburg 36, German Federal Republic

Projects:
- 3.1. Nomenclature of scales of working
- 3.2. List of synonyms and trivial names
- 3.3. Development and publication of methods of analysis
  - 3.3.1. Spectrophotometric procedures
  - 3.3.2. Gravimetric procedures
  - 3.3.3. Ion selective electrode procedures
- 3.4 Nomenclature of liquid–liquid extraction
- 3.5. Nomenclature of kinetic methods of analysis
- 3.6. Nomenclature of ion selective electrodes
- 3.7. Selectivity index
- 3.8. Criteria for sensitivity, detection limits, precision and accuracy
- 3.9. Nomenclature of data processing
- 3.10. Compendium of analytical nomenclature
- 3.11. Nomenclature of sampling
- 3.12. Information storage and retrieval

Commission V.4. Spectrochemical and Other Optical Procedures for Analysis

Chairman: Prof. V. A. Fassel (U.S.A.)
Secretary: Mr. B. F. Scribner, National Bureau of Standards, U.S. Department of Commerce, Washington D.C. 20234, U.S.A.

Projects:
- 4.1. Nomenclature of analytical X-ray spectroscopy
- 4.2. Systematic classification of spectromechanical excitation sources
- 4.3. Nomenclature of analytical molecular fluorescence spectroscopy

Commission V.5 Electroanalytical Chemistry

Chairman: Prof. R. G. Bates
Secretary: Prof. J. F. Coetzee, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 51260, U.S.A.

Projects:
- 5.1. Purification of electrolytes
- 5.2 Half-wave potentials in dimethylformamide
- 5.3. Symbols and terminology for electroanalytical techniques
- 5.4. Pretreatment of solid electrodes
- 5.5. Conditional diffusion coefficients
- 5.6. Standard potentials in fused salts
- 5.7. Purification of background electrolytes
- 5.8. Diffusion coefficients in mercury
- 5.9. Sign convention for currents
- 5.10. Conditional equilibrium constants
- 5.11. Recommendations on reporting of electroanalytical data
- 5.12. Selectivity of ion selective electrodes
- 5.13. Indicator and reference electrodes in non-aqueous solvents
- 5.14. Half-wave potentials in propylene carbonate and hexamethylphosphoramide
- 5.15. Purification of dimethylformamide
- 5.16. Application and potentialities of electroanalytical methods in environmental analysis

Commission V.6 Equilibrium Data

Chairman: Prof. G. H. Nancollas (U.S.A.)
Secretary: Dr. S. Ahrland, Department of Inorganic and Physical Chemistry, Chemical Center, University of Lund, POB 740, S-220 07 Lund 7, Sweden

Projects:
- 6.1. Stability constants
- 6.2. Distribution equilibria
- 6.3. Critical surveys
- 6.4. Ionic media
- 6.5. Information retrieval (data flagging)
- 6.6. Symbols for mixed ligand complex constants
- 6.7. Solubility data

Commission V.7. Analytical Radiochemistry and Nuclear Materials

Chairman: Dr. M. B. A. Crespi (Argentina)
Secretary: Dr. J. C. White, Analytical Chemistry Division, Oak Ridge National Laboratory, POB X, Oak Ridge, Tennessee 37830, U.S.A.

Projects:
- 7.1. Light element analysis
- 7.2. Trace analysis reference materials for radiochemical analysis
- 7.3. Reference materials for uranium analysis
- 7.4. Analysis of nuclear materials
- 7.5. Nomenclature for radioanalytical chemistry
- 7.6. Nuclear methods for analysis of key elements in environmental pollution
- 7.7. Nuclear methods for analysis of fissile and fertile elements
- 7.8. Nuclear methods for analysis of molecular compounds in environmental pollution
- 7.9. Critical compilation of radioanalytical data
- 7.10. Non-nuclear methods of analysis of fissile and fertile elements
- 7.11. Charged-particle-induced X-ray fluorescence
- 7.12. Separations in radioanalytical chemistry
  - 7.12.1. Ion exchange
  - 7.12.2. Liquid–liquid extraction
  - 7.12.3. Precipitation and adsorption
  - 7.12.4. Miscellaneous
- 7.13. State of the art of thorium analysis

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TWO-PHASE TITRATION OF ORGANIC AMMONIUM IONS WITH LAURYL SULPHATE AND METHYL YELLOW AS INDICATOR

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(*Received* 16 *May* 1973. *Revised* 22 *February* 1974. *Accepted* 1 *March* 1974)

Summary—Conditions for determination of quaternary ammonium compounds and amines by two-phase titration have been calculated on the basis of extraction constants for the ion-pairs between the titrant (lauryl sulphate), the indicator (Methyl Yellow) and the sample. Methods for determination of extraction constants are presented. The precision and selectivity of the method are demonstrated by titrations of ammonium ions with different structures and degrees of substitution. The results are in agreement with the theoretical calculations.

Two-phase titration with lauryl sulphate is a frequently used method for the determination of cationic surfactants as well as amines and quaternary ammonium ions of pharmaceutical interest.[1–3] The reverse procedure, *i.e.*, titration of anionic tensides with large quaternary ammonium ions also has a wide application.[4–7]

The publications have in most cases an empirical approach to the method. Han[5] gives a theoretical treatment of the titration error and Pellerin *et al.*[3] have made a systematic study of structural factors of importance for the application of the titration procedure.

The aim of the present paper is to demonstrate how equilibrium constants for the reaction between titrant (lauryl sulphate), sample (organic ammonium ion) and indicator can be used in the computation of suitable conditions for the titration. Expressions are computed for the relation between titration error, extraction constant, concentration of the ammonium ion and pH of the aqueous phase in titrations with Methyl Yellow as indicator.

THEORY

The essential process in a two-phase titration of an organic ammonium ion (Q^+) with lauryl sulphate (X^-) is an ion-pair extraction:

$$Q^+_{aq} + X^-_{aq} = QX_{org}$$

The quantitative expression for this equilibrium is given by the extraction constant, E_{QX}, defined by

$$E_{QX} = [QX]_{org}[Q^+]^{-1}[X^-]^{-1} \tag{1}$$

where $[QX]_{org}$ denotes the molar concentration of the ion-pair in the organic phase and $[Q^+]$ and $[X^-]$ the concentrations of the ions in the aqueous phase.

The magnitude of the extraction constant depends on the structure of the ion-pair and its components as well as on the properties of the organic phase.[8] All ion-pairs have a more or less polar character and non-polar solvents such as aliphatic hydrocarbons or carbon tetrachloride give in most cases low degrees of extraction. Chloroform and methylene chloride are often suitable as extracting agents, but hydrophilic compounds may require more strongly hydrogen-bonding solvents, *e.g.*, lipophilic alcohols. However, alcoholic solvents have the disadvantage of being rather unselective[9–11] and extract for instance sodium ion-pairs with large anions to a significant degree.

In a *titration procedure* based on extraction of QX, the relation between the extraction constant, the total concentrations of sample (C_Q) and titrant (C_X) and the concentration of the titrant in the aqueous phase (X^-) is given by equation (2). It is obtained by combination of equation (1) with the definitions for C_X and C_Q.

$$E_{QX} = \frac{(C_X - [X^-])}{(C_Q - C_X + [X^-])[X^-]R} \tag{2}$$

$C_X = [X^-] + R[QX]_{org}$

$C_Q = [Q^+] + R[QX]_{org}$

$R = V_{org}/V_{aq}$, where V_{org} and V_{aq} are the volumes of the organic and aqueous phase respectively.

The equivalence criterion is $C_X = C_Q$, but in order to obtain an acceptable result in the titration Q^+ and X^- have to be present almost entirely in the organic layer at the equivalence point, *i.e.*, the prerequisite $C_X \gg [X^-]$ has to be fulfilled. Under these conditions, equation (2) takes the form

$$[X^-]_{eq} = (C_Q)^{1/2}(E_{QX}R)^{-1/2} \tag{3}$$

where $[X^-]_{eq}$ is $[X^-]$ at the equivalence point. The equation shows that not only the concentration and the extraction constant of the sample but also the volume ratio of the phases (R) will have an influence on $[X^-]_{eq}$.

Indication of the end-point

The end-point of the titration can be indicated by use of a colour indicator that can form ion-pairs in the organic phase. Both $[Q^+]$ and $[X^-]$ will change very rapidly in the vicinity of the equivalence point and an indicator which forms an ion-pair either with Q^+ or with X^- can be used. It is usually convenient to use an indicator which forms an ion-pair with the titrant, X^-, since the extraction constant of the indicator will be independent of the properties of the sample.

If the uncomplexed indicator during the titration is present in the aqueous phase, the end-point of the titration is indicated by the transfer of the coloured titrant–indicator ion-pair to the organic phase. It is also possible to use an indicator that is present in the organic phase both in the uncomplexed form and as an ion-pair, but the two forms must then have distinctly different colours. The reaction of such an indicator (In) with the titrant (X^-) is illustrated by the equation

$$In_{org} + H^+_{aq} + X^-_{aq} = HInX_{org}$$

From the equilibrium constant of this process, E'_{In}, the following expression can be derived.

$$\frac{[HInX]_{org}}{[In]_{org}} = E'_{In}a_{H^+}[X^-] \tag{4}$$

The equation shows that the colour of the indicator, expressed by the quotient $[\mathrm{HInX}]_{\mathrm{org}}/[\mathrm{In}]_{\mathrm{org}}$, depends on the concentration of the titrant in the aqueous phase ($[\mathrm{X}^-]$) and the hydrogen ion activity (a_{H^+}).

The titration is usually finished at a predetermined value of the quotient $[\mathrm{HInX}]_{\mathrm{org}}/[\mathrm{In}]_{\mathrm{org}}$ (the indicator end-point), and by pH adjustment it is possible to make this end-point correspond to different values of $[\mathrm{X}^-]$.

The magnitude of the end-point quotient is also of some importance. A low quotient will broaden the range for variation of $[\mathrm{X}^-]$ and will also decrease the consumption of titrant by the indicator.

Calculation of titration conditions

The aim of the calculations is to find a pH interval where the indicator end-point is so close to the equivalence point that results with sufficient accuracy and precision are obtained.

The first step is a calculation of $[\mathrm{X}^-]_{\mathrm{eq}}$ from equation (3), based on the sample concentration and the extraction constant between sample and titrant. $[\mathrm{X}^-]_{\mathrm{eq}}$ is then substituted into equation (4) which gives the pH where the indicator end-point coincides with the equivalence point.

It is furthermore necessary to make an estimate of the precision that can be obtained in the titration. The error, F, in titration of a cation (Q^+) with lauryl sulphate (X^-) is given by equation (5).

$$F = C_{\mathrm{X}} - C_{\mathrm{Q}} = [\mathrm{X}^-] + R[\mathrm{HInX}]_{\mathrm{org}} - [\mathrm{Q}^+] \tag{5}$$

$[\mathrm{HInX}]_{\mathrm{org}}$ is the concentration of the ion-pair between the indicator and lauryl sulphate at the end-point of the titration. The indicator will give rise to a positive systematic error which has exactly the same magnitude for all titrations as long as the end-point quotient and the total concentration of the indicator are the same. An error of this kind can usually be compensated by a blank titration.

It is assumed in the discussion below that a compensation for the indicator error is made. $R[\mathrm{HInX}]_{\mathrm{org}}$ will then disappear from equation (5). The relative titration error, F_{rel}, can then be expressed by

$$F_{\mathrm{rel}} = \frac{[\mathrm{X}^-] - [\mathrm{Q}^+]}{C_{\mathrm{Q}}} \tag{6}$$

The titration error will have a minimum when the indicator end-point coincides with the equivalence point. Under practical conditions there will always be a deviation: there is some uncertainty in the determination of $[\mathrm{HInX}]_{\mathrm{org}}/[\mathrm{In}]_{\mathrm{org}}$, there is often a deviation between the calculated pH and that obtained in the solution and there is always some uncertainty in E_{QX} and C_{Q} which influence the calculated $[\mathrm{X}^-]_{\mathrm{eq}}$ [equation (3)]. The deviation, ΔpX, is defined by

$$\Delta\mathrm{pX} = \mathrm{pX}_{\mathrm{end}} - \mathrm{pX}_{\mathrm{eq}} \tag{7}$$

or in exponential form

$$[\mathrm{X}^-]_{\mathrm{end}} = [\mathrm{X}^-]_{\mathrm{eq}} 10^{-\Delta\mathrm{pX}} \tag{8}$$

$[\mathrm{X}^-]_{\mathrm{end}}$ is the concentration of the titrant in the aqueous phase at the end-point.

The influence of such a deviation on the precision of the titration can be calculated by using equation (9). It is obtained from equations (1), (3) and (6), by using the substitutions $[X^-] = [X^-]_{end}$ and $[QX]_{org} = C_Q/R$.

$$F_{rel} = (E_{QX}C_QR)^{-1/2}(10^{-\Delta pX} - 10^{\Delta pX}) \tag{9}$$

This equation shows that the error of the titration decreases with increasing extraction constant and sample concentration and increases with increasing deviation from the equivalence point.

The relation between F_{rel} and the extraction constant at different sample concentrations is summarized in Table 1. The calculation of the conditions was made with the assumption that $R = 1$ and $\Delta pX = \pm 0{\cdot}1$. The error in pX will usually not exceed this value if the titration is made with photometric end-point determination, as will be discussed below.

Table 1. Conditions for quantitative titrations, with photometric end-point determination

$-\log C_Q$	$\log E_{QX}$	F_{rel}
2·3	≥5·6	≤0·01
	≥6·2	≤0·005
3·3	≥6·6	≤0·01
	≥7·2	≤0·005

C_Q = total molar concentration of organic ammonium ion at the end-point of the titration, taken as being entirely in the aqueous phase.

E_{QX} = extraction constant defined by equation (1).

F_{rel} = relative titration error defined by equation (6) and valid when $\Delta pX = \pm 0{\cdot}1$.

The table shows that a sample with concentration $10^{-2\cdot 3}M$ can be titrated with a relative error of 0·01 (1%), if its extraction constant is $10^{5\cdot 6}$. When the extraction constant is higher, titrations can be made with a higher precision and/or a lower sample concentration can be used.

Selectivity

The selectivity of the lauryl sulphate titration method can be illustrated by a determination of a compound A^+ in the presence of a compound B^+, both extractable into the organic phase as ion-pairs with X^-. The equivalence point of the titration is defined in equation (10):

$$[X^-] + R[BX]_{org} = [A^+] \tag{10}$$

B^+ has a dominating influence on the location of the equivalence point when $R[BX]_{org} \gg [X^-]$. Equation (10) can then be simplified to

$$R[BX]_{org} = [A^+] \tag{11}$$

A calculation of $[X^-]_{eq}$ can be based on equation (11) and the definitions of E_{AX}, E_{BX}, C_A and C_B. A combination of these expressions gives:

$$\frac{C_B E_{BX}[X^-]_{eq}R}{1 + E_{BX}[X^-]_{eq}R} = \frac{C_A}{1 + E_{AX}[X^-]_{eq}R} \tag{12}$$

This equation will give a rather complicated expression for $[X^-]_{eq}$ but a simplification can be achieved by dividing the further discussion into two cases.

1. B^+ is titrated to a small degree, *i.e.*, $R[BX]_{org} \ll C_B$.
2. B^+ is almost completely titrated, *i.e.*, $[B^+] \ll C_B$.

Only case 1 will be discussed in detail, since it is obvious that the titration in case 2 will give the sum of A and B with a systematic error that will be directly proportional to the total concentration of B.

The calculation of $[X^-]_{eq}$ in case 1 is made with the further assumption that $C_A \gg [A^+]$, since this is a basic prerequisite for an acceptable titration accuracy. Equation (12) then gives:

$$[X^-]_{eq} = \frac{1}{R}\left(\frac{C_A}{C_B E_{AX} E_{BX}}\right)^{1/2} \tag{13}$$

The pH of the titration is calculated by substitution of $[X^-]_{eq}$ from equation (13) into equation (4).

The relative titration error, F_{rel}, for a deviation ΔpX, from the equivalence point, can be calculated according to the principles used above. A combination of equations (11) and (13) with an expression for F_{rel} analogous to equation (6) gives:

$$F_{rel} = \left(\frac{C_B E_{BX}}{C_A E_{AX}}\right)^{1/2} (10^{-\Delta pX} - 10^{\Delta pX}) \tag{14}$$

This equation shows that the error of the titration decreases with increasing $(C_A E_{AX})$ and increases when $(C_B E_{BX})$ increases.

The relative titration error in case 2 can be derived according to the same principles. The following equation is obtained:

$$F_{rel} = \frac{C_B}{C_A}(1 - 10^{\Delta pX}) \tag{15}$$

Equation (15) shows, as expected, that good precision can only be obtained when C_B/C_A is low.

Determination of extraction constants

The determination of extraction constants by batch procedures has been discussed in detail in several previous publications.[12,13] The limiting factor is the sensitivity of the method for determination of the ion-pair and its components. The determination of very high constants will also require a specialized technique.

Extraction constant determination by the titrimetric method given in the experimental section has not been previously discussed in a corresponding manner. The constant is calculated from equation (2) and the precision in the constant determination will depend on the error in the end-point determination, ΔpX, and the corresponding error in the titrant concentration, ΔC_X (the error in C_Q is assumed to be negligible). The error in C_X can be estimated from the lauryl sulphate buffer capacity of the system, β_L, defined by

$$\beta_L = dC_X/dpX. \tag{16}$$

An expression for β_L can be derived from the combination of the definitions of C_Q, C_X and E_{QX}:

$$C_X = [X^-] + E_{QX}C_Q[X^-]R(1 + E_{QX}[X^-]R)^{-1} \tag{17}$$

which gives

$$\beta_L = \frac{dC_X}{dpX} = -2{\cdot}3\left(\frac{[QX]_{org}[Q^+]R}{C_Q} + [X^-]\right) \tag{18}$$

When $C_X \gg [X^-]$, the equation can be given the form

$$\beta_L/2{\cdot}3 = -\frac{(C_Q - C_X)C_X}{C_Q} \tag{19}$$

The buffer capacity is almost constant over the interval $C_X = (0{\cdot}25\text{–}0{\cdot}75)C_Q$ with a maximum at $C_X = 0{\cdot}5C_Q$.

E_{QX} is usually calculated by means of the following simplified form of equation (2), valid when $C_X \gg [X^-]$:

$$\log E_{QX} = \log C_X - \log(C_Q - C_X) - \log R + pX \tag{20}$$

The relative errors in C_X and $(C_Q - C_X)$ for the range $C_X = (0{\cdot}25 - 0{\cdot}75)C_Q$ can be calculated from equation (19). The following expression is obtained when $\Delta pX = \pm 0{\cdot}05$ and $C_X = 0{\cdot}5C_Q$:

$$\log E_{QX} = \log C_X \pm 0{\cdot}02 + \log(C_Q - C_X) \pm 0{\cdot}02 - \log R + pX \pm 0{\cdot}05 \tag{21}$$

Equation (21) shows that the error in $\log E_{QX}$ is not higher than 0·1 units for the C_X range given above. It will, however, increase at higher and lower C_X.

The discussion above has not included the influence of side-reactions, since no such processes have been observed during the titration of any of the compounds dealt with in this paper.

It is, however, possible to include the influence of side-reactions (*e.g.*, protolysis in the aqueous phase, partition of ion-pair components in uncharged form, dissociation or association of the ion-pair in the organic phase) without any change of the general principle by use of a conditional extraction constant.[8]

EXPERIMENTAL

Apparatus

The photometric determinations were made with a Zeiss PMQ II and a Bausch and Lomb Spectronic 505 spectrophotometer. The pH measurements were performed with a Radiometer pH Meter 4 provided with glass and calomel electrodes. The titrations were performed in an EEL photometric titrator.

Chemicals and reagents

Sodium lauryl sulphate (BDH, specially pure).

Methyltriethylammonium, methyltripropylammonium and dimethylprotriptyline. Prepared from the corresponding amines and methyl iodide in acetone.

Methyl Yellow (*4-dimethylaminoazobenzene, Merck* 3055). Recrystallized from diethyl ether–petroleum ether.

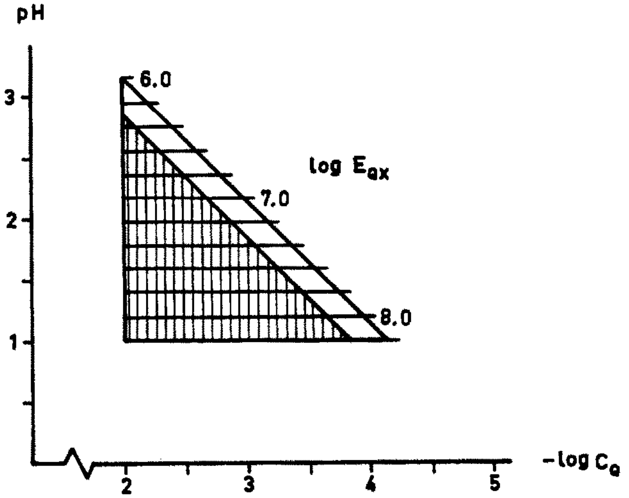

Fig. 1. pH and sample concentration (C_Q) for titration of compounds with log $E_{QX} \geq 6{\cdot}0$. Relative titration error $\leq 1{\cdot}0\%$ within the framed area, $< 0{\cdot}5\%$ in the shaded part (equal phase volumes). pH and C_Q of the titration are obtained from the triangular area above the horizontal line corresponding to log E_{QX} of the sample. The whole framed area is valid when log $E_{QX} > 8{\cdot}2$. *Example.* A compound with log $E_{QX} = 7{\cdot}2$ can be titrated with a relative error of $< 1\%$ at pH 2·0–3·3. For titration at pH 2·0, a sample concentration of $10^{-2{\cdot}0}$–$10^{-3{\cdot}2}M$ must be used, while a concentration of $10^{-2{\cdot}0}$–$10^{-2{\cdot}7}M$ can be used at pH 2·5.

All other ammonium compounds were of pharmacopoeia or analytical grade. Chloroform was of analytical grade and saturated with water before use. The buffers were prepared from sodium phosphate and phosphoric or sulphuric acid. They had an ionic strength of 0·1.

Titration procedure

Dissolve 10^{-4}–10^{-5} mole of the ammonium salt in 10 ml of buffer in the titration vessel. Add 20 ml of $2 \times 10^{-5}M$ Methyl Yellow in chloroform. Titrate the mixture (magnetic stirring) with buffered 10^{-2}–$10^{-3}M$ sodium lauryl sulphate in a photometric titrator at about 545 nm (filter 605 in the EEL titrator), *i.e.*, close to the absorbance maximum of the ion-pair between Methyl Yellow and lauryl sulphate. The first perceptible red colour of the organic phase (equivalent to a rise of the absorbance to 0·12 in the EEL titrator) is used as the end-point of the titration. Compensation for the indicator error will not be necessary when the sample concentration is $> 10^{-3}M$.

The pH of the buffer must be adapted to the extraction constant (E_{QX}) and the concentration of the sample (C_Q). When $E_{QX} > 10^{6{\cdot}0}$, the pH and concentration ranges can be calculated by means of Fig. 1 which gives conditions for titrations with maximum relative errors of 0·5 and 1·0%.

When $E_{QX} < 10^{6{\cdot}0}$, the pH must be more closely adapted to the sample concentration. The calculation of the pH can then be made by means of

$$\mathrm{pH} = 7{\cdot}15 + 0{\cdot}5 \log C_Q - 0{\cdot}5 \log(E_{QX}R) \qquad (22)$$

The precision that can be obtained is calculated by equation (9), using $\Delta\mathrm{pX} = \pm 0{\cdot}1$, if the deviations from the calculated conditions are within the limits $\Delta\mathrm{pH} = \pm 0{\cdot}05$ and $\Delta \log C_Q = \pm 0{\cdot}1$.

The sample and the titrant (lauryl sulphate) are dissolved in buffer solutions of the same composition. Buffers prepared from phosphoric acid and sodium dihydrogen phosphate and with an ionic strength of 0·1 are recommended.

Determination of extraction constants

Two methods are presented: a batch extraction procedure which is generally applicable, and a titration procedure which is more rapid but of limited use.

Batch extraction method. Known amounts of the organic ammonium ion (Q) and lauryl sulphate (X) are dissolved in 10 ml of buffer, and the solution is extracted with 10 ml of chloroform for 20 min in a glass-stoppered centrifuge tube at 25·0 ± 0·1°. After centrifugation the lower phase is separated by a capillary siphon.

The concentration of the ion-pair in the organic phase $[OX]_{org}$ is determined by photometry, compounds with low ultraviolet absorbance being determined by the Bromothymol Blue[14] or the hexanitrodiphenylamine method,[15] and highly-absorbing compounds by direct photometric measurements. The extraction constant, E_{QX}, is calculated from

$$E_{QX} = [QX]_{org}(C_X - [QX]_{org})^{-1}(C_Q - [QX]_{org})^{-1} \tag{23}$$

Titration method. A known amount of the organic ammonium ion is titrated with lauryl sulphate as described under titration procedure. As discussed above, the constant will be determined with the highest precision in the interval $C_X = (0{\cdot}25–0{\cdot}75)C_Q$, *i.e.*, by titration approximately to the "half-titre point". This criterion is fulfilled by compounds with extraction constants of the order $10^{3\cdot5}$–$10^{6\cdot5}$, when they are titrated with Methyl Yellow as indicator at a suitable pH in the range 3·2–1·2.

Data sufficient for calculation of a constant will be obtained by one or at most two titrations if the following working order is used.

1. Titrate at pH 2·2 with $C_Q = 10^{-3\cdot2}M$. Calculate the quotient C_X/C_Q. If the quotient is about 0·25–0·75, no further titration is necessary.
2. *a.* If the quotient is <0·25 repeat the titration at pH 3·2 with $C_Q = 10^{-2\cdot2}M$.
2. *b.* If the quotient is >0·75 repeat the titration at pH 1·2 with $C_Q = 10^{-4\cdot2}M$.

The extraction constant is calculated by equation (2). $[X^-]$ at the end-point is obtained by using equation (26).

Determination of indicator properties of Methyl Yellow

Absorbance measurements in $10^{-5}M$ chloroform solutions showed that Methyl Yellow (basic form) has an absorbance maximum at 410 nm while its ion-pair with lauryl sulphate has absorbance maxima at 522 and 545 nm.

The molar absorptivity of the ion-pair was determined by the following procedure. Known solutions of Methyl Yellow in chloroform were equilibrated with $10^{-3}M$ solutions of sodium lauryl sulphate (pH 1·80–2·40). The absorbance of the organic phases was determined at the absorbance maxima of the ion-pair (522 and 545 nm) and the base (410 nm). The measurements were made in the presence of small amounts of the aqueous phase in order to prevent equilibrium displacements.

The molar absorptivity was calculated by means of the equation

$$\varepsilon^{545} = A^{545}\Big/\left(C_{\text{In,org}} - \frac{A^{410}}{\varepsilon^{410}}\right) \tag{24}$$

$C_{\text{In,org}}$ is the total concentration of Methyl Yellow in the organic phase and A^{545} and A^{410} the measured absorbances. The absorbance of the base at above 520 nm and of the ion-pair below 420 nm was negligible.

The determination gave: Methyl Yellow (base), $\varepsilon^{410} = 2{\cdot}79 \times 10^4$ l.mole^{-1}.cm^{-1}; Methyl Yellow–lauryl sulphate (ion-pair), $\varepsilon^{522} = 4{\cdot}96 \times 10^4$, $\varepsilon^{545} = 4{\cdot}95 \times 10^4$.

The equilibrium constant of the reaction between lauryl sulphate and Methyl Yellow in a two-phase system [E'_{In}, equation (4)] was determined by the batch extraction method at pH 1·2–2·5. The concentration of the ion-pair was determined at 545 nm, and the concentration of the base at 410 nm. $[X^-]$ was obtained as the difference between C_X and $[\text{HInX}]_{org}$.

The determination gave $E'_{\text{In}} = 10^{5\cdot70}$.

RESULTS AND DISCUSSION

End-point indication

Methyl Yellow has several properties that make it suitable as indicator for ion-pair extraction titrations with lauryl sulphate. It has a high molar absorptivity both as base and as ion-pair with lauryl sulphate, and the two forms have distinctly different absorbance maxima. It is, furthermore, possible by pH variation to shift the colour change interval of the indicator to different $[X^-]$. The relation between the indicator end-point, given by the quotient $[\text{HInX}]_{org}/[\text{In}]_{org}$, and the lauryl sulphate concentration at the end-point, $[X^-]_{end}$, is given in logarithmic form in equation (25)[(cf. equation (4)].

$$pX_{end} = \log E'_{\text{In}} - pH - \log[\text{HInX}]_{org}/[\text{In}]_{org} \tag{25}$$

The equation shows that a decrease in the quotient $[\text{HInX}]_{org}/[\text{In}]_{org}$ will increase the width of the pX interval that can be achieved by pH variation.

It is advisable to use as low an end-point quotient as possible, since the broadening of the end-point interval will give opportunities to improve the titration conditions. Studies showed that even such a low end-point quotient as $10^{-1.45}$, corresponding to the first perceptible colour change of the indicator, could be used to indicate the end-point with good precision. By substitution of this end-point quotient and $\log E'_{\text{In}} = 5.70$ into equation (25) the following expression for pX_{end} is obtained:

$$\text{pX}_{\text{end}} = 7.15 - \text{pH} \tag{26}$$

By pH variation it is possible to confine the indicator end-point to the interval $\text{pX}_{\text{end}} =$ 3–6·1. The upper limit corresponds to pH = 1·0. Titrations at pH < 1 cannot be recommended owing to the difficulties in determining pH in this range with sufficient precision. The ionic strength will also be higher than 0·1, which may necessitate a special determination of the extraction constant. The lower limit of the pX_{end} interval is mainly due to the tendency of lauryl sulphate to give emulsions in the aqueous phase when pX < 3.

The precision in the determination of the end-point quotient $[\text{HInX}]_{\text{org}}/[\text{In}]_{\text{org}}$ has a considerable influence on the titration error and photometric end-point detection is recommended. An illustration of the precision that can be obtained by use of an EEL titrator to measure the absorbance of the ion-pair (HInX) is given in the following example. A series of samples was titrated according to the titration procedure to an end-point absorbance of 0·12 ± 0·01. Determination of $[\text{HInX}]_{\text{org}}$ and $[\text{In}]_{\text{org}}$ in the titrated samples by a Zeiss photometer gave the following interval for the end-point quotient:

$$0.030 < \frac{[\text{HInX}]_{\text{org}}}{[\text{In}]_{\text{org}}} < 0.040 \tag{27}$$

Substitution of (27) in (25) gives

$$\text{pX}_{\text{end}} = \log E'_{\text{In}} - \text{pH} + 1.45 \pm 0.05 \tag{28}$$

Table 2. Extraction constants of n-alkylammonium ions (determination by the titration method).
Conditions as given in Table 4 except for constants within brackets where a lower C_Q had to be used, owing to the formation of emulsions. Titrant $10^{-3.0}M$ lauryl sulphate

Cation	*pH*	$-\log C_Q$	$\log E_{QX}$
Hexylamine	3·05	3·1	(3·7)
Octylamine	1·97	3·2	5·2
Decylamine	1·07	3·3	6·9
Dipropylamine	2·51	3·2	(4·2)
Dibutylamine	1·92	3·2	5·7
Triethylamine	1·95	3·1	4·6
Tripropylamine	1·07	3·3	6·6
Tetraethylammonium	3·02	3·1	(3·4)*
Tetrapropylammonium	1·74	2·2‡	5·5†
Methyltriethylammonium	3·05	3·1	(3·1)
Methyltripropylammonium	2·40	3·2	4·9
Nonyltrimethylammonium	1·07	3·2	6·6

* 3·41 by batch extraction.
† 5·55 by batch extraction.
‡ $10^{-2.0}M$ titrant.

Table 3. Extraction constants of ammonium ions used as drugs (determination by the titration method).
Conditions as given in Table 4. Titrant $10^{-2.0}M$ lauryl sulphate

Cation	Method	pH	$-\log C_Q$	$\log E_{QX}$
Atropine	batch extr.	2·4	2·3	5·34
	titration	1·76	2·1	5·4
Codeine	titration	1·79	2·1	5·4
Ephedrine	titration	3·15	2·3	3·8
Lidocaine	titration	1·68	2·1	5·4
Procaine	titration	1·94	2·1	4·7
N,*N*-Dimethylprotriptyline	batch extr.	2·4	3·3-5·6	7·42
N-Hydroxyethylpromethazine	batch extr.	2·4	3·1–3·4	6·80
N-Methylpromethazine	batch extr.	2·4	2·9–3·7	7·01
N-Methylscopolamine	batch extr.	2·4	3·2–4·2	3·60

which shows that the uncertainty in the photometric end-point corresponds to 0·05 pX units.

Extraction constants

It is usually much simpler to determine extraction constants by titration than by batch extraction, but the use of the titration method is limited by the fact that the end-point must be located in the interval pX = 4–6, owing to the properties of the indicator.

The extraction constants of lauryl sulphate ion-pairs of a number of organic ammonium compounds are given in Tables 2 and 3. Most of the constants were determined by the titration method. The batch extraction method was used for some of the compounds in Table 3, the constants for which were too low or too high to be determined with sufficient precision by titration. Controls showed that the two methods give results in good agreement.

Recommended conditions for extraction constant determinations by titration are given in Table 4. Extraction constants of the order of $10^{3.5}$–$10^{6.5}$ can be determined with an error of ≤ 0.1 log units when $\Delta pX = \pm 0.05$, as discussed in the theory section.

Table 4. Extraction-constant determination by titration

pH	pX^*_{end}	$\log C_Q$	C_X/C_Q	$\log E_{QX}$
3·2	4·0	> -2.2	<0·25	<3·5
			0·25–0·75	3·5–4·5
2·2	5·0	> -3.2	0·25–0·75	4·5–5·5
1·2	6·0	> -4.2	0·25–0·75	5·5–6·5
			>0·75	>6·5

* pX_{end} Calculated by equation (26).

Extraction constants larger than $10^{6.5}$ cannot be determined with good precision by the titration method. Good estimations of the constant for n-alkylammonium ions can, however, be based on the data in Table 2 and the well-known fact that the addition of one CH_2 group will increase the constant by 0·5–0·6 log units (*cf.* ref. 13).

Lauryl sulphate ion-pairs with alkylammonium ions with different degrees of substitution show extraction-constant differences that agree well with earlier observations made with picrate and Bromothymol Blue as anions.[13]

No extraction of lauryl sulphate as the acid or sodium salt was observed.

Titration conditions

$[X^-]$ at the equivalence point of a titration depends on the extraction constant and the concentration of the sample, while $[X^-]$ at the indicator end-point, depends on pH. The adaptation of $[X^-]_{end}$ to $[X^-]_{eq}$ which is made by adapting the pH of the solution to the extraction constant and the concentration of the sample, is of fundamental importance for the precision of the titration.

When the extraction constant is high, good precision can be obtained within rather wide limits of both sample concentration and pH. The choice of conditions can be based on Fig. 1. The construction is based on the conditions

$$[Q^+]/C_Q < F_{rel}; \quad [X^-]/C_Q < F_{rel}; \quad \log C_Q < -2{\cdot}0; \quad pH > 1{\cdot}0$$

and negligible errors in E_{QX} and the end-point detection. Figure 1 shows that the concentration ranges that are suitable for titration increase with decreasing pH. It also shows that samples with $C_Q < 10^{-4{\cdot}2}M$ cannot be titrated with acceptable precision. Titrations at pH < 1 are not recommended as discussed earlier.

The discussion above has dealt only with titrations with photometric end-point detection. In visual titrations, the error in the end-point is about 5 times larger, *i.e.*, 0·25 pX units. Computations made by using equation (12) show that only compounds with $E_{QX} > 10^7$–10^8 can be titrated with acceptable precision when the error in the end-point determination is of this order.

Applications

The titration procedure was tested on a number of organic ammonium ions with different degrees of substitution. The main part of the work was concentrated on compounds with $\log E_{QX} < 6{\cdot}5$, since the discussion above has shown that substances with higher extraction constants can be titrated with good precision even if the conditions are not optimized.

Table 5. Titration of organic ammonium ions

Cation	*log* E_{QX}	$-$ *log* C_Q	*pH*	Yield,%	C.V.
Decylamine	6·9	3·32	1·99	101·3	0·4
Dibutylamine	5·7	2·32	2·95	98·8	0·2
Dihexylamine	7·7*	3·28	1·60	100·9	0·8
Tripropylamine	6·6	2·49	2·57	99·2	0·4
Tributylamine	8·6*	2·49	1·57	99·1	0·4
Tetrapropylammonium	5·5	2·32	3·00	100·0	1·1
Tetrabutylammonium	7·6*	3·30	1·67	100·2	0·3
Nonyltrimethylammonium	6·6	3·32	2·17	100·8	0·5
Atropine	5·4	2·32	3·15	101·5	1·3
Codeine	5·3	2·32	3·14	102·6	1·6
Lidocaine	5·4	2·32	3·13	100·5	0·6
N,N-Dimethylprotriptyline	7·4	3·06	1·80	99·8	0·4
N-Hydroxyethylpromethazine	6·8	3·03	2·20	99·0	0·6
N-Methylpromethazine	7·0	3·09	2·11	98·1	0·6

* Estimated (*cf.* ref. 13).

Table 6. Selectivity of the titration method.

Sample (A^+)	Additive (B^+)	$log\ E_{AX}$	$log\ E_{BX}$	$-log\ C_A$	$-\log C_B$	pH	Yield of A^+	C.V.
Decylamine	Hexylamine	6·9	3·7	3·32	2·57	1·50	100·3	0·7
Dihexylamine	Hexylamine	7·7	3·7	3·30	2·52	1·07	99·7	0·2
Tetrabutylammonium	Tetraethylammonium	7·6	3·4	3·00	2·07	1·07	100·3	0·3
Nonyltrimethylammonium	Methyltriethylammonium	6·6	3·1	3·24	1·98	1·87	101·8	1·1

The results of the studies are given in Table 5. It comprises ammonium ions from primary to quaternary, containing straight-chain alkyl substituents, as well as some ammonium compounds of pharmaceutical interest. The substances were titrated under conditions as close to the optimum as possible [*c.f.* equation (22)].

The precision, given in the table as the coefficient of variation (C.V.), is in agreement with the theoretical calculations.

Long-chain alkylamines have a tendency to give emulsions during the titration, which will spoil the observation of the end-point. The disturbance by emulsions decreases with decreasing concentrations, but can appear even with $10^{-3.3}M$ samples. The titrations in such cases can be done at a low stirring speed. Short-chain alkylammonium ions have been titrated without disturbance even at concentrations of $10^{-2}M$.

Selectivity

The lauryl sulphate titration is particularly suited for quaternary ammonium ions which are devoid of other good methods for titrimetric determination. However, it may also find use in titrimetric determination of aliphatic amines, as an alternative to the acidimetric method, since the two methods have quite different selectivity. The selectivity of the acidimetric method is based on differences in base strength, and it will not give discrimination between aliphatic amines which have very similar protonation constants. The two-phase titration with lauryl sulphate has a selectivity based on differences in partition properties, which are due to the number of alkyl and aryl carbon atoms as well as the number and character of the hydrophilic groups.[8,13,16]

The influence of an additive B^+ on the titration of A^+ can be demonstrated by use of equation (14). Substitution of $F_{\mathrm{rel}} = 0{\cdot}01$ and $\Delta \mathrm{pX} = 0{\cdot}10$ gives

$$\frac{E_{\mathrm{AX}}C_{\mathrm{A}}}{E_{\mathrm{BX}}C_{\mathrm{B}}} = 10^{3\cdot4} \qquad (29)$$

This equation shows that $(E_{\mathrm{AX}}C_{\mathrm{A}})$ must be at least 2500 times larger than $(E_{\mathrm{BX}}C_{\mathrm{B}})$ in order to keep the titration error within 1%.

The validity of these calculations is illustrated in Table 6 for titration of some organic ammonium ions in the presence of cations with lower extraction constants. The experiments were performed close to the conditions given by equations (14), (25) and (26), and the results lie well within the expected limits for the maximum relative error.

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Zusammenfassung—Die Bedingungen zur Bestimmung quartärer Ammoniumverbindungen und Amine durch Zweiphasentitration wurden berechnet auf Grund von Extraktionskonstanten der Ionenpaare, die sich aus Titriermittel (Laurylsulfat), Indikator (Methylgelb) und Probe bilden. Methoden zur Bestimmung von Extraktionskonstanten werden angegeben. Die Genauigkeit und Selektivität der Methode werden an Titrationen von Ammoniumionen verschiedener Struktur und verschiedenen Substitutionsgrades veranschaulicht. Die Ergebnisse sind in Einklang mit den theoretischen Berechnungen.

Résumé—On a calculé les conditions de dosage de composés ammoniums quaternaires et d'amines par titrage à deux phases sur la base des constantes d'extraction pour les paires d'ions entre l'agent de titrage (sulfate de lauryle), l'indicateur (Jaune de Méthyle) et l'échantillon. On présente les méthodes de détermination des constantes d'extraction. La précision et la sélectivité de la méthode sont démonstrées par des titrages d'ions ammonium de différentes structures et degrés de substitution. Les résultats sont en accord avec les calculs théoriques.

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CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF NOBLE METALS IN MATTE-LEACH RESIDUES

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Summary—The practical application of various chromatographic methods to the analysis of residues obtained from the leaching of copper–nickel mattes is described. The procedure involves the separation of gold on a TBP-treated Porasil column, the separation of base metals by cation-exchange. the separation of tellurium from platinum-group metals, and the separation of the non-volatile platinum-group metals on one cellulose column.

Most metallurgical processes for the recovery of the noble metals involve their concentration by a smelting procedure to produce a matte, which consists essentially of copper, nickel, iron and sulphur, and which has a noble-metal content of between 1000 and 3000 ppm. Further concentration of the matte by various leaching processes results in a matte-leach residue having a noble-metal content of > 1%. Because of the economic value of these concentrates, the accurate determination of their noble-metal content is important.

Relatively fast methods for the analysis of matte-leach residues have been developed at the National Institute for Metallurgy, South Africa, and are used on a routine basis. These methods involve the dissolution of a sample in acid under pressure or by fusion with sodium peroxide, and atomic-absorption spectrophotometry (AAS).

However, it was felt that an alternative method independent of AAS would be useful as an umpire method and also when, because of the complexity of a sample, direct AAS procedures might give doubtful results. In view of the findings of a recent investigation[1] it was decided to include the chromatographic separation of gold, rhodium and iridium so that all the noble metals could be present in a sufficiently pure state to warrant their gravimetric determination.

It was felt that this approach would result not only in a method independent of AAS but also in an assessment of the accuracy and precision of gravimetric methods, which are still favoured by some refineries, after separations considerably more involved than those proposed in this paper, in the belief that they are much more accurate than direct AAS measurement.

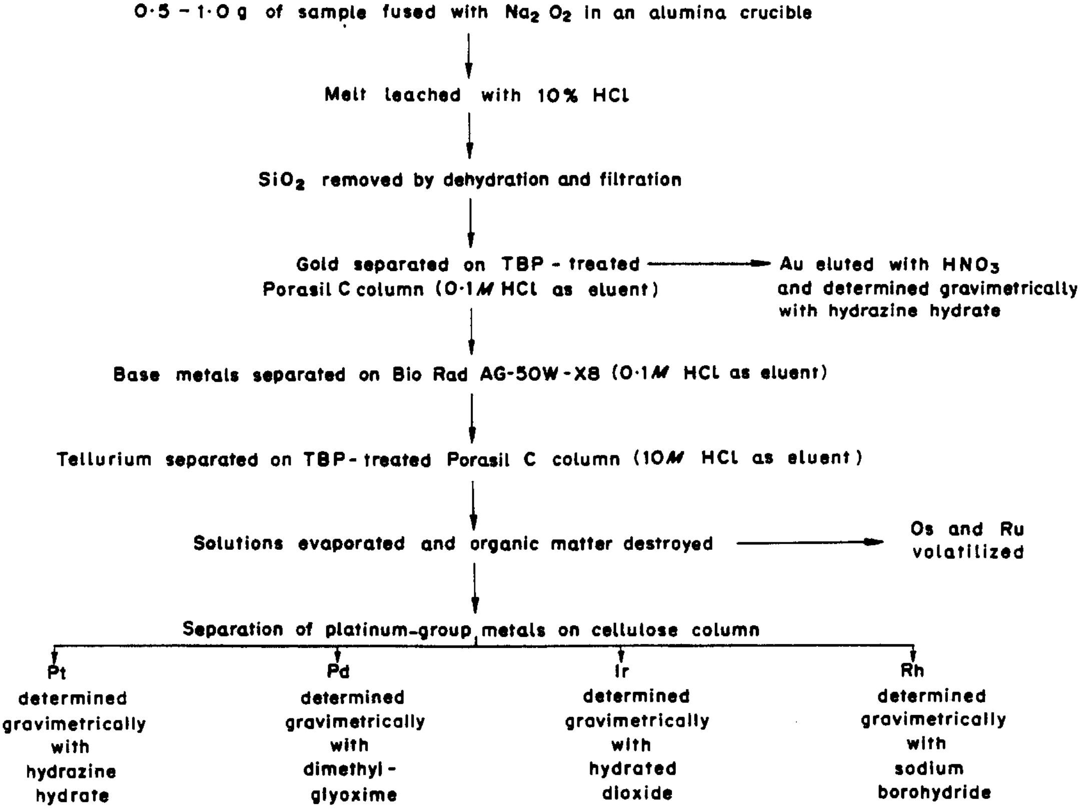
EXPERIMENTAL

Apparatus and reagents

Glass columns with sintered-glass discs or perforated porcelain discs at the bottom were used for the chromatographic separations. The cation-exchange resin Bio Rad AG-50W-X8 was obtained from Bio Rad Laboratories, Richmond. California. and the support material. Porasil C. from Waters Associates, Inc., Framingham, Mass., U.S.A. Whatman's fibrous cellulose CF 11 was used in the preparation of the columns. Platinum, palladium, rhodium, iridium and gold as metals were supplied by Engelhard Ind., U.S.A. The preparation of standard solutions of gold, platinum and palladium has been described elsewhere.[2] Rhodium and iridium solutions were prepared by dissolution of the metal in a sealed tube by chlorination.[3]

Procedures

The chemistry involved in the separation of the non-volatile platinum-group metals on a cellulose column, as well as column parameters and elution characteristics, have been discussed previously.[1] In the following sections an account is given of the various stages of the proposed procedure for application to the analysis of matte-leach residues. The method[4] is summarized in Scheme 1.



Scheme 1. Separation and gravimetric determination of the noble metals.

Fusion of sample. Zirconium crucibles were previously used for fusions with sodium peroxide.[1] However, since any zirconium dissolved during fusion tends to hydrolyse at the low acid concentrations used in the proposed procedure, particularly when left standing, it was decided to use alumina crucibles instead. The alumina crucibles were found to be resistant to sodium peroxide attack, and complete dissolution of a sample was readily obtained. Before leaching, the crucibles were allowed to cool to avoid breakage. Any aluminium dissolved during fusion was conveniently removed during the separation of the base metals on the cation-exchange column.

Removal of silica. Silica, usually present in matte-leach residues in amounts up to 40%, has to be removed at an early stage in the analysis, because it would otherwise cause difficulties in the analytical procedure. Attempts were made to volatilize the silica by treatment of the sample with hydrofluoric acid in the alumina crucible before fusion with sodium peroxide. However, this treatment resulted in unsatisfactory fusion, and leaching produced an insoluble precipitate consisting mainly of aluminium and iron.

It was therefore decided to remove the silica by the conventional procedure of dehydration and filtration. It was, however, observed that, depending on the type of sample, the silica precipitate was not always free from noble metals and had to be treated for their recovery.

Separation of gold. Gold was initially separated by precipitation with sodium sulphite and determined gravimetrically,[1] but this method was considered tedious and lacking in precision. Greater advantages were expected if the gold could be separated chromatographically from all the other metals present in a sample and then determined by a suitable method. The separation of gold on the ion-exchange resin Amberlite XAD-7 or on a TBP-treated Porasil C column was considered.

Separation of gold on XAD-7. The separation of gold from various other metals Amberlite XAD-7 has been described by Fritz *et al.*,[5] who showed that gold is strongly adsorbed from 1*M* hydrochloric acid, whereas base metals, platinum, palladium, and ruthenium were not adsorbed. Gold was readily recovered by elution with a mixture of acetone and hydrochloric acid.

We conducted further tests with respect to the behaviour of rhodium and iridium, which had not been investigated by Fritz. The results of these tests (Table 1) showed that complete separation of gold from base metals and platinum-group metals was obtained and that recoveries were quantitative.

Separation of gold on TBP-treated Porasil C. Various authors[6–8] have described the separation of microgram amounts of gold by reversed-phase extraction chromatography with TBP as the stationary phase and a mineral acid as the eluent. It has been shown that up to 20 mg of gold per g of TBP-treated Porasil C can be separated from platinum-group metals and base metals when these are eluted with 0·1*M* hydrochloric acid.[8] A few further tests with mixtures of noble metals and base metals likely to be present in matte-leach residues confirmed that complete separation is obtained on a TBP-treated Porasil C column 3 cm long (1·5 g) and that the recovery of the noble metals is quantitative, as shown in Table 1. The gold can be easily eluted from the column with 14*M* nitric acid.

It was thus ascertained that gold can be separated quantitatively on either XAD-7 or on TBP-treated Porasil C. However, in the analysis of matte-leach residues, it became apparent that a smaller amount of acid was needed to wash the TBP-treated Porasil C column free from foreign metals, and that the concentration of the eluate (0·1*M* hydrochloric acid) allowed direct transfer of the sample solution to the cation-exchange column for the separation of base metals, whereas if the gold had been separated on XAD-7 (1*M* hydrochloric acid), an evaporation step would have been necessary. It was therefore decided that the TBP-treated Porasil C column should be used for the separation of gold in the analytical scheme for matte-leach residues.

Behaviour of elements other than noble metals

Silica is removed by dehydration and filtration. Dissolution of the residue, obtained after evaporation of the filtrate, in 0·1*M* hydrochloric acid and filtration removed residual silica and probably Ag, Bi and Sb, which can precipitate at very low acid concentration. From published distribution coefficients[9] it can be assumed that the following species are retained on the cation-exchange column from 0·1*M* hydrochloric acid: Al(III), Zr(IV), Th(IV), Ba(II), Ga(II), Fe(II), Fe(III), Ni(II), Co(II), Mg(II), Mn(II), Cu(II), Zn(II), Be(II), Ti(IV), Sn(IV), Cd(II).

Cr(III) and large amounts of Na^+ were found to be only partially retained. According to distribution coefficients published by Ishimori,[10] V, Mo, Sb, Ta, W and As, if present in 10*M* hydrochloric acid, would be separated from the platinum-group metals together with Te on a TBP-treated Porasil C column. It can be further assumed that, in addition to Ru and Os, elements such as Se and Hg would be partially or completely lost during the evaporation steps or during wet oxidation with perchloric acid.[11,12]

In the analysis of matte-leach residues, only chromium was found to accompany the platinum-group metals through the entire procedure. Since chromium is not extractable into TBP, it was retained on the cellulose column and eluted together with rhodium. However, when rhodium was precipitated as the metal by reduction with sodium borohydride, chromium remained in solution and did not interfere in the gravimetric determination of rhodium.

Table 1. Separation of gold from platinum-group metals on XAD-7 or TBP-treated Porasil C

Method		Au Added, *mg*	Au Found, *mg*	Pt Added, *mg*	Pt Found, *mg*	Pd Added, *mg*	Pd Found, *mg*	Rh Added, *mg*	Rh Found, *mg*	Ir Added, *mg*	Ir Found, *mg*
XAD-7	Base metals absent	9·7	9·69	53·6	53·4	25·2	25·4	9·92	9·92	2·52	2·52
	Base metals present	10·0	10·2	50·3	—	30·3	—	10·0	—	2·5	—
TBP-Porasil	Base metals absent	10·0	10·0	53·6	53·6	25·2	26·2	9·92	9·92	2·52	2·80
	Base metals present	10·0	10·2	50·3	—	30·3	—	10·0	—	2·5	—

— Not determined.

Separation of tellurium

Since tellurium, usually present in a matte-leach residue, is not retained on the cation-exchange column under the experimental conditions described, it was considered a possible interference in the gravimetric determination of rhodium and iridium. Moreover, it had been observed previously[13] that tellurium can seriously interfere in the determination of platinum if the ratio of tellurium to platinum exceeds 1:45.

It was therefore decided to investigate the separation of tellurium from platinum-group metals by reversed-phase extraction chromatography with tri-n-butyl phosphate (TBP) as the stationary phase and hydrochloric acid as the eluent. The system TBP–HCl has been widely investigated with respect to the behaviour of the noble metals, and of tellurium and selenium.[14–17] Although the separation of tellurium and platinum-group metals had not been attempted, it appeared from published distribution coefficients[8,10] that it would be possible to separate them at hydrochloric acid concentrations of more than 10*M*. To confirm this prediction, the behaviour of tellurium and the platinum-group metals on a TBP-treated Porasil C column with 10*M* hydrochloric acid as the eluent was investigated.

Sodium chlorate was added to the sample solutions in a few experiments to show whether the presence of an oxidizing agent would affect the separation. On columns 5 cm long and 1·2 cm wide (approximately 3 g of TBP-treated Porasil), tellurium was found to be retained as a narrow yellow band, while the platinum-group metals were eluted with approximately 50 ml of 10*M* hydrochloric acid. The results in Table 2 show that, within the limits of experimental error for the methods of determination, complete separation was obtained. The platinum-group metals were determined by AAS, and tellurium, after elution with hydrochloric acid of concentration less than 2*M*, was determined gravimetrically by precipitation with hydrazine hydrate.

It can also be seen in Table 2 that the presence of sodium chlorate did not affect the separation and that the recoveries were quantitative.

Separation of platinum, palladium, iridium and rhodium on one column

It has been shown previously[1] that rhodium and iridium are not separated on a cellulose column when eluted with TBP. In the present investigation, the separation scheme was extended to include the separation of the two metals to facilitate their respective gravimetric determination (see Scheme 2).

Payne[18] has described a semi-chromatographic separation of iridium from rhodium by first extracting the iridium with an oxidizing solution (a mixture of methyl isobutylketone, hydrochloric acid and sodium chlorate) and then passing the organic extracts containing the iridium through a cellulose column. An attempt was made to modify Payne's method by oxidizing the iridium directly on the column to its mobile quadrivalent state and to elute it with TBP–toluene mixture (rather than with methyl isobutylketone as in Payne's method) from the rhodium. After elution of the platinum and palladium, 10–15 ml of an oxidizing solution consisting of chlorine dissolved in TBP and toluene was allowed to penetrate the column bed. After 5 min, elution was continued with the TBP–toluene without the oxidant. Under these conditions, the brown, oxidized iridium band moved slightly ahead of a very broad yellow chlorine band, while rhodium remained unaffected in the upper part of the column. Rhodium was next eluted with water, and the iridium was stripped from the organic eluate with water. That the proposed procedure is quantitative can be seen from the mean amounts recovered when twelve synthetically prepared sample solutions containing gold, platinum, palladium, rhodium and iridium were analysed (Table 5).

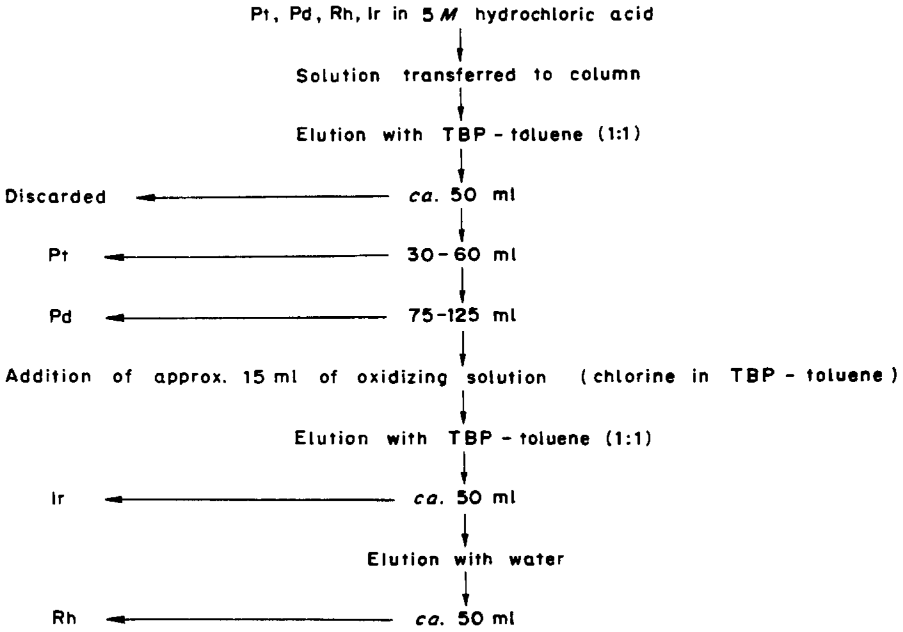
Determination of the noble metals

The precipitation of platinum and palladium with hydrazine hydrate and dimethylglyoxime respectively has been described previously.[13] The separation of rhodium from small amounts of iridium by the selective reduction of the former with sodium borohydride has been reported by McKay.[19] Since, however, the subsequent precipitation of iridium proved to be difficult, the two metals were first separated chromatographically as described earlier. Rhodium was then precipitated with sodium borohydride according to McKay's method, and iridium was precipitated as the hydrated dioxide as described by Beamish.[20] An indication of the accuracy obtainable for comparatively small amounts of rhodium and iridium is given in Table 3.

Table 2. Separation of tellurium from platinum group metals

$NaClO_3$ added, *mg*	Te Added, *mg*	Te Found, *mg*	Pt Added, *mg*	Pt Found, *mg*	Pd Added, *mg*	Pd Found, *mg*	Rh Added, *mg*	Rh Found, *mg*	Ir Added, *mg*	Ir Found, *mg*
50	1·0	1·2	9·95	10·02	—	—	—	—	—	—
50	5·0	4·8	9·95	9·92	5·0	5·08	3·60	3·55	1·0	1·1
50	5·0	4·9	9·95	10·02	5·0	5·12	—	—	—	—
Nil	5·0	5·1	9·95	9·90	5·0	5·05	—	—	—	—

—Not determined.



Scheme 2. Separation of platinum-group metals on cellulose.

Gold in the presence of a small amount of nitric acid was successfully precipitated with hydrazine hydrate, and some of the results are shown in Table 4.

Provided that in the determination of rhodium, iridium and gold, use is made of small porcelain crucibles having porous bottoms and a constant weight under the experimental conditions, relatively accurate results can be obtained for amounts of metal larger than 2 mg.

RESULTS

The precision obtainable with the proposed analytical procedure was tested by the analysis of twelve synthetically prepared samples containing platinum, palladium, rhodium, iridium, and gold in the amounts shown in Table 5. The results obtained for rhodium, iridium and gold show that the difference between the mean amounts recovered and the amounts added is well within the expected precision of the analytical procedure. Platinum and palladium were not determined in this analysis.

Table 3. Accuracy obtainable with mg amounts of Rh and Ir

	Rhodium			Iridium	
Added, *mg*	Found, *mg*	Difference, *mg*	Added, *mg*	Found, *mg*	Difference, *mg*
1·0	1·25	+0·25	1·0	1·24	+0·24
1·0	1·24	+0·24	1·0	1·32	+0·32
2·0	2·10	+0·10	2·0	2·08	+0·08
2·0	2·14	+0·14	2·0	1·99	−0·01
2·0	2·10	+0·10	2·0	2·04	+0·04
3·0	3·08	+0·08	3·0	3·11	+0·11
3·0	2·96	−0·04	3·0	3·05	+0·05

Table 4. Gravimetric determination of gold with hydrazine hydrate

Au added, *mg*	Au found, *mg*	Difference, *mg*
6·06	6·08	+0·02
7·07	7·14	+0·07
8·08	8·13	+0·05
10·10	10·09	−0·01

Table 5. Analysis of synthetic samples

Element	Amount added, *mg*	Mean amount recovered, *mg*	Difference, *mg*	Coeff. of variation, %	
Gold	10·10	10·09	−0·01	1·2	(1·0)
Platinum	49·55	49·20	−0·35	1·3	
Palladium	54·56	54·21	−0·35	0·5	
Rhodium	4·0	4·04	+0·04	1·47	(0·9)
Iridium	2·0	2·05	+0·05	2·49	(2·8)

Table 6. The determination of noble metals in matte-leach residues

Sample No.		Au, %	Pt, %	Pd, %	Rh, %	Ir, %
	Proposed procedure	1·47	$18{\cdot}4_8$	7·84	0·86	0·29
1	AAS	1·35	$18{\cdot}1_8$	8·06	0·81	0·19
	Proposed procedure	1·52	$18{\cdot}1_0$	7·67	0·85	0·27
2	AAS	1·28	$18{\cdot}2_6$	7·82	0·82	0·19
	Independent lab.	1·51	$18{\cdot}6_4$	7·91	0·87	0·23
	Proposed procedure	1·10	$14{\cdot}0_6$	5·73	0·61	0·21
3	AAS	1·16	$14{\cdot}2_4$	5·97	0·61	0·18
	Independent lab.	1·15	$14{\cdot}5_0$	5·89	0·62	0·20

The coefficients of variation given in brackets in Table 5 were obtained previously[8] by the proposed procedure, but with an atomic-absorption finish, instead of gravimetry. The difference in the coefficients of variation for rhodium is probably due to AAS analysis being applied to a rhodium level of 10 mg, instead of 4 mg.

The proposed procedure was also applied to the analysis of samples of matte-leach residues. The results obtained are shown in Table 6 and can be compared with those obtained when the noble metals were determined in the presence of one another by AAS, and with results obtained by an independent laboratory.

CONCLUSION

It has been shown that the noble metals can be separated by a simple chromatographic procedure in a sufficiently pure state to permit gravimetric determination with a relatively high degree of accuracy and precision. However, because of the absence of any interfering elements after the chromatographic separation, the same degree of accuracy and precision can be obtained when the metals are subsequently determined by AAS. Moreover, this work has shown that, while accurate results have been obtained with the proposed procedure, they are not outstandingly more accurate than those obtained by the much faster method of direct AAS measurement.

The proposed procedure, nevertheless, is very useful as an umpire method when an analysis independent of AAS is required, and also when, because of the complexity of a sample, or because of unsuspected interferences, the more direct AAS procedure may give doubtful results.

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Zusammenfassung—Die praktische Anwendung verschiedener chromatographischer Methoden auf die Analyse von Rückständen aus der Auslaugung von Kupfer–Nickel–Stein wird beschrieben. Gold wird dabei an einer TBP-behandelten Porasilsäule abgetrennt, die unedlen Metalle durch Kationenaustausch; Tellur wird von den Metallen der Platingruppe und die nichtflüchtigen Metalle der Platingruppe werden voneinander auf einer Cellulosesäule getrennt.

Résumé—On décrit l'application pratique de diverses méthodes chromatographiques à l'analyse de résidus obtenus à partir de l'épuisement de mattes cuivre–nickel. La technique comprend la séparation de l'or sur une colonne de Porasil traitée au TBP, la séparation des métaux basiques par échange de cations, la séparation du tellurium des métaux du groupe du platine, et la séparation des métaux du groupe du platine non volatils sur une colonne de cellulose.

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SEPARATION OF MONOSUBSTITUTED PHENOLS BY GAS–LIQUID CHROMATOGRAPHY

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Summary—The factors influencing the separation of monosubstituted phenols on silicone oil, poly(ethylene glycol) (1500), Apiezon L + Bentone 34, squalane, Versamide and diethylhexyl sebacate are discussed. Specific retention volumes, height equivalent to a theoretical plate and thermodynamic quantities are reported. Diethylhexyl sebacate and Versamide are selective for quantitative separation of all the isomers studied.

Methods of separation and characterization of phenols, chlorophenols, and cresols have already been reported.[1–6] Smith and Norman[7] suggested gas chromatographic conditions for the analysis of seven groups of isomeric monosubstituted phenols. They discussed the effect of the *ortho*-substituent on retention times, but nothing was proposed for the *meta* and *para* isomers. Hrivnak *et al.*[8] studied the gas chromatographic behaviour of nitrophenols on polyester and silicone columns. Ress and Higginbotham[9] demonstrated the use of a variety of polar substrates containing phosphoric acid for the electron-capture gas-chromatographic analysis of free chlorophenols.

Most of the work reported did not discuss the interactions involved, but a discussion of the efficiencies of some systems was given. However, quantitative separations for the isomers dealt with in this study have not previously been reported.

EXPERIMENTAL

Apparatus

A Perkin–Elmer Model 451 Fractometer equipped with a thermistor-type thermal conductivity detector was used. The recorder was a 2·5 mV Honeywell Brown Electronic Unit. Nitrogen was used as the carrier gas. The average column temperature was controlled to within ±0·2°.

Columns

These were obtained from Perkin–Elmer, U.K., in the form of stainless-steel tubing (2 m long and 6 mm o.d.) bent into a U-shape and covered with asbestos sleeves (to ensure uniform heating). The packing specifications of all the columns used and the chemical compositions of the liquid phases are shown in Table 1.

Materials

Pure *o*- and *m*-chlorophenol, *o*- and *p*-bromophenol, *o*-iodophenol, *o*-, *m*- and *p*-cresols and methoxyphenols were obtained from B.D.H. Ltd. Pure *o*-, *m*- and *p*-fluorophenol, *m*-bromophenol and *p*-iodophenol were obtained from Hopkin and Williams Ltd.

Sampling

Equal weights of the isomers were blended in a 3 ml cylindrical Pyrex glass cell. Sample sizes ranged from 0·6 to 2 μl for liquid isomers and from 1 to 4 μl of 10% w/w solution in acetone for solid isomers. The injections were done with a 10 μl Hamilton syringe.

Table 1. Packing specifications of the columns*

Stationary phase	Molecular weight	Density at 20°, *g/ml*	Loading, % *w/w*	Weight of liquid phase, *g*		Operating temp., °*C*	Solid support
Poly(ethyleneglycol), (PEG)	$1{\cdot}5 \times 10^3$	1·152	20	3·40		225	Chromosorb P
Silicone oil MS 200/50 (SO)	—	0·971	20	3·40	60–80	200	Chromosorb P
Apiezon L + Bentone 34 (APL + 34)	—	—	10 + 10	1·814	80–100	250	Chromosorb W
2,6,10,15,19,23-Hexamethyltetracosane (squalane) (SQ)	422·5	0·829	20	3·40	60–80	160	Chromosorb P
Versamide (VS)	—	—	2	0·191	80–100	250	Chromosorb W AW-DMCS
Diethylhexyl sebacate (Ectoil S) (DEHS)	426·6	—	20	3·40	60–80	175	Chromosorb P

* Information from Perkin–Elmer Ltd., Beaconsfield, Bucks, Great Britain.

RESULTS

The optimum flow-rate for the carrier gas was found to be 25 ml/min at NTP except for DEHS (45 ml/min). Each injection for an individual isomer or mixture of isomers was repeated at least twice and the results were found to be reproducible.

The specific retention volumes, V_g^0, were calculated according to the method of Littlewood *et al.*[10] The retention volume for the air peak was taken as zero. Specific retention volumes for halophenols, cresols and methoxyphenols at different column temperatures are listed in Table 2.

The number of theoretical plates, *n*, separation factor, α, height equivalent to a theoretical plate, HETP, electron polarizabilites per unit volume, α_e^v, dipole moment, DM, activity coefficients at infinite dilution, γ_2^0, the partial molar excess free energy, $\Delta\bar{G}_e^0$, partial molar excess entropy, $\Delta\bar{S}_e^0$, and partial molar excess enthalpy $\Delta\bar{H}_e^0$ of mixing at infinite dilution were calculated according to the methods used in previous work.[11] Tables 3–6 give these

Table 2. Specific retention volumes (*ml/g*) for monosubstituted phenols

Isomer	(SO)			(PEG)			(APL + 34)			(SQ)		(VS)		(DEHS)
	150°	168°	185°	150°	168°	185°	150°	168°	185°	130°	150°	168°	185°	168°
o-cresol	76	49	34	14	11	8	47	23	18	306	190	420	280	364
m-	88	51	36	20	13	9	64	28	20	453	234	574	364	507
p-	88	51	36	20	13	9	64	28	20	453	234	561	364	471
o-methoxyphenol	99	47	43	15	10	4	47	26	18	230	116	308	224	307
m-	174	76	73	54	31	12	96	74	43	230	97	1883	1219	1301
p-	174	76	73	54	31	12	96	74	43	230	97	1646	1093	1253
o-chlorophenol	60	42	29	9	8	5	34	17	14	183	81	293	196	203
m-	159	96	60	38	24	14	128	49	35	1785	733	2004	813	1303
p-	159	96	60	38	24	14	128	49	35	1785	733	1976	784	1256
o-bromophenol	89	50	41	13	10	8	49	28	18	307	123	462	322	343
m-	245	106	89	53	34	22	200	106	62	Not eluted		3266	1793	Not eluted
p-	245	106	89	53	34	22	200	106	62	Not eluted		2943	1793	Not eluted
o-fluorophenol	30	19	17	8	6	5	23	14	11	98	55	196	168	121
m-	57	30	26	15	11	9	52	25	17	432	202	659	449	441
p-	57	30	26	15	11	9	52	25	17	410	202	532	778	385
o-iodophenol	162	106	68	22	15	11	75	46	31	433	321	1046	674	607
p-	442	248	150	121	78	54	227	189	106	Not eluted		6938	3980	Not eluted

Table 3. Number of theoretical plates, *n*, separation factor, α, and height equivalent to a theoretical plate, HETP, for monosubstituted phenols on different liquid phases at 168°C

		SO			PEG			APL + 34			VS			DEHS	
Isomer	*n*	HETP	α	*n*	HETP	α	*n*	HETP	α	*n*	HETP	α	*n*	HETP	α
o-cresol	1600	0·125		196	1·020		225	0·888		144	1·388		2254	0·089	
			1·03			1·21			1·20			1·33			1·29
m-	1707	0·117		94	2·127		106	1·886		212	1·945		984	0·203	
			1·00			1·00			1·00			1·02			1·10
p-	1707	0·117		94	2·127		106	1·886		222	0·899		562	0·356	
o-methoxyphenol	2079	0·096		55	3·636		128	1·562		310	0·645		1469	0·136	
			1·63			3·15			2·81			5·34			4·08
m-	1143	0·174		121	1·652		455	0·439		1181	0·169		2634	0·055	
			1·00			1·00			1·00			1·14			1·03
p-	1143	0·174		121	1·652		455	0·439		2053	0·079		3785	0·053	
o-chlorophenol	1665	0·120		100	2·000		121	1·652		784	0·255		2187	0·091	
			2·29			3·00			2·91			6·73			6·20
p-	2290	0·088		41	4·878		31	6·451		1414	0·141		2473	0·081	
			1·00			1·00			1·00			1·01			1·03
m-	2290	0·088		41	4·878		31	6·451		1454	0·137		2728	0·054	
o-bromophenol	1661	0·120		55	3·636		144	1·388		697	0·286		1835	0·109	
			2·11			3·46			3·83			6·36			—
p-	1849	0·108		52	3·846		30	6·666		183	1·094		Not eluted		
			1·00			1·00			1·00			1·10			
m-	1849	0·108		52	3·846		30	6·666		277	0·722		Not eluted		
o-fluorophenol	2116	0·094		114	1·754		324	0·617		256	0·781		458	0·436	
			1·56			1·87			1·78			2·71			3·17
p-	1294	0·154		56	3·571		114	1·754		138	1·451		3341	0·060	
			1·00			1·00			1·00			1·23			1·14
m-	1294	0·154		56	3·571		114	1·754		180	1·109		3975	0·050	
o-iodophenol	1575	0·127		53	3·773		73	2·739		411	0·486		1711	0·117	
			2·35			5·20			4·10			6·63			—
p-	1044	0·191		141	1·411		72	2·777		425	0·470		Not eluted		

Table 4. Some physical constants of monosubstituted phenols

Isomer	b.p., °*C*	Refr. index	T, °*C*	E.P. 10^{-26} *cm*^{3}	D.M. *Debye*
o-chlorophenol	152	1·5473	40	12·5883	1·519
m-	178	1·5565	40	12·7632	2·625
p-	185	1·5579	40	12·7697	3·030
o-bromophenol	175·6	1·5643	66	12·9105	1·508
m-	214	1·5751	66	13·1130	2·607
p-	217	1·5790	66	13·1858	3·010
o-fluorophenol	194	1·4998	50	11·1625	1·469
m-	236·5	1·5007	50	11·6834	2·537
p-	238	1·5020	50	11·7091	2·930
o-iodophenol	186	—		—	1·426
p-	d.	—		—	2·850
o-cresol	191·5	1·5453	20	12·5501	1·496
m-	202·8	1·5398	20	12·4448	1·403
p-	202·5	1·5395	20	12·4390	1·080
o-methoxyphenol	205	1·5255	57	12·1689	2·383
m-	244·3	1·5340	57	12·3333	1·381
p-	243	1·5370	57	12·3910	0·150

Table 5. Vapour pressures and activity coefficients at various temperatures

	Temperature, °C	Cresols *ortho*	Cresols *meta*	Cresols *para*	Chlorophenols *ortho*	Chlorophenols *meta*	Chlorophenols *para*
Vapour pressure, *mmHg*	130	96·61	68·39	62·66	192·8	59·57	43·65
	150	218·8	151·4	138	400	123	100
	168	389	280	275	660·7	223	178
	185	631	473·2	446·7	984	354·8	317
Activity coefficient γ_2^0 (on PEG)	150	3·63	3·71	4·06	3·16	2·40	2·96
	168	2·79	3·10	3·20	2·27	2·12	2·60
	185	2·38	2·67	2·82	2·20	2·24	2·54
Activity coefficient γ_2^0 (on SQ)	130	1·36	1·30	1·42	1·14	0·38	0·52
	150	0·96	1·13	1·24	1·24	0·45	0·55

Table 6. Thermodynamic data for cresols and chlorophenols on different phases

			Thermodynamic data					
			cresols			chlorophenols		
Stationary phase	Isomer	Temp. °C	$\Delta\bar{G}^{\circ}_{e}$ *cal.mole*$^{-1}$	$\Delta\bar{H}^{\circ}_{e}$ *kcal.mole*$^{-1}$	$\Delta\bar{S}^{\circ}_{e}$ *cal.mole*$^{-1}$. *deg*$^{-1}$	$\Delta\bar{G}^{\circ}_{e}$ *cal.mole*$^{-1}$	$\Delta\bar{H}^{\circ}_{e}$ *kcal.mole*$^{-1}$	$\Delta\bar{S}^{\circ}_{e}$ *cal.mole*$^{-1}$. *deg*$^{-1}$
PEG	*ortho*	150	1078			962		
		168	872	4·75	8·75	721	5·91	11·7
		185	784			710		
	meta	150	1094			732		
		168	986	2·28	2·93	647	1·74	2·48
		185	889			730		
	para	150	1172			908		
		168	1014	3·82	6·37	833	1·36	1·19
		185	938			841		
SQ	*ortho*	130	247			104		
		150	31	4·94	11·7	180	−2·24	−5·73
	meta	130	209			−776		
		150	102	1·40	3·07	−676	−3·62	−6·96
	para	130	279			−528		
		150	180	1·31	2·66	−502	−1·86	−3·22

parameters and some important physical constants for the isomers studied. The *o*-halophenols, cresols and methoxyphenols were best resolved on DEHS, and less well by VS, SQ, SO, PEG and (APL + 34) (in order of decreasing efficiency). The corresponding *p*- and *m*-isomers were not resolved.

DISCUSSION

The order of elution of the isomers of cresols, halophenols and methoxyphenols was *o*-, *p*- and *m*-. The *o*-isomers were well resolved from the *m*- and *p*-isomers and had the smallest retention volumes. This is mainly due to the "*ortho* effect" of steric and intramolecular hydrogen bonding that minimizes the occurrence of the intermolecular hydrogen bonding observed with the *m*- and *p*-isomers.

The consistently higher retention of the *m*-halophenols compared with that of the *p*-halophenols does not accord with the activity coefficients. This may be due to an intramolecular electronic effect, *e.g.*, by resonance-induced electron transfer to one of the ring substituents when it is under the influence of a solvent dipole. For cresols and methoxyphenols the longer retention of the *m*-isomers correlates with their higher dipole moments (as seen in Tables 2 and 3).

The most selective liquid phase for separation and quantitative determination is DEHS (followed by VS) as can be seen in Tables 2 and 3. This is explained by the solute-solvent interaction due to hydrogen bonding which can exist in more than one position. The straight line obtained by plotting log V_g^o for some of the isomers on DEHS against log V_g^o for the same isomers on VS showed that similar interactions occur between the isomers and the two liquid phases.[12]

SO, AP + 34, SQ and PEG did not resolve the *m*- and *p*-isomers. The overlap of *m*- and *p*-isomers on the first three liquid phases is due to the fact that these liquid phases are non-polar, and do not polarize the two isomers sufficiently to permit adequate resolution. Furthermore the isomers have closely similar vapour pressures. In PEG, the solvent–solvent[13] and solute–solute interactions play a greater role than solute–solvent interaction, and this together with the high density of this liquid phase causes complete overlap of the two isomers.

Excess partial quantities

In PEG, the potential energies of interaction between two solvents and two solute molecules (W_{11} and W_{22}) are greater than that of solute–solvent molecular interaction (W_{12}). This will result in higher values of $\Delta \bar{H}_e^o$, and hence higher values of $\Delta \bar{G}_e^o$ and γ_2^o and positive deviation from Raoult's law according to the equation:

$$\Delta \bar{H}_e^o = Z\,(\tfrac{1}{2}W_{11} + \tfrac{1}{2}W_{22} - W_{12})$$

In SQ, the solvent–solvent interaction is very weak and lower than in PEG, while there is a little solute–solvent interaction, that is dipole–induced dipole interaction; moreover, SQ contains 6 branching methyl groups in its structure, so $\Delta \bar{G}_e^o$ and γ_2^o would be expected to be lower than in PEG (as seen in Tables 5 and 6).

The values of $\Delta \bar{G}_e^o$ for chlorophenol–PEG systems are lower than those for cresol–PEG systems at the same temperature (as shown in Table 6). The interaction of the former pair is stronger than that of the latter. This can be explained by the fact that the former pair forms donor–acceptor systems, which the cresols cannot do since the solute and solvent both contain electron-donating groups, (CH_3) and (OH) respectively. Dipole moments of cresols are lower than those of chlorophenols.

These results are in good agreement with those cited by Langer and Purnell[12] for the increase of $\Delta \bar{G}_e^o$ on passing from electron-withdrawing substituted aromatic solutes to those with electron-donating groups.

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Zusammenfassung—Die Faktoren werden diskutiert, die Einfluß auf die Trennung monosubstituierter Phenole an Siliconöl, Poly(äthylenglycol) (1500), Apiezon L + Bentone 34, Squalan, Versamid und Diäthylhexylsebacat haben. Es werden spezifische Retentionsvolumina, das Höhenäquivalent eines theoretischen Bodens und thermodynamische Größen angegeben. Diäthylhexylsebacat und Versamid sind für die quantitative Trennung aller untersuchten Isomeren selektiv.

Résumé—On discute des facteurs qui influencent la séparation de phénols monosubstitués sur l'huile de silicone, le poly(ethylèneglycol) (1500), l'Apiezon L + Bentone 34, le squalane, le Versamide et le sébaçate de diéthylhexyle. On rapporte des volumes de rétention spécifique, hauteurs équivalentes à un plateau théorique et quantités thermodynamiques. Le sébaçate de diéthylhexyle et le Versamide sont sélectifs pour la séparation quantitative de tous les isomères étudiés.

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ALKALI- UND ERDALKALISPURENANALYSE IN WOLFRAM UND WOLFRAM-VERBINDUNGEN NACH WOLFRAMMATRIXABTRENNUNG AN DEAE-SEPHADEX*

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Zusammenfassung—Es wird eine neue, säulenchromatographische Matrixabtrennungsmethode für Wolfram an DEAE-Sephadex beschrieben. Alkali- und Erdalkalispuren gelangen dabei quantitativ ins Säuleneluat und können so ohne störenden Matrixeinfluß mittels AAS erfaßt werden. Einige Verfahrens-Kenndaten: mittlere, relative Standardabweichung für Na, K und Mg bis etwa 50 ppm: ±5–10%, für Ca 10–20%; über 50 ppm: ±2–5%, für Ca 5–10%. Nachweisgrenzen: Na, K: 10 ppm; Mg: 1 ppm; Ca: 20 ppm; Zeitbedarf einer Einzelbestimmung: 1,5 Mannstunden. Die Methode ist durch pH-Änderung der Aufgabe- und Elutionslösung auch zur Molybdänmatrixabtrennung geeignet.

Untersuchungen über den Einfluß von Alkali- und Erdalkalispuren auf das Reduktions- und Sinterverhalten der hochschmelzenden Metalle Wolfram und Molybdän sowie auf deren Materialeigenschaften sind relativ selten,[1–4] da es bislang an verläßlichen und einfach zu handhabenden diesbezüglichen Spurenanalysenmethoden fehlte.[5] Lediglich der Einfluß des Kaliums in Verbindung mit Aluminium und Silizium auf Wolfram ist schon seit langem Gegenstand intensiven Studiums, da diese Elemente als Dopesubstanzen zur Herstellung von NS-Wolfram für Glühlampenwendeln dienen.[2–4] Von kaufmännischem Interesse ist darüber hinaus die Erfassung des Alkali- und Erdalkaligehaltes in technischem Wolframtrioxid, Ammoniumparawolframat, Wolframsäure *etc.*, da der Preis dieser Produkte von ihrem Reinheitsgrad begreiflicherweise entscheidend mitbestimmt wird.

Es hat nicht an Versuchen gefehlt, für die Analyse der Alkalien und Erdalkalien in Wolfram und Molybdän und deren Verbindungen den bequemsten und raschesten Weg einzuschlagen: die direkte Bestimmung dieser Elementspuren ohne Matrixabtrennung. Dies ist prinzipiell nur mit wenigen physikalisch chemischen Analysenverfahren möglich:[5] durch Festkörpermassenspektrometrie,[6] Emissionsspektralanalyse,[6] Atomabsorption[7,8] oder Aktivierungsanalyse.[9,10] Praktisch erreicht man jedoch ohne Matrixabtrennung mit keiner dieser Methoden für alle interessierenden Alkali- und Erdalkalispuren befriedigende Ergebnisse.

Alle diese Methoden können jedoch mit einer meist entscheidenden Empfindlichkeitssteigerung und vielfach auch mit besserer Reproduzierbarkeit zur Alkali- und Erdalkalianalyse herangezogen werden, nachdem die Matrix abgetrennt wurde. Wolfram- und Molybdänmatrixabtrennmethoden, die sich zur Alkali- und Erdalkalispurenanalyse

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* Herrn Prof. Dr. Friedrich Hecht zum 70. Geburtstag gewidmet.

eignen, sind wenige bekannt.[11–15] Mit keiner dieser Methoden ist eine gemeinsame Abtrennung von Alkali- und Erdalkalispuren aus Wolfram oder Molybdän möglich. Deshalb wurde versucht, entsprechende Verfahren durch den Einsatz von Dextrangelen zu entwickeln.

Für die Isopolysäuren des Wolframs und Molybdäns wurde an Dextrangelen mit sinkendem pH-Wert steigende Chelatkomplexbildungstendenz mit den Hydroxylgruppen der Gelmatrix festgestellt.[16,17] Die nur im sauren Bereich stabilen Komplexe werden unter Hydroxylionenabgabe gebildet. Dadurch, daß bei Molybdän und Wolfram Komplexbildungstendenz mit der Gelmatrix und Isopolysäurebildungsbestreben miteinander konkurrieren, prägen Molekülsiebeffekte als zweiter dominanter Faktor die Elutionsprofile. Während jedoch bei Molybdän im stärker sauren Medium die Komplexbildung mit der Dextranmatrix dominiert, treten bei dem als trägen Komplexbildner bekannten Wolfram Molekülsiebeffekte mit ausgeprägter Zeitabhängigkeit in den Vordergrund. Letztere vereiteln eine Wolframmatrixabtrennung an Dextrangelen. Hier gelingt eine vollständige Matrixsorption erst durch Verwendung von DEAE-Sephadex, also durch den kombinierten Sorptionseffekt von Ionenaustausch und Chelatkomplexbildung an der Dextranmatrix, worüber im folgenden berichtet wird.

EXPERIMENTELLER TEIL

Geräte

Gamma-Aktivitätsmessungen erfolgten mit einem Zählgerät der Firma Frieseke & Hoepfner, FH 49A, Grundsonde FH 421 AS, NaJ-Bohrlochszintillationskristall Z 11, in Verbindung mit einem 100-Kanal Gammaspektrometer TMC-Gammascope II* in Einkanalschaltung. Zur β-Zählung wurde ein Methandurchflußproportionalzählrohr mit Schirmzählrohr und eingebauter Antikoinzidenzschaltung der Firma Frieseke & Hoepfner FHT 650 D1, Zählrohreinsatz 42267/10 (für Proben bis 30 mm Durchmesser) verwendet.

Flammenemissionsspektrophotometrische und atomabsorptionsphotometrische Messungen wurden an einem Perkin-Elmer Modell 403 durchgeführt.

Säulenchromatographie: Es kamen selbstgefertigte Säulen aus Plexiglasrohren, gestanzten Filterplatten aus Hochdruckpolyäthylen (Plastibrand-Labpor, Dicke 1,6 mm, Porosität 70 µm und mit Auslauftrichtern aus Vinidur zum Einsatz. Die Proben- und Elutionsmittelaufgabe erfolgte anfangs mit einer Mikropumpe der Firma Bühler & Co., Tübingen, BRD, Typ mp 1. Für Routinebestimmungen wurde die Probelösung bzw. das Nachelutionsmittel auf oben trichterförmig erweiterte Säulen aufgegeben. Die dadurch bedingte Variation der Durchflußgeschwindigkeit hat auf die Wolfram-Matrixabtrennung keinen Einfluß. Es wurden ausschließlich Silikonschläuche verwendet. Ein automatischer Fraktionssammler "Fraktomat", Buchler Instruments, Fort Lee, USA, wurde bei Bedarf eingesetzt. Es wurde durchwegs in PVC-, Polyäthylen- bzw. Teflongefäßen gearbeitet.

Materialien

DEAE-Sephadex A-25 fine (Chloridform) und QAE-Sephadex A-25 fine (Chloridform) von Pharmacia, Uppsala. WO_3 und H_2WO_4 von H. C. Starck, Goslar, BRD. ^{22}Na, ^{45}Ca, ^{133}Ba, ^{185}W von The Radiochemical Centre, Amersham, England. ^{42}K wurde durch Bestrahlung von KCl im ASTRA-Reaktor der Österreichischen Studiengesellschaft für Atomenergie in Seibersdorf selbst hergestellt.

Alle übrigen Reagenzien waren von Merck, Darmstadt, BRD. Ihr erforderlicher Reinheitsgrad ist in der Arbeitsvorschrift jeweils dezidiert angeführt.

DIE SORPTION VON WOLFRAM(VI) AN SEPHADEX-ANIONENAUSTAUSCHERN

Aus früheren Untersuchungen betreffend das Verhalten von Wolfram(VI) an Dextrangelen[17] ging eindeutig hervor, daß die Sorptionstendenz des Wolframs an diesen Gelen allein nicht zu einer vollständigen Matrixabtrennung ausreicht. Im Gegensatz zu

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* Das Gerät wurde vom österreichischen Fonds zur Förderung der wissenschaftlichen Forschung zur Verfügung gestellt.

Molybdän(VI)[16] treten bei Wolfram(VI) im sauren und im Neutralbereich Molekülsiebeffekte mit ausgeprägter Zeitabhängigkeit in den Vordergrund. Deshalb wurde versucht, durch die Anwendung von Sephadex-Anionenaustauschern die Sorptionstendenz von Wolframatlösungen an Dextrangelen zu steigern. Tatsächlich führt der kombinierte Effekt von Chelatkomplexbildung und Sorption an den Ionenaustauschgruppen zu einer ganz wesentlichen Steigerung der Wolframsorption:

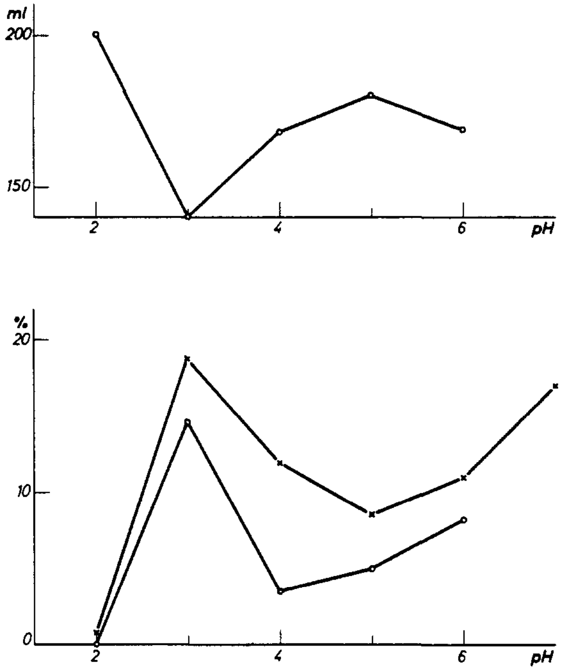

Abb. 1. pH-Abhängigkeit der Wolfram(VI)-Sorption an QAE- und DEAE-Sephadex. Oberes Diagramm: Abhängigkeit des Durchbruchselutionsvolumens für Wolfram auf DEAE-Sephadex A-25. Ordinate: Elutionsvolumen in ml, bei dem die ersten W-Spuren im Eluat nachweisbar sind. Unteres Diagramm: % der Aufgabeaktivität im Gesamteluat x—x Werte für QAE-Sephadex A-25; o—o Werte für DEAE-Sephadex A-25.

Versuchsbedingungen: Säulendimensionen: 9,0 × 2,0 cm; Säulenfüllung: jeweils 5 g QAE- bzw. DEAE-Sephadex A-25, Chloridform; Zimmertemperatur; Durchflußgeschwindigkeit 38 ml hr^{-1} cm^{-2} (= 120 ml/hr) Aufgabelösung: 200 ml 0,1*M* Wolframatlösung (4,64 g WO_3, mit ^{185}W markiert), Nachelution mit 200 ml 0,01*M* HCl.

Erste Versuche wurden sowohl mit dem stark basischen Sephadex-Anionenaustauscher QAE A-25 als auch mit dem schwach basischen Anionenaustauscher DEAE A-25 ausgeführt. Die pH-Abhängigkeit der Wolframsorption an den beiden Austauschertypen ist in Abb. 1 dargestellt. Für beide Austauschertypen ergab sich ein ähnlicher Verlauf der pH-Abhängigkeit. Beste Resultate werden bei pH 2,0 erzielt, bei pH 3,0 ist die Sorption am schlechtesten. Auf DEAE-Sephadex ist die Sorption durchwegs vollständiger als auf QAE-Sephadex. Dies läßt den Schluß zu, daß die gegenüber unsubstituierten Sephadexgelen gesteigerte Wolframsorption an Sephadex-Anionenaustauschern nicht auf einen reinen Ionenaustauscheffekt zurückzuführen ist. Vielmehr scheinen in Analogie zum Sorptionsverhalten des Molybdäns an Sephadex G-10 bei Anwesenheit von NH_4Cl[16] die

Austauschgruppen ebenfalls eine stabilere Chelatkomplexbildung zu bewirken. Dieser Effekt ist bei DEAE-Sephadex offensichtlich ausgeprägter als bei QAE-Sephadex. Im folgenden wurde daher nur DEAE-Sephadex zur W-Matrixabtrennung eingesetzt. Der Austauscher wurde in der Chloridform belassen, da bei anderen Säureanionen erhöhte Gefahr der Komplexbildung mit Wolfram besteht und das Chlorid für die AAS-Endbestimmung das günstigste Anion darstellt. Die Chelatkomplexbildung des Wolframs mit den Gelhydroxylgruppen gibt sich auch hier durch pH-Erhöhung während der Sorption deutlich zu erkennen, wie aus Abb. 2 ersichtlich ist. Auf eine Pufferung der Aufgabelösung zur Hintanhaltung dieses pH-Sprunges bei beginnender Sorption muß verzichtet werden, da sämtliche infrage kommenden Puffergemische organische Säureanionen enthalten, die durch Komplexbildung mit Wolfram(VI) zu einer Verminderung der Durchbruchskapazität führen.

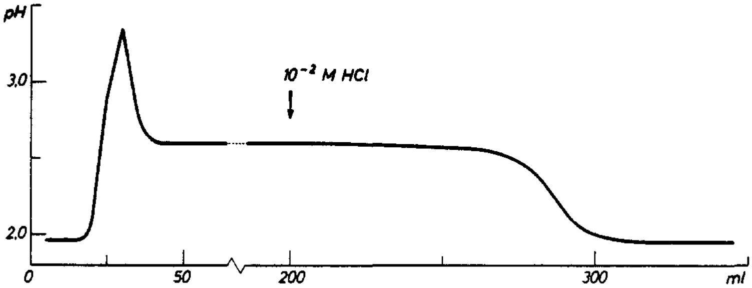

Abb. 2. pH-Elutionsprofil für die Wolframsorption an DEAE-Sephadex A-25. Versuchsbedingungen: Säulendimensionen: 15 × 2 cm; Durchflußgeschwindigkeit: 120 ml/hr; Aufgabelösung: 200 ml 0,1*M* Wolframatlösung, pH 2,0; Nachelution mit 200 ml 0.01*M* HCl.

Durchflußgeschwindigkeit

Wie für die Molybdänsorption an Sephadex G-10[16] war auch für die Sorption des Wolframs an DEAE-Sephadex aufgrund des ähnlichen Sorptionsvorganges mit beträchtlichen Sorptionsungleichgewichten bei höheren Durchflußgeschwindigkeiten zu rechnen. Dies ist jedoch überraschenderweise bis etwa 50 $ml.hr^{-1}.cm^{-2}$ nicht der Fall (Tabelle 1). Es kann also mit relativ hohen Tropfgeschwindigkeiten gearbeitet werden.

Tabelle 1. Einfluß der Durchflußgeschwindigkeit auf die Vollständigkeit der Wolframsorption an DEAE-Sephadex A-25

Tropfgeschw., *ml/hr*	Durchflußgeschw., $ml\ hr^{-1}\ cm^{-2}$	W im Eluat, %
60	26,4	<0,01
120	52,7	0,01
130	57,1	0,03
150	65,9	0,1
180	79,1	3,5

Versuchsbedingungen: innerer Säulendurchmesser: 1,70 cm; Säulenfüllung: 2,5 g DEAE-Sephadex A-25, Chloridform; Gelbetthöhe *ca.* 8 cm; Zimmertemperatur; Aufgabelösung: 40 ml Wolframatlösung (Einwaage 1.0 g WO_3); pH 2,0; Nachelution mit 60 ml 0,1 %iger NH_4Cl-Lösung, pH 2,0. Probenvorbereitung nach Arbeitsvorschrift.

Elutionsverhalten von Alkali- und Erdalkalispuren bei der Wolfram-Matrixabtrennung an DEAE-Sephadex

Tabelle 2 gibt eine Übersicht der durchgeführten Ausbeuteuntersuchungen. Dabei wurde zunächst 0,01*M* HCl zur Nachelution eingesetzt. Natrium und Kalium sind auf

Tabelle 2. Ausbeuteuntersuchungen zur Wolframmatrixabtrennung an DEAE-Sephadex A-25

		Ausbeute, %	
Element	aufgegeben (ppm)	durch Aktivitätsmessung ermittelt	durch Flammenphotometrie ermittelt
1. Nachelution mit 0,01*M* HCl			
^{22}Na	trägerfrei	98	—
Na	25	—	97
Na	50	—	97
Na	75	—	95
Na	100	—	100,5
Na	200	—	99,4
^{42}K + K	0,01	99,5	—
K	25	—	104
K	50	—	104
K	75	—	98
K	100	—	103
K	200	—	102
^{45}Ca + Ca	5 pbb	96; 98	—
Ca	25	—	72,5
Ca	50	—	75
Ca	75	—	94
Ca	100	—	100
Ca	200	—	100
Mg	25	—	99,5
Mg	50	—	99
Mg	75	—	91
Mg	100	—	89
Mg	200	—	91,5
2. Nachelution mit 0,1% NH_4Cl, pH 2,0			
^{22}Na	trägerfrei	100	—
^{22}Na + Na	50	99,5	98,5
^{22}Na + Na	100	99,5	100
Na	200	—	99
^{22}Na + Na	300	100	—
^{42}K + K	10 pbb	100	—
^{42}K + K	50	99,5	101,5
^{42}K + K	100	100	103
K	200	—	102
^{42}K + K	300	100	—
^{45}Ca + Ca	5 pbb	99,5	—
^{45}Ca + Ca	50	99	98
^{45}Ca + Ca	100	99,5	101
Ca	200	—	102,5
Mg	50	—	98
Mg	100	—	100,5
Mg	200	—	99
Mg	300	—	100

Versuchsbedingungen: Säulendimensionen: 15 × 2 cm; DEAE-Sephadex A-25, Chloridform; Tropfgeschwindigkeit: 120 ml/hr: Zimmertemperatur: Aufgabelösung: 200 ml 0,1*M* Wolframatlösung, pH 2,0: Nachelution mit 0,01*M* HCl oder 0,1% NH_4Cl (pH 2,0) bis zu einem Gesamtelutionsvolumen von 400 ml.

diese Weise vollständig eluierbar, bei Calcium ist die Ausbeute erst ab etwa 100 ppm quantitativ und Magnesium zeigt schließlich ein etwas ungewöhnliches Verhalten, indem es bei höheren Konzentrationen, etwa ab 75 ppm, nur mehr unvollständig eluiert wird. Generell ist die Sorptionstendenz für Alkali- under Erdalkalispuren wesentlich geringer als bei dem für Molybdän ausgearbeiteten Verfahren an Sephadex G-10.[16] Bei Nachelution mit 0,1 % NH_4Cl-Lösung werden sämtliche interessierende Alkali- und Erdalkalispuren quantitativ eluiert. Im Laufe vorliegender Untersuchungen gewannen auch Bariumspuren in Wolfram steigendes technologisches Interesse. Barium kann jedoch nicht quantitativ mit 0,1%iger NH_4Cl-Lösung eluiert werden. Seine quantitative Elution gelingt erst durch Nachelution mit 200 ml 1%iger NH_4Cl-Lösung (pH 2,0) unter den in Tabelle 2 angeführten Bedingungen.

Versuche zur Säulenregenerierung

Alle Versuche, das sehr stark sorbierte Wolfram wieder quantitativ von DEAE-Sephadexsäulen zu eluieren, verliefen erfolglos. Wohl gelingt mit größeren Elutionsvolumen von ADTE, Oxalsäure, Salicylsäure oder Citronensäure eine weitgehende Wolframdesorption (80–90 %), jedoch ist schon der dafür erforderliche Zeitaufwand zu groß. Es ist daher wesentlich einfacher und bei den geringen eingesetzten Austauschermengen auch rationeller, die Austauscherfüllung jeweils nach vollendeter Matrixabtrennung zu verwerfen.

Optimierung der Säulendimensionen

Als optimale Säulendimensionen ergaben sich für die Sorption von maximal 2,5 g Wolframtrioxid und im Hinblick auf eine möglichst rasche, aber dennoch vollständige Matrixabtrennung 150 × 20 mm. Die Höhe des Gelbettes beträgt bei einer eingesetzten Menge von 5 g DEAE-Sephadex A-25 (Chloridform) etwa 10 cm.

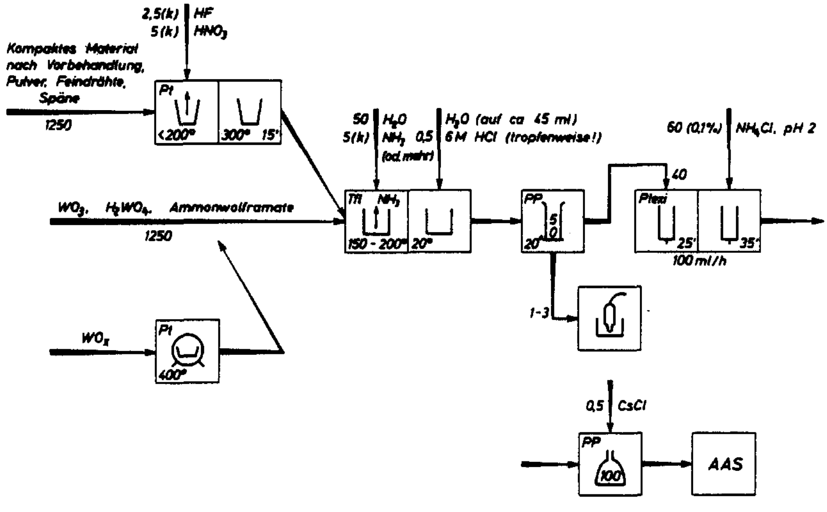

Abb. 3. Ablaufplan zur Wolframmatrixabtrennung auf DEAE-Sephadex A-25 zwecks Alkali- und Erdalkalispurenanalyse in Wolfram und Wolframverbindungen. Die hier angewandte Symbolik zur übersichtlichen Darstellung von Analysenabläufen wurde im Rahmen des Arbeitskreises "Analytik hochschmelzender Metalle"[18] erarbeitet. Sie stellt eine Modifizierung der von Malissa und Jellinek[20] vorgeschlagenen Symbolik dar.

Im Rahmen der Untersuchungen des Arbeitskreises "Analytik hochschmelzender Metalle"[18] ergab sich vor allem für die Analyse von Wolfram-Lampenwendeln die Notwendigkeit, die WO_3-Einwaagen auf 1 g zu verringern (Aufgabevolumen: 40 ml). Damit mußten auch die Säulendimensionen dieser Einwaage angepaßt werden: 100 × 17 mm (Gelbetthöhe: *ca.* 8 cm). Die DEAE-Sephadex A-25-Einwaage beträgt 2,5 g. Nachelution mit 60 ml 0.1%iger NH_4Cl-Lösung, pH 2,0.

Zur Lösung von WO_3

Je nach Dehydratisierungsgrad und Korngrößenverteilung des zu analysierenden Wolframoxids sind sehr verschiedene Ammoniakmengen zur Lösung erforderlich. Für H_2WO_4 und Ammoniumwolframate genügen immer 5 ml konz. Ammoniak pro 1 g Einwaage. Speziell bei calcinierten Wolframoxiden wurden jedoch bis zu 80 ml Ammoniak zur Lösung benötigt. Letzte Trübungen solcher Lösungen blieben unberücksichtigt. Ein krasses Ansteigen der Blindwerte wurde bei Anwendung auch von 80 ml suprapurem Ammoniak zwar nicht beobachtet, jedoch ist dies im Einzelfall jeweils zu überprüfen. Eine Lösung unter Druck in Teflonbomben brachte keine Verbesserung (Aufschlußzeit: 45 min; Temp.: 170°; Aufschluß in Uni Seal Decomposition Vessels, P.O. Box 9463, Haifa, Israel). Eine Lösungsbeschleunigung für grobkörnige, hochgeglühte Oxide durch Ultrabeschallung erscheint möglich. Eine diesbezügliche Apparatur stand jedoch nicht zur Verfügung.

In letzter Zeit wurde untersucht, ob sich in Ammoniak nicht vollständig lösliche Wolframoxide in suprapurem Lithiumkarbonat lösen. Dabei zeigte sich, daß sämtliche Wolframoxide durch Druckaufschluß in Teflonbomben in 30 min und bei 180° löslich sind. Es wurden jeweils 0,5 g Lithiumkarbonat und 10 ml Wasser pro 1,25 g WO_3 eingesetzt. Eine Beeinträchtigung der Wolframsorption an DEAE-Sephadex findet dabei interessanterweise nicht statt, d.h. die Matrixabtrennung verläuft auch nach Lösung in Lithiumkarbonat problemlos. Zur pH-Einstellung auf 2,0 werden *ca.* 1,2 ml 6*M* HCl benötigt. Die Eichlösungen müssen im Falle der Lösung in Lithiumkarbonat entsprechende Mengen an Lithiumkarbonat anstelle von Ammoniumchlorid enthalten. Deshalb wird eine Lösung in Lithiumkarbonat derzeit nur für calcinierte Wolframoxide eingesetzt, um für den Großteil der im Metallwerk Plansee anfallenden Wolfram- und Molybdänrohstoffproben eine gleichartige Probenvorbereitung und eine Art von Eichlösungen anwenden zu können. Auch die Verfahrenskenndaten der Arbeitsvorschrift (s.u.) beziehen sich auf in Ammoniak gelöste Wolframoxidproben.

Anwendung des Verfahrens zur Molybdänmatrixabtrennung

Es wurde auch versucht, das für Wolfram ausgearbeitete Verfahren zur Molybdänmatrixabtrennung einzusetzen. Bei pH 2,0 waren diese Versuche nicht erfolgreich, wohl aber bei pH 3,0. Dieses pH-Optimum ist für die Molybdänsorption an DEAE-Sephadex A-25 weit weniger scharf ausgeprägt wie das für die Molybdänsorption an Sephadex G-10.[16] Erste Versuche ergaben, daß die Ausbeuten an Natrium- Magnesium- und Calciumspuren auch bei Molybdänsorption quantitativ sind. Bei Kalium scheinen hingegen konzentrationsunabhängige Verluste von etwa 10% aufzutreten. Näheres über die Anwendung der hier beschriebenen Matrixabtrennmethode für Molybdän wird in einer folgenden Arbeit mitgeteilt werden.

Im folgenden sind nun Merkmalsmatrix und Arbeitsvorschrift zur Wolframmatrixabtrennung an DEAE-Sephadex wiedergegeben, wie sie den Richtlinien für standardisierte Analysenmethoden nach Gottschalk[19] entsprechen (Tabelle 3).

Tabelle 3. Merkmalsmatrix und Arbeitsvorschrift für Natrium, Kalium, Magnesium und Calcium in Wolfram. Wolframmatrixabtrennung auf DEAE-Sephadex A-25 Säulen; Endbestimmung mit AAS

Anwendungsbereich	Natrium/Kalium	Magnesium	Calcium
Gehaltsbereich in ppm für Probemenge von 1 g	10–100	5–50	20–200
Konzentrationsarbeitsbereich in µg/l für ein Ausgangsvolumen von 100 ml	100–1000	50–500	200–2000
Standardabweichung, mittlere, relative, %			
für <50 ppm			
für >50 ppm			
Nachweisgrenzen (ermittelt nach H. Kaiser aus 3 × Standardabweichung der Blindwerte + Mittelwert der Blindwerte)			
ppm	10	1	20
Ursache	Reagenzienkontamination		Empfindlichkeit der AAS-Bestimmung

Arbeitsvoraussetzungen

Geräte

Hartmetallmörser; Muffel- bzw. Simon–Müller–Ofen; Pt-Tiegel (hohe Form), Teflonbecher (500 ml); Plastikmeßzylinder (200 ml); Teflonrührstab, Chromatographiesäule aus Plexiglas (Länge 150 mm, innerer Durchmesser 17 mm) mit trichterförmigem Aufsatz; pH-meter. Die Endbestimmung erfolgte auschließlich durch Atomabsorptionsspektrometrie. Verwendetes AAS-Gerät: Perkin–Elmer Modell 403. Die Geräteeinstellungen entsprachen den von Perkin–Elmer als optimal angegebenen Meßparametern. Die Meßwertablesung erfolgte nach Integration über 2 bzw. 10 sec.

Reagenzien

HNO_3, min. 65%		Merck Suprapur
HF, min. 40%		
Ammoniaklösung, min. 25%		
6*M* HCl, aus HCl, min. 30%		
0,1% NH_4Cl-Lösung, mit HCl auf pH 2,0		
CsCl-Lösung, 254 mg/ml		
DEAE-Sephadex A-25		Pharmacia Fine Chemicals, Uppsala
Eichlösungen:	Na 0,1–1,00 ppm	NaCl, z.A.
	K 0,1–1,00 ppm	KCl
	Mg 0,05–0,50 ppm	$MgCl_2$
	Ca 0,2–2,00 ppm	$CaCO_3$

Diese Eichlösungen müssen 0,01*M* an HCl sein, sowie 0,1%ig. an NH_4Cl und 1,267 g/l CsCl enthalten. Alle Lösungen sind mit bidestilliertem Wasser aus einer Quarzdestillationsapparatur anzusetzen.

Durchführung

Probenvorbereitung

Metallpulver, Drähte, Späne: 1250 mg Probe in Pt-Tiegel mit 2,5 ml konz. HF versetzen; durch tropfenweise Zugabe von 5 ml konz. HNO_3 lösen. Eindampfen, auf Sand- oder Luftbad bis zur Trockene abrauchen und 15 min. bei 300° belassen.

Kompaktes Material: 1 min. mit HF konz.-HNO_3 konz (10 : 1) abbeizen, mit Wasser und dann mit Äthanol z.A. waschen und trocknen. Im Hartmetallmörser zerkleinern und wie oben weitserbehandeln.

Mischoxide, WO_x: Bei $x<3$ (blaue, braune, schwarze Pulver) vor der Einwaage ausreichende Probemengen im Pt-Tiegel bei 300–400° (nicht höher, sonst Alkaliverluste möglich) zu gelbem WO_3 oxidieren.

WO_3 und H_2WO_4, Ammonwolframate: ohne Vorbehandlung einwiegen und lösen.

Tabelle 3. *Fortsetzung*

Durchführung

1250 mg WO_3 (H_2WO_4) oder die mit HF und HNO_3 vorbehandelten Proben werden in einem Teflonbecher in 50 ml H_2O suspendiert und mit 5 ml konz. NH_3 (bei Bedarf auch wesentlich mehr) gelöst (Heizplatte 150–200).

Das Ammoniak wird *vollständig* verkocht (Prüfung mit pH-Papier *über* der Lösung). Dabei wird bis auf 5–10 ml eingeengt (zur Verhinderung der Bildung von Ψ-Metawolframat). Nun wird abgekühlt, mit Wasser auf *ca.* 45 ml gebracht und 0,5 ml 6*M* HCl *tropfenweise unter Rühren* zugegeben. Bei sehr unreinen Produkten bleibt vorhandenes SiO_2, Fe_2O_3, Cr_2O_3 etc. ungelöst. Die Lösung wird nun in einen Plastikmeßzylinder überführt und auf 50 ml aufgefüllt: 1–3 ml werden zur pH-Messung entnommen. Der pH-Wert liegt meist bei 2–4. Nach Zugabe einiger Tropfen 6*M* HCl und Umrühren wird der pH-Wert nochmals gemessen. Dies wird fortgesetzt, bis der pH-Wert von 2,0 erreicht ist. Auf diese Weise vermeidet man eine eventuelle Kaliumkontamination der Probelösung durch die kombinierte Glaselektrode. 40 ml der so hergestellten Lösung (entsprechend einer Probemenge von 1,0 g) werden zur chromatographischen Matrixabtrennung eingesetzt.

Säulenchromatographie

Gleichbleibende Parameter: Zimmertemperatur, Durchflußgeschwindigkeit: unter 50 ml/hr cm^2; Säulenvorbereitung: 2,5 g DEAE-Sephadex A-25 (Chloridform) werden in 0,01*M* HCl einen Tag quellen gelassen und in die Säule gefüllt. Ein Einlaufenlassen der Säule ist nicht nötig. Die Säulenfüllhöhe beträgt etwa 8 cm.

Probelösung (40 ml) wird auf die Säule aufgebracht. Darauf wird mit 0,1%iger NH_4Cl-Lösung, pH 2,0, nacheluiert, bis ein Eluatvolumen von 100 ml erreicht ist. Das Eluat wird in einem Plastikmeßkolben gesammelt. Die Säulenfüllung wird nach erfolgter Matrixabtrennung verworfen.

Endbestimmung

Die flammenphotometrische Alkali- und Erdalkalianalyse erfolgt ohne Einengung im Eluat. Zu 100 ml Eluat werden jeweils 0,5 ml einer CsCl-Lösung zugesetzt, die 254 mg CsCl/ml enthält. Dies entspricht einer Dotierung mit 1000 ppm Cs.

Störungen

Bei ungenügender Einengung der Probelösung oder bei zu schneller HCl-Zugabe zur Einstellung der Probelösung auf pH 2,0 vor Aufgabe auf die Säule kann die Matrixabtrennung unvollständig sein (vermutlich infolge Bildung von Ψ-Metawolframat oder noch höherer Wolfram-Isopolysäureaggregationen durch zu schnelles Ansäuern).

RINGANALYSENERGEBNISSE FÜR KALIUM

Im Rahmen eines ersten, vorläufigen Ringversuches des Arbeitskreises "Analytik hochschmelzender Metalle"[18] wurde die Verläßlichkeit des ausgearbeiteten Verfahrens für die Kalium-Analyse in verschiedenen Wolframproben unter Beweis gestellt, Tabelle 4. Die von der Technischen Hochschule Graz erhaltenen Werte galten bald als Leitwerte für

Tabelle 4. Ergebnisse der ersten Ringuntersuchung für die Bestimmung von Kalium in Wolfram

Ausführendes Labor:	TH Graz		Radium Wipperfürth	Osram Studienges. München	
	Matrixabtrennung			direkte Bestimmung	
	an DEAE-Sephadex		durch Chlorierung		
Angewandte Methode Endbestimmung mit	AAS	FES	FES	FES	AAS
Probenbezeichnung und Art					
03 W-Pulver	130	110	74	122	—
05 W-Pulver	154	135	97	148	148
06 W-Feindraht	50	50	64	32	40
R-1 oxidierter W-Draht	100	—	76	102	98

Angaben in ppm, auf Wolframmetall bezogen. FES = Flammenemissionsspektrometrie.

andere Untersuchungen. Die etwas zu niedrigen Resultate von Radium Wipperfürth sind auf die Anwendung etwas zu großer Säulen zur Matrixabtrennung und daher auf unvollständige Elution zurückzuführen. Ganz deutlich zeigt sich, daß bei Matrixabtrennung durch Chlorierung vor allem bei Wolframpulvern beträchtliche Kaliumverluste auftreten. Trotz ausgeprägter Matrixeffekte ist für Kalium auch die direkte Erfassung ohne Matrixabtrennung möglich.[7] Die Erfassung des Kaliumgehaltes von Wolframtrioxid machte dabei besondere Schwierigkeiten, da interessanterweise nur ein Lösen in H_2O_2 zu brauchbaren Resultaten führt. Hochgeglühte oder grobkörnige Oxide sind nicht oder nur sehr schwer in H_2O_2 löslich. Der bisher von Osram–München beschrittene Weg der Reduktion der Oxide im Wasserstoffstrom bei etwa 800°C dürfte bisweilen zu Alkaliverlusten führen, was jedoch noch einer experimentellen Klärung bedarf. Gegebenenfalls führt auch hier die Lösung mittels Lithiumkarbonat zum Ziel.

Im Gegensatz zu Kalium tritt bei Calcium eine derartige Depression der Meßsignale durch die Wolfram-Matrix auf, daß dieses ohne Matrixabtrennung nicht unter 100 ppm erfaßbar ist. Für Natrium und Magnesium stehen schlüssige Ergebnisse noch aus.

Die größten Vorteile bietet demnach die hier beschriebene Matrixabtrennung bei der Erfassung *aller* interessierenden Alkali- und Erdalkalispuren. Die Eignung der Methode zur Isolierung weiterer Metallspuren aus Wolfram- und Molybdänmatrices wird geprüft.

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Summary—A new column-chromatographic method is described, for the separation of tungsten on DEAE-Sephadex, enabling trace amounts of alkali and alkaline earth metals in tungsten to be determined quantitatively by AAS without matrix interference. Mean relative S.D. for <50 ppm Na, K, Mg, are 5–10% and for <50 ppm Ca 10–20%, and for >50 ppm, 2–5% and 5–10% respectively. Limits of detection in tungsten are 10 ppm Na and K, 1 ppm Mg, and 20 ppm Ca. Time for a determination is about 90 min. By appropriate changes in pH and other conditions, the method can be used for the separation of molybdenum from traces of alkali metal ions.

Résumé—On décrit une nouvelle méthode chromatographique sur colonne, pour la séparation du tungstène sur Sephadex DEAE, permettant la détermination quantitative de traces de métaux alcalins et alcalino-terreux dans le tungstène par spectrométrie d'absorption atomique sans interférence de la matrice. Les écarts types relatifs moyens pour < 50 ppm de Na, K, Mg, sont 5–10%, et pour < 50 ppm de Ca 10–20%, et pour > 50 ppm, 2–5% et 5–10% respectivement. Les limites de détection dans le tungstène sont 10 ppm de Na et K, 1 ppm de Mg, et 20 ppm de Ca. Le temps pour un dosage est d'environ 90 mn. Par des changements appropriés du pH et d'autres conditions, la méthode peut être utilisée por la séparation du molybdène de traces d'ions de métaux alcalins.

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CONTROLLED-POTENTIAL IODOMETRIC TITRATION OF NITRITE

APPLICATION TO THE DETERMINATION OF NITRITE IN MEAT PRODUCTS

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Summary—A controlled-potential coulometric method using iodine as an intermediate has been devised for the determination of nitrite. Nitrite is reduced by iodide and the iodine formed is then reduced coulometrically. The reduction of nitrite in the pH range 0–6 has been studied and the optimum conditions for an accurate determination are stated. The time of analysis for a determination in the range 0·005–5 mg of nitrite is about 2–5 min and the error ± 0·1%. The method is applied to the determination of nitrite in some meat products.

A large number of methods for the determination of nitrite can be found in the literature. Classical titrimetric procedures are based on the permanganate method where nitrite is oxidized to nitrate. and the iodometric method where nitrite is reduced to nitric oxide. These methods are all rather complicated and have limited accuracy. Besides, they require samples containing around 50 mg of nitrite for each analysis. Cool and Yoe[1] have examined more than thirty of these titrimetric procedures, of which only a few proved relatively satisfactory.

Electroanalytical approaches to the determination of nitrite are usually based on oxidation of nitrite to nitrate. An amperometric titration with permanganate was investigated by Stock and Björk[2] but the errors were not less than a few per cent. Constant-current coulometry using manganese(III) as oxidant was proposed by Buck and Crowe.[3] In the presence of an excess of pregenerated manganese(III), nitrite was oxidized to nitrate. and the excess of manganese(III) was then determined by back-titration with electrolytically generated iron(II). With this method small samples could be analysed but the use of two intermediates seems rather complicated. A more straighforward method, in which the nitrite was directly oxidized to nitrate at a platinum electrode by coulometry at controlled potential, has been described by Harrar.[4] The accuracy obtained was very good but the time of electrolysis was more than 20 min. The analysis time could be shortened appreciably by the use of predictive coulometry, investigated earlier by the same author, but in that case the accuracy was lower. Owing to the high potential required for the oxidation of nitrite in this method the possibility of interfering reactions is increased and therefore special pretreatment procedures must be followed in order to obtain low background currents.

The disadvantages of most of the existing methods for the determination of nitrite in meat and similar products are the relatively poor precision and accuracy. The colorimetric methods using different modifications of the Griess reagent[5] are most commonly used but they are limited by low precision. Landmann and Worland[6] found, using statistical methods according to Youden,[7] that the use of an iodometric method for the determination of nitrite in meat products proved superior to the colorimetric methods. Therefore, we found it attractive to use controlled-potential coulometry with iodine as an intermediate[8,9] for the determination of nitrite and to apply this method to nitrite in meat products.

The reaction for the iodometric determination of nitrite is:

$$2HNO_2 + 2I^- + 2H^+ \rightarrow I_2 + 2NO + 2H_2O \tag{1}$$

Air must be carefully excluded because of the reactions

$$2NO + O_2 \rightarrow 2NO_2 \tag{2}$$

$$NO_2 + 2I^- + 2H^+ \rightarrow I_2 + NO + H_2O \tag{3}$$

In the earlier iodometric methods proposed in the literature[10–12] the main problem was the difficulty in preventing reactions (2) and (3) occurring because of contamination from aerial oxygen during the analysis. In the electrolysis cells used in this investigation (and used earlier by the authors[8,9] for rapid and precise coulometric analysis) the exclusion of air is not at all difficult. The nitrite sample is added to an acid solution of sodium iodide in an electrolysis cell. The iodine formed in the reaction is then reduced coulometrically and the amount of electricity required is measured with an electronic integrator. By maintenance of a nitrogen atmosphere over the solution in the electrolysis cell, and passage of a rapid stream of nitrogen through the solution, the oxygen is effectively removed from the system and the nitric oxide liberated according to reaction (1) is expelled from the solution. Hence, reactions (2) and (3) cannot occur. Samples of nitrite in the range 0·005–5 mg can be determined with a relative standard deviation of about 0·1% and with analysis times in the range 2–5 min.

EXPERIMENTAL

Reagents

Standard solutions of nitrite were prepared from dried sodium nitrite of *pro analysi* quality (E. Merck, Darmstadt). All solutions were prepared with distilled water that had been boiled and cooled under a nitrogen atmosphere. The nitrogen used was 99·998% pure. Two titrimetric methods were used to assay the sodium nitrite.

Titration with permanganate

A 0·1*N* potassium permanganate solution was standardized against arsenic(III) oxide (NBS No. 83c, purity 99·99%, dried at 115 for 8 hr). The nitrite solutions were titrated according to the method proposed by Kolthoff and Sandell.[13]

Titration with chloramine-T ($CH_3C_6H_4SO_2NClNa.3H_2O$)

The chloramine-T solution was prepared from *pro analysi* reagent (E. Merck, Darmstadt). It was standardized and the sodium nitrite solutions were titrated according to the method described by Agterdenbos.[14]

With each of the two titration procedures 10 titrations were performed on each of the standard sodium nitrite solutions. The accuracies of the two methods were not significantly different and the sodium nitrite assayed as 99·96 ± 0·10% pure.

Preparation of samples from meat products

The sample is first carefully minced and mixed. A weighed portion of the sample (5 20 g) is then mixed with boiling distilled water and quantitatively transferred with boiling water to a 100 ml volumetric flask. Then 15% potassium ferrocyanide solution and 30% zinc sulphate solution (1 ml of each) are added to clarify the sample solution. The solution is made up to 100 ml and allowed to stand for 15 min before being filtered. Oxygen is then removed from the sample by a stream of nitrogen and the sample is placed in a refrigerator if not to be analysed immediately.

Apparatus

The controlled-potential coulometric circuit and the electrolysis cells have been described in detail earlier.[8,9] Cells of different sizes were used, depending on the nitrite content of the samples. The cells were fitted with an additional nitrogen inlet for rapid passage of nitrogen through the test solution. The solution in the working electrode compartment was made $1M$ in sodium iodide and $1M$ in sodium sulphate, and sufficient sulphuric acid and or acetic acid was added to obtain the appropriate pH. The counter-electrode compartment and bridge compartment were filled with $2M$ sodium sulphate. The bridge compartment solution was continuously deoxygenated with nitrogen. A glass electrode (Radiometer GK 2321C) was used to monitor the pH in the working electrode compartment during the analysis.

Procedure

The nitrogen stream passing over the solution in the cell is adjusted to about 150 ml/min, which prevents any oxygen from entering, and that passing through the solution is adjusted to about 250 ml/min. After 10 min passage of nitrogen, an appropriate amount of iodine is generated coulometrically in the cell and then immediately reduced. This is a check of the electrolysis system.

After this start-up a sample of nitrite is added to the cell. The amount of iodine liberated according to reaction (1) is immediately reduced and determined coulometrically. The analysis is followed by a check procedure in which an amount of iodine approximately equal to that liberated in the determination just finished, is generated and then immediately reduced. After this check procedure the nitrite content in the sample can be calculated. The corrections from the check procedure will normally not exceed 0·05% of the total integral obtained in an analysis.

RESULTS AND DISCUSSION

In order to establish the best conditions for the determination of nitrite a series of measurements was performed in which the pH was varied between 0 and 6. Table 1 shows the results obtained when 50·45 μmole of nitrite were added to the cell in each analysis. From the table it can be seen that the reaction between nitrite and iodide is rather slow at above pH 4 and practically negligible at pH 6. We interrupted the analysis after 30 min at pH 5 and 6 because of the very slow reaction rates, which made coulometric analysis impossible. At pH 4 the reaction goes appreciably faster but the result obtained was 1·1% low. Probably loss of nitrous acid, together with uncertain blank corrections, cause low results because of the relatively long time of analysis. Also the reaction:

$$HNO_2 + I_2 + H_2O \rightleftharpoons NO_3^- + 2I^- + 3H^+$$

can give rise to an error since both nitrous acid and iodine are consumed. This reaction is slow but may be a source of error with long analysis times. The high iodide concentration effectively prevents errors which might be due to volatilization of iodine.

The reaction:

$$4I^- + O_2 + 4H^+ \rightleftharpoons 2I_2 + 2H_2O$$

is a possible source of error at low pH. Kinetic studies[15] of this reaction have shown that the rate of aerial oxidation of iodide increases greatly at high hydrogen concentrations and that both light and oxides of nitrogen will catalyse this reaction. According to Kolthoff *et al.*[16] even the smallest trace of nitric oxide will have a considerable influence. However, with the high rate of passage of nitrogen through the cell solution any dissolved oxygen will be effectively expelled. If these conditions are fulfilled, precise coulometric determinations of nitrite can be performed even at pH 0. Only the very first analysis will result in a somewhat high value, probably because of traces of residual oxygen in the cell, but these will be consumed during the first analysis by the nitric oxide then formed.

Table 1. pH-Dependence for the determination of nitrite

pH	Time of analysis, *min*	Recovery, %
0	3·7	100·15
0·5	3·6	100·06
1·0	3·4	99·95
1·5	3·5	99·96
2·0	3·5	99·93
2·5	3·8	99·90
3·0	4·5	99·78
4·0	17	98·9
5·0	30	22
6·0	30	< 1

The high reaction rate between nitrite and iodide in the pH range 0–2 results in very rapid analysis, which minimizes the usual errors in the coulometric determination.

A series of tests was performed to find whether the passage of nitrogen could be diminished or even eliminated by the use of other methods. The use of carbon dioxide, from sodium bicarbonate or "dry ice", as a substitute for nitrogen for removing the dissolved oxygen and nitric oxide, as proposed in the literature, does not work satisfactorily in our method. The results were always a few per cent high. Urea will reduce nitrous acid and nitric oxide to nitrogen and water but these reactions are rather slow, whereas the reaction between iodide and nitrous acid is very rapid in acid medium. Even with a large excess of urea the results obtained were too high, indicating that the urea could not reduce the nitric oxide during the analysis.

A series of determinations on pure solutions of sodium nitrite was performed at the optimum pH of 0·5–1·5 and with sufficient nitrogen bubbling. Since the reaction between iodide and nitrite consumes hydrogen ions the pH in the working compartment will increase somewhat during a series of analyses, owing to the low buffer capacity of the system. Consequently, we adjusted the pH to 0·5 with sulphuric acid to avoid reaching too high a pH during the analysis. The results of the nitrite determinations in the range 0·005–5 mg are shown in Table 2, where the accuracy and precision are also quoted. The times of analysis were 2–5 min. These short times, with background currents always below 5 μA, lead to corrections not exceeding 0·05% of the result obtained in a determination.

Table 2. Determination of nitrite in the range 0·005–5 mg

Nitrite, μg added	Nitrite, μg found	Number of determinations	Precision* at a confidence limit of 95%, μg	Rel. error, %
5·22	5·21	6	0·05	−0·2
10·44	10·42	5	0·05	−0·2
34·57	34·61	5	0·08	+0·1
103·7	103·6	5	0·10	−0·1
345·7	346·0	5	0·22	+0·09
1160·1	1160·7	5	0·5	+0·05
4640	4639	4	2	−0·03

* Student's *t*-test.

Table 3. Determination of nitrite in meat products

Meat product	Sodium nitrite added before the extraction, *μg*	Meat sample, *g* (in 100 ml)	Aliquot analysed, *ml*	Nitrite calc., *μg*	Nitrite found, *μg*
Pork sausage	1250	5·00	1	12·5	12·7
	250	5·00	5	12·5	12·6
	1250	5·00*	1	12·5	12·5
	250	5·00*	5	12·5	12·4
Ham	—	5·00	5	0	0
	—	5·00*	5	0	0
	250	5·00	5	12·5	12·5
	250	5·00*	5	12·5	12·4

Meat product	Sodium nitrite added before the extraction, *μg*	Meat sample, *g* (in 100 ml)	Aliquot analysed, *ml*	Determined spectrophotometrically,† *μg*	Nitrite found, *μg*
German sausage	—	5·00	10	1·5 ± 0·7	1·1
	—	20·00	5	3 ± 0·7	2·3
	250	5·00	10	26·5 ± 2	26·2
	1000	20·00	5	53 ± 3	52·1
Bacon	—	5·00	5	1·3 ± 0·7	0·8
	—	20·00	5	5·2 ± 1	3·3
	125	5·00	5	7·6 ± 1	7·1

* Protein not precipitated.

† The error limits quoted correspond to a 95% confidence level.

Determination of nitrite in meat products

Table 3 gives the results of nitrite analyses in different meat products. (Each value is the mean of three measurements.) Some determinations of nitrite were performed without precipitation of the protein before analysis and the results in these cases showed no significant differences from those obtained for the treated solutions. However, with protein in the sample the time of analysis was increased owing to the diminished rate of mass transfer. The background currents became higher and the cell solution had to be changed after a few analyses in these cases. Addition of the precipitating ferrocyanide and zinc solutions to the cell alone (blank test) caused no disturbances. In general, the protein should be precipitated from the solution.

Nitrite in meat products reacts in different ways—for example it reacts with myoglobin to form the stable, coloured nitrosylmyoglobin. Also, oxides of nitrogen and free nitrogen are formed in different nitrite reactions, and nitrate is formed by disproportionation of nitrite. Therefore, calculations of nitrite contents based on experiments with a known amount of nitrite added are only relevant for freshly prepared samples.

We added nitrite to the samples just before the extraction step and the results obtained by immediate analysis agreed well with the values calculated, as may be seen in Table 3.

We also made simultaneous determinations with the standard spectrophotometric method using sulphanilic acid and α-naphthylamine, measuring the red coupling-product at 525 nm. The results obtained with the spectrophotometric method are given in Table 3 with confidence limits at the 95% level.

From the results in Table 3 it can be seen that the coulometric method is convenient for the determination of nitrite in meat. The method is rapid and the standard deviation is as low as 0·5% which makes the method an excellent alternative to the standard spectrophotometric method. In a further investigation the coulometric method will be extended to determination of nitrite contents below the μg level and also to include determination of nitrate.

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Zusammenfassung—Ein coulometrisches Verfahren mit geregeltem Potential mit Jod als Zwischenprodukt wurde zur Bestimmung von Nitrit entwickelt. Nitrit wird durch Jodid reduziert und das gebildete Jod anschließend coulometrisch reduziert. Die Reduktion von Nitrit wurde im pH-Bereich 0–6 studiert; die besten Bedingungen für eine genaue Bestimmung werden mitgeteilt. Die Analysenzeit für eine Nitritbestimmung bei 0,005–5 mg beträgt etwa 2–5 min, der Fehler ±0,1%. Das Verfahren wird auf die Bestimmung von Nitrit in einigen Fleischprodukten angewandt.

Résumé—On a élaboré une méthode coulométrique à potentiel contrôlé utilisant l'iode comme un produit intermédiaire pour le dosage du nitrite. Le nitrite est réduit par l'iodure et l'iode formé est alors réduit coulométriquement. On a étudié la réduction du nitrite dans le domaine de pH 0–6 et l'on fournit les conditions optimales pour un dosage précis. Le temps d'analyse pour un dosage dans le domaine de 0,005–5 mg de nitrite est d'environ 2–5 mn et l'erreur ±0,1%. La méthode est appliquée au dosage du nitrite dans quelques produits à base de viande.

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DETERMINATION OF THE OXIDIZING CAPACITY OF MANGANESE ORES

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Summary—An accurate method is described for determining the amount of active oxygen in manganese ores, based on the oxidation–reduction reaction between the ore and arsenic(III) in presence of ammonium molybdate, followed by the back-titration of excess of arsenic(III) with cerium(IV), using osmium tetroxide as catalyst and Disulphine Blue V as indicator. A survey has been made of the applicability of this method to various pyrolusite ores containing less than 0·2% phosphorus. Aluminium(III), copper(II), iron(III), manganese(II), and molybdenum(VI) do not interfere. Up to 30% phosphorus(V) causes no interference.

The active oxygen in a manganese ore is regarded as the amount in excess of that required by the formula MnO. It is usually described as being present in the form of manganese dioxide MnO_2 and is quoted as such throughout this work. A variety of methods have been used for its estimation. In the classical oxalate method[1] the sample is digested with oxalate in dilute sulphuric acid, and the excess of oxalate titrated with permanganate. However, this method has been criticized by several workers,[2–4] who found that oxalate is decomposed catalytically by Mn(II). Katz, Clarke and Nye[4] discovered that the loss of oxalate was reduced when the space above the reaction mixture was filled with carbon dioxide, and suggested that "decomposition" was due to reaction with atmospheric oxygen. This could be present in solution[5] or adsorbed on the surface of the ore.[6] Other workers[7] found that decomposition was also brought about by light and acid. Freeman and Chapman[8] obtained more accurate results in the presence of copper(II), or iron(III), both of which stabilize the oxalate, and a method was developed which used iron(III) as additive. The present author, following the procedure of Freeman and Chapman, found that it was necessary to adhere very closely to the specified conditions to obtain reproducible results and that the method was not suitable for small samples.

The British Standards method,[9] based on the oxidation of iron(II) sulphate, was found to be accurate but tedious. Moreover, the reaction had to be carried out in an atmosphere of carbon dioxide to prevent the oxidation of iron(II) by aerial oxygen.

In Bunsen's method[10] the ore is treated with hydrochloric acid and the evolved chlorine is passed into potassium iodide solution, the released iodine being titrated with thiosulphate. This method was regarded as satisfactory by Belcher and Kolthoff[11] and by Pantony and Siddiqi,[6] but Mrgudich and Clark[12] questioned its accuracy. In any case, it too is tedious and time-consuming. Modified procedures,[12–19] in which manganese dioxide is made to react directly with potassium iodide, can be used only in the analysis of reactive materials and are not generally applicable to ores of a refractory nature. The same criticism can be made of the methods of Schaeffer[20] and Stognii[21] in which hydrogen peroxide is used as the reducing agent. Tanino[2] has used fusion with potassium hydrogen fluoride as a means of reducing manganese(IV) and manganese(VII) to manganese(III). The fused mixture was extracted and titrated with ammonium iron(II) sulphate. However, this method did not give satisfactory results in presence of a high proportion of Mn(II), and therefore it is suitable only for samples with a high manganese dioxide content.

Wilson[23] and Schweigart[24] reduced the ore with vanadium(IV) at room temperature. They allowed the ore to dissolve in a solution containing excess of vanadium(IV) sulphate and hydrofluoric acid, and then titrated the resultant vanadium(V) produced with ammonium iron(II) sulphate. However, although some ores dissolve with ease in the reducing mixture, others take several days to go into solution.

The manganese ores analysed in the present work fall into the marketing categories of "metallurgical", "catalytic", "ceramic" and "battery" grade ores, all of which contained manganese as pyrolusite (MnO_2) in concentrations varying from 30 to 90%. With the exception of Caucasian ores, each type of ore analysed had characteristics unsuited to the methods reviewed above.

Moroccan ores with high Mn(II) contents give high results by the oxalate method, owing to catalytic decomposition of the oxalate. Congo manganese, while initially reacting quickly with oxalate, leaves behind a residue of a refractory nature which decomposes very slowly. Mamatwan type ores have high iron contents and decompose at only moderate rates; further, the colour of the reaction products makes end-point detection difficult. Amapa I and Hotazel manganese ores are of metallurgical grade and contain insoluble matter together with iron and other metals. In the analysis of these ores it is difficult to ascertain the completeness of the reaction and again end-point detection is difficult. The oxalate method for the determination of the oxidizing capacity of "electrolytic" manganese was found to be unreliable in this laboratory.

This paper describes a method anticipated by Cantoni's arsenite method.[25] It is based on reduction by arsenic(III) followed by back-titration of the excess of arsenic(III) with cerium(IV) sulphate, ammonium molybdate being present to reduce the depressive effect of phosphorus.

EXPERIMENTAL

Reagents

Arsenic(III) solution, 0·025*M*. Dissolve about 4·9 g (accurately weighed) of analytical grade arsenic(III) oxide, previously dried at 108 ± 2° for 2 hr, in about 200 ml of cold 20% sodium hydroxide solution to obtain a clear solution. Add just enough dilute sulphuric acid to bring the pH to below 7 (indicator paper). Dilute it accurately to 1 litre.

Ammonium cerium(IV) sulphate solution, 0·050*M*. Dissolve about 33 g of analytical-grade ammonium cerium(IV) sulphate in 500 ml of 5% v/v sulphuric acid and dilute to 1 litre with water. Standardize it with the arsenic(III) solution as in the procedure.

Ammonium molybdate solution, 1%. Dissolve 1 g of analytical-grade ammonium paramolybdate tetrahydrate in 100 ml of water and add 1 ml of 2*M* ammonia.

Osmium tetroxide solution, 0·01*M*. Dissolve 0·025 g of osmium tetroxide in 100 ml of 0·05*M* sulphuric acid.

Disulphine Blue V indicator solution, 1%.

Sodium hydroxide solution, 20%.

Sulphuric acid, 25% *v/v*.

Procedure

Grind the sample to pass through a 150-μm aperture sieve and dry it at 110 ± 2° for 2 hr. Transfer about 170 mg of sample, accurately weighed, into a 500-ml conical flask which contains 50·0 ml of standard 0·025*M* arsenic(III) solution and 30 ml of 25% v/v sulphuric acid, and dilute to about 200 ml with water. Place in the neck of the flask a funnel with a short wide stem and boil the solution gently for an hour, keeping the volume at 200 ml by adding water from time to time. Crush any unreacted solid particles with a glass rod, add 1 ml of 1% ammonium molybdate solution and boil the solution gently for 1 hr or until no dark brown particles

Table 1.

	MnO_2, %			
Sample	B.S.I. method[9]*	Present method without molybdate*	Present method*	Phosphorus in ore, %
Congo I	$80{\cdot}1_0\ (0{\cdot}1_3)$	$77{\cdot}9_4\ (0{\cdot}4_0)$	$80{\cdot}1_4\ (0{\cdot}1_0)$	0·18
Congo II	$82{\cdot}1_2\ (0{\cdot}1_0)$	$80{\cdot}3_1\ (0{\cdot}3_1)$	$82{\cdot}1_6\ (0{\cdot}1_1)$	0·14
British Chemical Standard 176/1	$73{\cdot}4_9\ (0{\cdot}1_4)$	$72{\cdot}4_2\ (0{\cdot}2_8)$	$73{\cdot}5_3\ (0{\cdot}1_0)$	0·14
Amapa (Brazil)	$72{\cdot}9_8\ (0{\cdot}1_0)$	$72{\cdot}0_0\ (0{\cdot}2_8)$	$72{\cdot}9_9\ (0{\cdot}0_8)$	0·09
Lagos (Nigerian)	$77{\cdot}2_1\ (0{\cdot}0_7)$	$76{\cdot}5_3\ (0{\cdot}2_3)$	$77{\cdot}1_8\ (0{\cdot}0_8)$	0·06
Immini I (Moroccan)	$74{\cdot}2_8\ (0{\cdot}1_1)$	$74{\cdot}0_5\ (0{\cdot}1_9)$	$74{\cdot}3_0\ (0{\cdot}0_7)$	0·05
Immini II	$81{\cdot}4_8\ (0{\cdot}1_0)$	$81{\cdot}0_7\ (0{\cdot}1_8)$	$81{\cdot}5_0\ (0{\cdot}0_8)$	0·04
Australian	$65{\cdot}0_3\ (0{\cdot}1_4)$	$64{\cdot}9_5\ (0{\cdot}0_9)$	$65{\cdot}0_2\ (0{\cdot}0_6)$	0·03
Indian	$93{\cdot}9_8\ (0{\cdot}1_6)$	$93{\cdot}9_3\ (0{\cdot}0_9)$	$93{\cdot}9_7\ (0{\cdot}0_9)$	0·02

* The values in brackets represent standard deviations from the mean of 5 determinations.

remain, whichever is the shorter. Cool the flask to room temperature, add two drops of osmium tetroxide solution and three drops of indicator and titrate with standard 0·05*M* cerium(IV) until the colour changes from green-yellow to red.

RESULTS AND DISCUSSION

A series of results obtained by the present procedure with and without the addition of molybdate is presented in Table 1. Standard deviations are given in brackets. Each figure is the average obtained from 5 different samples of the ore. The phosphorus contents of the ores were determined by an absorptiometric method.[26] The figure in column 2 represents the results obtained by the British Standards method.[9] The absolute standard deviation is seen not to exceed 0·16% regardless of the weight and nature of sample used. By comparison the standard deviation of the set of five separate analyses of the MnO_2 content of sample B.C.S. 176/1 as quoted in the sample specification is 0·37. This figure is in agreement with the results reported by the British Institute for its standard method.[9] However the figures in columns 2, 3, and 5 indicate that when the phosphorus content of the ores exceeds about 0·04%, the results obtained in the absence of molybdate are low and somewhat less reproducible. It is believed that these losses are caused by some type of association of phosphorus with manganese.

Ammonium molybdate was added to see whether this effect could be reduced by converting the phosphorus into phosphomolybdate. A comparison of columns 3 and 4 indicates marked improvement. The influence of phosphate was further studied by adding trisodium phosphate to the reaction flask together with the sample. Results obtained on samples of B.C.S. 176/1, Imini(I) and Imini(III) manganese are presented in Table 2. The addition of 2 mmole of phosphorus, which corresponds to 30% phosphorus being present in

Table 2. Effect of phosphorus(V)

		MnO_2 found, %*	
Phosphate added, *mmole*	B.C.S. 176/1 $(73{\cdot}5_3)$†	Imini I $(74{\cdot}3_0)$†	Imini III $(84{\cdot}0_8)$†
0·5	$73{\cdot}5_0$	$74{\cdot}2_8$	$83{\cdot}9_1$
1·0	$73{\cdot}4_8$	$74{\cdot}3_2$	$84{\cdot}0_0$
1·5	$73{\cdot}5_9$	$74{\cdot}3_9$	$84{\cdot}1_9$
2·0	$73{\cdot}4_4$	$74{\cdot}2_9$	$84{\cdot}1_0$

* Average of three determinations.
† True value, obtained by standard method.[9]

Table 3. Effect of additives to manganese ores

	MnO$_2$ found, %*		
Ion added, *mmole*	B.C.S. 176/1 (73·5$_3$)†	Imini I (74·3$_0$)†	Imini III (84·0$_8$)†
Mn(II)			
0·5	73·6$_1$	74·3$_4$	84·1$_8$
1·0	73·4$_5$	74·3$_1$	84·0$_9$
1·5	73·5$_4$	74·2$_9$	84·1$_4$
2·0	73·4$_6$	74·3$_8$	84·1$_4$
Al(III)			
0·5	73·4$_3$	74·3$_0$	84·0$_5$
1·0	73·6$_0$	74·4$_3$	84·1$_3$
1·5	73·3$_8$	74·2$_9$	84·1$_7$
2·0	73·4$_7$	74·3$_2$	84·0$_9$
Fe(III)			
0·5	73·3$_9$	74·2$_1$	84·2$_0$
1·0	73·4$_8$	74·3$_8$	84·1$_3$
1·5	73·6$_3$	74·1$_4$	84·0$_6$
2·0	73·5$_0$	74·3$_6$	84·1$_7$
Cu(II)			
0·5	73·4$_0$	74·2$_4$	84·1$_3$
1·0	73·3$_2$	74·4$_2$	84·1$_4$
1·5	73·5$_1$	74·1$_8$	84·2$_1$
2·0	73·4$_9$	74·3$_9$	84·0$_0$
Mo(VI)			
0·5	73·3$_8$	74·4$_1$	84·1$_0$
1·0	73·4$_1$	74·3$_6$	83·9$_0$
1·5	73·6$_0$	74·4$_6$	84·0$_0$
2·0	73·4$_3$	74·2$_9$	84·1$_9$
All five			
0·5 of each	73·4$_8$	74·4$_0$	83·9$_3$
1·0	73·3$_0$	74·1$_5$	84·0$_0$
1·5	73·5$_8$	74·3$_9$	84·2$_6$
2·0	73·6$_4$	74·1$_8$	84·1$_0$

* Average of three determinations.

† True value obtained by standard method.[9]

the ore sample, did not cause any interference. The molybdate had to be added after the initial reaction, because if it was added at the start, the reaction between manganese dioxide and arsenic(III) was retarded.

Manganese(II), copper(II), iron(III), aluminium(III), molybdenum(VI), and phosphorus(V) (in 2-mmole amounts) do not interfere with either the titration of arsenic(III) with cerium(IV) or with the determination of manganese dioxide by the method described (Table 3).

The maximum relative standard deviation found was 0·18% for electrolytic manganese dioxide, which is better than that obtained by other methods, particularly the oxalate method. For the other samples analysed (18 in all) the absolute standard deviation was generally 0·07–0·11%.

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Zusammenfassung—Es wird eine genaue Methode zur Bestimmung des aktiven Sauerstoffs in Manganerzen angegeben. Sie beruht auf der Oxidations-Reduktions-Reaktion zwischen dem Erz und Arsen(III) in Gegenwart von Ammoniummolybdat. Nach dieser Reaktion wird das überschüssige Arsen(III) mit Cer(IV) zurücktitriert, wobei Osmiumtetroxid als Katalysator und Disulfinblau V als Indikator verwendet werden. Es wurde eine Übersicht über die Anwendbarkeit dieses Verfahrens auf verschiedene weniger als 0·2% Phosphor enthaltende Pyrolusit-Erze zusammengestellt. Aluminium(III), Kupfer(II), Eisen(III), Mangan(II) und Molybdän(VI) stören nicht, bis zu 30% Phosphor(V) ebenfalls nicht.

Résumé—On décrit une méthode précise pour déterminer la quantité d'oxygène actif dans les minerais de manganèse, basée sur la réaction d'oxydation-réduction entre le minerai et l'arsenic(III) en présence de molybdate d'ammonium, suivie par le titrage en retour de l'excès d'arsenic(III) par le cérium(IV), en utilisant le tétroxyde d'osmium comme catalyseur et le Bleu Disulfine V comme indicateur. On a effectué une étude de la possibilité d'application de cette méthode à divers minerais de pyrolusite contenant moins de 0.2% de phosphore. Les aluminium(III), cuivre(II), fer(III), manganèse(II) et molybdène(VI) n'interfèrent pas. Le phosphore(V) jusqu'à 30% ne cause pas d'interférence.

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SHORT COMMUNICATIONS

COULOMETRIC DETERMINATION OF DISSOLVED OXYGEN IN WATER

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Of all the methods published for the determination of oxygen dissolved in water that of Winkler[1] and its numerous modifications are most widely used. From the critical reviews of these methods made by Potter[2] and later by Caritt and Carpenter[3] it can be seen that rather large sample volumes are required and that several of the procedures used are time-consuming. The final step in most of these methods, and in some others such as those in which oxygen is allowed to react with chromous ion,[4,5] is based on the determination of iodine titrimetrically or photometrically. The accuracy of these determinations is often affected by difficulties in determining the end-point exactly.

Electrochemical approaches to oxygen measurements have been made by Caritt and Kanwisher[6] who used membrane-type electrodes and by Lilley *et al.*[7] who improved these electrode measurements by the use of a chronoamperometric technique. The need for calibration curves and the sensitivity of the electrodes to temperature variations however. make these methods time-consuming and less accurate.

In an earlier paper we presented a coulometric method for the determination of nitrite,[8] using the reaction:

$$2HNO_2 + 2I^- + 2H^+ \rightarrow 2NO + I_2 + 2H_2O \qquad (1)$$

and found it necessary to prevent oxygen from entering the coulometric cell. Oxygen will otherwise interfere according to the reactions

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

and

$$NO_2 + 2I^- + 2H^+ \rightarrow NO^+I_2 + H_2O \qquad (3)$$

In our method for the determination of oxygen, sufficient nitric oxide is produced according to reaction (1) for reactions (2) and (3) to occur. The iodine formed is then reduced coulometrically and the amount of oxygen can be determined. Since all the reactions involved are rapid and stoichiometric the determinations are accurate and take only a few minutes.

EXPERIMENTAL

Apparatus

The controlled-potential coulometric apparatus was the same as for the determination of nitrite[8] and as described earlier.[9,10]

Preparation of oxygen samples

A thermostat bath was built containing about 8 l. of water and with very well insulated walls. A four-necked 250 ml flask containing 150 ml of doubly-distilled water was immersed in the bath to the top of the necks. Carbon dioxide-free thermostated air saturated with water vapour was bubbled through the water in the flask at about 50 ml/min. The flask was also furnished with a mercury thermometer calibrated against a platinum resistance thermometer.

When the desired temperature was reached the air stream through the water was decreased and only a small stream of air was blown over the surface of the water to renew the atmosphere in the flask continuously and allow the system to be completely equilibrated.

Procedure

The electrolyte in the coulometric cell was the same as in the determination of nitrite and the pH was adjusted to 0·5 with sulphuric acid. The nitrogen streams through and above the solution in the working electrode compartment were adjusted to 250 and 150 ml/min. respectively.

The following sequence of operations was performed for a determination of oxygen.

1. The nitrogen bubbling through the cell solution was stopped.
2. A coulometric determination of about 25 μmole of sodium nitrite was performed.
3. An identical amount of sodium nitrite together with the oxygen-containing sample was determined.
4. The oxygen content of the sample was calculated from the difference of the integrator read-outs obtained in steps 2 and 3.

Determination of oxygen in air-saturated water

Water was saturated with air at seven different temperatures in the interval 10–40°. Three samples were taken at each temperature with a carefully calibrated 1 ml "Misco" pipette, working from the lowest to the highest temperature and then back again. The results from the two series of determinations agreed within 0·2%, which indicated that equilibrium was reached at each temperature.

RESULTS AND DISCUSSION

The results for the determination of oxygen in water saturated with air are shown in Table 1 together with data from some often-cited studies. The values calculated by Whipple and Whipple,[11] based on a gasometric determination by Fox,[12] and quoted in several books on standard methods for the determination of oxygen are somewhat high over the whole range in comparison with our results. Probable explanations are supersaturation with dissolved oxygen and systematic errors due to the gasometric method used. A modification of the Winkler technique was used by Truesdale *et al.*[13] Their values up to about 30° are appreciably lower than any others available in the literature. A probable reason for this is that iodine had been lost by volatilization and that the loss was greater for samples saturated with oxygen at low temperatures than for samples saturated at high temperatures. This has also been shown by Montgomery *et al.*[14] who used a modification of the Winkler technique but eliminated the loss of iodine by using a large excess of iodide. Their values agree rather well with those obtained in our investigation.

Table 1. Oxygen content of air-saturated water, expressed in *ppm* (w/w)

Temp, °C	Whipple and Whipple	Truesdale *et al.*	Montgomery *et al.*	This work
10	11·33	10·92	11·28	11·20
15	10·15	9·76	10·07	10·10
20	9·17	8·84	9·08	9·10
25	8·38	8·11	8·26	8·28
30	7·63	7·53	7·57	7·60
35	7·10	7·04	6·98	7·04
40	6·60	6·59	6·47	6·48

Our values presented in Table 1 are the mean of six determinations and all values are adjusted to a pressure of 760 mmHg according to the formula

$$S_{760} = S\frac{760 - p}{P - p}$$

where S_{760} is the saturation value at 760 mmHg, S is the observed saturation value at the actual barometric pressure P, and p is the saturated water vapour pressure in mmHg. The relative humidity measured with a dew-point apparatus indicated that the water vapour pressure was within a few per cent of the saturation value at every temperature measured. The temperature was controlled to ±0·03° which gave an uncertainty of less than 0·05% in the results. Volume–weight conversions for the pipette at the different temperatures gave an error of about 0·1% and together with the uncertainty in the coulometric determination gave a total maximum error of about 0·4% for each value obtained.

An empirical equation for the solubility of oxygen was calculated by the method of least-squares:

$$S = 14{\cdot}1271 - 0{\cdot}33935t + 5{\cdot}1333 \times 10^{-3}t^2 - 3{\cdot}5556 \times 10^{-5}t^3$$

where S is the solubility of oxygen in water (ppm w/w) and t is the temperature in °C. The root mean square deviation of the experimental values from those calculated from the equation above is 0·021 ppm.

The enthalpy and entropy changes for the following reaction can be calculated:

$$O_2(g, p_{O_2}) \rightleftharpoons O_2(aq, X_{O_2})$$

where p_{O_2} is the partial pressure of oxygen in atmospheres in the gas phase and X_{O_2} is the solubility of oxygen expressed as a mole-fraction.

The solubility of individual gases in a mixture is directly proportional to their partial pressures and nearly independent of the presence of the others. If we express the solubility of oxygen in water at different temperatures as a mole fraction and use the equation

$$\ln X_{O_2} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln p_{O_2}$$

which is relevant if we assume that ΔH° and ΔS° for the transfer of 1 mole of oxygen from the gas phase to the water phase are independent of the temperature in the measured interval (25 ± 15°) a plot of ln X_{O_2} *vs.* the reciprocal of the absolute temperature will then result in a straight line. The line was evaluated by means of a least-squares fit and from the slope ΔH° was estimated to be −13·40 kJ/mole and from the intercept on the ordinate ΔS° was found to be −134 J.mole.deg^{-1}. The deviation of the solubility values from the calculated line is only 0·3%, which supports the assumption that ΔH° and ΔS° are almost independent of the temperature in this relatively small interval. The attractive forces between the oxygen molecules and the water molecules are probably of van der Waals type as the order of magnitude of such forces usually lies in the range 10–15 kJ/mole.

The good accuracy obtained for the solubility determinations and the small sample volumes required make the coulometric method very convenient for the determination of oxygen dissolved in water.

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Summary—The oxygen content of air-saturated distilled water has been determined at between 10 and 40° by using a controlled-potential coulometric method based on an earlier published method for the iodometric determination of nitrite. The maximum error for the determinations was ±0·3% over the whole range, and the time of analysis about 3 min. An equation is given for the solubility in the measured range, and some thermodynamic functions are calculated.

Zusammenfassung—Der Sauerstoffgehalt von luftgesättigtem destilliertem Wasser wurde zwischen 10 und 40° mit Hilfe einer coulometrischen Methode mit geregeltem Potential bestimmt; diese beruht auf einer vorher publizierten Methode zur jodometrischen Bestimmung von Nitrit. Der maximale Fehler der Bestimmungen betrug im ganzen Bereich ±0.3%, die Analyse dauerte etwa 3 min. Es wird eine Gleichung für die Löslichkeit im gemessenen Bereich angegeben, und es werden einige thermodynamische Funktionen berechnet.

Résumé—On a déterminé la teneur en oxygène de l'eau distillée saturée d'air entre 10° et 40° en utilisant une méthode coulométrique à potentiel contrôle basée sur une méthode publiée précédemment pour le dosage iodo-métrique du nitrite. L'erreur maximale pour le dosage est ±0,3% dans tout l'intervalle, et le temps d'analyse est d'environ 3 mn. On donne uneéquation pour la solubilité dans l'intervalle mesuré, et quelques fonctions thermodynamiques sont calculées.

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SIMULTANEOUS DETERMINATION OF DIMETRIDAZOLE AND FURAZOLIDONE IN FEED-PREMIXES BY D.C. POLAROGRAPHY

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Dimetridazole (1,2-dimethyl-5-nitroimidazole) and furazolidone [*N*-(5-nitro-2-furfurylidene)-3-amino-2-oxazolidone] are active ingredients of some veterinary feed-premixes used for the preparation of animal feeds effective against some diseases of pigs. A rapid polarographic method for the simultaneous determination of both these active constituents has been established.

The sample is treated with DMF to facilitate the dissolution of dimetridazole and furazolidone. A Britton–Robinson buffer, pH = 6·8, is used as supporting electrolyte and both constituents are determined polarographically in a single determination. Sugars, antibiotics of the tetracycline group, and most vitamins do not interfere. Vitamin B_2 and compounds with an aromatic nitro-group interfere.

EXPERIMENTAL

Reagents

N,N-*Dimethylformamide (DMF), analytical grade.*

Britton–Robinson buffer, pH = 6·8. Mix 100 ml of a solution which is 0·04*M* in acetic acid, 0·04*M* in orthophosphoric acid and 0·04*M* in boric acid, with 50 ml of 0·2*M* sodium hydroxide.

Standard solution. Weigh 120 mg of dimetridazole reference standard and 60 mg of furazolidone reference standard into a 100 ml volumetric flask. Dissolve them in 80 ml of DMF and add water to volume. This standard solution is used when the ratio dimetridazole: furazolidone in the sample is expected to be about 2:1. In general the ratio dimetridazole:furazolidone in the standard should be about the same as that in the sample, and other standards can be prepared appropriately.

Preparation of sample

Weigh a portion of finely ground sample containing 1·2–2·4 mg each of metronidazole and furazolidone into a 50 ml volumetric flask, add 5 ml of DMF and shake the flask for some minutes. Then add 0·75 ml of 0·2% aqueous solution of Triton X-100 (Rohm and Haas Co.), or of 0·2% aqueous solution of gelatin and dilute to volume with Britton–Robinson buffer, pH = 6·8. Mix well and filter the solution if necessary.

Polarography

Pipette 25 ml of the clear solution into a polarographic cell and purge with oxygen-free nitrogen for 10 min. Record the polarogram *vs.* SCE from +0·1 to −1·1 V with a sensitivity of 7–20 μA full-scale deflection and suitable damping. Use of a drop-life timer is recommended, to give a drop-time of 2–3 sec. Under these conditions $E_{1/2}$ of furazolidone is −0·35 V and that of dimetridazole about −0·69 V, so that $\Delta E_{1/2}$ is sufficient for separation of the two waves.

After obtaining the polarogram, add 1 ml of the standard solution to the solution in the cell, deaerate with oxygen-free nitrogen for 1 min and again record the polarogram under the same conditions.

Measure the wave heights and calculate as follows:

$$\text{mg of furazolidone in 1 g of sample} = \frac{20\,ah_1}{(1{\cdot}04\,h_2 - h_1)w}$$

$$\text{mg of dimetridazole in 1 g of sample} = \frac{20\,bH_1}{(1{\cdot}04\,H_2 - H_1)w}$$

where a = mg of furazolidone reference standard in 100 ml of standard solution
b = mg of dimetridazole reference standard in 100 ml of standard solution
w = weight of the sample in mg
h_1 = wave-height of furazolidone before standard addition
h_2 = wave-height of furazolidone after standard addition
H_1 = wave-height of dimetridazole before standard addition
H_2 = wave-height of dimetridazole after standard addition.

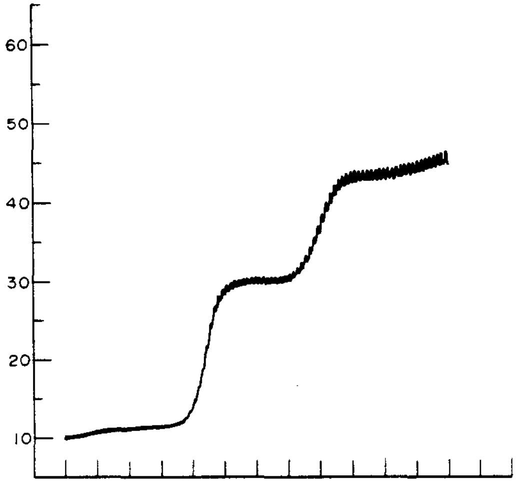

Fig. 1. Polarogram of an equimolar ($2 \times 10^{-4}M$) solution of dimetridazole and furazolidone in Britton–Robinson buffer, pH = 6·8. The solution contains 20% v/v of DMF. Recording of the curve starts at +0·1 V *vs.* SCE. One abscissa division corresponds to 0·1 V and one ordinate division to 1·5 μA.

RESULTS AND DISCUSSION

The method is especially suitable for rapid control during the manufacture of feed-premixes. One analysis for both components takes about 30 min. The precision is fairly good (see Table 1). The polarographic currents of both components are diffusion-controlled and increase linearly with concentration in the range used for the determination. The supporting electrolyte chosen (Britton–Robinson buffer pH = 6·8 with 10% of DMF) was found to be the most suitable. At lower pH values the separation of the waves is not so good, and in the alkaline region furazolidone decomposes.[1] An addition of DMF improves the solubility of both components. Other supporting electrolytes,[1,2] were also tested but their buffer capacity is too low for the purpose. The standard-addition method is preferred because more accurate results are obtained and it is more rapid than the concentration–diffusion current plot method.

Table 1. Results of 10 analyses on a feed-premix containing 12% metronidazole and 6% furazolidone

	Furazolidone		Dimetridazole	
	Found, %	Recovery, %	Found, %	Recovery, %
	5·86	97·7	11·86	98·8
	6·07	101,1	11,95	99·6
	5·87	97·8	12·10	100·7
	5·97	99·4	12·04	100·3
	5·91	98·4	11·88	99·0
	6·13	102·1	11·92	98·4
	5·90	98·3	12·11	100·9
	6·08	101·4	12·04	100·3
	6·04	100·6	11·87	98·8
	6·01	100·2	11·88	98·9
Average	5·98	99·7	11·96	99·6
Std. devn.		±1·6%		±0·9%

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Summary—A polarographic method has been proposed by which dimetridazole and furazolidone can be determined in combination in feed-premixes in a single determination. The sample is treated with DMF to facilitate the dissolution of dimetridazole and furazolidone, Britton–Robinson buffer of pH = 6·8 is added and the solution is polarographed at the dropping mercury electrode *vs.* SCE. The waves are sufficiently separated to allow quantitative determination. The standard-addition method is used. The method is simple and very fast.

Zusammenfassung—Es wird ein polarographisches Verfahren vorgeschlagen, mit dem Dimetridazol (1,2-Dimethyl-5-nitroimidazol) und Furazolidon nebeneinander in einer Bestimmung in vorgemischtem Futter bestimmt werden können. Die Probe wird mit DMF behandelt, um die Auflösung von Dimetridazol und Furazolidon zu erleichtern, Britton–Robinson-Buffer von pH 6,8 zugegeben und die Lösung an einer Quecksilbertropfelektrode gegen eine gesättigte Kalomelelektrode polarographiert. Die Stufen liegen genügend voneinander entfernt, um eine quantitative Bestimmung zu erlauben. Es wird die Methode der Standardzugabe verwendet. Das Verfahren ist einfach und geht sehr schnell.

Résumé—On propose une méthode polarographique par laquelle le dimétridazole et la furazolidone peuvent être dosés en combinaison dans des prémélanges alimentaires en une seule détermination. L'échantillon est traité au DMF pour faciliter la dissolution du dimétridazole et de la furazolidone, on ajoute du tampon Britton–Robinson de pH = 6,8 et la solution est passée au polarographe à l'électrode à gouttes par rapport à l'électrode au calomel saturée. Les vagues sont suffisamment séparées pour permettre le dosage quantitatif. On utilise la méthode d'addition d'étalon. La méthode est simple et très rapide.

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POLYSTYRENES IMPREGNATED WITH ETHERS—A POLYMERIC REAGENT SELECTIVE FOR GOLD

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The use of polymeric reagents in the recovery of metals offers many advantages over the use of liquid–liquid extraction. The most important of these is the ease with which the solid–liquid separation can be achieved. However, the choice of polymeric reagents is restricted by the complexity of their preparation, to the common ion-exchangers containing acidic or basic functional groups. The emergence of the high surface-area polymeric absorbants of the macroreticular or macroporous types now permits the preparation of polymeric reagents, not by chemical reactions, but by impregnation of a suitable compound having a high affinity for the polymeric matrix.

In the work described here, polymeric reagents *selective* for gold were prepared by the impregnation of ethylene diglycol dibutyl ether, according to the method reported by Morris and Khan,[1] so that the following points could be tested: (*i*) whether an impregnated polymeric reagent is completely analogous to a liquid reagent in selectivity.

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Summary—A polarographic method has been proposed by which dimetridazole and furazolidone can be determined in combination in feed-premixes in a single determination. The sample is treated with DMF to facilitate the dissolution of dimetridazole and furazolidone, Britton–Robinson buffer of pH = 6·8 is added and the solution is polarographed at the dropping mercury electrode *vs.* SCE. The waves are sufficiently separated to allow quantitative determination. The standard-addition method is used. The method is simple and very fast.

Zusammenfassung—Es wird ein polarographisches Verfahren vorgeschlagen, mit dem Dimetridazol (1,2-Dimethyl-5-nitroimidazol) und Furazolidon nebeneinander in einer Bestimmung in vorgemischtem Futter bestimmt werden können. Die Probe wird mit DMF behandelt, um die Auflösung von Dimetridazol und Furazolidon zu erleichtern, Britton–Robinson-Buffer von pH 6,8 zugegeben und die Lösung an einer Quecksilbertropfelektrode gegen eine gesättigte Kalomelelektrode polarographiert. Die Stufen liegen genügend voneinander entfernt, um eine quantitative Bestimmung zu erlauben. Es wird die Methode der Standardzugabe verwendet. Das Verfahren ist einfach und geht sehr schnell.

Résumé—On propose une méthode polarographique par laquelle le dimétridazole et la furazolidone peuvent être dosés en combinaison dans des prémélanges alimentaires en une seule détermination. L'échantillon est traité au DMF pour faciliter la dissolution du dimétridazole et de la furazolidone, on ajoute du tampon Britton–Robinson de pH = 6,8 et la solution est passée au polarographe à l'électrode à gouttes par rapport à l'électrode au calomel saturée. Les vagues sont suffisamment séparées pour permettre le dosage quantitatif. On utilise la méthode d'addition d'étalon. La méthode est simple et très rapide.

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In the work described here, polymeric reagents *selective* for gold were prepared by the impregnation of ethylene diglycol dibutyl ether, according to the method reported by Morris and Khan,[1] so that the following points could be tested: (*i*) whether an impregnated polymeric reagent is completely analogous to a liquid reagent in selectivity.

and (*ii*) whether it compares favourably with a conventional polymer, in spite of the fact that permeability inside the pores could be impaired during the impregnation process.

EXPERIMENTAL

Preparation of the polymeric reagent

XAD-2 polymeric absorbant (50 g) obtained from Rohm and Haas, was impregnated by being stirred in a solution of ethylene diglycol dibutyl ether (20 g) in hexane (150 ml) for 1 hr, followed by evaporation of the solvent in a rotary flash-evaporator, until freely flowing beads were obtained. The beads contained 28·6% of ethylene diglycol ether (or 1·31 mmole/g).

Test of gold adsorption

In all the tests, the resin was shaken with a known amount of tetrachloroaurate in hydrochloric acid, and the amount adsorbed was calculated from analyses of solutions before and after the tests either by spectrophotometric or by atomic-absorption methods.[2]

First the rate of adsorption from 3*M* hydrochloric acid was determined, and it was found that a contact time of 30 min is sufficient (see Table 1) for constant extraction (53%).

Table 1. Rate of adsorption of Au(III) onto resin from 3*M* hydrochloric acid (Au 177 mg in 10 ml; 1 g of resin)

Time, *min*	0	5	10	15	20	25	30
Au(III) in filtrate, *mg/ml*	17·7	12·5	10·1	9·0	8·4	8·3	8·3
Au(III) in resin, *mg/g*	0	52	76	87	93	94	94

Next, the influence of hydrochloric acid concentration on adsorption was tested. The results, which indicate that adsorption is not strongly dependent on acid concentration, are given in Table 2 (see also Fig. 1).

Table 2. Influence of acidity on adsorption of gold (Au 17·7 mg in 10 ml, 1 g of resin)

Hydrochloric acid, *M*	Au(III) in filtrate, *mg/ml*	Au(III) adsorbed on resin, *mg/g*
1·0	1·02	7·5
2·0	0·84	9·3
3·0	0·79	9·8
4·0	0·69	10·8
5·0	0·67	11·0
6·0	0·65	11·2

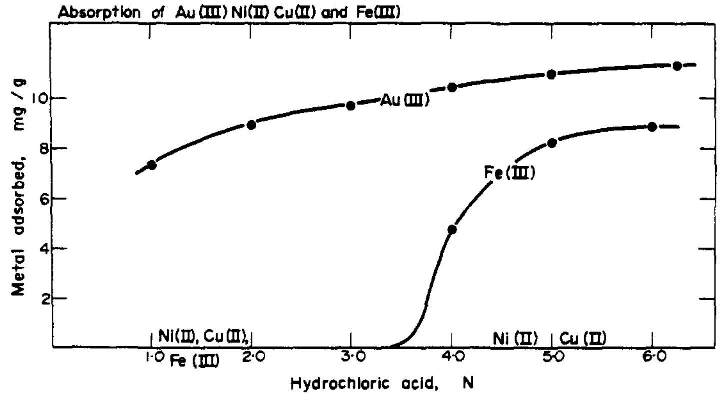

Fig. 1. Adsorption of Au(III), Fe(III), Cu(II) and Ni(II) as a function of hydrochloric acid concentration.

Adsorption of platinum-group metals

Individual platinum-group metal ions—Pt(IV), Pd(II), Rh(III), Ru(IV) and Ir(IV)— in 10 ml of 1*M* hydrochloric acid containing 17·7 mg of Au(III) were passed through a column of 1 g of resin at a rate of 1 ml min. and the column was rinsed with 1*M* hydrochloric acid. The solutions from the column were analysed by atomic absorption, the results indicating that the resin did not adsorb any of the metals except gold (Table 3).

Table 3. Adsorption of platinum-group metals from 1*M* hydrochloric acid

Metal	Amount added, *mg*	Amount recovered, *mg*
Pt	0·367	0·367
Pd	0·255	0·257
Ir	2·75	2·75
Rh	0·978	0·98
Ru	2·90	2·90

Adsorption of base metals by the resin

Iron(III), copper(II) and nickel(II) chloride solutions [10 ml, containing 17·7 mg of Au(III) and of varying hydrochloric acid concentrations] were shaken with 1 g of resin, and the solutions were analysed by atomic absorption before and after. The results (Fig. 1) indicate that only the iron(III) is adsorbed from solutions of hydrochloric acid concentration higher than 3*M* (see Fig. 1).

Recycling tests

To see whether the resin could be used several times, a limited number of recycling tests were performed. Each cycle involved loading of the resin (500 mg) by shaking it with a solution of 5·4 mg of Au(III) in 2*M* hydrochloric acid; the resin was then separated from the solution and stripped with 5% thiourea stripping solution, after which it was washed and loaded again. The loading of the resin for successive cycles was 9·0, 8·0, 10·6 and 9·6 mg/g.

DISCUSSION

The results show that the polymeric reagent tested has high selectivity for gold in preference to platinum-group metals and base metals. These results are in remarkable agreement with the behaviour of a solution of the reagent in a paraffin-type solvent.

The performance of the polymeric reagent is also very satisfactory when compared with that of ordinary ion-exchange resins. No detrimental effects were encountered, and the resin has fairly good ion-exchange capacity. It seems that the high surface areas of the polymeric absorbants ensure that the reagent is distributed evenly inside the pores in a thin layer, or perhaps even in a molecular monolayer, as the impregnation does not affect permeability to ions.

Although the recycling tests are not by any means conclusive, they indicate that the impregnation process affords a stable, easy-to-handle reagent. The impregnation technique therefore provides a fast way of preparing selective polymeric reagents by simple methods.

Although the evidence obtained is insufficient to decide which of the two possible mechanisms (ion-solvation or anion-exchange) is operative, the second seems the more likely since it accounts better for the behaviour of iron(III). The fact that the platinum-group metal anionic complexes are not adsorbed by the resin shows the bond between the resin and tetrachloro-aurate(III) to be rather weak in nature.

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Summary—A polymeric reagent selective for gold was obtained by impregnating XAD-2 polymeric absorbant with ethylene diglycol dibutyl ether, a gold-selective liquid. The reagent showed a high selectivity for gold over the platinum group metals, nickel(II) and copper(II), but the selectivity relative to iron(III) was pH-dependent.

Zusammenfassung—Ein für Gold selektives polymeres Reagens wurde gewonnen durch Imprägnieren des polymeren Absorptionsmittels XAD-2 mit Äthylendiglycoldibutyläther, einer für Gold selektiven Flüssigkeit. Das Reagens zeigte eine hohe Selektivität für Gold gegenüber den Platinmetallen, Nickel(II) und Kupfer(II); die Selektivität gegenüber Eisen(III) war pH-abhängig.

Résumé—On a obtenu un réactif polymère sélectif pour l'or en imprégnant l'adsorbant polymère ÖAD-2 avec l'éthylènediglycoldibutyl éther, un liquide sélectif pour l'or. Le réactif a montré une haute sélectivité pour l'or par rapport aux métaux du groupe de platine, au nickel(II) et au cuivre(II), mais la sélectivité relativement au fer(III) dépend du pH.

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ANALYTICAL APPLICATIONS OF THIO-, SELENO- AND TELLURO-ETHERS—III

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH DIBENZYL SELENIDE

(*Received* 23 *October* 1973. *Accepted* 26 *February* 1974)

Although a wide variety of reagents for palladium is known, relatively few are selenium compounds.[1–8] However, the purpose of this paper is not to describe yet another method for palladium, but to continue our systematic comparison of organic sulphur, selenium and tellurium compounds as analytical reagents. Previous work[5,7] has shown the highly selective behaviour of some selenium compounds towards palladium, in basic agreement with ideas advanced previously.[9–10] By analogy,[10] probably any "soft base" compound[11] R–Se–R should be a potential reagent for palladium determination by solvent extraction and spectrophotometric measurement of $PdX_2(R\text{–}Se\text{–}R)_2$ where X = Cl,Br,I. The selectivity should be enhanced because selenides reduce Au(III).[9]

EXPERIMENTAL

Reagents

Dibenzyl selenide. Synthesized by the Chugaeff method for aliphatic selenides.[12] (Yield 80%; recrystallized from ethanol: m.p. 44·5–45·0°.)

Benzene. Distilled before use. Commercial benzene was purified by the usual method.

Standard palladium solution (~ 1·15 *mg/ml*). Prepared from palladium(II) chloride and 0·1*M* hydrochloric acid. Standardized gravimetrically with dimethylglyoxime.

Solutions of diverse ions. Prepared from the chlorides in 0·1*M* hydrochloric acid; silver and lead were used as the nitrates; cations such as tin(IV), thorium(IV), zirconium(IV) and bismuth required more concentrated acid. Stock solutions of anions were made from the sodium salts. All contained *ca.* 10 mg of the relevant ion per ml.

All inorganic chemicals were of analytical grade.

Preparation of $PdCl_2\cdot 2[(C_6H_5CH_2)_2Se]$

The palladium complex was obtained by the Mann and Purdie method.[13] Anhydrous $PdCl_2$ (0·44 g) was dissolved in 75 ml of 0·1*M* hydrochloric acid, and 75 ml of ethanol containing 1·3 g of dibenzyl selenide were added dropwise. After stirring for 1 hr a yellow solid was formed, and was filtered off and dried. Yield 1·3 g, 77%; m.p.

Summary—A polymeric reagent selective for gold was obtained by impregnating XAD-2 polymeric absorbant with ethylene diglycol dibutyl ether, a gold-selective liquid. The reagent showed a high selectivity for gold over the platinum group metals, nickel(II) and copper(II), but the selectivity relative to iron(III) was pH-dependent.

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139–141° (decomp.) Calculated for $C_{28}H_{28}Se_2PdCl_2$: C 48·1%, H 4·0% Pd 15·2%; found, C 47·9%, H 4·0% Pd 14·8%. Palladium was determined after mineralization with concentrated sulphuric and perchloric acids, by the dibenzyl sulphide method.[10]

Conductivity measurements on nitromethane solutions of the complex showed it to be a non-electrolyte.

Characteristics

The complex, $PdCl_2 \cdot 2[(C_6H_5CH_2)_2Se]$, extracted into benzene from acidic palladium chloride solution, had an absorption spectrum with a well-defined maximum at 342 nm (Fig. 1) Benzene solutions of the reagent also absorb strongly at this wavelength, and all absorbance measurements were made against a reagent blank. The molar absorptivity is $2{\cdot}7 \times 10^4$ $l.mole^{-1}.cm^{-1}$.

The effect of reagent concentration was tested by extracting palladium with 1, 2 and 3% w/v dibenzyl selenide solution in benzene, and was found to be immaterial over this range. A 2% solution was therefore chosen. The pH of the palladium solutions before extraction was varied from 1·0 to 5·5 by addition of perchloric acid and acetate buffer and extraction was found to be quantitative over the pH range 1·0–4·5. The chloride concentration was varied from 0·1 to 10*M* without effect on the extraction. Temperature variation between 20° and 25° was also without effect. The absorbance remained constant for at least one day if the solution of palladium complex was kept in the dark.

When the palladium complex is extracted from 0·1*M* hydrochloric acid with 2% benzene solution of reagent and measured at 342 nm against a reagent blank, Beer's law is obeyed over the concentration range 0·38–3·0 ppm. The optimal concentration range, according to the Ringbom method, is 0·66–3·0 ppm in the final solution.

In extraction of 1·00 ml of aqueous solution containing 3·30 μg or 13·3 μg of palladium, with 1·0 ml of 2% solution of reagent, it was found that 80% of the palladium was extracted in a single pass, at either concentration.

Interferences

Earlier work[9,10] had indicated that separation and determination of palladium with thio- or seleno-ethers should be possible in the presence of various cations and anions. Interference by gold(III)[10] is avoided because the reagent reduces the gold, presumably to gold(I).

Platinum(IV) gives a positive interference, and cannot be prevented by addition of Fe(III) chloride or nitrate,[10] Ce(IV), Ir(IV) or chloramine-T or by pH adjustment. However, if the aqueous phase is saturated with LiCl or $CaCl_2$ and the Pt concentration kept below 250 μg/ml this interference is avoided.

Potentially interfering anions such as bromide, iodide, azide, thiocyanate, sulphide, sulphite or thiosulphate are easily eliminated by heating with *aqua regia*.[10]

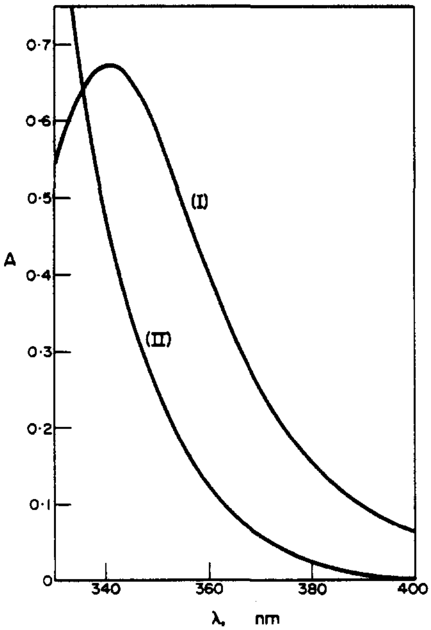

Fig. 1. (I) Absorption spectrum of the benzene extract containing the species $[PdCl_2 \cdot 2(C_6H_5{-}CH_2)_2Se]$; Pd(II) 13·3 μg/ml. (II) Absorption spectrum of 2% benzene solution of $(C_6H_5{-}CH_2)Se$ measured against benzene.

It was found that 3·30 μg of Pd(II) could be determined within ±2% and 13·3 μg within ±3% in the presence of 1·0 mg of Rh(III), Ir(IV), Ru(IV), Ni(II), Co(II), Zn(II), Cd(II), Cr(III), Fe(III), UO_2(II), Mn(II), Al(III), In(III), Ga(III), Be(II), Cu(II), Ag(I), Bi(III), V(III), Pb(II), Sn(IV), Zr(IV), Th(IV), Au(III), $HAsO_4^{2-}$, HPO_4^{2-}, NO_3^-, ClO_4^-, SO_4^{2-}, Br^-, I^-, N_3^-, SCN^-, S^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ and in the presence of 250 μg of Pt(IV); the presence of 1 mg of MoO_4^{2-} or WO_4^{2-} caused an error of <3% in determination of 13·3 μg of Pd(II); 1·0 mg of Hg(II) caused a positive error of about 7% in determination of 3·3 μg of Pd.

Precision

The standard deviation calculated from all the interference studies was 0·0022 for the absorbance of 3·3 μg of Pd, and 0·009 for the absorbance of 13·3 μg of Pd, corresponding to a range of ±0·09 and ±0·36 μg respectively (95% confidence limit, 36 variates in each case).

Recommended procedure

Take 1·00 ml of the test solution, which should be about 0·1*M* in hydrochloric acid, [if Pt(IV) is suspected to be present, saturate with LiCl or $CaCl_2$] in a ground-glass-stoppered 10-ml test-tube and shake it vigorously for 5 min with 1·0 ml of 2% benzene solution of dibenzyl selenide. Centrifuge to separate the phases and transfer the organic layer to a 5·0 ml volumetric flask (protected from the light) with an extraction pipette.[10] Repeat the extraction three times, dilute the combined extracts to volume with reagent, and read the absorbance at 342 nm, against a reagent blank run in parallel.

DISCUSSION

Although Pt(IV) is considered a moderately "hard acid", it unexpectedly interferes. Increasing the chloride ion concentration (palladium chloride is extracted even from 10*M* chloride) to keep $[PtCl_6]^{2-}_{(aq)}$ associated as much as possible to avoid the extraction of Pt(IV), was successful only when the Pt(IV) concentration was below 250 μg/ml. Although this limit is lower than for the other ions tested, the ratio Pd:Pt is acceptable and realistic.

The substitution mechanisms for Pt(IV) systems are arguable as reported before[10] and to this problem two new experimental facts may be added. During attempts to inhibit the effect of Pt(IV), solutions of $[PtCl_6]^{2-}$ in 0·1*M* hydrochloric acid were saturated with zinc chloride, and on extraction, yellow instead of colourless extracts were obtained. After two extractions, the aqueous phase became colourless, it appearing that all Pt(IV) was extracted; the extract had a well-defined absorption maximum at 355 nm. Studies to interpret and apply this fact are in progress. It is interesting that zinc chloride apparently had no effect when dibenzyl sulphide was used, but the same yellow extracts were obtained with dibenzyl selenide and platinum solution saturated with chloramine-T. The first fact indicates a salting-out effect but the second is very difficult to interpret.

The absorption band of the palladium selenium complex occurs at lower energy (29,200 cm^{-1}) than that of the sulphur complex[10] (31,400 cm^{-1}). A bathochromic trend had already been observed for benzene solutions of palladium chloride complexed with diphenyl sulphide, selenide and telluride (27,000, 26,700 and 25,000 cm^{-1}),[10] and for alcohol solutions,[14] it being suggested that the assignment should be an S_{nb} or $Se_{nb} \rightarrow ag^*$ charge-transfer metal-reduction type.

The molar absorptivity of the selenium complex is roughly 50% higher than that of the sulphur compound, and the sensitivity is therefore increased.

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Summary—Palladium chloride is very efficiently extracted with a benzene solution of dibenzyl selenide. The extract can be used to determine palladium spectrophotometrically in the range 0·38–3·00 ppm. Determination of palladium in presence of platinum metals and many cations and anions, is reported.

Zusammenfassung—Palladiumchlorid läßt sich mit einer Lösung von Dibenzylselenid in Benzol sehr gut extrahieren. Der Extrakt kann zur spectrophotometrischen Bestimmung von Palladium im Bereich 0,38–3,00 ppm verwendet werden. Es wird über eine Bestimmung von Palladium in Gegenwart von Platinmetallen und vielen Kationen und Anionen berichtet.

Résumé—Le chlorure de palladium est extrait très efficacement par une solution de séléniure de dibenzyle dans le benzène. L'extrait peut être utilisé pour doser le palladium spectrophotométriquement dans le domaine 0,38–3,00 ppm. On rapporte le dosage du palladium en présence de métaux du platine et de nombreux cations et anions.

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TITRIMETRIC ESTIMATION OF CYSTEINE ALONE AND IN THE PRESENCE OF OTHER AMINO-ACIDS

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There are several methods of estimating amino-acids, but the chemical methods are generally non-selective. However, simple titrimetric methods have been reported for sulphur-containing amino-acids.[1,2]

This paper reports simple and brief direct compleximetric titrations of cysteine either alone or in the presence of other amino-acids. The methods are based on use of mercury or lead solutions as titrants with a metallochromic indicator.

EXPERIMENTAL

Reagents

Doubly distilled water was used throughout. Standard solutions of cysteine hydrochloride monohydrate were prepared by dissolving exactly weighed amounts. Mercuric chloride and lead nitrate solutions were prepared by dissolving the reagents and standardizing.

Indicator solutions were 0·005% PAR, 0·1% Catechol Violet and 0·1% diphenylcarbazone in ethanol. The diphenylcarbazone solution must be freshly prepared.

Citrate buffer, pH 6·2, was prepared by diluting a mixture of 7·2 ml of 0·1*M* citric acid and 42·8 ml of 0·1*M* sodium citrate to 100 ml. Carbonate–bicarbonate buffer, pH 9·2, was made by diluting a mixture of 4 ml of 0·2*M* sodium carbonate and 46 ml of 0·2*M* sodium bicarbonate to 200 ml. Boric acid–borax buffer, pH 9·2, was made by diluting a mixture of 115 ml of 0·05*M* borax and 50 ml of 0·2*M* boric acid to 200 ml.

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Summary—Palladium chloride is very efficiently extracted with a benzene solution of dibenzyl selenide. The extract can be used to determine palladium spectrophotometrically in the range 0·38–3·00 ppm. Determination of palladium in presence of platinum metals and many cations and anions, is reported.

Zusammenfassung—Palladiumchlorid läßt sich mit einer Lösung von Dibenzylselenid in Benzol sehr gut extrahieren. Der Extrakt kann zur spectrophotometrischen Bestimmung von Palladium im Bereich 0,38–3,00 ppm verwendet werden. Es wird über eine Bestimmung von Palladium in Gegenwart von Platinmetallen und vielen Kationen und Anionen berichtet.

Résumé—Le chlorure de palladium est extrait très efficacement par une solution de séléniure de dibenzyle dans le benzène. L'extrait peut être utilisé pour doser le palladium spectrophotométriquement dans le domaine 0,38–3,00 ppm. On rapporte le dosage du palladium en présence de métaux du platine et de nombreux cations et anions.

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TITRIMETRIC ESTIMATION OF CYSTEINE ALONE AND IN THE PRESENCE OF OTHER AMINO-ACIDS

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There are several methods of estimating amino-acids, but the chemical methods are generally non-selective. However, simple titrimetric methods have been reported for sulphur-containing amino-acids.[1,2]

This paper reports simple and brief direct compleximetric titrations of cysteine either alone or in the presence of other amino-acids. The methods are based on use of mercury or lead solutions as titrants with a metallochromic indicator.

EXPERIMENTAL

Reagents

Doubly distilled water was used throughout. Standard solutions of cysteine hydrochloride monohydrate were prepared by dissolving exactly weighed amounts. Mercuric chloride and lead nitrate solutions were prepared by dissolving the reagents and standardizing.

Indicator solutions were 0·005% PAR, 0·1% Catechol Violet and 0·1% diphenylcarbazone in ethanol. The diphenylcarbazone solution must be freshly prepared.

Citrate buffer, pH 6·2, was prepared by diluting a mixture of 7·2 ml of 0·1*M* citric acid and 42·8 ml of 0·1*M* sodium citrate to 100 ml. Carbonate–bicarbonate buffer, pH 9·2, was made by diluting a mixture of 4 ml of 0·2*M* sodium carbonate and 46 ml of 0·2*M* sodium bicarbonate to 200 ml. Boric acid–borax buffer, pH 9·2, was made by diluting a mixture of 115 ml of 0·05*M* borax and 50 ml of 0·2*M* boric acid to 200 ml.

Procedure

Citrate buffer (pH 6·2, 40 ml), 0·1 ml of PAR and 1–5 ml of 0·001M cysteine hydrochloride solution were mixed in a 100 ml beaker and titrated with 0·001M mercuric chloride from a microburette, to a sharp change in colour from yellow to intense pink.

Similarly 0·04M cysteine hydrochloride was titrated with 0·01M lead nitrate with Catechol Violet as indicator and boric acid–borax buffer (pH 9·2, 5 ml), the end-point colour change being from pink to blue.

Further, 0·001M cysteine hydrochloride was titrated with 0·001M mercuric chloride, in carbonate–bicarbonate buffer (pH 9·2, 5 ml) and diphenylcarbazone as indicator, the end-point colour change being from yellow to violet.

RESULTS AND DISCUSSION

Micro-amounts of cysteine were estimated by the methods given both alone and in the presence of a mixture of lysine monohydrochloride, L-arginine hydrochloride, DL-leucine, DL-threonine, DL-methionine, hydroxyproline, asparagine, DL-aspartic acid, DL-alanine, DL-valine, DL-isoleucine, proline, DL-norleucine, DL-phenyl alanine, cystine, glutamic acid, glycine and DL-serine and it was found that these acids in up to ten times the concentration of the cysteine did not interfere.

Table 1. Titration of cysteine hydrochloride with mercuric chloride (PAR indicator and 4 ml of citrate buffer, pH 6·2)

Cysteine hydrochloride, 0·001M, *ml*	Mercuric chloride, 0·001007M, *ml*	Cysteine hydrochloride monohydrate, *mg* Taken	Found	Error, %
1·00	1·00	0·176	0·177	+0·7
2·00	2·00	0·351	0·353	+0·7
3·00	3·00	0·527	0·530	+0·7
4·00	4·00	0·702	0·707	+0·7
5·00	5·00	0·878	0·884	+0·7

Table 2. Titration of cysteine hydrochloride with lead nitrate (Catechol Violet indicator and 5 ml of boric acid–borax buffer, pH 9·2)

Cysteine hydrochloride, 0·04M, *ml*	Lead nitrate, 0·01009M, *ml*	Cysteine hydrochloride monohydrate, *mg* Taken	Found	Error, %
0·50	1·96	3·51	3·47	−1·1
0·70	2·74	4·91	4·85	−1·3
0·90	3·53	6·32	6·25	−1·1
1·10	4·31	7·72	7·63	−1·2
1·30	5·10	9·13	9·03	−1·0

Table 3. Titration of cysteine hydrochloride with mercuric chloride (diphenylcarbazone indicator and 5 ml of carbonate–bicarbonate buffer, pH 9·2)

Cysteine hydrochloride, 0·001M, *ml*	Mercuric chloride, 0·001008M, *ml*	Cysteine hydrochloride monohydrate, *mg* Taken	Found	Error, %
1·00	0·98	0·176	0·173	−1·3
2·00	1·96	0·351	0·347	−1·2
3·00	2·94	0·527	0·520	−1·2
4·00	3·94	0·702	0·697	−0·7
5·00	4·92	0·878	0·870	−0·8

Typical results are shown in Tables 1–3, and indicate that the lead method has a negative bias of about 1·2%, and the mercury method has a positive bias of 0·7% at pH 6·2 and a negative bias of about 1·2% at pH 9·2.

The cysteine solution must not be allowed to stand in air for too long, or there is partial oxidation to cystine and a change in the stoichiometry.

Up to about 10 mg of cysteine hydrochloride can be titrated. With larger amounts a white precipitate appears in the reaction mixture an addition of the titrant, and it is difficult to judge the end-point.

A 1:1 complex is formed in agreement with earlier reports[3–4] of both 1:1 and 1:2 complexes.

Acknowledgement—Thanks are due to the University Grants Commission (Government of India), New Delhi, for providing the financial support for this investigation.

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Summary—Cysteine has been determined alone and in the presence of other amino-acids by titration with mercury(II) at pH 6·2 or 9·2, and with lead at pH 9·2. In all three procedures, a 1:1 complex is formed.

Zusammenfassung—Cystein wurde allein und in Gegenwart anderer Aminosäuren durch Titration mit Quecksilber(II) bei pH 6,2 oder 9,2 und mit Blei bei pH 9,2 bestimmt. Bei allen drei Methoden bildet sich ein 1:1-Komplex.

Résumé—On a dosé xa cystéine seule et en la présence d'autres acides aminés par titrage avec le mercure (II) à pH 6,2 ou 9,2, et avec le plomb à pH 9,2. Dans les trois techniques, il se forme un complexe 1:1.

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REACTION BETWEEN COPPER(I)–THIOUREA AND BISMUTH(III)–THIOUREA COMPLEXES IN PRESENCE OF IODIDE. NEW SPOT-TESTS FOR COPPER(II) AND BISMUTH(III)

(*Received* 2 *October* 1973. *Accepted* 29 *November* 1973)

Bismuth(III) has been detected by various workers[1–4] by the development of a deep yellow colour caused by the action of thiourea on an acidic solution of this metal. Depending upon the conditions of the

Typical results are shown in Tables 1–3, and indicate that the lead method has a negative bias of about 1·2% and the mercury method has a positive bias of 0·7% at pH 6·2 and a negative bias of about 1·2% at pH 9·2.

The cysteine solution must not be allowed to stand in air for too long, or there is partial oxidation to cystine and a change in the stoichiometry.

Up to about 10 mg of cysteine hydrochloride can be titrated. With larger amounts a white precipitate appears in the reaction mixture an addition of the titrant, and it is difficult to judge the end-point.

A 1:1 complex is formed in agreement with earlier reports[3-4] of both 1:1 and 1:2 complexes.

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Summary—Cysteine has been determined alone and in the presence of other amino-acids by titration with mercury(II) at pH 6·2 or 9·2, and with lead at pH 9·2. In all three procedures, a 1:1 complex is formed.

Zusammenfassung—Cystein wurde allein und in Gegenwart anderer Aminosäuren durch Titration mit Quecksilber(II) bei pH 6,2 oder 9,2 und mit Blei bei pH 9,2 bestimmt. Bei allen drei Methoden bildet sich ein 1:1-Komplex.

Résumé—On a dosé xa cystéine seule et en la présence d'autres acides aminés par titrage avec le mercure (II) à pH 6,2 ou 9,2, et avec le plomb à pH 9,2. Dans les trois techniques, il se forme un complexe 1:1.

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(*Received* 2 *October* 1973. *Accepted* 29 *November* 1973)

Bismuth(III) has been detected by various workers[1-4] by the development of a deep yellow colour caused by the action of thiourea on an acidic solution of this metal. Depending upon the conditions of the reaction, a variety of bismuth(III)-thiourea complexes, *viz.*, $Bi(tu)X_3$, $Bi(tu)_2X_3$, and $Bi(tu)_3X_3$ [where tu = thiourea; X = a univalent anion][5,6] are formed. Like bismuth, copper(II) also reacts with thiourea, giving complexes of varying composition,[7-9] predominantly $Cu(tu)_3X$. In these complexes, copper is stabilized in the copper(I) state. When a solution containing bismuth(III)-thiourea complex is mixed with another containing a copper(I)-thiourea complex, there is apparently no major colour development. However, if a soluble iodide is then added, there is immediately formed a heavy, deep red or red-orange precipitate like that obtained with bismuth(III) in presence of iodide and organic bases.[10] The coloured product in the present case is most likely due to the formation of a mixed bismuth-copper-iodide-thiourea complex, which may be represented as $[Bi(tu)_3I_3.Cu(tu)_3I]$. Since the reaction is sensitive, and also is characteristic of bismuth and copper, it has been used for the spot-test detection of these metal ions when present alone or together, and also when present with iodide. This reaction is also characteristic of iodide, but the sensitivity is poor.

EXPERIMENTAL

Reagents

Hexakis(thioureato)sulphatomonoaquodicopper(I) $[Cu_2(tu)_6SO_4.H_2O]$ *solution (A).* Prepared by the method of Cavalca *et al.*[9] About 1 g of this complex was suspended in 30 ml of conc. sulphuric acid, and 50 ml of water were then added. The clear solution thus obtained was filtered and stored.

Potassium iodide solution, 4% *w/v in water.*

Thiourea solution, 2·5% *w/v in water.*

Bismuth(III) nitrate solution, 1% *w/v in dil. nitric acid.*

Copper(II) solution. A 2% w/v solution of cupric chloride or sulphate in acidified water.

Procedures

Bismuth(III). Mix a drop of the acidic test-solution with 1 drop of solution *A* in the depression of a spot plate, and add 1 drop of 4% potassium iodide solution. Appearance of a deep orange or red-orange precipitate indicates bismuth.

Limit of detection: 2μg of Bi(III).

Limit of dilution: 1 : 2·5 × 10^4.

Alternatively, to 1 drop of the acidic test solution on a spot plate, add 1 drop of 2·5% thiourea solution and 1 drop of 2% cupric chloride or sulphate solution with stirring. (More thiourea should be added if a precipitate persists on addition of copper solution.) Then add a drop of 4% potassium iodide solution. An orange or red-orange precipitate indicates bismuth.

Copper(II) by conversion into copper(II) complex. Mix 1 or 2 drops of 2·5% thiourea solution with 1 drop of test solution on a spot plate, and add successively 1 drop each of 1% bismuth nitrate or chloride solution and 4% potassium iodide solution. An orange or red-orange precipitate indicates copper(II).

Limit of detection: 8 μg of Cu(II).

Limit of dilution: 1 : 6·25 × 10^3.

Iodide. To 1 drop of 1% acidic bismuth nitrate solution on a spot plate add 1 drop each of the reagent solution (A) and neutral or slightly acidic test solution. An orange or red-orange precipitate is formed if iodide is present.

Limit of detection: 75 μg of I^- in a drop (0·05 ml).

Bismuth(III) when present with iodide. Place 1 drop of the acidic test solution (which is invariably yellow owing to *in situ* formation of BiI_4^- ions) on the spot plate, and add 1 drop of solution (*A*). A deep orange or red-orange precipitate indicates both bismuth and iodide.

Limit of detection: 2 μg of Bi(III); 75 μg of I^-/0·05 ml.

Bismuth(III) when present with copper(II). Mix on a spot plate 1 drop of the slightly acidic test solution and 1 or 2 drops of 2·5% thiourea solution. Then add 1 or 2 drops of 4% potassium iodide solution. A red or red-orange precipitate indicates both bismuth(III) and copper(II).

Limit of detection: 2 μg of Bi(III) and 8 μg of Cu(II)/0·05 ml.

Bismuth(III) when present with copper(II) and iodide. To 1 drop of the slightly acidic test solution on a spot plate add 1 or 2 drops of 2·5% thiourea solution. A deep orange or red-orange precipitate indicates the combined presence of bismuth(III), copper(II), and iodide ions.

Limit of detection: 2 μg of Bi(III), 8 μg of Cu(II); 75 μg of I^-/0·05 ml.

Interferences

Most cations and anions (coloured or colourless) do not interfere in any of the tests above. Only Tl(I), Cs, SO_3^{2-}, $S_2O_3^{2-}$, EDTA, and oxidizing ions (*e.g.*, NO_2^-, IO_3^-, IO_4^-, BrO_3^-, and MnO_4^-) interfere.

The interference by thallium(I) is because it forms a wine-red or maroon-red precipitate of thallium bismuth iodide (Tl_2BiI_5)[11-13] with Bi^{3+} and I^- ions. Similarly, caesium interferes because it forms with Bi^{3+} and I^- ions a bright red precipitate of caesium bismuth iodide (Cs_2BiI_5).[14,15]

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Summary—New and very simple spot tests are described for the detection of Bi(III), Cu(II) and I$^-$ ions with limits of detection of 3, 8, and 75 µg/0·05 ml respectively. Tests are also described for such combinations as Bi(III) + I$^-$; Bi(III) + Cu(II); and Bi(III) + Cu(II) + I$^-$. All the tests are based on the formation of an orange or red-orange precipitate of bismuth(III)-copper(I)-iodide-thiourea complex, for which the formula [Bi(tu)$_3$I$_3$.Cu(tu)$_3$I] (where tu = thiourea) is proposed. This complex is produced in various ways by the interaction of Bi(III), Cu(II), and I$^-$ ions with thiourea. Most cations and anions do not interfere, but Tl(I), Cs(I), SO$_3^{2-}$, S$_2$O$_3^{2-}$, EDTA, and oxidizing ions such as NO$_2^-$, IO$_3^-$, IO$_4^-$, BrO$_3^-$, and MnO$_4^-$ do. The complex hexakis(thioureato)sulphatomonoaquodicopper(I) [Cu$_2$(tu)$_6$SO$_4$.H$_2$O] is proposed as a new spot-test reagent for Bi(III) and I$^-$ ions, although the sensitivity for the latter is poor.

Zusammenfassung—Neue und sehr einfache Tüpfelreaktionen zum Nachweis von Bi(III), Cu(II) und J$^-$ mit Nachweisgrenzen von 3, 8 bzw. 75 µg/0,05 ml werden beschrieben. Auch für Kombinationen wie Bi(III) + J$^-$; Bi(III) + Cu(II); Bi(III) + Cu(II) + J$^-$ werden Tests beschrieben. Alle Tests beruhen auf der Bildung eines orange oder orangeroten Niederschlags eines Komplexes von Wismut(III), Kupfer(I), Jodid und Thioharnstoff, für den die Formel [Bi(tu)$_3$J$_3$.Cu(tu)$_3$J] (tu = Thioharnstoff) vorgeschlagen wird. Dieser Komplex wird auf verschiedene Weise durch die Reaktion von Bi(III), Cu(II) und J$^-$ mit Thioharnstoff erhalten. Die meisten Kationen und Anionen stören nicht, es stören jedoch Tl(I), Cs(I), SO$_3^{2-}$, S$_2$O$_3^{2-}$, EDTA und oxidierende Ionen wie NO$_2^-$, JO$_3^-$, JO$_4^-$, BrO$_3^-$ und MnO$_4^-$. Der Komplex Hexakis(thioharnstoff)sulfatomonoaquodikupfer(I) [Cu$_2$(tu)$_6$SO$_4$.H$_2$O] wird als neues Tüpfelreagens für Bi(III) und J$^-$ vorgeschlagen, obgleich die Empfindlichkeit für J$^-$ nur gering ist.

Résumé—On décrit des essais à la touche nouveaux et très simples pour la détection des ions Bi(III), Cu(II) et I$^-$ avec des limites de détection de 3,8 et 75 µg/0,05 ml respectivement. Des essais sont aussi décrits pour des combinaisons telles que: Bi(III) + I$^-$; Bi(III) + Cu(II); et Bi(III) + Cu(II) + I$^-$. Tous les essais sont basés sur la formation d'un précipité orangé ou rouge-orangé de complexe bismuth(III)-cuivre(I)-iodure-thiourée, pour lequel on propose la formule [Bi(tu$_3$I$_3$, Cu(tu)$_3$I] (ou tu = thiourée). Ce complexe est produit de diverses manières par l'interaction d'ions Bi(III), Cu(II) et I$^-$ avec la thiourée. La plupart des cations et anions n'interfèrent pas, mais Tl(I), Cs(I), SO$_3^{2-}$, S$_2$O$_3^{2-}$, l'EDTA t les ions oxydants tels que NO$_2^-$, IO$_3^-$, IO$_4^-$, BrO$_3^-$ t MnO$_4^-$ gênent. On propose le complexe hexakis (thiouréato) sulfato-monoaquodicuivre (I) [Cu$_2$(tu)$_6$SO$_4$, H$_2$O] comme un nouveau réactif d'essai à la touche pour les ons Bi(III) et I$^-$, quoique la sensibilité soit faible pour le dernier.

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NEW SPOT-TEST FOR SILVER(I) BASED ON DOUBLE IODIDE FORMATION WITH BISMUTH(III)

(*Received 2 October* 1973. *Accepted* 29 *November* 1973)

Various spot-test methods for the detection of silver have been reported. They mostly involve organic reagents,[1,2] although certain inorganic reagents[1] such as manganous nitrate/alkali, manganic nitrate/hydrochloric acid, ceric ammonium nitrate/nitric acid, potassium chromate, stannous chloride, and cuprous thiocyanate have also been used. The present paper describes a new and unusually simple spot-test for silver involving the use of bismuth(III) solution and a soluble iodide. The test is based principally on the tendency of bismuth(III) halides to combine with one or more molecules of halides of other elements to form double halides.[3–7] Thus, for example, a spot-test for thallium(I) has recently been described which is based on the formation of a wine-red thallium bismuth iodide ($2TlI.BiI_3$).[8] Similarly, a spot-test for copper and bismuth has been reported[9] which is based on the formation of a red-orange complex $[Bi(tu)_3I_3Cu(tu)_3I]$, produced by the interaction of bismuth(III)-thiourea-iodide and copper(I)-thiourea-iodide complexes.

The present test for silver is based on the formation of a deep red-maroon or brownish-maroon precipitate of bismuth silver iodide (Ag_2BiI_5) when a silver salt solution is treated with a solution of potassium iodobismuthate $KBiI_4$ or its acid, iodobismuthic acid $HBiI_4$. No work has so far been reported on this compound. The test is highly sensitive, and is capable of detecting submicrogram quantities of silver.

EXPERIMENTAL

Reagents

Bismuth(III) solution. A 1% w/v solution of bismuth trinitrate pentahydrate or bismuth trichloride in dilute nitric or hydrochloric acid.

Silver nitrate solution. A 1% w/v solution in distilled water acidified with a few ml of nitric acid.

Potassium iodide solution. A 2% w/v solution in water.

Procedure

Place 2 or 3 drops of 2% potassium iodide solution in the depression of a spot plate and mix with it 1 drop of 1% bismuth nitrate or bismuth chloride solution. To the resulting yellow solution of potassium bismuth iodide add 1 drop of neutral or slightly acidic test solution. Immediate formation of a deep red-maroon or brownish-maroon precipitate or colour indicates the presence of silver. When, however, ultramicrogram quantities of silver are present in the test solution, a positive response is indicated by the appearance of a green colour either immediately or after a few sec. The green colour is often accompanied by a brownish precipitate.

Limit of detection: 0·01 μg Ag(I).

Limit of dilution: $1 : 5 \times 10^6$.

RESULTS AND DISCUSSION

Interferences

Most cations and anions, including the following, do not interfere: Cu(II), Ni, Co(II), Mn(II), Fe(II), Mg, Ca, Sr, Ba, Zn, Cd, Fe(III), Al, Cr(III), In(III), Eu(III), Ru(III), Ce(IV), Zr, V(IV), La, V(V), Mo(VI), W(VI), U(VI), $Fe(CN)_6^{3-}$, SO_3^{2-}, $Fe(CN)_5NO^{2-}$, $Cr_2O_7^{2-}$, NO_3^-, CN^-, F^-, PO_4^{3-}, SO_4^{2-}, and small quantities of Hg(I) and Hg(II).

$Fe(CN)_6^{4-}$ and CrO_4^{2-} hinder the reaction, but their interference is avoided by rendering the test solution acidic with a few drops of conc. sulphuric acid. Pd(II) and Pt(IV), although they form dark ionic species with iodide, *viz.* PdI_4^{2-} and PtI_6^{2-}, generally do not interfere because if silver is present, the dark maroon-red precipitate is clearly visible. In the presence of thiourea, an orange precipitate is formed instead of maroon-red. Excess of thiourea, however, hinders the reaction. In presence of α,α′-bipyridyl, a deep scarlet-red precipitate appears. α,α′-bipyridyl otherwise forms an orange precipitate with $KBiI_4$.

Serious interference is caused by Tl(I),[8] Cs,[10] $S_2O_3^{2-}$, and oxidizing species, such as NO_2^-, BrO_3^-, IO_3^-, IO_4^-, MnO_4^-, $S_2O_8^{2-}$, and hydrogen peroxide. Pyridine and EDTA also interfere. When they are present in the sample, 8 ions such as Cl^-, Br^-, I^-, SCN^-, and N_3^- which cause precipitation of silver, also cause interference.

Nature of the product

Bismuth iodide, BiI_3, when allowed to react *in situ* with the iodide of a univalent metal (MI), results in the formation of a double iodide of the type $2MI.BiI_3$ or M_2BiI_5. It is interesting to note that only a few such double iodides possess a specific colour of analytical importance. The M_2BiI_5 may also be formed by the interaction of a univalent metal ion (M^+) with potassium bismuth iodide, $KBiI_4$, in presence of a slight excess of iodide ions. Thus, the following series of reactions is likely to be involved:

$$Bi^{3+} + 3I^- \xrightarrow{\quad} BiI_3 \xrightarrow{KI} KBiI_4 \xrightarrow{M^-} MBiI_4 \xrightarrow{MI} M_2BiI_5$$

Thallium(I) and caesium are known to form beautifully-coloured double iodides of this type with bismuth in presence of iodide.[3-5,8,10] Silver(I) most probably forms a similar compound.

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Summary—The formation of an intense brownish-maroon or maroon-red product by the interaction of silver(I) and bismuth(III) solution in the presence of iodide forms the basis of a new and specific spot-test procedure for silver. The test is conducted on a spot plate with 2 or 3 drops of 2% potassium iodide solution, 1 drop of 1% bismuth(III) nitrate solution, and 1 drop of test solution. Limit of detection is 0·01 μg; limit of dilution is 1:5 × 10^6. Most cations and anions do not interfere. Only Tl(I), Cs, $S_2O_3^{2-}$, EDTA, pyridine, excess of thiourea, oxidizing ions (NO_2^-, IO_3^-, IO_4^-, MnO_4^-, BrO_3^-, and $S_2O_8^{2-}$) and ions such as Cl^-, Br^-, I^-, SCN^-, and N_3^- which cause precipitation of silver, interfere. The product formed is most probably Ag_2BiI_5.

Zusammenfassung—Die Bildung eines intensiv kastanienbräunlichen oder kastanienroten Produktes durch die Reaktion von Silber(I)- und Wismut(III)-Lösungen in Gegenwart von Jodid bildet die Grundlage einer neuen und spezifischen Tüpfelprobe auf Silber. Auf eine Tüpfelplatte werden 2 oder 3 Tropfen 2% Kaliumjodidlösung, 1 Tropfen 1% Wismut(III)-nitratlösung und 1 Tropfen Probelösung gegeben. Die Nachweisgrenze ist 0,01 μg, die Verdünnungsgrenze 1 : 5 × 10^6. Die meisten Kationen und Anionen stören nicht. Es stören nur Tl(I), Cs, $S_2O_3^{2-}$, EDTA, Pyridin, ein Überschuß an Thioharnstoff, oxidierende Ionen (NO_2^-, JO_3^-, JO_4^-, MnO_4^-, BrO_3^- und $S_2O_8^{2-}$) und Silber ausfällende Ionen wie Cl^-, Br^-, J^-, SCN^- und N_3^-. Höchstwahrscheinlich wird Ag_2BiJ_5 gebildet.

Résumé—La formation d'un produit marron-brunâtre ou marron-rouge intense par l'interaction de solutions d'argent (I) et de bismuth (III) en la présence d'iodure constitue la base d'une technique d'essai à la touche nouvelle et spécifique pour l'argent. L'essai est mené sur une plaque pour touches avec 2 ou 3 gouttes de solution d'iodure de potassium à 2%, 1 goutte de solution de nitrate de bismuth (III) à 1%, et 1 goutte de la solution essai. La limite de détection est 0·01 μg; la limite de dilution est 1:5 × 10^6. La plupart des cations et anions n'interfèrent pas. Seuls Tl(I), Cs, $S_2O_3^{2-}$, l'EDTA, la pyridine, un excés de thiourée, les ions oxydants (NO_2^-, IO_3^-, IO_4^-, MnO_4^-, BrO_3^- et $S_2O_8^{2-}$) t es ions tels que Cl^-, Br^-, I^-, SCN^- et N_3^- qui provoquent la précipitation de l'argent sont gênants. Le produit formé est très probablement Ag_2BiI_5.

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ON THE THEORY OF THERMOMETRIC TITRATION

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In recent years, the thermometric titration method has become extensively used in analytical and physico-chemical laboratories. Many aspects of the theory have been clarified,[1–5] yet there remains the question of the role of heat emission during the thermometric measurements.

That heat transfer between ambient medium and thermometric cell has an important effect on the measurements has been confirmed many times (*cf.* Tyrrell and Beezer[1]). However, in the formulae used for thermometric titration calculations this factor is, unfortunately, either not accounted for[2,3,6] or the formulae are complicated to such an extent as to become unsuitable for practical calculations.[4,5,7] This paper is an attempt to fill this gap.

Thermometric titration yields a curve which is plotted in terms of solution temperature T *vs.* time t, or T *vs.* volume V of titrant added. Such curves are equivalent to each other at a constant titration rate. Figure 1 represents a general curve, which may be subdivided into three sections. The first corresponds to the period before titration is started. In this period, heat sources are friction during mixing, and heat transfer with the ambient medium. The second section is the main one, and the additional heat sources are the chemical reaction and mixing or dilution of the solution. The third section represents the final step of the experiment. The reaction is completed, but the titrant continues to flow into the solution at a constant rate. The heat sources are the same as those in the second section, with the exception of the chemical reaction.

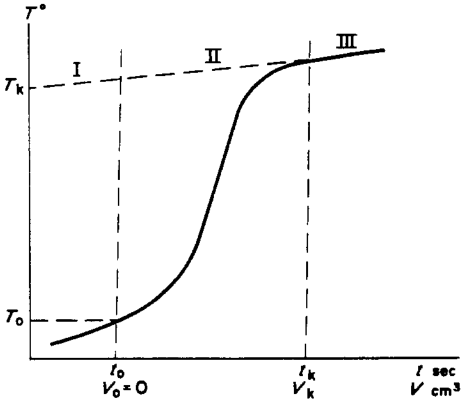

Fig. 1. Thermometric titration curve $t_0(V_0)$ = start of titration, $t_k(V_k)$ = end-point.

Only the second step is of interest to us here. We assume that the titrant is added at constant rate, that heat transfer between the solution and the ambient medium occurs in accordance with Newton's law, with a constant heat-transfer coefficient, that mixing is so efficient that temperature and concentration are uniform throughout the solution, that the temperature-dependence of the specific heat capacity, heat-transfer coefficient and heats of mixing and reaction may be neglected, that frictional heat is generated at a constant rate of ω cal/sec, that the solution composition and ionic strength do not influence the results, and that the reaction rate is infinitely high.

To make the argument general, the initial temperature of the solution T_0 (at time $t_0 = 0$), temperature of titrant T_T, and temperature of the ambient medium T_c are taken as not equal to one another.

We consider reactions of the type

$$mA + nB \rightarrow A_mB_n \qquad (1)$$

where B is the titrant.

The thermal balance of the thermometric cell may be expressed as:*

$$a(M_0C_0 + \rho_T GV)\frac{dT}{dV} + q + \alpha F(T - T_c) + \rho_T C_T a(T - T_T) = 0 \qquad (2)$$

where a is the titration rate (cm^3/sec), m_0 and C_0 are the mass (g) and the specific heat capacity (cal.g^{-1}.deg^{-1}) respectively of the thermometric cell + starting solution system, ρ_T and C_T are the density (g/cm^3) and the specific heat capacity respectively of the titrant (cal.g^{-1}.deg^{-1}); V is the volume of titrant (cm^3) added in time t, α is the heat-transfer coefficient (cal.cm^{-2}.deg^{-1}.sec^{-1}); F is the surface area for heat-transfer (cm^2), q is the rate of production of internal heat:

$$q = Q_R C_B am/n + Q_V \rho_T a + \omega/\rho_T a \qquad (3)$$

where Q_R is the heat of chemical reaction (cal/mole); C_B is the concentration of the titrant (mole/cm^3), Q_V is the heat of mixing (cal/g of titrant), and T is the solution temperature at time t. The initial condition is that $V = 0$ and $T = T_0$.

Equation (2) can be solved in a conventional manner[8] to yield

$$\Delta T = T - T_0 = \frac{l + T_0 - T_c + K_2(T_0 - T_T)}{1 + K_2}\left[\frac{1}{\left(1 + \frac{K_2}{K_1}V\right)^{[(1+K_2)/K_2]}} - 1\right] \qquad (4)$$

where $l = q/\alpha F$, $K_1 = m_c C_0 a/\alpha F$ and $K_2 = \rho_T C_T a/\alpha F$.

Since $K_2 V/K_1 \ll 1$, then to a good approximation

$$\left(1 + \frac{K_2}{K_1}V\right)^{[(1+K_2)/K_2]} \quad 1 + \frac{V(1 + K_2)}{K_1}$$

Equation (4) may then be written as

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV} \qquad (5)$$

where

$$A = \frac{l + T_0 - T_c + K_2(T_0 - T_T)}{K_1}, \quad B = \frac{1 + K_2}{K_1},$$

both being constants. Since usually $l \gg T_0 - T_c$ and $l \gg K_2(T_0 - T_T)$ the sign of ΔT is determined by the sign of q.

By comparing equations (2) and (5) with those in the literature, it can be proved that the Keily and Hume equation[6] is a special case of equation (2). Although the thermal-balance equations proposed by others[4,5] agree in general with equation (2) except in some details, the authors cited could not find a concise and simple solution of their equations.

Equation (5) represents the experimental data satisfactorily. Table 1 presents as an example the experimental and calculated data from Keily and Hume's work.[6] Comparison with the results calculated by the use of (5) shows that the deviation between the experimental and calculated values is an order of magnitude smaller when equation (5) is used.

Table 1. Comparison between the experimental and calculated values of the temperature change (°C) in titration of sodium acetate with perchloric acid (in glacial acetic acid as medium)

V, *ml* of 0·5M HClO$_4$	ΔT (exp.)	ΔT_1 (theor.)*	ΔT_2 (theor.)†	$\Delta T - \Delta T_1$	$\Delta T - \Delta T_2$
0·5	0·045	0·047	0·045	−0·002	0
1·50	0·134	0·136	0·131	−0·002	+0·003
2·50	0·213	0·225.	0·211	−0·012	+0·002
3·50	0·285	0·314	0·285	−0·029	0
4·50	0·353	0·399	0·355	−0·046	−0·002
5·50	0·418	0·483	0·421	−0·065	−0·003
5·95	0·442	0·521	0·449	−0·079	−0·007

* Calculations according to Keily and Hume.[6]

† Calculations according to equation (5), $A = -0{\cdot}092$, $B = 0{\cdot}0368$.

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* We have chosen the titrant volume V as an independent variable, because it is directly proportional to the titration time, as indicated by the assumed condition $a = dv/dt = \text{const}$.

The most interesting conclusion which may be drawn from (5) is that in the general case the value of ΔT is not directly proportional to V, as is sometimes assumed to be the case. The linear dependence should exist between the inverse values: $1/\Delta T$ and $1/V$.

Consequently, it would be better to plot not ΔT *vs.* V, the usual practice, but $1/\Delta T$ *vs.* $1/V$, which should give a straight line. This can easily be proved if (5) is written in the form

$$\frac{1}{\Delta T} = -\frac{1}{AV} - \frac{B}{A} = -\frac{a}{V} - b$$

where $a = 1/A$ = const., $b = B/a$ = const.

In these graphs, the point of inflexion corresponding to the end-point should become more conspicuous.

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Summary—The general equation defining the change in solution temperature ΔT during a thermometric titration is

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV}$$

where A and B are constants, V is the volume of titrant used to produce temperature T, and T_0 is the initial temperature. There is a linear relation between the inverse values of ΔT and V:

$$\frac{1}{\Delta T} = -\frac{a}{V} - b$$

where $a = 1/A$ and $b = B/A$, both a and b being constants. A linear relation between ΔT and V is usually a special case of this general relation, and is valid only over a narrow range of V. Graphs of $1/\Delta T$ *vs.* $1/V$ are more suitable for practical calculations than the usual graphs of ΔT *vs.* V.

Zusammenfassung—Die allgemeine Gleichung, die die &nderung der Lösungstemperatur ΔT während einer thermometrischen Titration angibt, lautet

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV}$$

wo A und B Konstanten sind, V das Titrantvolumen, das die Temperatur T herbeiführt, und T_0 die Anfangstemperatur bedeuten. Es besteht eine lineare Beziehung zwischen den reziproken Werten von ΔT und V:

$$\frac{1}{\Delta T} = -\frac{a}{V} - b$$

wo $a = 1/A$ und $b = B/A$ ebenfalls konstant sind. Eine lineare Beziehung zwischen ΔT und V ist im allgemeinen ein Spezialfall dieser allgemeinen Beziehung und gilt nur in einem kleinen Bereich von V. Graphische Darstellungen von $1/\Delta T$ gegen $1/V$ sind für Berechnungen in der Praxis besser geeignet als die üblichen graphischen Darstellungen von ΔT gegen V.

Résumé—L'équation générale définissant la variation de la température de solution ΔT durant un titrage thermométrique est:

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV}$$

où A et B sont des constantes, V est le volume d'agent de titrage utilisé pour produire la température T, et T_0 est la température initiale. Il y a une relation linéaire entre les valeurs inverses de ΔT et V:

$$\frac{1}{\Delta T} = -\frac{a}{V} - b$$

où $a = 1/A$ et $b = B/A$, a et b étant toutes deux des constantes. Une relation linéaire entre ΔT et V est habituellement un cas spécial de cette relation générale, et est valable seulement dans un étroit domaine de V. Les graphiques de $1/\Delta T$ par rapport à $1/V$ sont plus convenables pour les calculs pratiques que les graphiques habituels de ΔT par rapport à V.

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TALANTA REVIEW*

SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS IN SOLUTION

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(*Received* 4 *September* 1973. *Accepted* 25 *March* 1974)

Summary—This paper reviews critically a number of published methods for using ultraviolet or visible spectrophotometric data for the determination of equilibrium constants in solution. Single-stage or overlapping equilibria are considered, and a number of ways in which the experimental data can be handled by electronic computers are suggested.

Equilibrium data continue to serve as important criteria of the stability of complexes or the strengths of acids and bases in solution. They provide the basis for speculations on linearity of free-energy relationships, structural factors influencing stability, or medium effects arising from change in solvent composition. Through the application of computers, equilibrium data may be utilized to predict the distribution of solute species in model systems representative of multicomponent solutions as complex as sea-water[1] or blood plasma.[2] In analytical work, equilibrium data provide the theoretical foundation for complexometric titrations, the choice of masking agents,[3] and broadly speaking the selectivity of reagents in general for solution procedures.

This paper presents an outline and some discussion of spectrophotometric methods for measuring equilibrium constants in solution. The examples particularly apply to the formation of metal complexes or acids, which may be regarded as proton complexes of bases, but the procedures are described with sufficient generality to be adapted to any association equilibrium.

The intention is not to be encyclopaedic but to discuss a number of methods in depth, especially those with which the author has had experience.

FEATURES OF THE SPECTROPHOTOMETRIC METHOD

An obvious requirement is that the reaction in question should be accompanied by appreciable changes in light-absorption at one or more convenient wavelengths. If the molar extinction coefficients are large enough very small concentrations can be used, which is an advantage in the case of sparingly soluble materials, or when it is desired to work at low ionic strengths so that activity coefficients can be estimated from theory.

The spectrophotometric method may be complementary to other methods, by giving access to regions of equilibrium not otherwise attainable,[4] or supplementary, *e.g.*, in investigating "micro" ionization constants of polyfunctional acids, where potentiometric evidence can only indicate "macro" constants (for example, in the ionization of tyrosine[5]).

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* For reprints of this Review see Publisher's announcement near end of this issue.

Moreover, spectrophotometry can provide confirmation of results obtained in other ways. It differs from, and has the advantage over, potentiometry in that a property of one or more of the reactants or products can be directly measured. Accordingly, the spectra measured in determination of an equilibrium constant must be consistent with all solution compositions predicted by that constant. Spectrophotometry can be used for solvent systems or reactions that may not be suitable for potentiometry, *e.g.*, the reaction between iron(III) and thiocyanate.

Each solution prepared for spectrophotometric measurement should be examined at several wavelengths, so that it provides several data points instead of just one. Such spectral observations may reveal the occurrence of other reactions or side-reactions which will perturb the calculation of an equilibrium constant, for instance, the oxidative or other degradation of a reagent, though some kinds of interactions may not be revealed (*e.g.*, protonation or deprotonation of a metal–ligand complex without apparent effect on the chromophore[6]). The appearance of isosbestic points in the spectra of a series of solutions in which some parameter other than reactant concentration is systematically varied will generally mean the system in equilibrium comprises just two absorbing species; this inference, as will be shown later, considerably facilitates interpretation of the data.

SOME PRACTICAL CONSIDERATIONS

Spectrophotometric study of chemical equilibrium has been mainly confined to the visible and ultraviolet regions. Infrared spectroscopy is restricted for this application owing to absorption by many solvents, *e.g.*, work with aqueous solutions is not possible. There are also problems, because of the common occurrence of narrow absorption bands, in the application of the Beer–Lambert law to infrared data. In recent years Raman spectra have been utilized, *e.g.*, by Irish and co-workers,[7] in the study of equilibria in fairly concentrated solutions. The integrated Raman intensity has been found to be a reliable measure of the concentration of a particular constituent. These spectra are also sometimes able, through inferences about symmetry, to yield structural information about complexes. Magnetic resonance spectroscopy will not be included in this review, but is capable of providing information from which equilibrium constants can be calculated and inferences made about structural features of complexes.[8]

To make a series of measurements of the equilibrium constant for a reaction such as

$$A + B = BA\,(\equiv C) \qquad (1)$$

in a particular solvent, A and B may be mixed together in various proportions, or solutions of C prepared at different concentrations. Then measurements are made directly or indirectly (spectrophotometrically or otherwise) of the activity or the concentration of one or more of these species when equilibrium is presumed to have been attained. When a particular concentration is measured by difference, it may be important for the degree of conversion of the reaction not to be too great or too small.

Many of the relationships in this paper presuppose the validity of the Beer–Lambert law. True variations of this law can arise when moderately concentrated solutions are used, but can usually be neglected when working with dilute solutions. Departures from the law, for dilute solutions, nearly always have their origin in dilution causing shifts of equilibria involving the absorbing species. It is an instrumental limitation of the absorptiometric method that absorbance (A) cannot be widely varied without decreasing the precision of its measurement, and is effectively confined to a range covering about one order of magnitude, *i.e.*, $0{\cdot}1 < A < 1{\cdot}2$,[9] though the range of concentrations measured can be increased by use of different path-lengths, *e.g.*, 5, 1, and 0·2 cm.

To incorporate measured concentrations into equilibrium constants requires a decision about activity coefficients. For non-electrolytes these are usually taken as unity in dilute solutions; for ionic species relationships such as the Davies equation[10] are used. However, the practice has become widespread of expressing equilibrium constants as concentration quotients, particularly for ionic systems, an indifferent background electrolyte being included in all solutions at a fairly high concentration. These quotients are thus conditional constants, and the medium to which they apply must be specified. This practice amounts to adopting a thermodynamic system based on a different standard state, namely unit concentration in the specified medium.[11] The use of concentration quotients to define equilibria presupposes that activity coefficients remain constant if the ionic strength arising from an indifferent supporting electrolyte is fixed and comparatively high.

HYDROGEN-ION EFFECTS

Many reactions involve a competition between metal ion (B) and hydrogen-ion (H) for a particular ligand (A):

$$\mathrm{B + HA \rightleftharpoons BA + H} \tag{2}$$

(charges will generally be omitted for simplicity). The degree of formation of BA can be controlled *via* the hydrogen-ion concentration which can be varied over a wide range, and can usually be measured easily without disturbing the equilibrium. Side-reactions may also be pH-dependent, *e.g.*, hydrolysis of the metal ion or protonation of the complex

$$\mathrm{B + H_2O \rightleftharpoons BOH + H} \tag{3}$$

$$\mathrm{BA + H \rightleftharpoons BAH} \tag{4}$$

A possible source of error that is often overlooked arises from the buffers used to control the hydrogen-ion concentration. Several common buffer components react with a fair number of metal ions and can give rise to competing side-reactions.[12]

In the complete study of equilibrium in a reaction such as (2) when side-processes such as (3) and (4) are also involved, two or more equilibrium constants have to be combined. If these have been obtained from separate investigations they must be compatible, *e.g.*, with respect to temperature, but more important, if they are concentration quotients they must refer to media essentially similar in nature of the background electrolyte and ionic strength (especially the latter). There are many instances in the literature where equilibrium data have been combined without proper regard for this requirement.

Some comments seem in order concerning hydrogen-ion functions. The concentration [H] is unambiguously defined; the activity {H} is conceptually defined, but cannot really be evaluated on its own; a third quantity $\mathrm{H} = 10^{-\mathrm{pH}}$ is operationally defined through the use of buffers. Considerable effort has gone into defining the pH of certain buffer solutions in such a way as to make H identical with what {H} is believed to be in these. However, in media of higher ionic strength than these buffers, specific ionic interactions and a liquid junction potential can give rise to differences between H and {H} which become appreciable at higher concentrations. In practice H has been found to be proportional to [H] within certain limits, so that pH-meters can be empirically calibrated as hydrogen-ion concentration probes,[13,14] even for mixed solvents.[15] Many acidity constants have been evaluated by means of the Henderson equation $\mathrm{p}K = \mathrm{pH} + \log([\mathrm{HA}]/[\mathrm{A}])$ or similar expressions. These are "mixed" or practical acidity constants of the form H.[A]/[HA]. There is no harm in the use of such quantities in conjuction with other compatible experimental data,[16] but because of uncertainty in the significance of the quantity H in many background solutions, "mixed" acidity constants can only be regarded as having limited physical significance. Published compilations of equilibrium constants for acids and bases do not as a rule reveal whether these are *thermodynamic*, *concentration*, or *mixed* quotients, and indeed many authors of original papers have not made clear which kind of "constant" is intended.

It may seem that undue stress is being placed on the precise significance and use of these hydrogen-ion functions in what is supposed to be a discussion of spectrophotometry, but the matter is often of considerable importance. As will be shown later, expressions such as $(1 + \beta_1^0[H] + \beta_2^0[H]^2 \ldots)$ often occur in calculations to compensate for portions of a ligand that may be protonated.* When [H] is large these expressions may become the determining factor in fixing the accuracy or precision with which an equilibrium constant may be evaluated. The use of an improper value of the acidity constants can thus lead to an incorrect value of the equilibrium constant sought.

EXPERIMENTAL CONSIDERATIONS

It should scarcely require mentioning that all possible pains should be taken to ensure the purity of reagents, the correctness of volumetric dilutions, the maintenance of constant temperature, and so forth. In the author's experience, the commonest and sometimes the most surprising source of erroneous results is dirty, etched, or otherwise unmatched absorption cells. No series of measurements should be begun without checking, by the interchange of cells, that no bias is being introduced into the results at any wavelength through non-equivalent absorption by the cells. Finally, if equilibrium data of high quality are sought, absorbance measurements should be made on a null-type spectrophotometer. In the writer's experience, results taken from even a high-quality ultraviolet-visible recording spectrophotometer have *never* yielded results in subsequent calculations that were as satisfactory as the same information gathered on a good null-type instrument.

STEPWISE FORMATION OF COMPLEXES

It is assumed that readers are familiar with the terminology and symbolism pertaining to stepwise formation of complexes,[17,18] which is briefly summarized below. For a series of n simple mononuclear complexes $BA \ldots BA_n$ the fraction of B that is in the jth complex is

$$\alpha_j = \beta_j[A]^j/X \tag{5}$$

where X is given by

$$X = 1 + \beta_1[A] + \beta_2[A]^2 + \ldots \beta_n[A]^n \tag{6}$$

The fraction of B that is uncomplexed, $\alpha_0 = [B]/C_B = 1/X$, and this leads to the convention of defining $\beta_0 = 1$. It also follows that

$$\sum_{j=0}^{n} \alpha_j = 1$$

---

* Throughout this paper the symbol β_j^0 will be used to denote overall proton *association* constants, *i.e.*, $\beta_j^0 = [H_jA]/[H]^j[A]$. The use of these, rather than the usual acid dissociation constants, permits more generalized representation of proton exchange reactions, particularly for computer programming.

The degree of complex formation is defined by

$$\bar{n} = \sum_{j=1}^{n} j\beta_j[\mathrm{A}]^j/x = \sum_{j=1}^{n} j\alpha_j \tag{7}$$

More complicated expressions are required to define these quantities when polynuclear species or complexes that undergo proton exchange with the solvent are formed. The cumulative equilibrium constants in these expressions apply to formation of the species in question; if dissociation constants are used, the polynomials must be altered accordingly.

The manner in which $\bar{n}$ and α_j vary with log[A] is depicted in Figs. 1 and 2 for two systems of complexes for which $n = 3$. In the first case, which is comparatively rare among

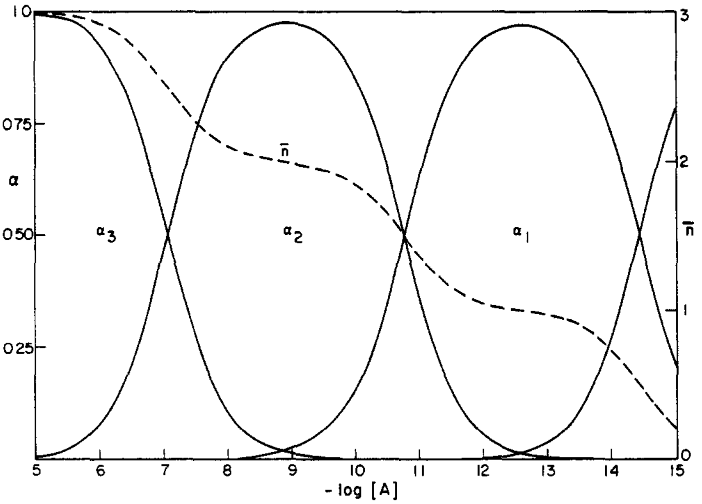

Fig. 1. Formation of iron(III)-sulphosalicylate complexes.
Log K_1 = 14·42; log K_2 = 10·76; log K_3 = 7·06. Solid line = α; broken line = $\bar{n}$.

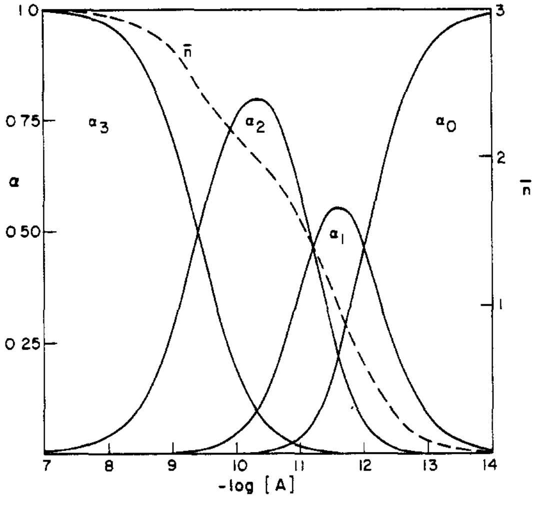

Fig. 2. Formation of iron(III)-oxine-sulphonate complexes.
Log K_1 = 12·0; log K_2 = 11·2; log K_3 = 9·4. Solid line = α; broken line = $\bar{n}$.

metal complexes, the formation of one complex is complete before that of the next begins. In the second case the formation of two or more complexes overlaps. The difference between the two systems arises from the ratios between the stepwise formation constants.[19] Systems of the first sort can be treated as a series of independent formations of 1:1 complexes, and are simple to handle. In systems where overlap occurs the treatment becomes more complicated and susceptible to error.

EXCESS ABSORBANCE

For a reaction

$$mB + nA = B_mA_n (\equiv C) \tag{1a}$$

$$A - \epsilon_B C_B - \epsilon_A C_A = [C](\epsilon_C - m\epsilon_B - n\epsilon_A) \tag{8}$$

where A represents the measured absorbance, adjusted if necessary for the path-length used in definition of the molar absorptivity ϵ. The quantity on the left is the difference between A and the absorbances of A and B if no reaction occurred. This quantity has sometimes been called *excess absorbance*, and although this term may not be very appropriate when it occurs with a negative value, we shall use it as occasion warrants and designate it A^*. The quantity $(\epsilon_C - m\epsilon_B - n\epsilon_A)$ may for some purposes be treated as a single coefficient which we shall represent by ϵ^*.

EQUILIBRIUM INVOLVING FORMATION OF ONE COMPLEX

Reaction of 1:1 *stoichiometry with* C_A *and* C_B *variable*

The equilibrium constant for equation (1) may be expressed in terms of absorptiometric quantities as follows:

$$K = \frac{A^*/\epsilon^*}{(C_A - A^*/\epsilon^*)(C_B - A^*/\epsilon^*)} \tag{9}$$

If ϵ^* or ϵ_C can be found by a suitable experiment, several independent estimates of K can be made by preparing a number of solutions with various C_A and C_B values and measuring A to find A^*.

It is sometimes assumed that by adding a large excess of one of the reactants the degree of conversion of the other into complex may be considered complete. Thus if $C_A \gg C_B$ it may be assumed that $[C] = C_B$, and that ϵ^* will be given by A^*/C_B. This may be tested by keeping C_B fixed and increasing C_A to see whether A^* becomes constant, but this method is impractical if the reactant in excess is a strong absorber, and in practice constant absorbance may not be obtained even when C_A/C_B is made quite large.

A brief digression will disclose the factors that render this particular assumption valid or invalid. Suppose C_A is put equal to nC_B in equation (9); when n is large enough A^*/ϵ^* may be neglected in comparison with nC_B. The result is a quadratic equation for which the positive root is

$$C_B = \frac{nKA^*/\epsilon^* + \sqrt{(nKA^*/\epsilon^*)^2 + 4(nKA^*/\epsilon^*)}}{2nK} \tag{10}$$

From this it is evident that $C_B \rightarrow A^*/\epsilon^*$ as the second term under the square root becomes small compared to the first. This only occurs if nKA^*/ϵ^* is fairly large. In fact, unless this quantity has a value greater than 100, the estimate of ϵ^* based on A^*/C_B will be in error by 1% or more. The following table gives an indication of the relationships defined by equation (10).

nKA^*/ϵ^*	A^*/C_B
4	$0{\cdot}829\,\epsilon^*$
40	$0{\cdot}976\,\epsilon^*$
400	$0{\cdot}997\,\epsilon^*$

Clearly, therefore, systems with small values of K or large values of ϵ^* are not well suited to this method, since A^* will generally be unity or less, and a number of practical factors may impose a limit on n.

Another approach to estimating ϵ^* which, like the preceding case, requires for practical reasons that ϵ_A be zero, entails finding by trial and error,[20] or preferably by computer,[21] the value of ϵ_C which yields the minimum standard deviation for K.

When ϵ^* is not or cannot be determined in this way, a common strategy is to treat it and K as a pair of unknowns to be extracted from the experimental data. Rearrangement of equation (9) gives:

$$C_AC_B - (C_A + C_B)A^*/\epsilon^* + (A^*/\epsilon^*)^2 = A^*/\epsilon^*K$$

As a rule the term $(A^*/\epsilon^*)^2$ will be smaller than the others, and may be temporarily or permanently dropped. This gives:

$$C_AC_B/A^* = 1/\epsilon^*K + (C_A + C_B)/\epsilon^* \qquad (11)$$

Then if C_AC_B/A^* is plotted against $(C_A + C_B)$ it should be possible to find ϵ^* and K from the slope and intercept of a straight line.[22] Many variations of this method have been suggested, according to the systems and stabilities involved.[23–25] Relationships of this sort may be extended to include coefficients for side-reactions, provided these do not interfere spectrally. For example, hydrolysis of a metal ion: $C_B - [C] = [B](1 + K_h/[H] + \ldots)$; protonation of a ligand: $C_A - [C] = [A](1 + \beta_1^0[H] + \ldots)$.

There are at least two potential problems with this method. One or two bad experimental values can markedly influence the slope and intercept of a straight line, even if fitted by a least-squares regression analysis. Thus the values of both ϵ^* and K can be prejudiced. Furthermore, for a slope and intercept to be well-defined by equation (11), $1/K$ and $(C_A + C_B)$ must be of comparable magnitude. For rather weak complexes the first term on the right of (11) is large compared to the second, so the slope and ϵ^* remain ill-defined, and one is left with only the product ϵ^*K. If the complex is strong and $(C_A + C_B) \gg 1/K$, the intercept will be small and probably poorly defined. In this case $\epsilon^* \sim A^*/C_A + A^*/C_B$, and can probably be estimated satisfactorily. There remains the risk, however, that a high degree of conversion into a strong complex could, as mentioned previously, impair evaluation of the equilibrium constant. A searching analysis of the propagation of errors in this type of analysis of data to secure an equilibrium constant has been given by Conrow *et al.*,[26] and Ramette[27] has reduced to a simple generalized numerical problem the treatment of data from a variety of spectrophotometric determinations of equilibrium constants, and demonstrated how this may be most readily solved with a computer.

In the method just considered ϵ^* and K were both regarded as unknown parameters. For weak complexes a good alternative is to arrange pairs of observations so as to eliminate ϵ^*.[28,29] For instance, for two solutions with the same C_B but different and much larger C'_A and C''_A undergoing reaction (1):

$$[C]'' = \frac{C_B(A''C'_A - A'C''_A)}{A'(C'_A - C''_A)} \tag{12}$$

whence

$$K = \frac{[C]''}{(C_B - [C]'')C''_A}, \ etc. \tag{13}$$

Equation (12) also establishes a value of $\epsilon^* = A^{*''}/[C]''$. In practice large numbers of solutions with fixed C_B and varying C_A may thus be compared in pairs to get a number of estimates of K, or better still analysed by computer to find what value of ϵ^* would most nearly make the two sides of equation (12) equal for all experimental values of A and C_A. It will be evident that this procedure will be less appropriate the stronger the complex, in which case $A''C'_A$ more nearly equals $A'C''_A$ and the quantity on the right of (12) is thereby less precisely defined. Another caveat: although ϵ^* is used in the discussion above, the suggested procedure entails the use of a considerable excess of A and is not likely to be successful unless $\epsilon_A \sim 0$.

Method of continuous variation[17,18]

For a reaction described by equation (1a) it is easily shown that the concentration of complex [C] will have its maximum value when $mC_A = nC_B$, and from equation (8) that the excess absorbance A^* will then show a maximum or minimum value. If C_A and C_B are varied but $(C_A + C_B)$ is kept constant, the maximum in [C] or A^* will occur when $x/(1-x) = n/m$, where $x = C_A/(C_A + C_B)$†. In practice, equimolar solutions are mixed to give a constant total volume, so that x is the volume fraction $V_A/(V_A + V_B)$.

Figure 3 shows the appearance of such plots for a system forming a 1:1 complex ($m = n = 1$; $x_{max} = 0{\cdot}5$). The different curves in this diagram might arise from sets of measurements (*i*) at different wavelengths; (*ii*) with different total $(C_A + C_B)$; (*iii*) on groups of solutions that differ in pH, where the complex formation is dependent on the hydrogen-ion concentration as in equation (2).

There are several features of this method that require further comment.

1. The relationship just described is valid for a single complex, and is independent of the wavelength at which A^* is measured. When more than one complex is simultaneously formed equation (8) must be changed to include on the right-hand side a term for each complex, and in consequence the ensuing relationships no longer apply. In practice, the value of x at which A^* shows an extremum becomes dependent on wavelength‡. Continuous-variation analysis incorporating measurements at several wavelengths can thus provide diagnostic evidence of whether one or more than one complex forms at a time (*cf.* Fig. 1).

2. The method is not vitiated by side-reactions such as (3) or (4), provided the products of these are spectrally non-absorbing, and that the degree of conversion in the side-reactions is kept constant (constant pH in these instances[30]).

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† It is convenient, though not strictly correct, to speak of this ratio as the "mole fraction" of A. Perhaps a better term would be the "molarity fraction".

‡ It is possible in principle for a second complex to be characterized by $\epsilon^* = 0$, in which case this effect would not appear, but the plot of A^* would assume a decidedly abnormal shape.

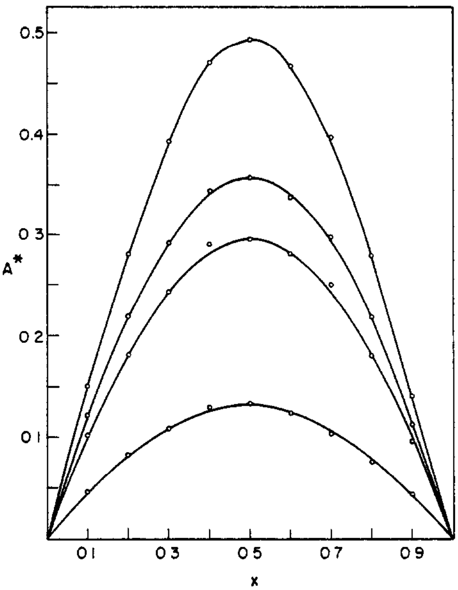

Fig. 3. Typical Job curves for 1:1 complex.

3. Only the empirical formula of the complex is established, and the method as originally conceived cannot discriminate between mononuclear ($m = 1$) and polynuclear ($m > 1$) complexes.

The method of continuous variations is unfortunately open to misuse on systems in which more than one complex-forming reaction takes place at a time.[31] Only in a few instances, where there has been considerable insight into the absorbing properties of a series of complexes, have continuous-variation plots been successfully interpreted for systems of more than one complex species.[32,33] A few authors have recently discussed how the formation of a polynuclear species B_mA_n ($m > 1$) affects the shape of the Job plots, and proved that the plots should then be concave at the ends;[34] however, this effect may be too small to be detectable, and the absorbances are necessarily small and so prone to measurement error; the effect may instead be caused by impure reagents or undesirable side-reactions.[35]

A number of ways have been suggested for calculating stability constants from continuous-variation analysis. Job showed[36] that when x volumes of C_0 molar B are mixed with $(1 - x)$ volumes of rC_0 molar A ($r \neq 1$), then at equilibrium for the formation of BA_n:

$$\beta C_0^n r^{n+1}[r - x_{\max}(n + r)]^{n+1} = (r - 1)^n[x_{\max}(n + 1) - 1] \tag{14}$$

For the value of $x_{\max}$ to be independent of C_0, r must equal unity. If non-equimolar solutions are mixed, Job plots for the solutions can in principle be used to evaluate β. In practice, however, this method may not yield particularly accurate values of β, owing to difficulties in precisely fixing values for $x_{\max}$.

A very simple approach is to assume that near the ends of the Job curve the degree of conversion into product is essentially complete,[37] and hence,

$$(\mathrm{d}A^*/\mathrm{d}x)_{x\to 0} = (n/m)\epsilon^*(C_A + C_B) \tag{15a}$$

$$-(\mathrm{d}A^*/\mathrm{d}x)_{x\to 1} = (m/n)\epsilon^*(C_A + C_B)\dagger \tag{15b}$$

† In these relationships can be seen the essence of the slope-ratio method.[38]

Given a value of ϵ^*, $[B_mA_n]$ for other solutions can be obtained and thence the equilibrium constant. However, the validity of the assumption should be checked by proving that the value of ϵ^* so derived is independent of $(C_A + C_B)$ and of pH. For instance, the Job curves in Fig. 3 will certainly not lead to a unique value of ϵ^* *via* equations (15a) and (15b) unless they correspond to measurements at different wavelengths, and further evidence would be required concerning the effect of pH or concentration.

Schwarzenbach has shown in a more rigorous analysis that equation (15a) is really a special case of a more general relationship.[39] For $m = n = 1$, this is

$$(\mathrm{d}A^*/\mathrm{d}x)_{x\to 0} = \frac{\epsilon^* K(C_A + C_B)^2}{K(C_A + C_B) + 1} \tag{16}$$

Only when $K(C_A + C_B)$ is considerably larger than unity does this expression converge with (15a), so that the applicability of the latter is restricted to complexes that are at least moderately stable. Buděšínský[35] has stated that the minimum stability of complexes for which the method is applicable is given by the equation

$$K_{mn} = 10^{3n-1}(C_A + C_B)^{1-(m+n)}$$

i.e., a 1:1 complex requires that $K(C_A + C_B) > 100$. Equation (16) contains both ϵ^* and K as unknowns which could, in principle, be evaluated from sufficient and suitable experimental results.

In passing, two other methods for extracting equilibrium constants from the data of Job curves may be mentioned. Heller and Schwarzenbach[40] applied an equation closely related to (11) to the results of continuous-variations analysis to find ϵ^* and K by a slope and intercept method. Hagenmuller[41] compared values of A^* for two different solutions within a series having $(C_A + C_B)$ constant $= C_0$. One of these solutions corresponded to the maximum (minimum) in A^*, the other to any other suitable value of x. With the respective molarity fractions, excess absorbances and concentrations of complex, designated $x_{\max}$, $A^{*\prime}$,$[C]'$ and x,A^*,$[C]$, the following relationships can be derived.

$$\{nC_0/(m + n) - m[C]'\}\{mC_0/(m + n) - n[C]'\} = [C]'/K_{mn}$$
$$\{(1 - x)C_0 - m[C]\}\{xC_0 - n[C]\} = [C]/K_{mn}$$
$$[C]/[C]' = A^*/A^{*\prime} = a$$

This set of equations can be solved for $[C]$, $[C]'$ and K_{mn} either algebraically or graphically.

Proportional absorbances

Some authors have made use of what have come to be called proportional absorbances in connection with continuous-variations analysis. Two "Job" series are prepared, corresponding solutions from each set having a constant ratio of reactant concentrations:

$$C_B/C'_B = C_A/C'_A = a \text{ (constant)}$$

The values of $x_{\max}$ and the corresponding excess absorbance are measured for the two Job curves. Then for a 1:1 complex, $C_B = C_A$ at $x_{\max}$, and if the maximum concentrations of complex are denoted by [C] and [C]′, we can write $[C] = zC_B$ and $[C]' = z'C'_B$ and

$$K = \frac{[C]}{(C_B - [C])^2} = \frac{[C]'}{(C'_B - [C]')^2}$$

$$= \frac{zC_B}{(C_B - zC_B)^2} = \frac{z'C'_B}{(C'_B - z'C'_B)^2} = \frac{z'C_B/a}{(C_B/a - z'C_B/a)^2}$$

Hence we can write

$$\frac{z}{(1 - z)^2} = \frac{az'}{(1 - z')^2} = \frac{1}{y} \tag{17}$$

and

$$K = \frac{1}{yC_B} \tag{18}$$

The two expressions in equation (17) may be given in terms of experimental quantities:

$$\frac{A^*/\epsilon^* C_B}{(1 - A^*/\epsilon^* C_B)^2} = \frac{aA^*/\epsilon^* C'_B}{(1 - A^*/\epsilon^* C'_B)^2}$$

All the quantities are known save ϵ^*, so this may be evaluated as a solution to a quadratic equation. With ϵ^* known, a value of K can be determined from equation (18).

If $m \neq n \neq 1$, these relationships can be modified [see equations (17a) and (18a)], but to find a value of K in this case would require the solution of an equation of higher degree in ϵ^*. Although this could be done, absorbance data of very high precision would be required for the values of the equilibrium constant to be acceptable.

A novel alternative to seeking explicit solutions to such equations has been developed by Buděšínský,[35] who has shown that equation (17) may be given in a more general form for the complex B_mA_n:

$$\frac{z_{mn}}{(1 - mz_{mn})^{m+n}} = \frac{a^{m+n-1}z'_{mn}}{(1 - mz'_{mn})^{m+n}} = \frac{1}{y} \tag{17a}$$

$$K_{mn} = \frac{(m/n)^n}{yC_B^{m+n-1}} \tag{18a}$$

The quantity y [in (17) and (17a)] depends functionally on z_{mn} or z'_{mn}, and may be evaluated for values of z_{mn} or z'_{mn} lying between 0 and $1/m$. It is evident that y becomes infinite if z or z' is zero, and y becomes zero when z or $z' = 1/m$. Figure 4, taken from Buděšínský's paper, shows how log y varies with z or z' corresponding to different coefficients m and n, with $a = 2$. Each value of y has a pair of corresponding values of z and z', the ratio of which can be expressed in terms of the respective absorbances, thus:

$$z_{mn}/z'_{mn} = [C]/a[C]' = A^*/aA^* = x_{mn} \tag{19}$$

The quantity x_{mn} has limiting values that are a consequence of the limits of y. From (17a) and (19) it appears that if y is zero, $x_{mn} = 1$, while if y is infinite, $x_{mn} = a^{m+n-1}$. The relationship between x_{mn} and log y is indicated in Fig. 5, which also suggests the approach to these limiting values.[42]

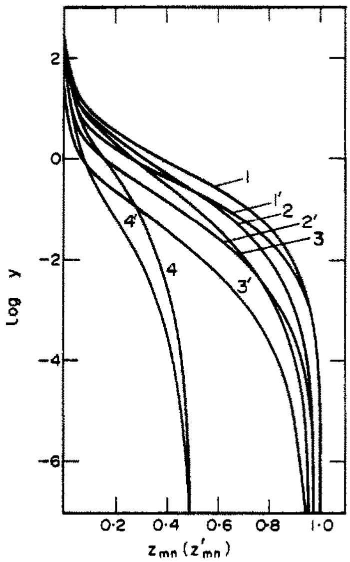

Fig. 4. Dependence of log y on z_{mn} or z'_{mn} (curves numbered with primes) for $a = 2$ and various complexes: 1,1' = BA; 2,2' = BA_2; 3,3' = BA_3; 4,4' = B_2A_2 (after Buděšinský,[35] reproduced with permission).

If several solutions are prepared having $x = x_{\max}$, but differing in C_B, the ratio of A^*/aA^* for pairs of these will establish values of x_{mn}. Inspection of the latter may, but not necessarily will, indicate a choice between alternative compositions of the complex, *e.g.*, BA or B_2A_2. For instance, values of $x_{mn} > 2$ are incompatible with the composition BA. However, if the indicated values of x_{mn} admit the possibility of more than one composition of the complex, a choice can still be made based on which gives the lesser variation in K_{mn} when appropriate alternative values of m and n and a value of y corresponding to x_{mn} are

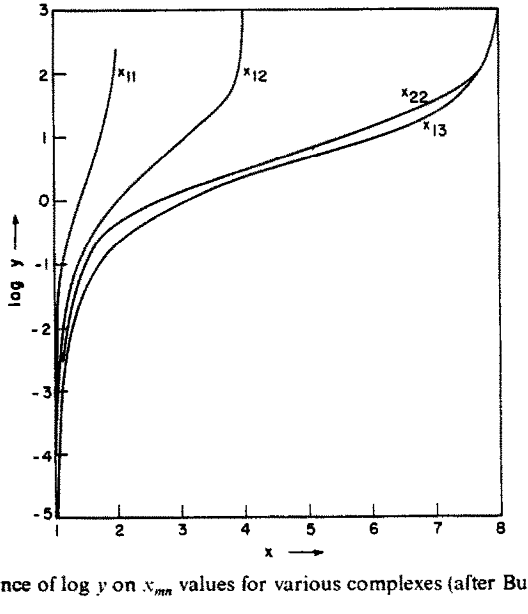

Fig. 5. Dependence of log y on x_{mn} values for various complexes (after Buděšinský,[35]).

inserted in equation (18a). Tables have been worked out[43] showing for various combinations of m and n the values of log y to enable this calculation to be made.

Buděšínský's treatment of continuous-variations analysis[44]

Equation (1a) can be generalized by considering the complex to be $B_mY_iH_jA_n$, which allows for formation of protonated species, or species incorporating some other ligand Y. If we call this complex C′, then

$$\beta_{mijn} = [C']/[B]^m[Y]^i[H]^j[A]^n \tag{20}$$

and an apparent stability constant can be written

$$K'_{mn} = [C']/(C_B - m[C'])^m(C_A - n[C'])^n \tag{21}$$

The effect of side-reactions may be expressed by side-reaction coefficients as usual (but note that $\alpha_{B(Y)}$ is dependent on $[H^+]$):

$$\alpha_{B(Y)} = (C_B - m[C'])/[B] \tag{22a}$$

$$\alpha_{A(H)} = (C_A - n[C'])/[A] \tag{22b}$$

Suitable substitution then gives

$$K'_{mn}\alpha^m_{B(Y)}\alpha^n_{A(H)} = [Y]^i[H]^j\beta_{mijn} \tag{23}$$

The coefficient $\alpha_{A(H)}$ relates to all forms of A other than metal complexes (*i.e.*, A, HA … H_QA):

$$\alpha_{A(H)} = \sum_0^Q \beta^0_q[H]^q$$

where $\beta^0_0 = 1$. Thus $\alpha_{A(H)}$ depends only on [H] as an experimental variable. The coefficient $\alpha_{B(Y)}$ relates to complexes formed by the metal with Y but not containing A, and can be made dependent on [H] and essentially independent of [B] if the complexes are mononuclear (BH_rY_s) and $C_Y \gg C_B$, since $[Y] = C_Y/\alpha_{Y(H)}$, and hence

$$\alpha_{B(Y)} = \sum_0^R\sum_0^S \beta_{rs}[H]^r(C_Y/\alpha_{Y(H)})^s \tag{24}$$

The side-reaction coefficients are thus defined in terms of experimental quantities and, hopefully, available and compatible equilibrium constants.

From experimental information it is usually possible to fix the values of i and j in C′. From equation (23)

$$\log K'_{mn} + m\log\alpha_{B(Y)} + n\log\alpha_{A(H)} = i\log[Y] + j\log[H] + \log\beta_{mijn}$$

It must be assumed that conditions can be chosen such that the side-reaction leads to a single complex BH_rY_s; this may occur naturally with some multidentate ligands such as EDTA, or be contrived by the use of an excess of Y so that $s = s_{max}$. In this case, at constant [H] the equation above becomes.

$$\log K'_{mn} = (i - ms)\log C_Y + \text{constant} \tag{25}$$

In a completely analogous way the dependence of log K'_{mn} on pH at fixed C_Y can lead to a value of j. Once i and j are established, values of β_{mijn} can be found from (20).

Obviously, for the necessary spectrophotometric measurements to be within the useful range, the relationship of the magnitudes of the equilibrium constant and the reactant concentrations must fall within certain limits. The apparent stability constant can be brought within this range through the use of side-reactions.

Hydrolysis of metal ions is an undesirable side-reaction. It can easily lead to polymeric condensation products, the formation of which is not immediately reversible, or to hydroxylated species of possibly uncertain composition. The first stage of the hydrolysis may be taken as formation of BOH. Budĕšínský[44] has suggested that a side-reaction coefficient of 1·25 for this first-stage hydrolysis is tolerable, *i.e.*,

$$\log \alpha_{\mathrm{BOH}} = \log(1 + K_{\mathrm{h}}^{*}/[\mathrm{H}]) = 0{\cdot}1 \qquad (26)$$

where $K_{\mathrm{h}}^{*} = [\mathrm{BOH}][\mathrm{H}]/[\mathrm{B}]$.

The pH corresponding to this side-reaction coefficient is $\mathrm{p}K_{\mathrm{h}}^{*} - 0{\cdot}4$. To work at higher pH, as may be required by the characteristics of a particular colour-forming reaction, it is recommended that hydrolysis be controlled by a masking agent Y. Then, according to the acid-forming and complex-forming characteristics of Y, the pH corresponding to some designated degree of hydrolysis of the metal ion can be calculated. For instance, for 1% of the metal ion not involved in complexation with A to undergo hydrolysis,

$$100[\mathrm{BOH}] = C_{\mathrm{B}} = [\mathrm{B}]\alpha_{\mathrm{B(Y)}}$$

or

$$100\,K_{\mathrm{h}}^{*} = [\mathrm{H}]\alpha_{\mathrm{B(Y)}}.$$

The corresponding pH will be an implicit function of C_{Y} and the β_{rs} and β_q^0 values for the masking ligand Y [equation (24)].

The spectrophotometric study should often be done at a pH at which the apparent formation constant of the absorbing species is a maximum. Below this pH A will be increasingly protonated and above it, any masking agent Y present will compete for the metal to an increasing extent. For the optimum pH,[45]

$$(\mathrm{d}\log K'_{mn}/\mathrm{dpH})_{\mathrm{opt}} = 0$$

and for a constant excess (C_{Y}) of Y,

$$m\left(\frac{\mathrm{d}\log \alpha_{\mathrm{B(Y)}}}{\mathrm{dpH}}\right)_{\mathrm{opt}} + n\left(\frac{\mathrm{d}\log \alpha_{\mathrm{A(H)}}}{\mathrm{dpH}}\right)_{\mathrm{opt}} = -i\left(\frac{\mathrm{d}\log \alpha_{\mathrm{Y(H)}}}{\mathrm{dpH}}\right)_{\mathrm{opt}} - j$$

and on appropriate substitution this yields

$$m(\bar{p}\bar{s} - \bar{r})_{\mathrm{opt}} - n\bar{q}_{\mathrm{opt}} = i\bar{p}_{\mathrm{opt}} - j \qquad (27)$$

in which

$$\bar{p} = \sum_{0}^{P} p\beta_p[\mathrm{H}]^p \Big/ \sum_{0}^{P} \beta_p[\mathrm{H}]^p$$

$$\bar{q} = \sum_{0}^{Q} q\beta_q[\mathrm{H}]^q \Big/ \sum_{0}^{Q} \beta_q[\mathrm{H}]^q$$

$$\bar{r} = \sum_{0}^{R}\sum_{0}^{S} r\beta_{rs}[\mathrm{H}]^r(C_{\mathrm{Y}}/\alpha_{\mathrm{Y(H)}})^s \Big/ \sum_{0}^{R}\sum_{0}^{S} \beta_{rs}[\mathrm{H}]^r(C_{\mathrm{Y}}/\alpha_{\mathrm{Y(H)}})^s$$

$$\bar{s} = \sum_{0}^{R}\sum_{0}^{S} s\beta_{rs}[\mathrm{H}]^r(C_{\mathrm{Y}}/\alpha_{\mathrm{Y(H)}})^s \Big/ \sum_{0}^{R}\sum_{0}^{S} \beta_{rs}[\mathrm{H}]^r(C_{\mathrm{Y}}/\alpha_{\mathrm{Y(H)}})^s$$

It will be evident that $\bar{p}$ and $\bar{q}$ refer respectively to those parts of the masking agent Y and the ligand A that are not bound in the complex C′, and specifically these are the degrees of protonation of each. Also $\bar{r}$ and $\bar{s}$ refer to the complexes MH_rY_s, and are respectively the average numbers of moles of protons and of masking agent Y bound per mole of metal in these complexes. It follows that these four variables can be evaluated for particular ligands and masking agents as functions of pH, and useful predictions derived therefrom.

ACID-BASE AND SIMILAR EQUILIBRIA

Many of the procedures thus far described have been devised to overcome the problem caused by inability to convert B completely into BA ($\equiv$ C), and hence to be able to measure ϵ_C. However, if A can be made large enough to achieve complete formation of C, then for a fixed C_B, and varying [A]

$$\epsilon\dagger = \frac{A - \epsilon_A[A]}{C_B} = \frac{\epsilon_B + \epsilon_C K[A]}{1 + K[A]} \qquad (28)$$

for a single complex, or, if a series of complexes forms

$$\epsilon\dagger = \frac{\epsilon_B + \epsilon_1\beta_1[A] + \epsilon_2\beta_2[A]^2 + \ldots\epsilon_n\beta_n[A]^n}{1 + \beta_1[A] + \beta_2[A]^2 + \ldots\beta_n[A]^n} \qquad (28a)$$

If only one complex forms, or formation of BA is complete before that of BA_2 begins, equation (28) applies. Then at very small [A], $\epsilon\dagger \rightarrow \epsilon_B$ and at very large [A], $\epsilon\dagger \rightarrow \epsilon_C$. At intermediate values of [A]

$$K = \frac{1}{[A]} \cdot \frac{\epsilon\dagger - \epsilon_B}{\epsilon_C - \epsilon\dagger} \qquad (29)$$

Unless a probe is available for the direct measurement of [A] this quantity will not be known, hence to evaluate $\epsilon\dagger$ it is necessary that ϵ_A be zero. These relationships are displayed in Fig. 6 in which [A] is represented on a logarithmic scale. When $K[A] = 1$, $\epsilon\dagger = (\epsilon_B + \epsilon_A)/2$. Several corresponding values of $\epsilon\dagger$ and [A] may be obtained, but the precision

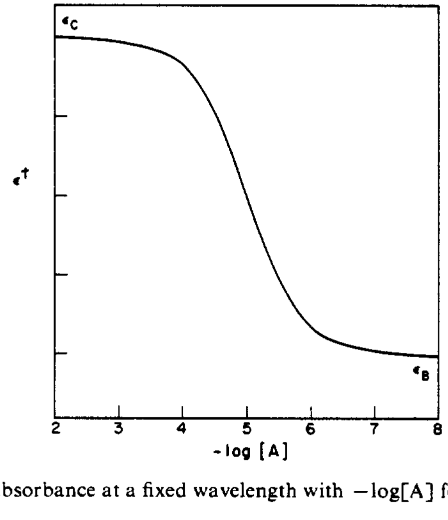

Fig. 6. Variation of absorbance at a fixed wavelength with −log[A] for reaction B + A = C.

of $(\epsilon\dagger - \epsilon_B)/(\epsilon_C - \epsilon\dagger)$ should be adequately defined by the data; the ratio should be in the range 0·1–10, and A may be measured at any wavelength for which ϵ_C and ϵ_B are well separated.

By far the most familiar application of (29) is to acid–base equilibria, where A is the hydrogen ion and B and C the conjugate base and acid respectively. The pH can be varied and measured over wide ranges in aqueous or partially aqueous solutions. A related use of (29) is to define acidity functions such as the Hammett function[46] by means of indicators. When pH is used to control formation of metal complexes, and these and the free metal have sufficiently different absorption spectra, plots of absorbance *vs.* pH can be used to measure the formation constants for the complexes. For this purpose (28) still applies, but it is necessary to find a value of [A] as follows:

$$[A] = (C_A - \bar{n}C_B)/\alpha_{A(H)} \tag{30}$$

where

$$\bar{n} = (\epsilon\dagger - \epsilon_B)/(\epsilon_C - \epsilon_B) \tag{31}$$

It is presupposed that A can be protonated and is non-absorbing in all its forms.

Even if ϵ_C is inaccessible to direct measurement, it is still feasible to estimate it by computer calculation of the value that gives the most consistent fit of the experimental results. This device has been used by the writer to determine some low pK_a values where it was apparent that conversion into the fully protonated species was incomplete.[47]

Isosbestic points as diagnostic tools

Isosbestic points in absorption spectra plotted for constant C_B and variable [A] arise at wavelengths where ϵ_B and ϵ_{BA} have the same value. The value of [A] is often varied by pH control. Usually occurrence of an isosbestic point is taken to imply that only *two* species in equilibrium are present over the appropriate range of conditions. This inference is normally warranted, but Schläfer[48] cautioned that a fortuitous combination of circumstances could give rise to a pseudo-isosbestic point for which the inference would be incorrect. Occurrence of an isosbestic point implies that equation (28) can be applied.

As shown by Vareille[49] in an analysis of the spectra of certain iron(III) complexes, systems of non-overlapping consecutive complex-formation reactions (as in Fig. 1) can be treated in the same way.

It has been shown [12] for a series of three complexes, typical of many metal chelates, that if equation (28a) is expressed in terms of α_j [see equation (5)]

$$\epsilon\dagger = \epsilon_0\alpha_0 + \epsilon_1\alpha_1 + \epsilon_2\alpha_2 + \epsilon_3\alpha_3 \tag{28b}$$

$$\begin{aligned} 0{\cdot}43\frac{d\epsilon\dagger}{d\log[A]} &= (\epsilon_1 - \epsilon_0)\alpha_0\alpha_1 + 2(\epsilon_2 - \epsilon_0)\alpha_0\alpha_2 + 3(\epsilon_3 - \epsilon_0)\alpha_0\alpha_3 \\ &\quad + (\epsilon_2 - \epsilon_1)\alpha_1\alpha_2 + 2(\epsilon_3 - \epsilon_1)\alpha_1\alpha_3 + (\epsilon_3 - \epsilon_2)\alpha_2\alpha_3 \end{aligned} \tag{32}$$

The expression on the right-hand side of (32) will be zero if any one of the values of α becomes unity, since then the other three must be zero. Thus $\epsilon\dagger$ will not change as [A] varies as long as all the B is present as a single species in solution. The same expression will be zero whenever any of the following pairs of relationships is fulfilled:

$$\begin{aligned} \epsilon_0 &= \epsilon_1 \quad \text{and} \quad \alpha_0 + \alpha_1 = 1 \\ \epsilon_1 &= \epsilon_2 \quad \text{and} \quad \alpha_1 + \alpha_2 = 1 \\ \epsilon_2 &= \epsilon_3 \quad \text{and} \quad \alpha_2 + \alpha_3 = 1 \\ \epsilon_0 = \epsilon_1 &= \epsilon_2 \quad \text{and} \quad \alpha_0 + \alpha_1 + \alpha_2 = 1 \\ \epsilon_1 = \epsilon_2 &= \epsilon_3 \quad \text{and} \quad \alpha_1 + \alpha_2 + \alpha_3 = 1 \end{aligned}$$

These are the conditions that would generate an isosbestic point, and as it is usually considered unlikely that three different species would have a common molar extinction coefficient at some particular wavelength, it is a reasonable inference from the occurrence of an isosbestic point that only two absorbing species are in equilibrium.

Within the appropriate ranges of [A], therefore, absorbances at any suitable wavelength may be applied to evaluate formation constants by means of equation (29a).

$$K_n = \frac{1}{[\mathrm{A}]} \cdot \frac{(\epsilon\dagger - \epsilon_{n-1})}{\epsilon_n - \epsilon\dagger} \tag{29a}$$

In evaluating [A], it is necessary to modify equation (31) to

$$\bar{n} = (n - 1) + (\epsilon\dagger - \epsilon_{n-1})/(\epsilon_n - \epsilon_{n-1}) \tag{31a}$$

Values of ϵ_0 can be found directly, and those of ϵ_3 can generally be found from solutions containing a large excess of A. It is more difficult to fix ϵ_1 and ϵ_2 precisely. However, ϵ_1 at the isosbestic point where $\epsilon_1 = \epsilon_2$ is easily found; we may denote this $\epsilon^{\prime}_1$. For a solution of lower [A] containing only B and BA, the value of A/C_{B} can be represented as $\epsilon^{\prime}$ at the isosbestic wavelength or ϵ at some different wavelength. For the other wavelength, then, $\epsilon_1 = \epsilon . \epsilon^{i}_1/\epsilon^{\prime}$. The best way to assign ϵ_2 is then by computer search to find the best fit to make $(\epsilon\dagger - \epsilon_2)/(\epsilon_3 - \epsilon\dagger)$ [A] constant for a set of solutions, and $(\epsilon\dagger - \epsilon_1)/(\epsilon_2 - \epsilon\dagger)$ [A] constant for another set at the same wavelength. In one such study[47] there was a marked improvement in the precision of the equilibrium constants, relative to that obtained by assignment of ϵ values by inspection.

OVERLAPPING EQUILIBRIA

With many polybasic acids and most metal complexes the equilibria overlap and most of the procedures and calculations just discussed are vitiated; at best they must be used only with the greatest caution. For example, the method of continuous variations can be quite misleading.[31]

The absorption at a particular wavelength can be described by equation (28a) if either $\epsilon_{\mathrm{A}} = 0$ or [A] can be determined by a suitable probe. There are two features of this relationship that place spectrophotometry at a disadvantage compared to some other methods of establishing β_j in systems of this sort. First, each complex species represented in the equation contributes two unknown parameters, ϵ and β, so that the number of unknowns requiring evaluation from experimental results is double that originating in some other procedures.[17] Secondly, the value of ϵ at a given wavelength often changes only a little as higher complexes are formed. This probably signifies that the relative change in the conditions of bonding from one complex to another decreases in passing to higher complexes.[50] Accordingly, values of β for the higher complexes can only be evaluated from small changes in $\epsilon\dagger$ and are therefore unreliable. Nevertheless, for systems of complexes, particularly those involving transition metal ions and chelate-forming organic ligands, where pronounced spectral changes occur in passing from one complex to another, the spectrophotometric method may be successfully applied.

The method of corresponding solutions[51]

Corresponding solutions in this sense are defined as having the same degree of complex formation, $\bar{n}$, and hence the same [A]. Since $\bar{n}$ is a single-valued function of [A] only if mononuclear complexes are formed, this method is restricted to such systems. For two corresponding solutions it may be shown [see equation (30)] that

$$\bar{n} = \frac{C'_{\mathrm{A}} - [\mathrm{A}]\alpha'_{\mathrm{A(H)}}}{C'_{\mathrm{B}}} = \frac{C''_{\mathrm{A}} - [\mathrm{A}]\alpha''_{\mathrm{A(H)}}}{C''_{\mathrm{B}}} \tag{30a}$$

whence

$$\bar{n} = \frac{C''_{\mathrm{A}}\alpha'_{\mathrm{A(H)}} - C'_{\mathrm{A}}\alpha''_{\mathrm{A(H)}}}{C''_{\mathrm{B}}\alpha'_{\mathrm{A(H)}} - C'_{\mathrm{B}}\alpha''_{\mathrm{A(H)}}} \quad \text{and} \quad [\mathrm{A}] = \frac{C''_{\mathrm{B}}C'_{\mathrm{A}} - C'_{\mathrm{B}}C''_{\mathrm{A}}}{C''_{\mathrm{B}}\alpha'_{\mathrm{A(H)}} - C'_{\mathrm{B}}\alpha''_{\mathrm{A(H)}}} \tag{33}$$

Since $\alpha_{\mathrm{A(H)}}$ depends only on [H], $\alpha' = \alpha''$ in solutions adjusted to the same pH, and then

$$\bar{n} = \frac{C''_{\mathrm{A}} - C'_{\mathrm{A}}}{C''_{\mathrm{B}} - C'_{\mathrm{B}}} \quad \text{and} \quad [\mathrm{A}] = \frac{C''_{\mathrm{B}}C'_{\mathrm{A}} - C'_{\mathrm{B}}C''_{\mathrm{A}}}{(C''_{\mathrm{B}} - C'_{\mathrm{B}})\alpha_{\mathrm{A(H)}}} \tag{33a}$$

Thus if we know C_{B} and C_{A} for two corresponding solutions we can calculate a pair of corresponding values of $\bar{n}$ and [A], that is to say, the co-ordinates of a point on the complex formation curve. Given sufficient such co-ordinates to be able to draw the formation function we may obtain β_j values by curve-fitting procedures.

It was shown earlier that

$$\epsilon\dagger = \epsilon_0\alpha_0 + \epsilon_1\alpha_1 + \epsilon_2\alpha_2 + \ldots \epsilon_n\alpha_n \tag{28b}$$

If we treat ϵ_0, ϵ_1, *etc.*, as constants, then corresponding solutions, having [A] fixed, also have α_j and $\epsilon\dagger$ fixed. Solutions are prepared in sets, each set having fixed C_{B} and variable C_{A}; then the values of $\epsilon\dagger$ and pH (if required) for each solution are measured (preferably more than one wavelength being used). The results are displayed as in Fig. 7. The points

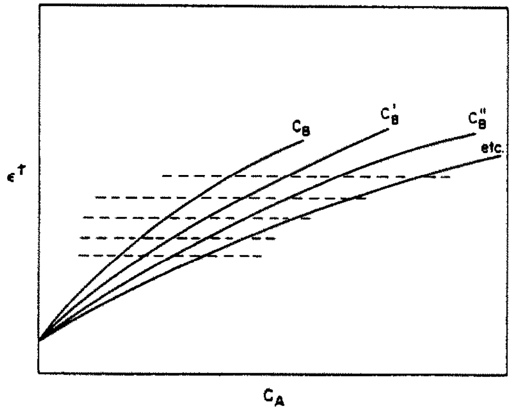

Fig. 7. Identification of corresponding solutions.

of intersection of the experimental $\epsilon\dagger$ curves and the horizontal lines define the composition of corresponding solutions; from these the co-ordinates of the formation curve can be obtained.

Insofar as this is almost the only spectrophotometric method that will generate a formation curve for a series of complexes it has a good deal to recommend it. However, it is time-consuming because so many solutions have to be prepared. Some care must be taken in choosing the experimental conditions to ensure that $C_A - [A]\alpha_{A(H)}$ is well-defined: thus $[A]\alpha_{A(H)}$ should lie well away from C_A. For various reasons connected with the values of ϵ_j and lack of differentiation among corresponding solutions, the method may yield only a portion of the formation curve.

An interesting extension of this method was based on competition of two metal species for the same ligand.[52] The ligand was 1,10-phenanthroline; one metal species was iron(II) which forms a stable, coloured tris complex (large β_3), the other was Co(II), Ni(II), Cu(II) or Zn(II) which give colourless complexes. All solutions were prepared with constant C_{Fe} but variable C_M and C_A. Solutions of constant absorbance contained the same $[FeA_3]$, hence the same $\bar{n}(Fe)$, and same $[A]$. For the second metal $\bar{n}(M)$ was equal to $\{C_A - [A] - \bar{n}(Fe)C_{Fe}\}/C_M$. The fraction of the iron(II) present as FeA_3 was given by the ratio of the absorbance observed in the presence of competing metal to that observed in the absence of the latter [the experimental conditions having been designed so that conversion of iron(II) into complex was complete in the absence of the second metal]. Thus A/A_{max} was equal to $\alpha_3(Fe)$, and since the stability constants for the iron(II) complexes were known, $[A]$ could be found from $a_3(Fe)$. The use of competing reactions to determine stability constants will be mentioned again in a later section.

Yatsimirskii's method[53]

This is an extrapolation method analogous to a procedure devised by Poulsen, Bjerrum and Poulsen[54] for finding stability constants from a set of corresponding values of $\bar{n}$ and $[A]$. The method has been described a number of times,[17,18,48] and will not be given in detail here. In the writer's opinion, there are two stumbling blocks which militate against the application of this procedure. First data must be available in the form of corresponding values of $\epsilon\dagger$ and $[A]$. It is clear from equation (30) that $[A]$ is not ordinarily available from the experimental quantities unless $C_A \gg C_B$, when it may be permissible to put $[A] = C_A/\alpha_{A(H)}$. However, when all experimental considerations such as solubility, working range of absorbance, *etc.*, are met, the ratio C_A/C_B may not be able to meet this additional requirement.

Secondly, extrapolation procedures such as the two cited in this section are extremely susceptible to "differencing errors"; they only work with exceedingly good data, and absorptiometric measurements seldom possess the necessary precision. At the best, it is doubtful if this method is capable of deriving stability constants for systems of more than two successive complexes.

Ang's method for two overlapping equilibria[55]

The following procedure was developed for the case of a dibasic acid, but is here generalized for any system of two overlapping equilibria. The essential requirement is that there be some wavelength(s) such that as $B \rightarrow BA \rightarrow BA_2$ with increase in C_A the absorbance goes through a maximum or minimum, at which presumably $[BA]$ is at a maximum. Such

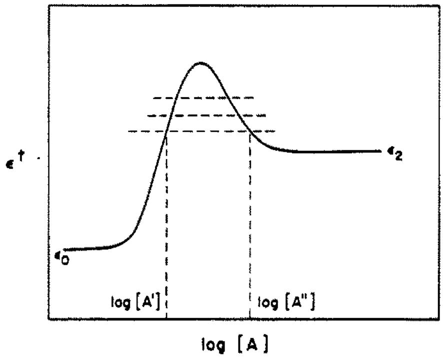

Fig. 8. Variation of absorbance suitable for Ang's method[55] for two successive complexes.

a situation is represented in Fig. 8. If we assume A is non-absorbing, then from equation (28)

$$(\epsilon^\dagger - \epsilon_0) + (\epsilon^\dagger - \epsilon_1)\beta_1[A] + (\epsilon^\dagger - \epsilon_2)\beta_2[A]^2 = 0 \tag{34}$$

The horizontal lines in Fig. 8 cut the absorbance curve at two points at which the $\epsilon^\dagger$ values are the same. If we designate by [A′] and [A″] the corresponding values of [A], substitute these in turn in (34), and then subtract, we obtain

$$\epsilon^\dagger - \epsilon_1 = -(\epsilon^\dagger - \epsilon_2)K_2([A'] + [A'']) \tag{35}$$

since $\beta_2/\beta_1 = K_2$. From Fig. 8 it is evident that ϵ_2 will be known from $\epsilon^\dagger$ at sufficiently great values of log [A]. Thus the quantity $(\epsilon^\dagger - \epsilon_2)([A'] + [A''])$ can be evaluated for each of several chosen values of $\epsilon^\dagger$. A plot of $\epsilon^\dagger$ *vs.* this quantity should yield ϵ_1 as intercept and K_2 as slope. Likewise

$$\epsilon^\dagger - \epsilon_0 = -(\epsilon^\dagger - \epsilon_1)\beta_1 \Bigg/ \left(\frac{1}{[A']} + \frac{1}{[A'']}\right) \tag{36}$$

from which β_1 can be obtained in the same way.

Method of Newman and Hume[56]

These authors have given a penetrating analysis of relationships that may arise whem simple or mixed complexes are formed through the interaction of metal and ligands in various overall proportions, and various species are absorbing or non-absorbing. The original paper should be consulted for the details, which are too lengthy to include here.

Computer-assisted study of overlapping equilibria

During the last 6–7 years the graphical and numerical procedures developed earlier have been greatly assisted, if not actually superseded, by the introduction of computer-based procedures. These are being introduced and modified in many laboratories and it would scarcely be practical to include a complete report of such methods in this survey. The problem in investigating stepwise equilibria spectrophotometrically is that both the stability constants *and* the molar extinction coefficients are unknown, and the best values of all of these are sought.

The method of corresponding solutions offers the possibility, not always realized, of reducing this problem to finding the stability constants only, by means of converting absorptiometric results into a formation function. Several computer programs exist for finding the values of the proper number of β's to give the best fit to a Bjerrum formation curve. The most obvious approach, and one of the earliest suggested,[57] was to seek optimum solutions to a set of simultaneous equations of the sort:

$$\bar{n} = (1 - \bar{n})\beta_1[\mathrm{A}] + (2 - \bar{n})\beta_2[\mathrm{A}]^2 + (3 - \bar{n})\beta_3[\mathrm{A}]^3 \ldots \tag{37}$$

Values of β are sought which yield a minimum in the sum of squares of residuals, a residual being the difference between $\bar{n}$ (observed) and the calculated value of the right-hand side. In the writer's laboratory a comprehensive program NLMAX was developed and used for a time for this purpose, but experience in its use revealed certain difficulties that should be kept in mind. The coefficients of β in (37) include values of $\bar{n}$ and [A] derived from experimental measurements. Uncertainties in the latter cause uncertainties in the coefficients and these may vary widely between, say, low and high values of [A]. To compensate for these uncertainties the residuals need to be weighted, but the manner of arriving at the proper weighting is somewhat discretionary. In this connection we found the approach outlined by Varga[58] to be quite effective.

There is a second problem in the solution of sets of linear equations like (37). This arises whenever the values of β span too wide a range. It is difficult to define "too wide", but a system that creates such problems is nickel–ethylenediamine ($\log \beta_1 = 7{\cdot}7$, $\log \beta_2 = 14{\cdot}1$, $\log \beta_3 = 18{\cdot}6$). In such a system the coefficients of β in (37), which constitute the elements of a matrix in the computer solution of the simultaneous equations, are too disparate in size to be effective in defining values of the several β's. The difficulty is eased but not eliminated by introducing scale reductions before submitting the equations to solution, followed by suitable subsequent adjustment of the stability constants. We also found it preferable in handling such a system to divide the data defining the formation curve ($\bar{n}$ [A]) into two lots covering different but overlapping regions of [A], the one capable of defining β_1 and β_2, the second β_2 and β_3. The resulting computation gave good approximations of β_1 and β_3 but not necessarily a single satisfactory value of β_2. A new grouping of data was then taken, encompassing the middle range of values of [A], and used with the first estimates of β_1 and β_3 to obtain an acceptable value of β_2.

In a recent publication Perrin *et al.*[59] employed essentially the same method for determining overlapping $\mathrm{p}K_a$ values. They used equation (34), treating β_1, β_2 and ϵ_1 as unknowns to be found by a least-squares computer solution to a set of equations, one from each experimental point. These authors allude to the problem of poor conditioning arising from the columns of the matrix having different orders of magnitude. They employed a scaling technique to limit to unity the modulus of any element in the matrix.

The exact form in which equation (37) is to be written will depend on what species are assumed to be present, and for which stability constants must be sought. As the assumed complexity of the system becomes greater, so does the chance of postulating spurious species. The chemist must therefore exercise considerable judgment in selecting reasonable constituents in accordance with experimental data. Fortunately, as mentioned before, spectrophotometric observations do provide some direct evidence concerning the reality of the assumptions. Negative values of β are not admissible, and if obtained generally indicate an unwarranted assumption of existence of the corresponding species.

A rather better, though less obvious, approach to computer-assisted evaluation of β's is typefied by the Swedish program LETAGROP,[60] which by now has appeared in a number of variations. If the stability constants are to be experimentally evaluated through the formation function $\bar{n}$, the values of β are sought which will minimize the weighted sum of squares of residuals defined as $\bar{n}$ (observed) $-$ $\bar{n}$ (calculated). This quantity to be minimized is denoted the "error square sum", U, and is assumed to bear some functional relationship to the stability constants sought. The nature of this relationship has been shown to be of the form of a generalized elliptic paraboloid in $(N + 1)$-dimensional space, where N is the number of β's sought, subject to the assumption that $\bar{n}$ is, as we normally express it, a linear function of the β's. The nature of the error function, so represented, can most easily be visualized in the case where $N = 2$, when U will describe an elliptic paraboloid in three dimensions, with $U_{\min}$ at the lowest point. This image has led to the practice of describing U in the vicinity of $U_{\min}$ (irrespective of the value of N) as a "pit", and the whole process of searching for $U_{\min}$ as "pit-mapping". Initially-guessed values of the various stability constants are used to find an initial value of U; the constants are then systematically adjusted and corresponding values of U evaluated. The characteristics of the error function are such that a set of $\frac{1}{2}(N + 1)\ (N + 2)$ values of it are sufficient to permit estimates of the N equilibrium constants corresponding to $U_{\min}$, and also of the standard deviations associated with these. Just as in the previous case negative values of β are forbidden, and some care and common sense must be used in the choice of species and their β values.

Since spectrophotometric data do not, except for suitable measurements on corresponding solutions, yield information about $\bar{n}$ and [A] for systems in which equilibria overlap, some other strategy must be resorted to. For a long time Mrs. J. L. McCourt and the writer have sought to develop a procedure along the following lines. Sets of solutions can be prepared containing the complexes to be studied in a wide range of proportions. Absorbance values of each of these can be measured at a reasonably large number of wavelengths of interest. These measurements yield two arrays of relationships; the first is for different solutions at a single wavelength;

$$\begin{aligned} \epsilon\dagger &= \epsilon_0\alpha_0 + \epsilon_1\alpha_1 + \epsilon_2\alpha_2 + \epsilon_3\alpha_3 \ldots \\ \epsilon\dagger^0 &= \epsilon_0\alpha_0^0 + \epsilon_1\alpha_1^0 + \epsilon_2\alpha_2^0 + \epsilon_3\alpha_3^0 \ldots \\ \epsilon\dagger^\infty &= \epsilon_0\alpha_0^\infty + \epsilon_1\alpha_1^\infty + \epsilon_2\alpha_2^\infty + \epsilon_3\alpha_3^\infty \ldots \end{aligned} \tag{38}$$

etc.

The second array involves one solution at different wavelengths:

$$\begin{aligned} \epsilon\dagger &= \epsilon_0\alpha_0 + \epsilon_1\alpha_1 + \epsilon_2\alpha_2 + \epsilon_3\alpha_3 \ldots \\ \epsilon\dagger\S &= \epsilon_0\S\alpha_0 + \epsilon_1\S\alpha_1 + \epsilon_2\S\alpha_2 + \epsilon_3\S\alpha_3 \ldots \\ \epsilon\dagger\| &= \epsilon_0\|\alpha_0 + \epsilon_1\|\alpha_1 + \epsilon_2\|\alpha_2 + \epsilon_3\|\alpha_3 \ldots \end{aligned} \tag{39}$$

to which may be added the non-spectrophotometric relationship:

$$1 = \alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 + \ldots. \tag{40}$$

These relationshps are treated by computer in such a way as to find the values of ϵ_i and α_i that will best satisfy all these relationships. The method was tried out on extremely precisely measured results gathered on a Cary Model 16 spectrophotometer for three much-studied systems of complexes, *viz.* nickel(II) + ethylenediamine, copper(II) + glycine, iron(III) + 5-sulphosalicylic acid. In addition a completely synthesized set of absorbance values was worked out for a hypothetical system of complexes of assumed stability constants, and used to study the behaviour of the computer program.

Working with the synthetic data, when the correct values of ϵ_i were supplied the computer could in one pass furnish the correct values of α_i and *vice versa*. Solutions to (38) and (39) are unbounded, and these equations by themselves can be satisfied by an infinite set of solutions. Accordingly, when values for both ϵ_i and α_i are sought there have to be additional constraints imposed. One such constraint is equation (40). The value of ϵ_0 can always be measured* and that of the highest complex can often also be found. Values for ϵ_1, *etc*., are supplied as estimates if they are not known. The computer in this case produces best first estimates of α_i.

It was found advantageous to arrange the data in the first array (38) in order of increasing $\bar{n}$ or [A]; this can be established without difficulty on the basis of chemical and optical evidence. The first estimates of α_i were then adjusted on the basis of chemical knowledge; for instance α_0 must decrease with increasing $\bar{n}$, while α for the highest complex must increase. For each intermediate species α rises to a maximum then falls ultimately to zero. After these adjustments the revised values of α_i were used to find a new set of values for all or some of the ϵ_i. This cyclical process was sometimes able to achieve reasonable stability with iteration, though not always. Failure to achieve refinement could not be traced to any single cause. It is clear from this description that our method involved a suitable blending of machine computation and human correction based on the known characteristics of sequential equilibria; it could in no way be represented as a fully automated procedure for characterizing such a system. In such cases as did succeed in establishing values of the complete set of α_i, it was a straightforward matter to apply equations (7) and (30) in order to obtain $\bar{n}$ and [A] and hence the corresponding values of β.

This method, although not really developed successfully, has, because of its directness and simplicity, afforded the writer an opportunity to discover many of the difficulties inherent in the problem of finding acceptable equilibrium constants for overlapping complexes by the spectrophotometric method. The procedure attempted is analogous, for two sets of unknowns (ϵ and α), to the simple solution of simultaneous equations described earlier. In addition to the problems mentioned there, such as the incidence of physically impossible negative roots, there are more subtle difficulties which arise from the interdependence of ϵ and α (or of ϵ and β). Thus at some wavelengths a particular ϵ_i may be quite small, and this can prejudice the determination of the corresponding α_i, and the same thing occurs in reverse for solutions in which α_i is small or zero. It will be recalled that earlier in this review attention was drawn to this interdependence in the case of single weak complexes for which it is sometimes easy to measure the product ϵK but difficult to assign a value to either individual quantity.

The application of "pit-mapping" to the problem of overlapping equilibria has been discussed in two important papers by Nagano and Metzler[61] and Sillén and Harnquist.[62] The first of these computer programs, known as PITMAP, was subsequently modified, with incorporation of some features of the second, by Thomson in this university. The essence of this procedure is as follows.[63] Suppose there are J species in solution to be characterized; various solutions designated by i are measured at several wavelengths indicated by k. Then

$$A_1 = \sum_{j=1}^{J} C_j \epsilon_j \tag{41}$$

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* When ϵ_0 is zero at all wavelengths, it proves advantageous to use equations (38) and (39) in the form

$$(\epsilon^\dagger - \epsilon_0)\alpha_0 + (\epsilon^\dagger - \epsilon_1)\alpha_1 + (\epsilon^\dagger - \epsilon_2)\alpha_2 + (\epsilon^\dagger - \epsilon_3)\alpha_3 = 0$$

and the error sum is given by

$$U = \sum_{ik} W_k(A_{ik} - C_{ji}\epsilon_{jk})^2 \tag{42}$$

where W_k is a suitable weighting factor. This is minimized when $\partial U/\partial\epsilon_{jk} = 0$, and a set of simultaneous equations is produced which may be solved to give values of ϵ_{jk}. However, initially estimates of C_{ji} must be supplied and are found from tentative estimates of the J stability constants and the overall composition of the solutions. The program then undertakes a systematic variation of the values of the equilibrium constants, working out for each set the corresponding value of the error sum. In this way the best set of equilibrium constants for the initial estimates of ϵ_{jk} is obtained. The program next undertakes to find an improved set of values of ϵ_{jk} consistent with the observed absorbances and compositions, and a cycle is established which will normally converge fairly promptly. The PITMAP program of Nagano and Metzler, refined by Thomson, is constantly undergoing improvement in performance, for instance, by replacing a subroutine EQUIL, described by Thomson, the purpose of which was to calculate values of C_{ji} from the solution parameters, by the apparently much more reliable subroutine COGSNR extracted from the published computer program SCOGS,[64] developed to secure equilibrium constants from pH-titration data. These are large complex computer programs, difficult to describe in a review of this sort, and they contain many practical devices, for instance, one for disposing of negative answers for values of ϵ_{jk}. The success with which the task of evaluating stability constants and molar extinction coefficients has been achieved can be judged by the ability of these parameters to give calculated absorbance values that match the experimentally observed quantities. Alternatively, values of equilibrium constants obtained from spectrophotometric observations should be compared with results derived from other procedures. Unfortunately, in the writer's opinion, there has been little effort made yet to subject different procedures, including computer programs, to well-controlled comparisons.

Some other experimental methods

We conclude with a mention of two other experimental strategies for spectrophotometric determination of equilibrium constants. One is the use of competitive equilibria, already mentioned in connection with corresponding solutions.[52] More direct procedures can also be used based on competition between two metals for a single ligand,[65–67] or two ligands for a single metal,[68–70] although in the latter case the absence of mixed complexes should be confirmed before calculations are made, and in the former the absence of ligand-bridged mixed metal complexes.

Another procedure which has proved particularly useful for determination of stability constants of metal complexes of 1,10-phenanthroline and 2,2′-bipyridyl[71,72] is based on distribution of the ligand between two immiscible solvents. The method in this case depends on the fact that only the free ligand is distributed between the phases and can readily be determined spectrophotometrically. By judicious choice of solvent a wide range of concentration of free ligand can be obtained in the aqueous phase. Solvent extraction can also be applied when a neutral complex is distributed between the two phases, and Rydberg[73] has given a thorough account of the theory. The distribution has usually been measured radiochemically by means of isotopic tracers, but in principle spectrophotometric methods could also be used, though they do not appear to have been by many workers, and there are practical limitations of sensitivity and difficulties in determining small differences between large values.

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Zusammenfassung—Die Arbeit gibt eine kritische Übersicht über eine Anzahl in der Literatur angegebener Methoden, aus spektrophotometrischen Daten im Ultraviolett oder im Sichtbaren Gleichgewichtskonstanten in Lösungen zu bestimmen. Es werden einstufige oder sich überlappende Gleichgewichte behandelt und auf eine Anzahl von Möglichkeiten hingewiesen, wie die Versuchsdaten mit Elektronenrechnern verarbeitet werden können.

Résumé—Ce mémoire passe en revue de manière critique un certain nombre de méthodes publiées pour l'emploi de données spectrophotométriques ultraviolettes ou visibles pour la détermination de constantes d'équilibre en solution. On considère les équilibres qui ne comportent qu'un temps ou qui s'imbriquent, et l'on suggère un certain nombre de voies selon lesquelles les données expérimentales peuvent être traitées par des calculatrices électroniques.

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PICOLINE-2-ALDEHYDE THIOSEMICARBAZONE: THE ACID DISSOCIATION CONSTANTS AND REACTIONS WITH VARIOUS METALS

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Summary—The acid association constants for picoline-2-aldehyde thiosemicarbazone have been determined by potentiometry and spectrophotometry. Results are calculated by the modified computer programs SCOGS and PITMAP. Protonation sites are suggested for these reactions. A spectrophotometric survey has been performed of the reaction between PATS and several metal ions.

Picoline-2-aldehyde thiosemicarbazone (PATS) came to our attention as a possible analytical reagent for some heavy metals. A method for the determination of silver with PATS, useful in the range 0·0–1·0 μmole, has been developed.[1] The present paper deals with our findings concerning the acidity constants of PATS, determined potentiometrically and spectrophotometrically. A broad survey of the reaction of PATS with various metals is reported. The pK_a's of PATS have been reported by F. Pino *et al.*[2,3] The validity of their results and that of those presented in this paper are compared.

EXPERIMENTAL

Apparatus and reagents

Glassware. Only Class A volumetric glassware was used, and all transfer pipettes were calibrated.

pH Measurement. Measurements of pH were made with an Orion Research 801 pH-meter and a Radiometer PHM52 pH-meter. The Orion meter was equipped with a Beckman 39301 glass electrode and a Leeds and Northrup 117208 saturated calomel reference electrode, whilst the PHM52 meter was equipped with manufacturer's G20213 glass electrode and K401 saturated calomel reference electrode. Before use the meters were calibrated with two buffer solutions[4] of pH 6·865 and pH 4·005 to compensate for the actual Nernst slope of the glass electrode. The meters were calibrated as hydrogen-ion concentration probes.[5,6]

Titration apparatus. Potentiometric titrations were performed with a Gilmot microburette. The piston travel was calibrated from known weights of delivered water. Flexing of the polypropylene tubing was avoided by mounting the microburette on a laboratory jack, thus enabling the whole assembly to be raised and lowered as desired. The pH-meter was restandardized at pH 6·865 after each titration.

Spectrophotometry. Spectrophotometric measurements were made at 25 ± 0·1° in 10-mm matched silica cells with a dual-beam Cary 14 recording spectrophotometer (purged with dry nitrogen). Absorbance values were estimated to 0·001. Measured values were key-punched, and processed by an IBM 360/75 computer, with graphical output plotted by a Calcomp 765 digital incremental plotter.

Potassium hydroxide solution. Commercial concentrates were diluted according to instructions, standardized against potassium hydrogen phthalate[7] and stored under nitrogen. The solution was frequently restandardized and discarded after three months.

Picoline-2-aldehyde and thiosemicarbazide Obtained commercially, and redistilled and recrystallized respectively before use.

Metal ion solutions. Prepared from hydrated perchlorates or nitrates and standardized by conventional methods Other chemicals used were of reagent grade purity.

Procedures

Preparation of picoline-2-aldehyde thiosemicarbazone. Thiosemicarbazide (4·55 g) was dissolved in 200 ml of ethanol and the solution boiled under reflux. Picoline-2-aldehyde (5·03 g) dissolved in 20 ml of ethanol was added and the mixture refluxed for 30 min. The solution was allowed to cool in the dark and the product separated by filtration, giving a crude yield of 82%. The product was recrystallized twice from boiling ethanol, forming white needles (m.p. 205–205·5°,[8] found: C 46·9%; H 4·7%; N 30·8%; S 18·0%; calculated for $C_7H_8N_4S$: C 46·67%; H 4·44%; N 31·11%; S 17·72%).

Compliance with Beer's law. Two sets of ten solutions each were prepared, which were 0·0–4·00 × $10^{-5}M$ in PATS. The mean pH of each set of solutions was adjusted with buffers[1,9] to give pH 1·31 and pH 8·25. These pH values had previously been shown to be favourable for the formation of only one of the three forms of PATS. Absorbances were obtained at 300, 320, 345 and 365 nm for the pH 1·31 set and at 280, 312, 325 and 330 nm for the pH 8·25 set. Compliance with Beer's law was observed at both pH's for all wavelengths.

Determination of pK_a's for PATS by various methods

(*i*) *Mixed (Brønsted) quotients.* The graphical spectrophotometric method for the determination of well-separated pK_a's[10–12] was used to evaluate the mixed quotients. A stock solution of 2·422 × $10^{-3}M$ PATS was mixed with stock buffer solutions and supporting electrolyte so that on dilution to final volume the ionic strength was 0·1*M* and the pH was in the range 1·10–12·70. Solutions of PATS were also prepared, in which the ionic strength was greater than 0·1*M*, to extend the range from H_0 3·0 to pH 14·0. These solutions were employed to investigate the existence of pK_a's greater than 13·0 and less than 1·0.

(*ii*) *Potentiometric titration.* The titration assembly was that described by Perrin.[13] Solutions containing various concentrations of PATS (in the range 1·0–2·0 × $10^{-3}M$) were titrated with potassium hydroxide solution from pH 2·0 to 12·0. Evaluation of concentration constants was possible from pH-meter readings by utilizing the experimental parameter, Γ_H.[5] The titrations were performed in 0·100*M* potassium chloride and nitrate. Γ_H for these background electrolytes was determined as 0·864 ± 0·005 and 0·875 ± 0·011 respectively. The titration data were processed with the computer program SCOGS modified from the original version[14] to deal with systems of one ligand and one metal.

(*iii*) *Spectrophotometric determination.* Thirteen solutions, each 3·968 × $10^{-5}M$ in PATS, approximately 2 × $10^{-3}M$ in nitric acid and 0·100*M* in potassium nitrate were prepared and the p[H] of each adjusted with molar potassium hydroxide to cover the range pH 2·36–11·86. The spectrum of each solution was recorded, digitized at 2·5-nm intervals between 260 and 390 nm and the data processed with the computer program LIGAND PITMAP,[15,16] based on Sillén's LETAGROP VRID.[17]

Location of the ionization sites in the PATS molecule. Stock solutions of thiosemicarbazide and picoline-2-aldehyde, each 2 × $10^{-3}M$, were prepared and suitably diluted. The spectrum of each compound was measured at various pH's.

Reaction of PATS with various metals as a function of pH. Stock solutions of PATS and various hydrated metal perchlorates or nitrates were prepared, each being 2 × $10^{-3}M$. Solutions were then prepared, by dilution, such that C_M:C_L was 1:2, the concentration of PATS in each final solution was 3·274 × $10^{-5}M$, and the pH was varied. The metal ions investigated were mercury(II), cobalt(II), silver, thorium, nickel, bismuth, copper(II) and palladium(II). The investigation of the iron(II)–PATS system will be published at a later date. Mercury(I) showed signs of rapid disproportionation and was not studied further.

Programs. The modified versions of SCOGS and LIGAND PITMAP are available on request from the authors.

RESULTS

pK_a values for PATS

Table 1 shows the pK_a values obtained, together with the method, medium, and type of constant.

Pino *et al.* have recently reported[2,3] pK_a values for PATS.* These results are not completely comparable with ours, since there will be an appreciable medium effect on measurements of pK_a in ethanolic solution which cannot be estimated without information concerning solvent composition and then only semiquantitatively.[18] Similar uncertainties apply to the measurement of p[H] in such solvents of unspecified composition.[4,5] These authors have given absorption spectra for PATS of 4·0 × $10^{-5}M$ aqueous solutions. Suitable measurements at various pH values would have enabled the determination of

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* The diagram showing these spectra (Fig. 1 in reference 2) was incorrectly labelled. We agree that spectrum A is correct for pH 7·2 but feel that the spectrum for pH 1·3 should be labelled C and that for pH 12·8 should be B.

Table 1. Values of pK_a's by various methods

Method	log β_{011}	σ_{011}	log β_{021} (pK_{a_1})	σ_{021}	Background electrolyte	Constant type
Graphical	11·06*	±0·21	14·81* (3·75 ± 0·02)	±0·08	0·1M, various buffers	Brønsted
LIGAND PITMAP (Spectrophotometric)	10·927†	±0·010	14·615† (3·688 ± 0·0004)	±0·012	0·100M KNO_3	Concentration
SCOGS (Potentiometric)	10·935‡	±0·002	14·608‡ (3·673 ± 0·001)	±0·003	0·100M KNO_3	Concentration
SCOGS	10·877¶	±0·001	14·551¶ (3·674 ± 0·001)	±0·002	0·100M KCl	Concentration

* Arithmetic mean value of those obtained at four wavelengths (312, 328, 336, 347 nm).

† Best values from twelve solutions, 53 wavelengths per solution. Standard deviation = ±0·005 absorbance units.

‡ Values obtained by combining four titrations—a total of 291 points. Standard deviation of the combined data = $\pm 2{\cdot}0 \times 10^{-3}$ml.

¶ Values obtained by combining three titrations—a total of 227 points. Standard deviation of the combined data = $\pm 1{\cdot}7 \times 10^{-3}$ ml.

pK_a's to be made in aqueous media at these concentrations, thus avoiding the mixed solvent.

The general problems with graphical evaluation[10–12] of Brønsted pK_a's is evidenced by the discrepancy of the first reported value in Table 1. The two different methods and background electrolytes employed for evaluation of concentration constants give values of both pK_a's that are in close agreement.

Figure 1 shows the individual spectra of PATS species and Figs. 2 and 3 indicate the fit between the observed spectra (symbols) and the theoretical ones based on three absorbing species having the log β_{011} and log β_{021} values shown in Table 1 and the molar absorptivities indicated by Fig. 1. (Eight of the total number of spectra are shown in Figs. 2 and 3).

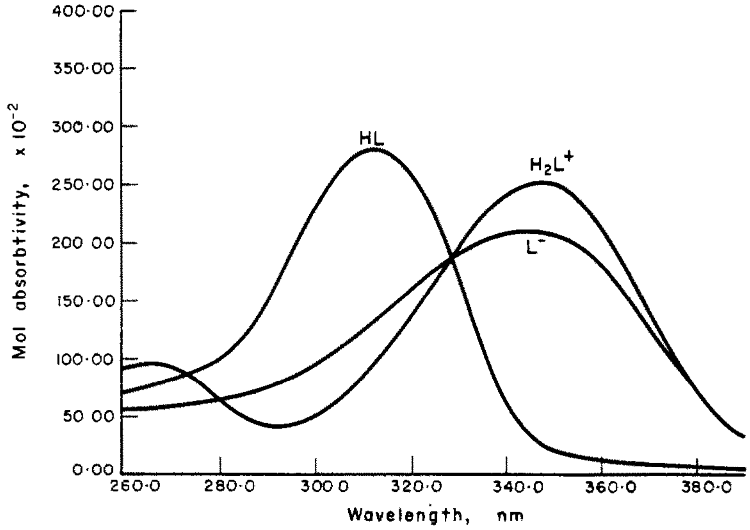

Fig. 1. Computed spectra of individual species of PATS.

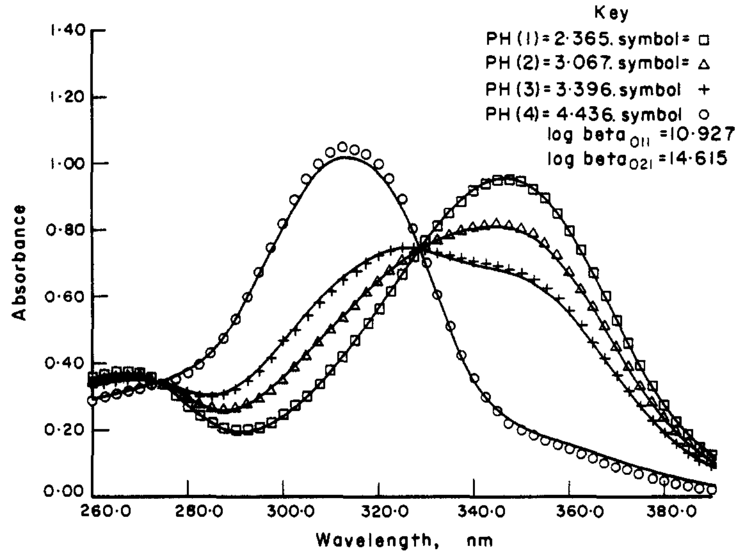

Fig. 2. Experimental (symbols) and computed (solid line) spectra at various acidities.

Location of the ionization sites for PATS

The potentiometric studies strongly indicate the proton reactions of PATS as

$$H^+ + L^- \rightleftharpoons HL \qquad \beta_{011}$$

$$H^+ + HL \rightleftharpoons H_2^+L \qquad \beta_{021}/\beta_{011}$$

Examination of the literature did not permit any deductions concerning the protonation sites, there being no suitably related compounds with evaluated pK_a's. The qualitative tests performed showed that for basic and neutral solutions of picoline-2-aldehyde the resultant

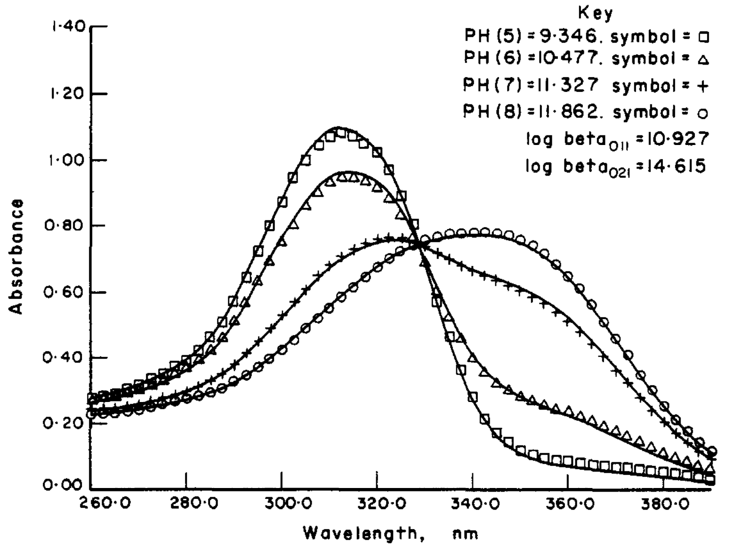

Fig. 3. Experimental (symbols) and computed (solid line) spectra at various acidities.

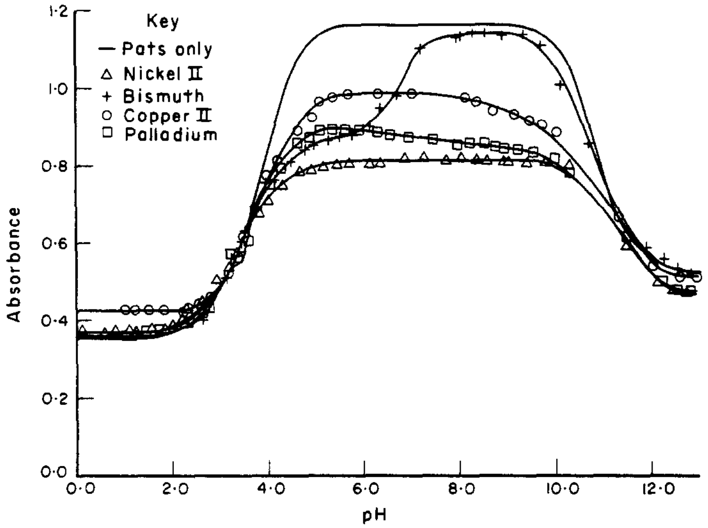

Fig. 4. The absorbance of several metal–PATS solutions as a function of acidity. $C_{PATS} = 2C_M = 3{\cdot}274 \times 10^{-5} M$. Absorbances were measured at 312 nm.

spectra were virtually identical whereas the acidic solutions exhibited markedly different spectra. However the addition of acid or base to a neutral solution of thiosemicarbazide led to a small bathochromic shift for only the alkaline solution. Although the changes observed here were not as dramatic as those for the aldehyde, when they are considered together with the resonance-stabilized anion $-N{=}C(NH_2)-S^-$ it seems probable that the proton is abstracted from the thiol group in alkaline solution and that protonation occurs at the heterocyclic nitrogen atom. It should be noted that these tests are only qualitative and a procedure such as quarternization of the ring nitrogen atom and/or methylation of the thiol group could be more informative.

Reaction of PATS with various metals

The absorbance of the PATS–metal ion system as a function of pH (measured at 312 nm) is shown in Figs. 4 and 5. A similar curve indicating the absorbance–pH behaviour of PATS is included for reference. Several broad conclusions may be drawn from these curves. First, all the metals studied, except thorium, gave an observable reaction with PATS. Nickel, palladium and copper showed similarities in their pH–absorbance relations but the effect was less intense than that for PATS alone.

Bismuth is only apparently anomalous. The sharp break in the curve at pH 7 can be attributed to the hydrolysis of the bismuth ion possibly with the formation of mixed ligand complexes. Whilst the nature of the complex bismuth hydroxides is not fully understood, the high stability of these complexes is well known.[19] The approach of the bismuth curve to that of PATS at pH 8 and higher confirms this argument.

The mercury(II)–PATS spectrum, on close examination, is not merely less intense than the PATS spectrum. More detailed studies of mercury–PATS and mercury–PATS–EDTA systems will be discussed in a forthcoming publication. The similarities of these curves to those of nickel, palladium and copper are superficial.

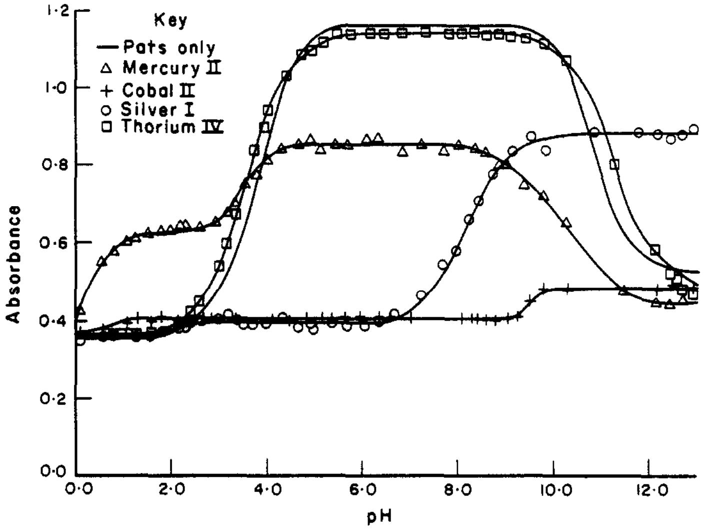

Fig. 5. The absorbance of several metal–PATS solutions as a function of acidity, (conditions as for Fig. 4).

Silver ions and PATS produce a spectrum very different from that of PATS, and this was the basis for the investigation of PATS as an analytical reagent for silver.[1] Both cobalt and iron give coloured solutions with PATS. The colours formed are pH-dependent: from colourless to yellow for cobalt in the range pH 1–3 without further change at pH > 3; rose through purple and blue to green for iron(II) at pH 1·5–11·0. The iron(II) colours were only observable after the addition of ascorbic acid.[20] The cobalt and iron(II) reactions will be discussed in further detail in a future communication.

This general method for the initial appraisal of the reactions of a particular ligand with various metals is qualitatively beneficial. It enables a rapid decision to be made concerning the wisdom of undertaking further studies with that ligand.

Definitions

The overall stability constant describes the reaction between the free components to give a particular complex. For instance β_{121} describes the reaction

$$M + 2H + L \rightleftharpoons MH_2L$$

(charges omitted for clarity)

where

$$\beta_{121} = [MH_2L]/[M][H]^2[L]$$

To avoid possible confusion in the terms pK_{a_1}, pK_{a_2} *etc.*, the overall stability constant notation has been used to describe the process $nH + L \rightleftharpoons H_nL$; $\beta_{0n1} = [H_nL]/[H]^n[L]$; $\log \beta_{011}$ has the same numerical value as pK_{a_2} and $\log \beta_{021}$ is the sum of pK_{a_1} and pK_{a_2}. This symbolism also simplifies computer algorithms. However, the synonym "pK_a's" has been retained to denote the collection of log β's related to a particular ligand.

Throughout the text pH is used to denote pH-meter reading and not the concentration of hydrogen ions in solution, which is denoted by p[H].

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Zusammenfassung—Die Säuredissoziationskonstanten von Picolin-2-aldehyd-thiosemicarbazon (PATS) wurden potentiometrisch und spektrophotometrisch bestimmt. Die Ergebnisse wurden mit den modifizierten Rechnerprogrammen SCOGS und PITMAP berechnet. Es werden Vermutungen darüber geäußert, wo das Molekül bei diesen Reaktionen protoniert wird. Ein spektrophotometrischer Überblick über die Reaktion zwischen PATS und mehreren Metallionen wurde erstellt.

Résumé—Les constantes d'association acide pour la thiosemicarbazone du picoline 2-aldéhyde ont été déterminées par potentiométrie et spectrophotométrie. Les résultats ont été calculés par les programmes de calculatrice modifés SCOGS et PITMAP. On suggère des positions de protonation pour ces réactions. On a effectué une étude spectrophotométrique de la réaction entre le PATS et plusieurs ions métalliques.

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SEPARATION OF TELLURIUM(IV) BY SOLVENT EXTRACTION METHODS

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Summary—A critical review is given of the contemporary state and the perspectives for development of solvent extraction methods for the separation of tellurium(IV). The literature (150 references) is covered up to the end of 1973.

In the last 5 years, in connection with the wide application of tellurium compounds in the electronics industry, numerous papers on the analytical chemistry of tellurium have been published.[1–3] The necessity to determine traces of tellurium in various samples, and impurities in tellurides, has raised difficult problems for analysts. This, however, also provided the impetus to search for rapid and selective methods for separation and determination of tellurium. Solvent extraction methods have given very good results when applied to the separation of rare elements.[4,5] Tellurium is a typical rare element (abundance in the earth's crust *ca.* $1 \times 10^{-7}\%$).

The mechanism of distribution of the compounds in both phases must be known if a separation method is to be developed. Thus far, however, only qualitative data on the state of tellurium in aqueous solutions are available.[6] Hence all equilibrium constants for systems of tellurium compounds are only conditionally valid.

Complexes of tellurium(II), tellurium(IV) and tellurium(VI) are known. The tellurium(II) compounds were found to disproportionate in aqueous solutions:

$$2\,\mathrm{Te(II)} \rightarrow \mathrm{Te(IV)} + \mathrm{Te}$$

Some of these compounds, however, *e.g.*, $Te(dtc)_2$, $Te(tu)_2(SCN)_2$* are stable in organic solvents.[7–9] Tellurium(VI) is a powerful oxidizing reagent, oxidizing many ions and almost all organic solvents. Further, very stable oxo- and hydroxo-complexes are formed by tellurium(VI), and these complexes reluctantly undergo substitution by other ligands.

In the analytical chemistry of tellurium, Te(IV) is much more important than Te(II) and Te(VI). The compounds of tellurium(IV) are stable in aqueous and organic solutions. The opinions of various authors on the state of tellurium(IV) in aqueous solutions are often contradictory. Hence we have summarized below the most probable ionic species of tellurium(IV).

Alkaline and moderately acidic solutions (the important medium for solvent extraction using most of the chelating reagents).[10–12]

pH ⩾ 8	pH = 3–7·5	pH = 3·5	from pH = 3 to 1*M* mineral acid
TeO_3^{2-}	$HTeO_3^-$	H_2TeO_3	$TeOOH^+$

Strongly acidic solutions. Stable complexes of tellurium(IV) are not formed by sulphuric and perchloric acids. These acids, however, affect the equilibrium in solutions by

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* For abbreviations see p 1014.

their high hydrogen-ion concentrations and thus suppress the formation of oxo- and hydroxo-complexes.

Hydrochloric acid.[6,13–18]

1–3M	3–7M	7–10M	10–12M
$TeOCl_2$?	$TeOCl_4^{2-}$	$Te(H_2O)_2Cl_4$	$TeCl_6^{2-}$
$TeOCl_3^-$?	$Te(OH)_2Cl_4^{2-}$	$TeCl_5^-$	
	$Te(H_2O)_2Cl_4$	$TeCl_6^{2-}$	

Hydrobromic acid.[13,19,21] If the concentration of the hydrobromic acid is higher than 3M the predominant ionic species in the solution is the co-ordinatively saturated complex $TeBr_6^{2-}$. In mixtures of HBr + $HClO_4$ (a total concentration of 4M) the predominant species are $TeBr_4$ and $TeBr_3^+$ (0·6–1·4M HBr), and $TeBr_6^{2-}$ (> 1·4M HBr).

Hydriodic acid.[13,22] The stability of the halide-complexes of tellurium(IV) increases from bromide to iodide. The co-ordinatively saturated complex TeI_6^{2-} is formed and it is the predominant species even when [HI] = 0·4M.

Instead of HI, a mixture of potassium iodide and a strong acid is often used. For smaller concentrations of hydriodic acid (*e.g.*, in mixtures of 3M H_2SO_4 + 0·04M KI or 1M H_2SO_4 + 0·2M KI), owing to the high hydrogen-ion concentration the species TeI_6^{2-} is predominant.

In the following summary the solvent extraction systems are classified according to their solvent extraction mechanisms. In some cases, for which thus far the extraction mechanism is not yet investigated, we have placed the corresponding extraction system in the most probable type.

The following abbreviations are used.

A—anion of the chelating reagent, HA
AmAc—amyl acetate
B—a bulky cation
dit—dithizonate
dtc—dithiocarbamate, $R_2NCS_2^-$
dtp—dithiophosphate, $R_2PS_2^-$
EtAc—ethyl acetate
Et_2dtc—diethyldithiocarbamate
HDEHP—di-(2-ethylhexyl)phosphoric acid
MIBK—methyl isobutyl ketone
R—alkyl radical
S—solvating reagent
TBP—tributyl phosphate
TOPO—trioctylphosphine oxide
tu—thiourea, $H_2N.CS.NH_2$
ϵ—molar absorptivity ($l.mole^{-1}.cm^{-1}$)

SOLVENT EXTRACTION OF NEUTRAL NON-POLAR COMPOUNDS

Tellurium(IV) aquo-species cannot be extracted from acid media with non-polar solvents. Tellurium(IV) bromide and especially the iodide are stable neutral non-polar compounds and it would be expected that they could be extracted.[23]

It seems that from hydrobromic acid medium tellurium(IV) is probably extracted as $TeBr_4$ into benzene.[24] Tellurium(IV) can be extracted into nitrobenzene with a high distribution coefficient (D > 100 from 0·05M HBr + 18N H_2SO_4, or 0·05M HBr + 7M $HClO_4$);[25] this solvent has no solvating groups, hence the extracted compound is probably of the composition $TeBr_4$.

From mixtures of sulphuric acid and potassium iodide, tellurium(IV) can be extracted with non-polar solvents.[24,26] The extractable tellurium compound is the neutral non-polar TeI_4;[26] previously it was assumed that a suspension of elementary tellurium is formed in the system.[24] This mistake was probably due to the very low solubility of TeI_4 in both phases: if the concentration of tellurium is higher than $10^{-4}M$ an almost black precipitate is formed, which consists of TeI_4, however, and not of elemental tellurium.

CHELATE COMPOUNDS

In this paper the solvent extraction systems are arranged according to the reactive group of the ligand.

Tellurium(VI) oxidizes nearly all ligands and this is the reason why co-ordination compounds of tellurium(VI) have not been extensively investigated. Tellurium(II) and tellurium(IV) can form stable neutral co-ordination compounds of the types TeA_2 and TeA_4, mainly with sulphur-containing ligands. Owing to their electroneutrality, these chelates can be very well extracted. The distribution coefficients are high for solvent extraction with both polar and non-polar solvents. It is interesting to know whether all four ligands are bonded to tellurium in an equivalent manner. For $Te(Et_2dtc)_4$ we have found that the ligands differ in their manner of bonding—two of the Et_2dtc groups are bidentate and two are unidentate.[8]

HDEHP forms neutral chelate compounds with tellurium(IV) which are extractable at pH 3 into non-polar solvents.[27] HDEHP is found to be more suitable for the separation of Mo(VI), Fe(III), rare earths, U(VI), Th(IV) *etc.* These ions are extracted with higher distribution coefficients than tellurium(IV).

Tellurium(IV) does not form co-ordination compounds with *cupferron* hence this reagent can be recommended for the separation of the other ions (*e.g.*, from a tellurium matrix).[28,37]

The *dithiocarbamate* ligand forms stable co-ordination compounds with both Te(II) and Te(IV).[7,8,31] The solvent extraction of tellurium with $NaEt_2dtc$ has been extensively studied.[30] At pH 8·5, $Te(Et_2dtc)_4$ can be precipitated and thus separated from a solution of Te(IV).[8] This complex may be extracted at pH $< 9{\cdot}5$ into non-polar solvents[1,28,30,33–35] ($\epsilon_{428} = 3{\cdot}6 \times 10^3$). This compound was found to be light-sensitive. The most widely used photometric method for the determination of small amounts of tellurium is Bode's method.[28,30,33] Bode used $NaEt_2dtc$ at pH 8·5 in the presence of masking reagents such as EDTA, tartrate and cyanide, and ultimately extracted the dithiocarbamate complex into carbon tetrachloride. In this extraction photometric method only Bi(III), Tl(III), Hg(II), Ag(I), and a high concentration of Cu(II) were found to interfere. The method is of great importance for the separation of tellurium(IV) from Se(IV). Selenium(IV) does not interfere until the ratio $Se{:}Te = 10^5{:}1$ is reached[28] and this is a great analytical advantage. The sensitivity of this photometric method may be enhanced if substitution of Te(IV) by Cu(II) is used; in this case, however, the separation of the phases is rather difficult and the selectivity smaller, since both Sb(III) and Cd(II) are found to interfere with the determination of tellurium.

Tellurium(II) forms the complex $Te(Et_2dtc)_2$ and this compound can be extracted, with a high distribution coefficient, into polar and non-polar solvents;[8,9,31] this compound was proposed for a selective determination of copper by using a substitution reaction.[7]

Bode's method is often used for the determination of tellurium.[30,36–39] If tellurium is subsequently to be determined by atomic absorption the solvent must burn, hence in this case the $Te(Et_2dtc)_4$ should be extracted into AmAc[40] or MIBK.[41] The solvent extraction of the tellurium(IV) diethyldithiocarbamate into TBP offers no advantages—the selectivity of the separation is worse.[47]

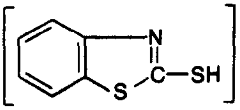
Solvent extraction using di-(2-hydroxyethyl)dithiocarbamate has also been described.[43] This reagent is less stable than $NaEt_2dtc$. Diethylammonium-N,N'-diethyldithiocarbamate is much more stable than $NaEt_2dtc$ (the C–N bond in the first compound is stronger), hence by use of this reagent tellurium(IV) can be extracted into carbon tetrachloride from 1*M* hydrochloric acid.[44–46] Ammonium bis(carboxymethyl)dithiocarbamate was found to react with Te(IV) and to form a complex compound extractable at pH 5; the reagent, however, was rapidly decomposed in the acid medium.[47] Ammonium pyrrolidinedithiocarbamate tellurium(IV) complexes can be prepared which are not sensitive to light and can also be extracted from acid medium.[48] Ammonium hexamethylenedithiocarbamate has been proposed as a reagent for the separation of tellurium.[49]

The molar absorptivity of all the tellurium dithiocarbamates mentioned is relatively small (less than 5×10^3). Higher absorptivity can be obtained if a dithiocarbamate is used which has an additional conjugated system: it is most advantageous if the CS_2^- group is in conjugation with the *N*-substituents. Such dithiocarbamates, however, are less stable; they are decomposed even in alkaline medium. Another possibility for increasing ϵ is to incorporate a dye molecule in the dtc molecule.[32,50] Thus 3-methyl-5(phenyl)-pyrazolidinedithiocarbamate was found[32] to form stable complexes at pH 8·5 with tellurium(IV) ($\epsilon_{max} = 5{\cdot}8 \times 10^4$).[50] Unfortunately the preparation of such a chromophoric dithiocarbamate is very complicated.

Tetramethylthiuramdisulphide $[(CH_3)_2NCS_2.S_2CN(CH_3)_2]$ (a product from the oxidation of dimethyldithiocarbamate) forms extractable tellurium(IV) complexes in 3*M* hydrochloric acid; this method was recommended as being very selective for the separation of tellurium(IV).[51]

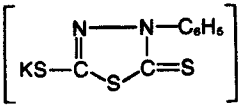
Similarly to the dithiocarbamates, the *dithiophosphate* ligand can form chelate compounds with Te(IV) and Te(II).[52–54] If di-n-butyldithiophosphoric acid is used (diluted with a non-polar solvent) tellurium(IV) can be extracted from 1–10*M* hydrochloric acid medium (or 0·2–8*M* sulphuric acid) and the distribution coefficient is greater than 10. The dithiophosphate ligand was found to reduce tellurium(IV) to tellurium(II) much more rapidly than the corresponding dithiocarbamate, and the oxidation product was a disulphide. When tellurium(IV) is analytically separated by a solvent extraction with dithiophosphate, a mixture of $Te(dtp)_4$ and $Te(dtp)_2$ is always obtained. The electronic spectra of these two compounds are different. Hence this solvent extraction method could not be recommended as a photometric method for the determination of tellurium.

Mercaptobenzthiazole



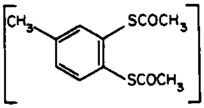
forms stable co-ordination compounds with tellurium(IV), of the type TeA_4;[55] the compounds have an absorption maximum in the near ultraviolet (360 nm). If the solvent extraction is performed with carbon tetrachloride from 4*M* hydrochloric acid medium the compound obtained has a molar absorptivity of $2{\cdot}4 \times 10^4$.[55,56] The complex obtained is not as sensitive to light as is the dithiocarbamate complex. It seems promising to study the naphthyl homologue as a reagent for tellurium: the conjugated system is greater, thus the molar absorptivity should be higher, and the absorption band of the tellurium complex shifted to the visible region of the spectrum.

Bismuthiol II



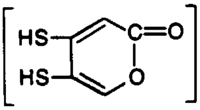
at pH 3 forms a co-ordination compound with tellurium(IV), which contains four ligands.[29,57,58] The compound is soluble in non-polar solvents,[1,59,61–63] and if it is extracted with chloroform its molar absorptivity is high: $\epsilon_{335} = 3{\cdot}4 \times 10^4$.[57] The great disadvantages of this method are the sensitivity of Bismuthiol II to aerial oxygen (a disulphide is formed which has strong light absorption at 335 nm) and the interfering effect of selenium(IV). Cheng has improved the method by changing the sequence of addition of the reagents, thus obtaining $\epsilon_{335} = 4{\cdot}0 \times 10^4$.[64] Busev *et al.*[29,65–67] have prepared many analogues of Bismuthiol II (the phenyl radical was replaced by another radical). These Bismuthiol derivatives are more stable in respect to aerial oxidation than Bismuthiol II, but the absorption coefficients of the corresponding tellurium compounds are smaller.[65]

Diacetyldithiol



reacts very selectively with tellurium(IV) in 12*M* hydrochloric acid.[68] Palladium(II) and rhenium(VII) are the only ions which form dithiolate complexes under these conditions. If a suitable non-polar solvent could be found which would extract this tellurium compound, a very selective separation method for tellurium(IV) might be developed.

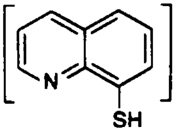
Dimercaptopyrone



forms extractable tellurium(IV) complexes.[69]

Thionaphthenic acid $C_{12}H_{23}C(O)SH$ forms easily extracted tellurium(IV) co-ordination compounds[70] in which a co-ordinative bond to the carbonyl group and a covalent bond to the sulphur atom are assumed to occur. Owing to the greater affinity of tellurium(IV) for sulphur, it may be expected that these compounds would not be as stable as the corresponding dithio co-ordination compounds. Thionaphthenic acid[70] also reacts with selenium(IV) in acid medium. This chelating reagent is very stable.

In slightly acidic medium *8-mercaptoquinoline*



diluted with non-polar solvents, can extract tellurium(IV).[71]

Tellurium(IV) can be extracted by a *dithizone* solution in carbon tetrachloride from a 0·1–1*M* mineral acid solution.[10,45,72,146] The composition of the extracted complex is assumed to be $Te(dit)_4$.[72,73] Marhenke and Sandell were the first to realize that the reaction product is an equimolar mixture of $Te(dit)_2$ and a disulphide from the dithizone.[10]

The resulting oxidation products of dithizone have almost the same absorption spectrum as that of the tellurium dithizonate. Consequently this extraction cannot be recommended as a photometric method since the reduction of Te(IV) to Te(II) does not always proceed completely.

Thiourea forms co-ordination compounds with both tellurium(IV) and tellurium(II) which can be extracted into polar solvents.[60,74,75] Tellurium(IV) in an acid medium is reduced by thiourea to tellurium(II)[75] and mixed complexes of the composition $Te(tu)_4X_2$ are obtained (X is the corresponding anion of the acid—Cl^-, Br^-, ClO_4^-, $1/2SO_4^{2-}$).[9] The solvent extraction of tellurium(IV) with tributyl phosphate and thiourea from 0·6–1·7*M* hydrochloric acid containing KSCN has been described.[1,9,60] Most probably this is an extraction of $Te(tu)_4(SCN)_2$—for this system a synergistic effect may be expected.

Tellurium(IV) was found to react with diphenylthiourea in 4·5–8·0*M* sulphuric acid.[76,77] The stable compound obtained is easily extracted into chloroform ($\epsilon_{380} = 2 \times 10^4$). The molar absorptivities of the tellurium complexes of other substituted thiourea compounds are smaller than those of the diphenylthiourea compounds. The solvent extraction–photometric method for the determination of tellurium with diphenylthiourea has a great advantage over the dithiocarbamate method—the reagent is stable with respect to light and oxygen (but selenium interferes).

It is of interest to study the solvent extraction of some organotellurium compounds which could easily be prepared. In this field there are new possibilities for the development of selective separation methods for tellurium. In all reactions known so far[78–82] the organotellurium compounds are prepared in the absence of water and this requirement creates great difficulties for the analytical separation.

SOLVENT EXTRACTION OF ION-ASSOCIATION COMPOUNDS

Tellurium(IV) can be easily extracted from hydrogen halide acid media as an ion-association complex with a bulky cation. In all cases studied so far the extracted compound is of the composition B_2TeX_6 (X is Cl, Br, or I).

A very useful method for the separation of tellurium from selenium(IV) is the solvent extraction of tellurium(IV) from 4–7*M* hydrochloric acid medium with the long-chain amines Amberlite LA-1 or Amberlite LA-2.[83] This separation is based on the great difference in stability of the chloro-complexes of these two elements. For the industrial purification of tellurium(IV), a similar solvent extraction from hydrochloric acid medium[84] was proposed, using commercial mixtures of aliphatic amines (C_{11}–C_{20}). Tellurium(IV) could be separated from a number of ions such as Se(IV), Cd(II), Tl(III), Sb(III), Cu(II) and Bi(III) by a solvent extraction reaction with 4,4′-methylenediantipyrene.[62,85,86] The solvent extraction of tellurium(IV) with $(C_6H_5)_4PBr$ from 3–5*M* hydrochloric acid medium has also been described.[1] For the selective separation of traces of tellurium, Bock has recommended solvent extraction with tetraphenylphosphonium chloride[1] from a mixture containing sulphuric acid and potassium iodide.

The recommended methods for the solvent extraction–photometric determination of tellurium(IV) are based on the extraction of the ion-association complexes of the halide-complexes ($TeCl_6^{2-}$, $TeBr_6^{2-}$, or TeI_6^{2-}) of tellurium(IV) with cations of some dyes[87,88] such as Rhodamine 4G,[89] Victoria Blue 4R[90] (solvent extraction with a mixture of nitrobenzene and carbon tetrachloride from an aqueous phase consisting of 9–10*N* H_2SO_4 and 0·7*M* KBr, $\epsilon_{max} = 8 \times 10^4$). These methods, however, are less selective and most other ions must be separated in advance.

Bismuthiol II and its derivatives extract tellurium(IV) very well from a 12–16*N* sulphuric acid + hydrobromic acid medium.[29] In this case, however, no chelates are formed (in contrast to the chelates found at low hydrogen-ion concentrations), the species being ion-association complex of the protonated molecule of the reagent and $TeBr_6^{2-}$. This is an example of how the solvent extraction mechanism may vary according to the experimental conditions.

Tellurium(IV) reacts with 1,4-diphenylthiosemicarbazide ($C_6H_5.NH.CS.NH.NH.C_6H_5$) in 5·4–6·3*M* sodium bromide ($\epsilon_{max} = 5 \times 10^4$), giving a tellurium compound of the composition Te:Reagent = 1:2 (probably an ion-association complex with $TeBr_6^{2-}$).[91] The reaction of tellurium with 1,4-diphenylthiosemicarbazide proceeds only in bromide-containing solutions. These compounds could probably be extracted into polar solvents and thus the selectivity of the photometric method might be enhanced.

EXTRACTION BY SOLVATION

These extraction methods are very often used for the separation of tellurium(IV) from hydrogen halide medium. With oxygen-containing extractive reagents (ethers, alcohols, esters, ketones and basic extractive reagents such as organophosphorus compounds), the halide-complexes of tellurium(IV) can be extracted. Tellurium(II) and tellurium(VI),[92,93] do not form halide-complexes which might be extracted into solvating extractive reagents. Tellurium(IV) is poorly extracted from *hydrofluoric acid* medium since its fluoro-complexes are not stable. The degree of extraction, however, is increased with increasing hydrofluoric acid concentration.[94]

The solvent extraction of tellurium(IV) from *hydrochloric acid* medium has been extensively studied. Tellurium(IV) can be extracted into alcohols from a 6–10*M* hydrochloric acid medium (the distribution coefficient shows a maximum for the 8·5*M* acid).[14] The composition of the compound extracted into octanol is $H_2(H_2O)_mS_n.TeCl_6$.[95] Another solvate, $HTeCl_5.S$ was found by Shitareva[18] when studying the extraction by n-hexanol. The ethers are weaker proton-donors than the alcohols and this is the reason why they are poorer extractants of tellurium(IV).[14,96,97] When studying the solvent extraction of tellurium(IV) from 9–12*M* hydrochloric acid medium with di-n-butyl ether, Iofa found a solvate of H_2TeCl_6 was extracted.[14] Brubaker[99] has found in the organic phase (β,β'-dichlorodiethyl ether) a solvate with Te:Cl = 1:4 when an aqueous phase of low hydrochloric acid concentration was used and another solvate (Te:Cl = 1:6) at higher hydrochloric acid concentrations.

Ketones[100] and TBP[101–104] can extract from 2–10*M* hydrochloric acid medium a tellurium complex with Te:Cl ratio 1:4 (but at concentrations of HCl more than 10*M*, Te:Cl = 1:6[148]). It seems that an ionic species $Te(OH)_2Cl_4^{2-}$ is formed; the hydroxy groups of these species are solvated through hydrogen-bonding by the relatively highly basic solvents.[100] Owing to the more strongly polarized P=O bond the TOPO has a greater extraction ability. In extraction of tellurium(IV) we have found the solvate $TeCl_4.2TOPO$ (unpublished observation). In this case the distribution process is based on the substitution of TOPO for water molecules in the co-ordination sphere of tellurium(IV).

The presence of alkali metal nitrates in these solvation extraction systems enhances the degree of extraction. The distribution coefficients of tellurium(IV) depend on the concentration of other ions.[96,105] In comparative studies on the extraction of tellurium(IV) into alcohols, ethers and ketones it was established that ketones are the best extractants and that the resulting distribution coefficient is inversely proportional to the length of the chain.[14,100,106,107]

An extensive literature exists on the solvent extraction of tellurium(IV) into MIBK from 4–7*M* hydrochloric acid medium.[37,92,93,98,106,108–111,147,149] This is an important method for the separation of tellurium(IV) from Zn(II), Cu(II), Pb(II), Cd(II), Se(IV) *etc.* With respect to selectivity, the solvent extraction of tellurium(IV) with MIBK in mixtures with amyl alcohol and AmAc,[112,113] or EtAc.[114] or methyl ethyl ketone[115] from 2–7*M* hydrochloric acid medium offers no advantages over the MIBK extraction. These separation methods are also suitable for the industrial purification of tellurium, the great advantage of these extractive reagents being their low price and high extraction capacity.

Solvent extraction with TBP is suitable for the separation of tellurium(IV) from tellurium(VI);[116] tellurium(VI) is not extracted from a 2–10*M* hydrochloric acid medium[117] (*D* is less than 10^{-2}). The great advantage of this separation is the stability of TBP with respect to strong oxidizing reagents such as tellurium(VI) [ketones, ethers and alcohols are slowly oxidized by Te(VI)]. Tellurium(IV) is easily extracted into TBP (diluted with saturated hydrocarbons)[87,104,118,119] or a cyclohexane solution of TOPO. The neutral organophosphorus compounds are appropriate for the separation of tellurium from other elements such as Fe(III), U(VI), Mo(VI), Au(III), Re(VII), Hg(II) and Tl(III), which are better extracted than tellurium(IV). In this case tellurium(IV) remains in the aqueous phase.

The extractive ability of sulphoxides was recently investigated.[120] The sulphoxides are less basic than the corresponding organophosphorus compounds. Di-n-hexylsulphoxide can easily extract tellurium(IV) from 2–10*M* hydrochloric acid medium and the extracted compound has a Te:Cl ratio of 1:5 (a disolvate).[121]

The bromo-complexes of tellurium(IV) are more stable than the corresponding chloro-complexes. Tellurium(IV) can easily be extracted from *hydrobromic acid* medium with ethers.[122,123] Shitareva has proposed the formula $(H_3O)_2(H_2O)_mS_3.TeBr_6$ for the compound extracted into hexanol.[20] Tellurium(IV) is better extracted by ketones;[111,147] in this case the organic phase may be directly subjected to an atomic-absorption determination.[124] In comparison with extraction from hydrochloric acid medium, the separation of tellurium from hydrobromic acid medium offers no advantages, since many elements form extractable bromo-complexes. This is the reason why this solvent extraction system has found limited application. Tellurium(IV) can be extracted with a high distribution coefficient from hydrobromic acid medium with TBP.[125] The solvate of TBP was found to be dissociated in the organic phase and the distribution coefficient for tellurium(IV) decreased at higher concentrations of indium(III).

Tellurium(IV) can be easily extracted from *hydriodic acid* medium with alcohols[126] and ethers.[127] The extracted ionic species is formulated as H_2TeI_6 or $HTeI_5$ (at lower HI concentrations).[21,22,128,129] We have established that the compound extracted into acetophenone (from mixtures of sulphuric acid and potassium iodide) has the composition $TeI_4.S_3$.[26] The solubility of this solvate in ketones is very low (less than $10^{-4}M$). Hence this extraction system with ketones can be used only for the separation of microgram amounts of tellurium(IV).[1,26,41,130–132] The other solvates of the tellurium(IV) iodo-complexes with ethers,[133] alcohols,[126] or mixtures of alcohols and polar diluents[127] have a substantially higher solubility, hence these methods can be used for higher concentrations of tellurium(IV).

Recently other techniques have been used for the separation of tellurium, namely thin-layer chromatography,[136–139] paper chromatography,[135,150] and extraction chromatography[134,140–145]—predominantly with oxygen-containing solvating extractants. These techniques are especially suitable for complicated separations since they are in fact a multistage extraction process and the selectivity of the separation is very high. It would be advantageous to develop such separation methods by using sulphur-containing chelating reagents,[138] which are more selective for separation of tellurium.

Unfortunately no solvent extraction method for the separation of tellurium has so far been published in which the organic phase consists of an active extractant which can be dissolved in a biphenyl melt. Such a method could eventually be important also for the treatment of fission products.

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Zusammenfassung—Es wird eine kritische Übersicht über den derzeitigen Wissensstand und die Aussichten auf die Entwicklung von flüssig–flüssig-Extraktionsmethoden zur Abtrennung von Tellur(IV) gegeben. Die Literatur (150 Zitate) ist bis Ende 1973 ausgewertet.

Résumé—On présente une revue critique de l'état actuel et des perspectives pour le développement de méthodes d'extraction par solvant pour la séparation du tellurium (IV). La littérature (150 références) est couverte jusqu'à la fin de 1973.

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ATOMIC-ABSORPTION DETERMINATION OF LEAD IN GEOLOGICAL MATERIALS

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Summary—A method is described for the determination by atomic-absorption spectrophotometry of lead, up to the milligram level, in samples of geological materials. After attack with perchloric-hydrofluoric acid mixture and the removal of perchlorate ion by precipitation as potassium perchlorate, lead is separated from matrix elements by means of anion-exchange in 2*M* hydrobromic acid on the strongly basic anion-exchange resin Dowex 1 × 8. Lead is adsorbed on the resin column while practically all other accompanying elements pass into the effluent. For the elution of lead 6*M* hydrochloric acid is used and after evaporation of the eluate lead is determined by atomic-absorption spectrophotometry. The method was tested by analysing numerous samples with contents ranging from a few ppm to milligram amounts of lead. In most cases very good agreement of results was obtained

Atomic-absorption methods have been used extensively for the determination of lead in a variety of materials, including silicates,[1–3] rocks and minerals,[4–7] soils,[8–9] glass,[10,11] ceramic ware,[12,13] bismuth oxychloride,[14] sodium chloride,[15] lead titanate zirconate,[16] food-grade phosphates and phosphoric acid,[17] iron oxide,[18] uranium compounds,[19–21] reagent-grade chemicals,[22] paints,[23–25] waters,[26–29] air and atmospheric particulate matter,[26,30–37] metallurgical products,[38–49] petrol and petroleum products,[50–55] plant material,[56–60] urine,[29,61–74] blood,[63–68,70,71,75–84] milk,[29] bone,[66,85] faeces,[66] tissue,[66] fish,[86–89] beer,[22] chocolate,[22] organic solvents,[90] and aqueous and organic media.[91]

To avoid interferences by matrix elements and to increase the sensitivity, suitable organic complexes of lead are often extracted into organic solvents and the organic extract is aspirated directly into the flame (usually air–acetylene). Reagents used include sodium and diethylammonium diethyldithiocarbamate,[7,17,22,48,84] ammonium tetramethylene-dithiocarbamate,[28,67,69,70,83] ammonium pyrrolidine-1-carbodithioate,[27,29,58,66,71,80–82] dithizone[3,18,43,68,81,85,89] and 8-hydroxyquinoline[22] and the solvents include isobutyl methyl ketone,[18,22,27,28,48,58,66,69–71,80–84] heptan-2-one,[29] chloroform,[7,81,89] carbon tetrachloride[3,43,68] and xylene.[17] Methods have also been described, based on the extraction of tetraiodoplumbate ion into isobutyl methyl ketone[44,45,47,55] or isopropyl methyl ketone,[91] followed by aspiration of the organic phase into the flame.

The sensitivity of lead determinations in various materials can also be increased by extraction of the matrix. An example is the removal of uranium nitrate by TBP-extraction before the atomic-absorption determination of lead in uranium compounds.[19–21]

Before the determination of lead by atomic-absorption measurements, especially in biological materials such as plant and animal products[59,60] and biological fluids such as urine[72–74] this element is occasionally separated from the matrix by co-precipitation methods. Suitable co-precipitants are strontium sulphate[59,60] and calcium phosphate[74] as well as bismuth[72] and thorium[73] which are added as nitrates.

Ion-exchange procedures in conjunction with atomic-absorption spectrophotometry have found but little application[46,49] to the determination of lead in various materials, although the technique of ion-exchange separation of lead is a very suitable means of obtaining solutions in which lead can be determined by atomic-absorption measurements free from interferences.

This paper describes an anion-exchange separation method and its application to samples containing from a few ppm to milligram amounts of lead.

EXPERIMENTAL

Solutions and reagents

All the reagents were of analytical-reagent grade unless otherwise stated.

Ion-exchanger. Dowex 1 × 8 (100–200 mesh; chloride form). The resin (4 g) was soaked in a few ml of 2*M* hydrobromic acid and the slurry transferred to the ion-exchange column, the same acid being used as a rinse. Subsequently 50 ml of 2*M* hydrobromic acid were passed through the resin bed to pretreat the resin, *i.e.*, to transform the chloride into the bromide form.

Lead standard solutions. Lead nitrate, $Pb(NO_3)_2$ (33·0 g), dissolved in 0·5% v/v nitric acid and the solution diluted to 1 litre with 0·5% nitric acid: 1 ml of this standard solution contained 20·36 mg of lead (the lead content of this solution was determined by EDTA titration). Aliquots were diluted with 0·5% nitric acid to give solutions with lead concentrations in the range 0·2–200 ppm.

Hydrobromic acid, 2M. This acid was prepared by diluting 235 ml of concentrated hydrobromic acid (about 47%; specific gravity ≅ 1·50) with water to 1 litre.

Other reagents. Potassium bromide, 6*M* and concentrated hydrochloric acid, concentrated hydrofluoric acid and concentrated perchloric acid.

Apparatus and operating conditions

A Perkin–Elmer 303 atomic-absorption spectrophotometer (equipped with a Hitachi–Perkin–Elmer Recorder 56 connected to a read-out accessory) was used with the following instrumental settings.

Grating:	ultraviolet
Wavelength:	283·3 nm
Scale expansion:	up to 30 ×
Slit:	4 (1 mm; 0·7 nm bandpass)
Source:	lead hollow-cathode lamp
Lamp current:	8 mA
Burner:	three-slot burner head
Acetylene pressure:	8 psig; 9·0 on flowmeter (arbitrary scale)
Air pressure:	30 psig; 9·0 on flowmeter (arbitrary scale)
Noise suppression:	up to 5

Under these conditions the sensitivity is 0·6 ppm of lead for 1% absorption (when the measurement of lead is carried out in 0·5% v/v nitric acid). In the determination of lead concentrations exceeding 40 ppm the burner has to be turned by 90°.

The ion-exchange separations were performed by using columns of the same type and dimensions as described earlier.[92]

Determination of distribution coefficients

The distribution coefficients (K_d values) and elution characteristics of lead and other elements were determined by using the batch and column methods.

Procedure

Dissolution of geological samples. To 1 g of the thoroughly homogenized sample in a platinum dish, add 1 ml of water (or 1 ml of lead standard solution when a spike is to be used and the whole procedure applied), 2 ml of concentrated perchloric acid and 10 ml of concentrated hydrofluoric acid, and heat the mixture (which is stirred occasionally) on a steam-bath until most of the hydrofluoric acid is removed. Then take the mixture to dryness on a sand-bath or on a hot-plate and add 10 ml of concentrated hydrofluoric acid. Evaporate the mixture to dryness on a steam-bath and take up the residue in 1 ml of water and 2 ml of concentrated perchloric acid.

Take the mixture to dryness on a sand-bath or on a hot-plate, dissolve the residue in 20 ml of 2*M* hydrobromic acid and let stand for about 1 hr (occasional swirling of the solution speeds up the dissolution of the residue).

Removal of perchlorate. Transfer the solution of the sample in 2*M* hydrobromic acid (see above) to a beaker and use 10 ml of 2*M* hydrobromic acid as a rinse. Then add 2 g of potassium bromide and after mixing let stand for several hr (preferably overnight or longer). Filter off the insoluble precipitate (mainly potassium perchlorate), rinse it with 10 ml of 2*M* hydrobromic acid and dilute the filtrate to 50 ml with the same acid. From this sample solution (= sorption solution) lead is separated by means of the ion-exchange procedure described below.

Ion-exchange separation. Pass the 2*M* hydrobromic acid sample solution (sorption solution) through the ion-exchange column containing 4 g of the resin (pretreated with 50 ml of 2*M* hydrobromic acid) at a flow-rate which corresponds to the back-pressure of the resin bed. Wash the resin with 30 ml of 2*M* hydrobromic acid and elute the lead with 50 ml of 6*M* hydrochloric acid (lead eluate).

Determination of lead. Evaporate the lead eluate to dryness on a steam-bath, take up the residue in 5 ml of 0·5% nitric acid and after about 30 min transfer the solution to a 10-ml standard flask, using the same acid as a rinse. Dilute to volume with 0·5% nitric acid and filter the solution through a dry filter paper to remove any solid particles which might block the capillary used for aspirating the solution into the air–acetylene flame. In this filtrate determine the lead by atomic-absorption spectrophotometry. Construct the calibration curve by aspirating suitable lead standard solutions (prepared in exactly the same way as the samples) before and after each batch of samples.

In the determination of ppm quantities of lead it is necessary to run a reagent blank through the whole procedure (starting with dissolution of geological samples; see above) and finally to deduct its lead concentration from the lead contents measured in the samples.

RESULTS AND DISCUSSION

Atomic-absorption spectrophotometry is a well-established method for the determination of lead in various materials, because it is almost free from interference effects. Thus, of 25 cations, 25 anions and 6 organic acids investigated by Dagnall and West[22] only aluminium, beryllium, thorium, zirconium, phosphate, pyrosulphate, formate and phthalate interfered slightly in the determination of lead in aqueous solution at 283·3 nm. As a consequence atomic-absorption spectrophotometry is frequently used in methods which involve the direct aspiration of the dissolved samples into the flame.[1,2,4–6,8–16,23–26,30–42,50–54,56,57,61–65,75–79,86–88,90]

By closely matching calibration standards and test samples in both lead content and matrix, good analyses can be obtained without preliminary separation of lead from the matrix elements. However, because of the presence of the sample matrix and the associated physical alteration of the sample solution, sample concentrations above 1 or 2 g/100 ml should be avoided. Therefore, lead contents less than 20–30 ppm cannot be determined accurately. However, high accuracy of lead determinations is attainable after separation of the lead by means of ion-exchange employing strongly basic or acidic ion-exchange resins or by extraction with long-chain amines.

On strongly basic anion-exchange resins such as Dowex 1 or Amberlite IRA-400 lead can be adsorbed quantitatively from solutions 1–2*M* in hydrochloric acid, and water or 0·005–0·02*M* and 6–12*M* hydrochloric acid solutions can be employed for its elution.[49,94–118] This "chloride method" of anion-exchange separation of lead has been used to separate lead from barium,[94] copper,[96] zinc,[96,106] thorium,[97] nickel,[104] cobalt,[104] iron,[104] manganese,[104] metallurgical products,[98–100,107–108,110–116] geological materials,[101,105,109,118] biological materials,[95,117] and clear solutions.[102,103] It is probably the most selective of all the methods available, but the low maximum value of the distribution coefficient of lead in about 1·5 *M* hydrochloric acid ($K_d \sim 27$) allows only limited amounts of solution to be passed through a column before lead appears in the effluent. In addition, the distribution coefficient of lead in 1–2*M* hydrochloric acid is further decreased in the presence of salts (*e.g.*, chlorides and perchlorates) so that a sorption solution which is obtained after acid dissolution of a sample has to be passed through a relatively large column of a strongly basic anion-exchange resin to effect quantitative retention of the lead.

Although anion-exchange of lead in mixed aqueous organic solvent systems containing nitric acid[119,120] or in a malonate solution[121] of pH 4·8 as well as adsorption of lead on the chelating resin Dowex A-1[122,123] show some advantages over the "chloride method", the difficulties mentioned above can be eliminated only when using systems in which hydrochloric acid is replaced by hydrobromic acid.

On cation-exchange resin columns dilute hydrobromic acid (0·5–0·6*M*) is a very effective eluent for lead and highly selective separations of this element from most metal ions can be achieved.[124–126] Unfortunately, most of the common elements remain adsorbed, a fact which limits the amount of sample material which can be handled and makes the method less suitable for the separation of small amounts of lead from large amounts of such elements as aluminium, iron, calcium and magnesium (which are main constituents of geological samples). This disadvantage of cation-exchange separations in hydrobromic acid media can be completely eliminated by the use of strongly basic anion-exchange resins[127–131] or long-chain liquid amines such as benzyldodecylmethylammonium bromide (in isobutyl methyl ketone)[46] and methyltrioctylammonium salts (in xylene).[132,133]

In the procedure described in the present paper, lead is adsorbed on a column of the strongly basic anion-exchange resin Dowex 1 from 2*M* hydrobromic acid solution and by means of this method lead can be separated from most accompanying elements. The elution characteristics of these metal ions are shown in Table 1 from which it is seen that lead is separated under these conditions from the majority of the elements investigated. Furthermore, most of the co-adsorbed metal ions are not co-eluted with lead when 6*M* hydrochloric acid is used as the eluent (see *Procedure*).[134] Since geological samples, especially silicates, do not contain amounts of the co-adsorbed elements which exceed ppm quantities, their presence in the sorption solution (see *Procedure*) will have no adverse effects on lead adsorption, such as replacing lead from the resin. However, a considerable decrease of lead adsorption was observed in the presence of perchlorates, which are formed when applying the dissolution technique described in the *Procedure*. Thus, the recovery of lead was reduced by 20–50% when the separation step involving the precipitation of perchlorate by the addition of potassium bromide to the 2*M* hydrobromic acid sample solution (see *Procedure*) was omitted.

A decrease of lead adsorption is also observed in the presence of excess of bromide ion but this effect (see results presented in Table 2) is not as pronounced as when the acid molarity is increased or hydrochloric acid used in place of hydrobromic acid (see Table 3).

Investigations with respect to the effects of perchlorate precipitation and of lead concentration on the recovery of lead gave the results presented in Tables 4 and 5.

From the results shown in Table 4 it is seen that lead was recovered quantitatively, which means that lead was not co-precipitated with the potassium perchlorate, which was precipitated by the addition of 2 g of potassium bromide to 30 ml of 2*M* hydrobromic acid containing 0·5 ml of concentrated perchloric acid and a known amount of lead. Following this precipitation the solution was treated in exactly the same way as described in the procedure. A quantitative recovery of μg and mg-quantities of lead is also possible in the presence of the entire amount of 2 g of potassium bromide (see Table 5).

The suitability of the anion-exchange method in combination with the atomic-adsorption technique described in this paper for the determination of lead was tested by analysing

Table 1. Elution characteristics of metal ions (1·0 mg each) in 2*M* hydrobromic acid (1 g column of Dowex 1 × 8)

Metal ion	BTV, *ml*	$\bar{V}$, *ml*	K_d	EV, *ml*
Pb(II)	60	110	109·3	210
Cu(II)	1	3	2·3	22
Fe(III)	1	2	1·3	13
Co(II)	1	2	1·3	4
Ni(II)	1	2	1·3	4
Mg(II)	1	2	1·3	5
Ca(II)	1	2	1·3	5
Sr(II)	1	2	1·3	4
Ba(II)	1	2	1·3	4
Mn(II)	1	3	2·3	5
Al(III)	1	2	1·3	4
Ga(III)	1	2	1·3	4
La(III)	1	2	1·3	4
Ce(III)	1	2	1·3	4
Cr(III)	1	2	1·3	5
Ti(IV)	1	2	1·3	4
Th(IV)	1	2	1·3	5
UO_2(II)	1	2	1·3	6
Mo(VI)	1	2	1·3	8
V(V)	1	2	1·3	4
Bi(III)	> 100	strong adsorption		
Zn(II)	> 108	strong adsorption		
Cd(II)	> 117	strong adsorption		
In(III)	> 144	strong adsorption		
Au(III)		strong adsorption		
Pt(IV)		strong adsorption		
Pd(II)		strong adsorption		

BTV = breakthrough volume; $\bar{V}$ = volume of elution peak; K_d = distribution coefficient = $\bar{V} - 0{\cdot}7$ (0·7 = void volume in ml); EV = elution volume.

Table 2. Effect of concentration of potassium bromide on batch distribution coefficient of lead

mg K Br/*ml* 2*M* HBr	K_d
0	130
10	96
20	87
30	76
40	66

Table 3. Batch distribution coefficients of lead in hydrobromic and hydrochloric acid solutions

Acid concentration, *M*	K_d in HBr	K_d in HCl
1	353	∼50
2	130	∼10
3	44	< 10

Table 4. Effect of perchlorate precipitation on lead recovery

Amount of lead used (μg, 50 *ml* $2M$ HBr)	Amount of lead found in $6M$ HCl eluate, μg
0·0	1·5
10	9·75
20	21·0
50	50·1
100	101
500	498
1000	998

Table 5. Effect of lead concentration on lead recovery (4 g column of Dowex 1 × 8; sorption solution: 50 ml of $2M$ HBr containing 2 g of KBr)

Amount of lead used, μg	Amount of lead found in $6M$ HCl eluate, μg
5	4·45
20	20·2
100	100
488	467
977	977
2442	2472

Table 6. Results of lead determinations (ppm) in Geological Survey Standards

Sample	This method A	B	Results obtained in other laboratories[13,5]
Granite G-1	43·9	—	21–58
Granite G-2	30·4	31·8 (20)	15–50
Diabase W-1	8·0	—	trace–20
Diabase Q.M.C. 13	7·0	7·6 (10)	<20; 14; 4
Peridotite PCC-1	10·1	9·4 (10)	<20
Tonalite T-1	45·0	41·0 (20)	37

A = Lead content determined by atomic-absorption spectrophotometry after separation of lead by anion-exchange.

B = Lead content determined by atomic-absorption spectrophotometry after separation of lead by anion-exchange and deduction of lead-spike which was added before dissolution of the sample (the number in parentheses gives the number of μg of lead added as a spike).

numerous samples with contents ranging from a few ppm to milligram amounts of lead. The results of these investigations are shown in Tables 6–8 from which it is seen that in most cases very good agreement of results was obtained. In the samples shown in Tables 7 and 8 lead was also determined directly, *i.e.*, without preliminary separation of lead by anion-exchange. These analyses (see columns *C* in Tables 7 and 8) show that results were obtained which, especially at low lead concentrations, deviate considerably from those listed in columns *A* and *B* (Tables 7 and 8). This is due to the effect of the matrix elements on the absorbance of lead, which is more pronounced at low than at high concentrations of this element.

Because the anion-exchange separation can be performed more or less automatically, numerous samples can be analysed simultaneously, *i.e.*, the procedure is very well suited for the routine determination of lead by atomic-absorption spectrophotometry.

Table 7. Results of lead determinations in geochemical standards from the Centre de Recherches Pétrographiques et Géochimiques

Sample	Lead content, *ppm* A*	B*	C	D
Granite GA	29·4	29·2 (20)	34·5	26
Granite GH	41·5	45·0 (20)	43·8	50
Basalte BR	4·2	5·4 (10)	21·3	16
Biotite Mica-Fe	8·0	9·2 (10)	14·1	17
Phlogopite Mica-Mg	11·2	11·4 (10)	21·1	10; 25
Diorite DR-N	52·9	54·0 (50)	57·5	75
Serpentine UB-N	12·1	13·2 (20)	24·8	12; 18; 30; 32
Bauxite BX-N	137·2	147·8 (100)	132·5	132; 155; 205; 215
Disthène DT-N	—	17·4 (50)	25·0	14; 25; 30
Verre Synthetique VS-N†	1058	1086 (500)	959	500–1293

* See footnotes to Table 6.

† The lead content of this synthetic glass standard is given in ppm PbO. Theoretically this sample should contain 1000 ppm of this oxide.

C = Lead content determined by atomic-absorption spectrophotometry without preliminary separation of lead by anion-exchange.

D = Lead content determined in other laboratories.[136,137]

Table 8. Results of lead determinations in Canadian radioactive ore standards [138]

Sample	Lead content, *ppm* A*	B*	C*
DH	18·1	18·2 (20)	27·5
DL	541	505 (500)	562
BL1	73·2	69·0 (50)	89·3
BL2	933	911 (1000)	890
BL3	1783	1640 (1000)	1720
BL4	358	334 (400)	383

* See footnotes to Tables 6 and 7.

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Zusammenfassung—Es wird ein Verfahren zur Bestimmung von Blei in geologischen Proben bis zum Milligrammbereich durch Atomabsorptions-Spektrophotometrie beschrieben. Nach Aufschluß mit einem Gemisch aus Überchlorsäure und Flußsäure und Entfernung von Perchlorat durch Fällung als Kaliumperchlorat wird Blei von den Hauptbestandteilen durch Anionenaustausch in 2*M* Bromwasserstoffsäure an dem stark basischen Anionenaustauschharz Dowex 1 × 8 getrennt. Blei wird an der Harzsäule adsorbiert, während praktisch alle Begleitelemente durchlaufen. Blei wird mit 6*M* Salzsäure eluiert; nach Eindampfen des Eluats wird Blei durch Atomabsorptions-Spektrophotometrie bestimmt. Das Verfahren wurde durch Analyse zahlreicher Proben mit Bleigehalten von einigen ppm bis zu Milligrammen getestet. In den meisten Fällen stimmten die Ergebnisse sehr tut überein.

Résumé—On décrit une méthode pour le dosage par spectrophotométrie d'absorption atomique du plomb, jusqu'à la teneur du milligramme, dans des échantillons de matières géologiques. Après attaque par le mélange acide perchlorique—acide fluorhydrique et élimination de l'ion perchlorate par précipitation à l'état de perchlorate de potassium, on sépare le plomb des éléments de la matrice au moyen d'échange d'anion en acide bromhydrique 2*M* sur la résine échangeuse d'anions fortement basique Dowex 1 × 8. Le plomb est adsorbé sur la colonne de résine tandis que pratiquement tous les autres éléments qui l'accompagnent passent dans l'effluant. Pour l'élution du plomb on utilise l'acide chlorhydrique 6*M*, et après évaporation de l'éluat on dose le plomb par spectrophotométrie d'absorption atomique. On a essayé la méthode en analysant de nombreux échantillons avec des teneurs allant de quelques ppm à des quantités de l'ordre du milligramme de plomb. Dans la plupart des cas, on a obtenu un très bon accord des résultats.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—IV

URAN, KOBALT UND KADMIUM

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Zusammenfassung—Es wird eine Methode beschrieben, die es ermöglicht ppM- Mengen an Uran, Kobalt und Kadmium aus natürlichen Wässern abzutrennen und der quantitativen Endbestimmung mittels fluorimetrischer und spektrophotometrischer Verfahren zugängig zu machen. Die Wasserprobe wird mit Salzsäure angesäuert, filtriert und nach Zugabe von Ascorbinsäure und Kaliumthiocyanat durch eine Säule des Anionenaustauscherharzes Dowex 1-X8 (Thiocyanatform) fließen gelassen. Dabei werden Uran, Kobalt und Kadmium nicht nur am Ionenaustauscher in Form ihrer anionischen Thiocyanatkomplexe quantitativ angereichert, sondern auch gleichzeitig von den meisten in der Wasserprobe anwesenden Begleitelementen getrennt. Koadsorbierte Ionen werden mittels eines salzsauren, gemischt wäßrig–organischen Lösungsmittelsystems entfernt und Kobalt mit 6*M* Salzsäure, Uran mit 1*M* Salzsäure und Kadmium mit 2*M* Salpetersäure eluiert. Die Methode wurde zur Bestimmung von Uran, Kobalt and Kadmium in zahlreichen österreichischen Gewässern herangezogen wobei Gehalte in den Konzentrationsbereichen 0,01 bis 5,0 ppM (Uran), 0,04 bis 1,9 ppM (Kobalt) und 0,04 bis 0,6 ppM (Kadmium) gefunden wurden.

Zur Uranprospektion werden häufig hydrogeochemische Methoden verwendet, da der Urangehalt natürlicher Wässer wertvolle Hinweise hinsichtlich der Lokalisierung von Uranvorkommen liefert.[1] Auf Grund von in Kanada[2,3] gemachten Erfahrungen ist es jedoch erforderlich, daß die Nachweisgrenze des zur Uranbestimmung verwendeten Verfahrens besser ist als einige Zehntel eines ppM, da ein Gehalt von mehr als 1 μg Uran pro Liter als Anomalie angesehen werden kann. Dazu eignen sich vor allem Bestimmungsmethoden, die es gestatten das Uran, möglichst ohne vorangehendes Eindampfen der Wasserprobe, mit großer Empfindlichkeit zu bestimmen und mit denen sich auch eine größere Anzahl Wasserproben gleichzeitig analysieren lassen. Diese Eigenschaften weisen Uranbestimmungsmethoden auf, die in Kombination mit Ionenaustauschverfahren[4-23] angewendet werden, wodurch eine Anreicherung des Urans und damit eine wesentliche Steigerung der Empfindlichkeit und Genauigkeit der Uranbestimmung erzielt wird. Zu diesen Methoden gehören die Fluorimetrie,[4-9] Polarographie,[10-14] Spektrophotometrie[15] und radiochemische Methoden[16,17] die nach vorangehender Isolierung des Urans auf Anionen[4-8,10-14,17] oder Kationenaustauscherharzen[9,15,16] benützt werden.

In früheren Arbeiten dieser Reihe werden Methoden beschrieben, die es ermöglichen die in natürlichen Wässern vorhandenen Spurenelemente Kobalt[24] und Kadmium[25] ohne vorangehenes Eindampfen der Analysenproben unter Anwendung von Anionenaustauschverfahren abzutrennen und der spektrophotometrischen Endbestimmung zugängig zu machen. Da auch Uran und Kadmium analog zum Kobalt[24] anionische Thiocyanatkomplexe bilden, können diese Elemente, wir in der vorliegenden Arbeit beschrieben wird, aus ein und derselben Wasserprobe quantitativ auf dem stark basischen Anionenaustauscher Dowex 1 adsorbiert und nach ihrer Elution mittels fluorimetrischer und spektrophotometrischer Methoden bestimmt werden.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1-X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4 g des Anionenaustauscherharzes in wenigen ml der Vorbehandlungslösung[24] aufgeschlämmt und nach Ablauf von etwa 15 Minuten wird der Austauscher so vollständig als möglich in die mit derselben Lösung gefüllte Ionenaustauschersäule gebracht. Danach wird mit 50 ml der Vorbehandlungslösung nachgewaschen, um den Austauscher weitestgehend in die Thiocyanatform überzuführen.

Kobalt- und Kadmium-Standardlösungen, Vorbehandlungslösung, THF–MG–HCl-Mischung, und Reagenzlösungen. Die Herstellung von diesen Lösungen wurde bereits in Teil I und Teil II dieser Reihe beschrieben.[24,25] THF = Tetrahydrofuran; MG = Methylglykol (2-methoxyethanol).

Andere Reagenzien. Ferner wurden verwendet: Kaliumthiocyanat (p.a.), Ascorbinsäure, 1*M*, 6*M*, 9*M* und konzentrierte Salzsäure und zahlreiche in den Beiträgen I und II dieser Reihe[24,25] angeführte Reagenzien.

Apparaturen

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[26] angegebenen Typs ausgeführt.

Die fluorimetrische Bestimmung des Urans erfolgte mit einem Galvanek–Morrison- Fluorimeter, Mark V, der Firma Jarrell–Ash.

Für die photometrischen Bestimmungen von Kobalt, Cadmium und Uran wurde ein Beckman Spektralphotometer, Modell B mit 1 cm-Küvetten verwendet.

Bestimmung der Verteilungskoeffizienten

Die Gleichgewichtsverteilungskoeffizienten (K_d-Werte) der stark adsorbierbaren Metallionen wurden unter Anwendung der Batch-Methode bestimmt.[27]

Vorbereitung der Wasserprobe

Ein Liter der Wasserprobe wird so bald als möglich nach der Probenahme (mittels einer gut verschließbaren Plastikflasche) mit 10 ml konzentrierter Salzsäure angesäuert und dann durch ein dichtes Filter filtriert. Dem Filtrat werden 5 g Ascorbinsäure und 20 g Kaliumthiocyanat zugesetzt, gut durchgemischt bis sich beide Reagenzien aufgelöst haben und danach wird die Mischung (Sorptionslösung) etwa 5 bis 6 Stunden stehengelassen. Wird für die Analyse ein kleineres oder größeres Volumen als 1 Liter benötigt, so müssen natürlich die der Wasserprobe zuzugebenden Mengen an Reagenzien entsprechend variiert werden.

Ionenaustauschtrennung

Die wie oben angegeben hergestellte Sorptionslösung wird durch eine mit 4 g des Ionenaustauscherharzes beschickte Säule (die vorher mit 50 ml der Vorbehandlungslösung gewaschen wurde) mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 70 bis 80 ml/Stunde) fließen gelassen. Anschließend wird mit 200 ml der THF–MG–HCl-Mischung nachgewaschen (wobei die, durch den am Harz adsorbierten Thiocyanatkomplex des Eisens während der Sorption gebildete, rote Adsorptionszone vollständig verschwindet) und das adsorbierte Kobalt (selbst 10 μg sind als grün-blaue Zone am Harz noch deutlich erkennbar) mit 100 ml 6*M* Salzsäure eluiert (Kobalteluat). Anschließend wird das Uran mit 50 ml 1*M* Salzsäure eluiert (Uraneluat), koadsorbiertes Zink mittels 100 ml 0,15*M* Bromwasserstoffsäure entfernt und danach das Kadmium mit 50 ml 2*M* Salpetersäure eluiert (Kadmiumeluat).

Uranbestimmung

Fluorimetrische Methode. Das Uraneluat wird auf dem Wasserbad zur Trockne eingedampft und der Rückstand in 2 ml 6*M* Salzsäure gelöst. Dieser Lösung wird ein geeignetes Aliquot (z.B. 0,1 ml) entnommen und das Uran fluorimetrisch bestimmt. Die angewendete fluorimetrische Methode beruht auf der Messung der Intensität des Fluoreszenzlichtes von Uran in erkalteten Schmelzflüssen und dem Vergleich mit ebenso bereiteten Standards mit bekannten Urankonzentrationen.[28] Zur Herstellung der Schmelzen werden Fluorbase-Tabletten

(Nordrhein-Chemie, Wolfgang Zeh jun., 41 Duisburg 12, Deutschland) bestehend aus 98 gew.% Natriumfluorid und 2 Gew.% Lithiumfluorid verwendet (Gewicht einer Tablette = 200 mg).

Spektrophotometrische Methode Dieses Verfahren, bei dem das Uran in 9*M* salzsaurer Lösung mittels Zinkgries zur vierwertigen Oxydationsstufe reduziert wird wonach dann in Gegenwart von Arsenazo III die Extinktionsmessung erfolgt, wird an anderer Stelle beschrieben.[29]

Kobaltbestimmung

Die spektrophotometrische Bestimmung des Kobalts im Kobalteluat erfolgt unter Anwendung der Nitroso-R-Salzmethode [24]

Cadmiumbestimmung

Im Eluat wird das Kadmium mittels der Dithizonmethode spektrophotometrisch bestimmt.[25]

Bemerkung

Obwohl die zur Abtrennung und Bestimmung von Uran, Kobalt und Kadmium benützten Reagenzien keine nachweisbaren Mengen dieser Elemente enthielten, ist es immer ratsam ihre Konzentrationen unter Anwendung der oben beschriebenen Arbeitsvorschrift zu ermitteln wobei 1 Liter destilliertes Wasser als Wasserprobe eingesetzt wird.

RESULTATE UND DISKUSSION

Die in der Arbeitsvorschrift beschriebene Methode zur direkten Abtrennung von Uran, Kobalt und Kadmium aus Proben natürlicher Wässer beruht darauf, daß diese Elemente mit Thiocyanationen sehr stabile anionische Komplexe bilden, die aus verdünnt salzsaurer Lösung relative stark auf dem stark basischen Anionenaustauscher Dowex 1 adsorbiert werden. Unter den angegebenen Bedingungen mit denen die Sorptionslösung durch die Ionenaustauschersäule fließen gelassen wird (siehe Arbeitsvorschrift) wurden Verteilungskoeffizienten von $8{,}5 \times 10^4$ (für Uran), $3{,}3 \times 10^3$ (für Kobalt) und $7{,}6 \times 10^2$ (für Kadmium) ermittelt. Es ist daher möglich, diese Elemente, nach Zugabe der zur Adsorption als Thiocyanatkomplexe erforderlichen Reagenzien, direkt durch einfaches Durchfließenlassen der Wasserprobe durch eine kleine Säule des Anionenaustauscherharzes quantitativ anzureichern und gleichzeitig von den in Gewässern in größeren Konzentrationen anwesenden Kalcium-, Magnesium- und Sulfationen zu trennen.

Hinsichtlich des Einflußes von varierenden Thiocyanat- und Salzsäurekonzentrationen auf die Absorption von Uran und Kadmium wurde festgestellt, daß sich diese Elemente ähnlich wie das Kobalt[24] verhalten, d.h. bei Zunahme der Thiocyanatkonzentration tritt eine Adsorptionserhöhung auf, während eine Adsorptionserniedrigung bei Salzsäurekonzentrationen die wesentlich über 0,1*M* liegen zu beobachten ist. Die Einflüsse dieser beiden Konzentrationsparameter sind jedoch bei Uran und Kobalt wesentlich geringer als beim Kadmium, da Uran und Kobalt um Zehnerpotenzen höhere Verteilungskoeffizienten aufweisen als Kadmium.

Der Zusatz von Ascorbinsäure zu den angesäuerten Wasserproben (siehe Arbeitsvorschrift) dient zur Reduktion von Eisen(III) zu zweiwertigem Eisen und das nach der Sorption von Uran, Kobalt und Kadmium als Waschlösung benützte THF–MG–HCl-Gemisch wird dazu verwendet, um die Thiocyanatkomplexe der adsorbierten Elemente in anionische Chlorokomplexe überzuführen (siehe auch Beitrag I dieser Reihe[24]). Mit diesem aus 50 vol.% Tetrahydrofuran, 40 vol.% Methylglykol und 10 vol.% 6*M* Salzsäure bestehenden, gemischt wäßrig-organischen System wird nicht nur jene Eisenmenge, die als anionischer Thiocyanatkomplex festgehalten wurde, entfernt,[24] sondern es werden damit auch die Thiocyanatkomplexe aller anderen koadsorbierten Elemente, wie z.B. Vanadin,[30,31] Molybdän,[32,33] Kupfer,[30] Zink,[30,34] Quecksilber[30,34] und Silber[30,34] wirksam zerstört. Dies hat zur Folge, daß Vanadin und Molybdän, die aus dem THF–MG–HCl-System nur schwach am Anionenaustauscher adsorbierbar sind,[6] weitgehend vom Harz entfernt und somit von Uran, Kobalt und Kadmium (in dieser Mischung sind die Verteilungskoeffizienten dieser Elemente größer als 10^3)[6] getrennt werden.

Tabelle 1. Elutionsverhalten des als Thiocyanatkomplex auf Dowex 1 (4 g Säule) adsorbierten Urans (100 μg)*

Elutionsmittel	Urangehalt des Eluats, μg
1. 200 ml THF–MG–HCl-Mischung + 100 ml $6M$ HCl + 50 ml $1M$ HCl	100
2. 50 ml konzentrierte HCl + 50 ml $1M$ HCl	97
3. 50 ml $1M$ $HClO_4$	50,5
4. 50 ml $6M$ HCl + 50 ml $1M$ HCl	0,08
5. 50 ml $1M$ HNO_3	0,00
6. 50 ml $2M$ H_2SO_4	0,00

* Diese Uranmenge wurde jeweils einem Liter destilliertem Wasser zugesetzt und das Uran wie für Analysenproben beschrieben (siehe Arbeitsvorschrift) am Harz adsorbiert.

Der entscheidenste Vorteil der sich aus der Anwendung der THF–MG–HCl-Mischung ergibt, ist darauf begründet, daß dabei der äußerst stabile Uranylthiocyanatkomplex[35–37] vollständig in den Chlorokomplex umgewandelt wird, wodurch es möglich ist das Uran quantitativ mittels $1M$ Salzsäure zu eluieren. Das Elutionsverhalten des Urans bei Anwendung dieses gemischt wäßrig–organischen Systems sowie einer Anzahl anderer Elutionsmittel wird in Tabelle 1 gezeigt. Aus dieser Tabelle geht hervor, daß auch das Elutionsmittel 2 sowie konzentrierte Salzsäure gefolgt von Wasser[30] zur quantitativen Elution des Urans geeignet ist. Allerdings wird mittels dieser Medien nicht nur das Uran sondern auch das adsorbierte Eisen[30,34] gleichzeitig eluiert und kann dann eine Störung der fluorimetrischen Uranbestimmung durch Fluoreszenzlöschung hervorrufen.[28] Bei Anwendung des Elutionsmittels 3[38] werden nur 50% des Urans eluiert.

Bei der, der Anwendung der THF–MG–HCl-Mischung, nachfolgenden Elution des Kobalts mittels rein wäßriger $6M$ Salzsäure (siehe Arbeitsvorschrift) werden von den ursprünglich als Thiocyanatkomplexe adsorbierten Metallen nur Kupfer, Silber und Vanadin (Restmenge) ebenfalls eluiert. Diese Elemente rufen jedoch keine Störungen bei der spektrophotometrischen Bestimmung des Kobalts hervor.[24] Weiter am Harz adsorbiert verbleiben Uran(VI) (K_d = 283), Zink(II) (K_d = > 100), Kadmium(II) (K_d = > 100) und Quecksilber(II) (K_d = > 100). Von diesen Ionen wird bei der darauffolgenden Behandlung des Harzes mittels $1M$ Salzsäure (siehe Arbeitsvorschrift) nur das Uran eluiert.

Durch die vor der Elution des Cadmiums angewendete $0,15M$ Bromwasserstoffsäure (siehe Arbeitsvorschrift) wird das koadsorbierte Zink qantitativ eluiert, so daß Kadmium im $2M$ salpetersauren Eluat störungsfrei spektrophotometrisch bestimmt werden kann.[25]

Um den Einfluß des Volumens der zur Analyse verwendeten Wasserprobe auf die Ionenaustauschtrennung und die Genauigkeit der Uran-, Kobalt- und Cadmiumbestimmungen zu untersuchen, wurden variierende Volumina Wiener Trinkwassers sowohl auf

Tabelle 2. Resultate von Uran-, Kobalt- und Kadmiumbestimmungen im Wiener Trinkwasser (Leitungswasser des Analytischen Instituts der Universität Wien)

Datum der Probenahme	Volumen der zur Analyse verwendeten Wesserprobe, l.	Urangehalt, $\mu g/l$.		Kobaltgehalt, $\mu g/l$.		Kadmiumgehalt, $\mu g/l$	
17 Dezember 1973	0,1	0.1	0.1*	0.0	0.0	0,0	0.0
14 November 1973	0.5	0.30	0.31†	0.42	—	0,22	—
14 November 1973	1	0.31	0.26§	0.39	0,29§	0,27	0,26§
18 Mai 1973	1	0.17	0.20§	—	—	—	—
9 Februar 1973[24]	1	—	—	0,20	—	—	—
23 Februar 1973[25]	1	—	—	—	—	0,10	—
14 November 1973	2	0.37	0.37§	0.28	0,32§	0.28	0,26§
14 November 1973	5	0.31	0.31§	0.18	0,28§	0.10	0,20§
2 August 1956	5	0.41–0.48‡		—	—	—	—
23 Februar 1973[25]	5	—	—	—	—	0,10	—

* Urangehalt nach Abzug von 0,025 μg Uran-Spike die 0.1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurde.

† Urangehalt nach Abzug von 0,125 μg Uran-Spike die 0,5 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurde.

§ Uran-, Kobalt- und Kadmiumgehalte nach Abzug von 0,25 μg U, 0.20 μg Co und 0,1 μg Kd-Spikes die pro 1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurden.

‡ Polarographisch bestimmter Urangehalt nach Eindampfen der Wasserprobe, Ätherextraktion und Anionenaustausch.[10]

ihren natürlichen Gehalt an diesen Elementen analysiert, als auch in Gegenwart bekannter Spurenkonzentrationen an Uran. Kobalt und Kadmium. Die Resultate dieser Versuche werden in Tabelle 2 gezeigt und aus ihnen ist ersichtlich, daß im Fall des Urans das Volumen keinerlei Einfluß auf die Ionenaustauschtrennung ausübt, da der hohe Verteilungskoeffizient von 8.5×10^4 eine quantitative Isolierung des Urans selbst aus 5 Litern Wasser ermöglicht. Dagegen hat aber das Volumen einen entscheidenden Einfluß auf die Genauigkeit der fluorimetrischen Uranbestimmung falls das Volumen der zur Analyse verwendeten Wasserprobe geringer ist als 0,5 Liter. Dies gilt auch für die Kobalt- und Kadmiumbestimmungen, da diese Elemente in vergleichbar geringen Konzentrationen anwesend sind (siehe auch Tabellen 3 bis 5). Da außerdem der Verteilungskoeffizient des Kadmiums nur einen Wert von $7,6 \times 10^2$ aufweist, ist die quantitative Abtrennung dieses Elementes mittels Anionenaustausches nur aus Wasserproben möglich, deren Volumen 2 Liter nicht überschreitet. Infolge dieser Einschränkung ist es daher unmöglich die Kadmiumgehalte natürlicher Wasser mit derselben hohen Genauigkeit, mit der ihre Urangehalte ermittelt werden können, zu bestimmen.

In den Tabellen 3 bis 5 werden die Ergebnisse von Uran-, Kobalt- und Kadmiumbestimmungen in Wasserproben gezeigt, die zahlreichen Gewässern österreichischer Bundesländer entnommen wurden. Diese Analysen wurden unter Anwendung der in der Arbeitsvorschrift beschriebenen Methode durchgeführt und zeigen, daß mit diesem Verfahren ebenso gute Ergebnisse bei Urananalysen erzielt werden, als mittels einer früher beschriebenen[6] Anionenaustauschmethode welche nur nach vorangehendem Eindampfen der Proben zur Uranabtrennung herangezogen werden kann (siehe Tabelle 3).

Mit der fallweise zur Bestimmung höherer Urangehalte benützten spektrophotometrischen Methode[15,39–41] (siehe Arbeitsvorschrift) wurden allerdings, wie aus Tabelle 5 ersichtlich ist, durchwegs höhere Urangehalte gefunden.

Tabelle 3. Resultate von Uran-, Kobalt- und Kadmiumbestimmungen in österreichischen Wasserproben mit Urangehalten unter 0,5 ppM

	Probenbezeichnung und Datum der Probenahme	Urangehalt, *μg/l.*	Kobaltgehalt, *μg/l.*	Kadmiumgehalt, *μg/l.*
95/1	Zinkenbach am Ausgang Steingraben, westl. der Ortschaft Zinkenbach, bei Straßenbrücke; Salzkammergut; 21.6.1973	0,16 (0,20)*	1,00	0,28
95/4	Rußbach, Abzweigung Pass Gschütt-Straße zum Kudlhaus westl. der Straßenbrücke vor der Einmündung der Lammer; Salzkammergut; 21.6.1973	0,338 (0,32)*	0,75	0,14
95/5	Lammer nahe des Zusammenflusses mit dem Rußbach, Salzkammergut; 21.6.1973	0,33 (0,32)*	1,00	0,21
204/1	Kollmannbach, nördl. von St. Kollmann bei 1. Brücke außerhalb von St. Kollmann; Kärnten; 16.7.1973	0,45	0,60	0,20
204/2	Grafenbach, nördl Stift Griffen, 1. Straßenbrücke nach Stift Griffen, Kärnten; 16.7.73	0,22	0,90	0,20
204/3	Haimburgerbach nördl. Haimburg an der Straße nach Diex, bei Harrich-Mühle; Kärnten; 16.7.1973	0,24	0,60	0,16
203/1	Diexerbach nördl. von Obertrixen bei Straßenbrücke oberhalb Mühle, Kärnten; 16.7.1973	0,33	0,90	0,13
186/1	Feistritzbach, an der Straße nach Hochfeistritz hinter 4. Straßenbrücke von der Hauptstraße bei Mühle, Kärnten, 16.7 1973	0,13	1,40	0,23
186/2	Tisäckerbach, westl. Eberstein an der Straße nach Kulm bei der 1. Brücke, Kärnten; 16.7.1973	0,10	0,60	0,16
186/3	Schreckenbach östl. unter St. Paul, Kärnten; 16.7.1973	0,12	0,11	0,20
186/4	Grünburgerbach, östl. Kitschdorf, 2. Brücke nach Kitschdorf in der Nähe der Quote 808, Kärnten; 16.7.1973	0,15	0,77	0,16
186/5	Weinsbergerbach, nordöstl. Wieting, Kärnten; 16.7.1973	0,075	0,09	0,20
187/1	Löllingbach, östl. Lölling, südl. Stöckl, Kärnten; 16.7.1973	0,29	0,35	0,13
187/2	Mosinzbach, östl. Plaggowitz, Kärnten; 16.7.1973	0,36	0,57	0,22
204/4	Wölfnitzbach, Kärnten; 17.7.1973	0,21	0,66	0,13
196/1	Lahnbach, 2 km westl. Obertilliach, Osttirol; 7.8.1973	0,18	0,86	0,20
196/3	Rabetzbach vor Einmündung in die Gail, bei Göll; Obertilliach, Osttirol; 7 8.1973	0,10	0,44	0,08
196/4	Frohnbach, 5 km südl. St. Lorenzen im Lesachtal bei Jagdhütte, Lesachtal, Südkärnten; 7.8.1973	0,23	0,93	0,25
197/1	Mattlingbach, bei Durnthal, 1 km westl. Mattling, bei Bachbrücke, Lesachtal, Südkärnten; 7.8.1973	0,26	0,98	<0,08

* Die eingeklammerten Urangehalte wurden nach Eindampfen der Proben und Anwendung der THF MG-HCl-Methode[6] ermittelt.

Tabelle 3

	Probenbezeichnung und Datum der Probenahme	Urangehalt, $\mu g/l$.	Kobaltgehalt, $\mu g/l$.	Kadmiumgehalt, $\mu g/l$.
197/9	Stelzlinghütte, 3 km nördl. Kötschach-Mauthen, bei Laas, Südkärnten; 7.8.1973	0,27	<0,08	0,35
198/5	Wiesergraben, 1 km oberhalb Grafendorf, Oberes Gailtal, Südkärnten; 10.8.1973	0,25	0,95	0,35
198/6	Reißkofelbach, oberhalb Reißkofelbad, bei Grafendorf, Oberes Gailtal, Südkärnten; 10.8.1973	0,43	0,65	0,56
198/8	Rudnigbach, oberhalb Oselitzen, bei Bachbrücke an der Straße zum Grenzübergang Naßfeld; Südkärnten, 10.8.1973	0,44	0,24	0,31
DR 1	Draßnitzbach, bei Draßnitz, oberhalb Dellach im Drautal, Kärnten; 11.8.1973	0,01	0,56	0,26
DR 2	Gnoppnitzbach, 10 km oberhalb Greifenburg, Drautal, Kärnten; 11.8.1973	0,35	0,88	0,32
DR 3	Grabach, 5 km oberhalb Steinfeld, Drautal, Kärnten; 11.8.1973	0,21	0,83	0,23
St. 1	Göriachbach bei Hintergöriach, 5 km nordwestl. von Tamsweg, Salzburg; 12.8.1973	0,064	0,56	0,09
St. 2	Lessachbach bei Lessach, 5 km nördl. von Tamsweg, Salzburg; 12.8.1973	0,11	0,64	0,15
Sb. 1	Larzenbach, 2 km nördl. Hüttau an der B112 Bischofshofen-Radstadt, Salzburg; 12.8.1973	0,36	0,80	0,28
Sb. 2	Imlaubach oberhalb Imlau, an der B159 Werfen-Bischofshofen, Salzburg; 12.8.1973	0,42	0,72	0,35
	Fieberbrunn, Tirol; 25.8.1973	0,13	<0,08	0,32
116/1	Silzerbach, unterhalb Wasserfall, Tirol; 26.8.1973	0,20	0,30	0,16
145/1	Leonhardsbach, Oberangern, Tirol; 26.8.1973	0,28	<0,08	0,24
196/6	Tuffbad-Bach von der Ostseite, Tirol; 26.8.1973	0,44	0,33	0,24
73/4	Traisenbachrotte oberhalb Prünstbachgraben, Niederösterreich; 31.5.1973	0,48	0,67	0,32
73/5	Traisen, Höhe Kienbiegl, Niederösterreich; 31.5.1973	0,04	0,67	0,24
73/6	Retzbach unterhalb Grieß, Niederösterreich; 31.5.1973	0,31	1,07	0,24
73/7	Traisen bei Auhof, Niederösterreich; 31.5.1973	0,26	1,05	<0,04
73/10	Scharbach oberhalb Bahnhof Türnitz, Niederösterreich; 31.5.1973	0,26	0,98	<0,04
73/11	Weißenbach oberhalb Bahnlinie, Niederösterreich; 31.5.1973	0,45	0,73	0,35
73/16	Moosbach oberhalb ÖBB-Haltestelle, Niederösterreich; 31.5.1973	0,28	0,73	0,21
S7	Klegerbach bei Weyer, Pinzgau, Salzburg; 16.6.1973	0,12	<0,1	0,16
S8	Mühlbach im Pinzgau, 1 km oberhalb Mühlbach, Salzburg; 16.6.1973	0,16	<0,1	0,16
S9	Hollersbach im Pinzgau, 2 km oberhalb Hollersbach, Salzburg; 16.6.1973	0,22	<0,1	0,08
S11	Stuhlfeldnerbach oberhalb Stuhlfelden, Pinzgau, Salzburg; 16.6.1973	0,16	0,80	0,20

Tabelle 3

	Probenbezeichnung und Datum der Probenahme	Urangehalt, µg/l.	Kobaltgehalt, µg/l.	Kadmiumgehalt, µg/l.
S13	Kapruner Ache oberhalb Kaprun, Salzburg; 16.6.1973	0,30	0,34	0,20
S14	Fuscher Ache oberhalb Fusch an der Glocknerstraße, Pinzgau, Salzburg; 16.6.1973	0,29	0,80	0,13
OÖ 1	Klammleitenbach bei Königswiesen an der B124 (Pierbach-Arbesbach), östl. Mühlviertel, Oberösterreich; 18.8.1973	0,13	0,67	0,15
OÖ 2	Große Mühl, 1 km unterhalb Haslach an der Mühl, nördl. Mühlviertel, Oberösterreich; 18.8.1973	0,09	0,59	0,18
OÖ 4	Fallauerbach oberhalb Engelhartszell, Sauwald, Oberösterreich; 18.8.1973	0,28	0,55	0,24
OÖ 5	Sausenderbach unterhalb Engelhartszell, Sauwald, Oberösterreich; 18.8.1973	0,07	0,35	0,15
73/17/2	Traisen oberhalb Moosbach, Niederösterreich; 18.8.1973	0,47 (0,50)*	0,25	0,15
	Leckbach, Habachtal, Tirol; 16.8.1973	0,16	1,52	<0,08
	Dobrachbach, Tirol; 16.8.1973	0,16	<0,08	0,32

Tabelle 4. Resultate von Uran-, Kobalt- und Cadmiumbestimmungen in österreichischen Wasserproben mit Urangehalten von 0,5 bis 1,0 ppM

	Probenbezeichnung und Datum der Probenahme	Urangehalt, µg/l.	Kobaltgehalt, µg/l.	Kadmiumgehalt, µg/l.
95/2	Königsbach, bei Straßenbrücke westl. Zinkenbach, Salzkammergut; 21.6.1973	0,71	0,80	0,14
95/3	Weißenbach südl. Unterberg zwischen erster und zweiter Wildbachmauer, Salzkammergut; 21.6.1973	0,75	0,67	0,28
200/1	Nötschgraben oberhalb Förk bei Nötsch, Gailtal, Kärnten; 6.8.1973	0,71	1,50	0,39
200/2	Erlachgraben oberhalb Erlachbach, westl. Bleiberg-Kreuth, Südkärnten; 6.8.1973	0,93	0,93	0,26
199/4	Untervellacher Almbach westl. Bergwerk Förolach, Unteres Gailtal, Südkärnten; 6.8.1973	0,97	0,28	0,24
199/5	Garnitzenbach, 2 km südl. Möderndorf, Unteres Gailtal, Südkärnten; 6.8.1973	0,80	0,68	0,18
198/1	Schwarzenbach, 1 km südwestl. Weißbriach, Gailtaler Alpen, Südkärnten; 6.8.1973	0,74	0,85	0,13
197/2	Wolayerbach, 7 km oberhalb Einmündung in die Gail bei Birnbaum, Lesachtal, Südkärnten; 7.8.1973	0,54	0,84	0,08
197/4	Lanerbach vor Einmündung in den Podlanigbach, oberhalb Kornat, Lesachtal, Südkärnten; 7.8.1973	0,55	0,38	0,44

Tabelle 4

	Probenbezeichnung und Datum der Probenahme	Urangehalt, µg/l.	Kobaltgehalt, µg/l.	Kadmiumgehalt, µg/l.
197/5	Strajachbach, 1 km östl. Strajach bei Bachbrücke, Lesachtal, Südkärnten; 7.8.1973	0,90	<0,08	0,24
198/4	Nöblingbach, 1 km oberhalb Nöbling, Oberes Gailtal, Südkärnten; 10.8.1973	0,96	0,39	0,32
117/2	Gießenbach bei Eisenbahnbrücke, Tirol; 26.8.1973	0,87	<0,08	0,48
117/3	Reitherbach, Tirol; 26.8.1973	0,83	0,11	0,10
117/4	Zirlerbach, Tirol; 26.8.1973	0,61	0,08	0,29
73/1	Gurgelbach zwischen Högerhof und Hofbauer, Niederösterreich; 31.5.1973	0,77	<0,04	0,16
73/2	Fischbach unterhalb Waldsteighof, Niederösterreich; 31.5 1973	0,68	0,35	<0,04
73/3	Koppeltal vor Einmündung Fischbach, Niederösterreich; 31.5.1973	0,64	0,10	0,32
73/8	Türnitz bei den Anthöfen, Niederösterreich; 31.5.1973	0,58	0,71	0,16
73/12	Stelzerbach, Höhe Schacherbauer, Niederösterreich; 31.5.1973	0,82	0,10	0,42
73/13	Klamm Höhe ÖBB-Haltestelle, Niederösterreich; 31.5.1973	0,71	0,73	0,14
73/14	Hauserbauernbach oberhalb Bachbrücke, Niederösterreich; 31.5.1973	0,84	<0,04	0,21
73/15	Thorbach oberhalb Bachbrücke, Niederösterreich; 31.5.1973	0,71	<0,04	0,35
73/17	Traisen oberhalb Moosbach, Niederösterreich; 31.5.1973	0,59	0,42	0,21
73/18	Traisen unterhalb Moosbach, Niederösterreich; 31.5.1973	0,59	0,32	0,28
S1	Krimmler Ache oberhalb Bahnhof Krimml, Pinzgau, Salzburg; 16.6.1973	0,50	0,71	<0,08
S2	Salzach bei Einmündung in die Krimmler Ache, Vorderkrimml, Pinzgau, Salzburg; 16.6.1973	0,78	0,28	<0,08
S3	Obersulzbach, 3 km oberhalb Einmündung Rosenthal, Pinzgau, Salzburg; 16.6.1973	0,66	0,25	<0,08
S4	Untersulzbach, 2 km oberhalb Einmündung bei Sulzau in die Salzach, Pinzgau, Salzburg; 16.6.1973	0,72	1,14	<0,08
S5	Dürrnbach, 2 km oberhalb Einmündung bei Neukirchen am Großvenediger, Pinzgau, Salzburg; 16.6.1973	0,66	<0,1	<0,08
S6	Habach oberhalb Bahnhof Habachtal, Pinzgau, Salzburg; 16.6.1973	0,94	<0,1	0,24
S15	Salzach unterhalb Bruck an der Glocknerstraße, Salzburg; 16.6.1973	0,62	0,54	0,33
Ö03	Kleine Mühl bei Peilstein im Mühlviertel (B128 Kollerschlag-Öepping), Oberösterreich; 18.8.1973	0,62	0,69	0,30
196/4	Aus dem Tuffbad 1420 m, Tirol; 26.8.1973	0,74	0,26	0,60

Tabelle 5. Resultate von Uran-, Kobalt- und Kadmiumbestimmungen in österreichischen Wasserproben mit Urangehalten über 1,0 ppM

	Probenbezeichnung und Datum der Probenahme	Urangehalt, µg/l.	Kobaltgehalt, µg/l.	Kadmiumgehalt, µg/l.
199/1	Gailwaldbach, 2 km oberhalb Kreuzen, Gailtaler Alpen, Südkärnten; 6.8.1973	1,20	0,38	0,21
199/2	Klausenbach, 4 km westl. Kreuzen, Gailtaler Alpen, Südkärnten 6.8.1973	1,39	0,38	0,16
199/3	Förolacherbach östl. Bergwerk Förolach, Unteres Gailtal, Südkärnten; 6.8.1973	2,40 (3,23)*	0,61	0,16
198/2	Gösseringbach, 1 km nordwestl. Weißbriach, Gailtaler Alpen, Südkärnten; 6.8.1973	1,26	0,66	0,20
198/3	Mocnikgraben, 1 km westl. Weißbriach, Gailtaler Alpen, Südkärnten; 6.8.1973	1,02	0,47	0,17
196/2	Gärberbach, 2 km östl. Obertilliach, bei Goll, Osttirol; 7.8.1973	1,24	<0,08	0,26
197/3	Podlanigbach, 7 km oberhalb Einmündung in die Gail, bei Kornat, Lesachtal, Südkärnten; 7.8.1973	2,20 (2,67)*	0,44	0,36
197/6	Sittmooserbach, bei Sittmoos (Bachbrücke), Lesachtal, Südkärnten; 7.8.1973	1,06	1,94	0,22
197/7	Mayengraben, 2 km oberhalb St. Daniel bei Kötschach-Mauthern, Oberes Gailtal, Südkärnten; 7.8.1973	1,64	0,24	0,49
197/8	Dellacherbach, 1 km oberhalb Dellach, Oberes Gailtal, Südkärnten; 7.8.1973	1,63	1,42	0,38
179/1	Sturzelbach, südl. Mittewald an der Drau, Drautal, Osttirol; 10,8.1973	3,52 (4,62)*	0,08	0,08
179/2	Gamsbach, östl. Mittewald an der Drau, Drautal, Osttirol; 10.8.1973	4,30 (4,62)*	0,20	0,24
179/3	Leisacher Almbach, östl. Mittewald an der Drau, Drautal, Osttirol; 10.8.1973	2,22 (2,46)*	0,24	0,28
198/7	Jeniggraben, 1 km oberhalb Jenig, vor Wasserfall, Oberes Gailtal, Südkärnten; 10,8,1973	1,44	0,50	0,21
145/2	Himmelswiesbergbach, oberhalb Zams, Tirol; 26.8.1973	2,19 (2,56)*	0,66	0,08
145/3	Breithaslachbach bei Klammaustritt, Tirol; 26.8.1973	2,52 (2,68)*	0,33	0,20
117/1	Steinbrennerei Seefeld, Bach, Tirol; 26.8.1973	1,04	<0,08	0,19
196/5	Quelle bei Tuffbad, Tirol; 26.8.1973	5,00 (6,67)*	0,38	0,24
73/9	Großer Sulzbach im Ort Türnitz, Niederösterreich; 31.5.1973	1,84	0,52	<0,04
S12	Stub-Ache, 1 km oberhalb Stubach, Stubachtal, Pinzgau, Salzburg; 16.6 1973	1,52	0,30	0,16

* Die eingeklammerten Urangehalte wurden spektrophotometrisch unter Anwendung der Arsenazo III-Methode[29] ermittelt

Da die vorliegende Methode auf der Anwendung der weitgehend automatisierbaren Anreicherung und Abtrennung von Uran, Kobalt und Kadmium auf Anionenaustauschersäulen beruht, ist es möglich, viele Wasserproben gleichzeitig nach deren Ansäuern und Filtration zu analysieren d.h. das Verfahren eignet sich vorzüglich zur serienmäßigen Bestimmung dieser Elemente in Gewässern.

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Summary—A method is described for separating and determining, by spectrofluorimetric or spectrophotometric measurement, traces of uranium, cobalt and cadmium at ppM levels in natural waters. The sample is acidified with HCl, filtered, and after addition of ascorbic acid and potassium thiocyanate, passed through a column of Dowex 1- × 8 anion-exchange resin in the thiocyanate form. The three ions are concentrated on the resin as thiocyanate complexes, being at the same time separated from most of the other ions present in the sample. Elution with a tetrahydrofuran–methylglycol–HCl mixture removes other interfering ions, then 6*M* HCl strips the cobalt, 1*M* HCl the uranium, and 2*M* HNO_3 the cadmium. Data are presented for concentrations of uranium (0·01–5 ppM) cobalt (0·04–1·9 ppM) and cadmium (0·04–0·6 ppM) in a large number of water sources in Austria.

Résumé—On décrit une méthode pour la séparation et le dosage, par mesure spectrofluorimétrique ou spectrophotométrique, de traces d'uranium, cobalt et cadmium aux teneurs de l'ordre de la ppM dans les eaux naturelles. L'échantillon est acidifié par HCl, filtré, et après addition d'acide ascorbique et de thiocyanate de potassium, passé sur une colonne de résine échangeuse d'anions 1-X8 sous la forme thiocyanate. Les trois ions sont concentrés sur la résine sous forme de complexes thiocyaniques, et sont en même temps séparés de la majeure partie des autres ions présents dans l'échantillon. L'élution avec un mélange tétrahydrofuran–méthylglycol–HCl élimine les autres ions gênants, puis HCl 6*M* arrache le cobalt, HCl 1*M* l'uranium et HNO_3 2*M* le cadmium. On présente les données pour les concentrations d'uranium (0,01–5 ppM), cobalt (0,04–1,9 ppM) et cadmium (0,04–0,6 ppM) dans un grand nombre de sources d'eau en Autriche.

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SYSTEMES AUTOMATIQUES D'ANALYSE PAR ACTIVATION NEUTRONIQUE POUR LA MESURE EN LIGNE DES PROCEDES INDUSTRIELS

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Résumé—Après avoir énoncé les principales conditions auxquelles un système d'analyse doit satisfaire pour être utilisé dans l'industrie, on étudie comment chacune des parties d'une installation d'activation doit être conçue pour répondre à ces impératifs: choix de la source de neutrons et du détecteur, adaptation du système de transfert en fonction de l'échantillonnage et de l'étalonnage, mise en ligne du traitement des informations. On indique quelques applications ayant donné lieu à des installations déjà en service dans l'industrie: dosages de l'oxygène, de l'azote, du fluor, du silicium. On mentionne enfin quelques essais de dosages en continu.

La radioactivation induite par les neutrons est un phénomène connu depuis quarante ans et ses premières applications à l'analyse chimique datent presque de la même époque. On connaît bien les nombreux avantages de cette méthode:

—analyse indépendante des liaisons chimiques,

—grande sensibilité pour la plupart des éléments (et en particulier pour plusieurs éléments légers, à condition d'utiliser des neutrons rapides),

—assez bonne précision,

—utilisation d'étalons primaires,

—bonne représentativité (gros échantillons, grande pénétration des neutrons et des rayons gamma),

—conservation souvent possible de l'échantillon.

Et pourtant, l'analyse par activation n'est encore pratiquement utilisée par les industriels qu'à l'intérieur des laboratoires d'accueil créés à leur intention dans les centres de l'Energie Atomique. Elle est donc limitée à la recherche plus ou moins appliquée et ne prend place que très rarement à l'intérieur des usines pour contrôler directement les procédés industriels.

IMPERATIFS D'UNE METHODE D'ANALYSE POUR PROCEDE INDUSTRIEL

Pour qu'une méthode d'analyse puisse s'appliquer au contrôle d'un procédé industriel, elle doit posséder les qualités suivantes:[1,2]

1—une sensibilité moyenne (les éléments recherchés constituent souvent au moins 0,1% du produit),

2—une bonne exactitude soit:

  2*a*—pas d'interférence due à la matrice,

  2*b*—pas d'erreur systématique de mesure,

3—une bonne précision (de l'ordre du % relatif),

4—une bonne fidélité (donc un réétalonnage commode),

5—une insensibilité aux liaisons chimiques,
6—une bonne représentativité soit:
  6*a*—une analyse dans la masse,
  6*b*—un volume d'échantillon analysé en un temps donné (ou un débit de matière analysée) aussi grand que possible,
7—une préparation facile de l'échantillon,
8—un temps de réponse assez bref (réaction rapide sur la fabrication),
9—une possibilité d'automatisation (économie de personnel):
  9*a*—au niveau de l'analyse,
  9*b*—au niveau de l'utilisation du résultat (contrôle en boucle fermée),
10—une souplesse d'installation pour s'adapter à des implantations diverses,
11—une sécurité d'emploi (aucun danger pour le personnel),
12—une grande robustesse (économie d'entretien, fonctionnement en environnement hostile).

Cependant, ce qui décide en dernier ressort de l'adoption d'une telle méthode, c'est de savoir si:

13—elle entraîne pour le produit fabriqué:
  —soit une diminution de son prix de revient, —soit une amélioration de sa qualité.

ADAPTATION DE L'ANALYSE PAR ACTIVATION A L'INDUSTRIE

Parmi les impératifs que nous venons d'énumérer, nous pouvons distinguer:
—ceux qui sont inhérents au principe même de la méthode choisie (impératifs 4, 5, 6*a*): l'activation neutronique semble très bien placée à cet égard,
—ceux qui dépendent à la fois de la méthode et du produit à analyser (impératifs 1, 2*a*, 7, 8): il faut étudier chaque cas particulier afin de déterminer, suivant l'élément à doser et la matrice, les meilleures conditions d'irradiation (énergie des neutrons, temps) et de comptage (refroidissement, temps);[3–5] cependant, la lecture des tables de sensibilités[6–8] montre que de nombreux éléments intéressant l'industrie produisent, après une brève irradiation aux neutrons thermiques ou rapides, des radioisotopes dont l'émission gamma est à la fois caractéristique et suffisante (tableau 1),
—enfin ceux qui dépendent à la fois de la méthode et de l'appareillage utilisé (impératifs 1, 2*b*, 3, 6*b*, 8, 9, 10, 11, 12, 13): c'est uniquement sur ces points que des progrès peuvent être faits afin d'adapter l'activation à l'industrie.

Nous allons donc étudier comment chacun des éléments constitutifs d'une installation d'activation (source de neutrons, transfert, comptage gamma, traitement des informations) doit être adapté afin d'obtenir un ensemble d'analyse:
—assez sensible (impératif 1),
—exact et précis (impératifs 2*b* et 3),
—représentatif (impératif 6*b*),
—rapide et automatique (impératifs 8 et 9),
—souple, robuste et non dangereux (impératifs 10, 11 et 12),
—rentable (impératif 13).

L'activation présentant l'avantage de permettre la conservation de l'échantillon, nous n'envisagerons pas la possibilité d'effectuer des séparations chimiques, souvent longues et délicates (impératifs 7, 8, et 9), avant ou après irradiation.

Tableau 1. Principaux éléments dosables par activation avec un générateur de neutrons[7]

Elément	Energie neutrons, *MeV*	Réaction	Seuil réaction, *MeV*	Radio-isotope formé	Période	Energie principal γ émis, *MeV*	Nombre de coups par mg sous le photopic	Principales interférences
N	14	n, 2n	10,6	^{13}N	10,0 mn	0,51	2.400†	Cu, Br, K...
O	14	n, p	9,6	^{16}N	7,4 s	6,13	420*	F
F	14	n, p	4,0	^{19}O	29,4 s	0,20	1.100*	Pd, Ag
	14	n, α	1,5	^{16}N	7,4 s	6,13	220*	O
Al	14	n, p	1,8	^{27}Mg	9,5 mn	0,84	3.000†	
	th	n, γ	—	^{28}Al	2,3 mn	1,78	1.100‡	Si, P
Si	14	n, p	3,9	^{28}Al	2,3 mn	1,78	500*	P
P	14	n, α	1,9	^{28}Al	2,3 mn	1,78	180*	Si
Cl	14	n, 2n	12,8	^{34m}Cl	32 mn	0,51	650†	Zn, Sn...
K	14	n, 2n	13,1	^{38}K	7,8 mn	0,51	550†	Br, Cu, N...
Ca	14	n, p	4,9	^{44}K	22 mn	1,16	12†	Cl
V	th	n, γ	—	^{52}V	3,8 mn	1,44	16.000‡	Cr, Mn
Fe	14	n, p	2,9	^{56}Mn	2,6 h	0,85	600†	Co
Cu	14	n, 2n	10,9	^{62}Cu	9,8 mn	0,51	27.000†	Br, N, K...
Br	14	n, 2n	10,7	^{78}Br	6,4 mn	0,51	21.000†	Cu, N, K...
Ag	14	n, 2n	9,6	^{106}Ag	24 mn	0,51	120*	Sb, Cl, Sn...
Ba	14	n, 2n	9,3	^{137m}Ba	2,6 mn	0,66	600*	Ag
Hf	th	n, γ	—	^{179m}Hf	19 s	0,22	9.000‡	Pd, F
Au	14	n, n′	0,4	^{197m}Au	7,4 s	0,28	550*	
Pb	14	n, 2n	9,0	^{207m}Pb	0,84 s	0,57	20*	

* 10^9 n.cm^{-2}.s^{-1}, irrad. = 30 s, refr. = 3 s, compt. = 30 s.
† 10^9 n.cm^{-2}.s^{-1}, irrad. = 5 mn, refr = 10 mn, compt. = 5 mn.
‡ 5.10^7 n.cm^{-2}.s^{-1}, irrad. = 10 mn, refr. = 3 s, compt. = 10 mn.

ADAPTATION DE LA SOURCE DE NEUTRONS

Les réacteurs

Les seules sources suffisamment intenses de neutrons ont longtemps été constituées par les réacteurs nucléaires. Or ceux-ci sont encore très coûteux; il en résulte qu'ils sont habituellement situés dans des centres d'études (d'où localisation de leur utilisation) et sont employés par de nombreux chercheurs (d'où partage du temps d'utilisation). Ils ne sont donc pas utilisables dans l'industrie puisqu'on a vu que le contrôle en ligne d'un procédé imposait que l'on disposât entièrement d'une source de neutrons et que l'on pût l'implanter à l'endroit même où avait lieu ce procédé. Des assemblages sous-critiques ont par ailleurs été utilisés, soit en tant que multiplicateurs des neutrons produits par une autre source,[9] soit en les rendant momentanément surcritiques.[10] Cependant, les flux obtenus sont faibles pour des installations assez lourdes.

Les générateurs de neutrons

Il a fallu attendre le développement des générateurs de neutrons, au début des années 1960,[11] pour posséder les premières sources assez souples et intenses pour être utilisables dans l'industrie. Ces générateurs sont des petits accélérateurs de particule qui permettent de bombarder une cible deutérée ou tritiée avec un faisceau de quelques mA de deutérons sous une tension de 150 ou 400 kV. Le vide à l'intérieur du tube accélérateur est soit entretenu par pompage, soit conservé par scellement.[12] On peut ainsi obtenir des flux de neutrons rapides assez importants[13] pour doser, directement ou après thermalisation, plusieurs dizaines d'éléments avec une sensibilité meilleure que 0,1% (tableau 1).[7,8,14]

Tableau 2. Comparaison des sources de neutrons

	Sources isotopiques			Générateurs de neutrons		
	^{124}Sb–Be	^{238}Pu–Be	^{252}Cf	Tube pompé réaction D–D	Tube pompé réaction D–T	Tube scellé réaction D–T
Energie des neutrons, *MeV*	0,024	4	2,3	2,6	14,7	14,7
Débit de neutrons, *n/s*	3.10^{10}/g	5.10^{7}/g	$2\ 10^{9}$/mg	quelques 10^{9}	quelques 10^{11}	quelques 10^{10}
Sensibilité	moyenne*	faible	bonne	faible	bonne†	moyenne†
Variations lentes	$T\frac{1}{2} = 60$j	$T\frac{1}{2} = 89$a	$T\frac{1}{2} = 2{,}6$a	cible autorégénérée	vie de la cible = 10 h	vie du tube = 1.000 h
Variations rapides	non	non	non	faisceau instable	faisceau instable	faisceau instable
Précision	bonne	bonne	bonne	moniteur utile	moniteur nécessaire	moniteur utile
Volume d'échantillon	1 dm^3	1 dm^3	1 dm^3	quelques cm^3	quelques cm^3	1 cm^3
Automatisation de l'analyse	simple	simple	simple	facile	facile	facile
Souplesse d'installation	bonne	bonne	bonne	moyenne	moyenne	moyenne
Robustesse	bonne	bonne	bonne	moyenne	moyenne	moyenne
Commande de l'émission	possible	non	non	oui	oui	oui
Frais d'investissement	200.000 FF/g	30.000 FF/g	100.000 FF/mg	150.000 FF	150.000 FF	100.000 FF
Frais de fonctionnement	75.000 FF/an	0	30.000 FF/an	0	50 FF/h‡	20 FF/h§

* Intérêt pour les réactions (n, γ).

† Intérêt pour les réactions à seuil élevé, inconvénient pour les solutions aqueuses.

‡ Changement de cible.

§ Changement de tube.

FF Francs français.

Les sources isotopiques

Pendant le même temps, les sources isotopiques ont progressé. Ces sources sont constituées d'un radioisotope émetteur γ (par exemple ^{124}Sb)[15] ou α (par exemple ^{238}Pu, ^{241}Am, ^{210}Po, ^{227}Ac, ^{244}Cm ou ^{239}Pu), qui, par réaction sur du béryllium, produit des neutrons. Cependant, les sensibilités sont encore plus faibles qu'avec un générateur de neutrons.[6] Mais, depuis quelques années, une nouvelle source très attrayante est disponible, seulement en très faible quantité: le californium 252 qui émet des neutrons par fission spontanée.[16]

Comparaison des sources de neutrons

Le tableau 2 résume les qualités comparées des sources qui semblent les mieux adaptées à l'industrie. On voit que:

—lorsqu'un flux moyen est suffisant, les sources (α, n) à longue vie sont les moins coûteuses et les plus souples (les sources isotopiques s'adaptent facilement à la forme et au volume des échantillons, ce qui augmente le flux utile),

—lorsqu'un flux élevé est nécessaire (et en particulier lorsque la réaction utile a un seuil énergétique très haut, comme pour le dosage de l'oxygène ou de l'azote), il faut utiliser un générateur de neutrons D–T à tube pompé mais on doit tenir compte des variations de flux et les protections sont évidemment plus lourdes; par contre, on peut commander l'émission de neutrons (par exemple au moyen d'un écran escamotable placé dans le faisceau de deutérons).

ADAPTATION DU TRANSFERT EN FONCTION DE L'ECHANTILLONNAGE

Analyse discrète (Fig. 1)

Pour la plupart des contrôles industriels, on se contente d'une analyse discrète, c'est-à-dire portant sur un échantillon prélevé dans la production. On a vu cependant que la méthode ne peut s'adapter à l'industrie que si le prélèvement conduit à un échantillon:

—représentatif (c'est-à-dire de même composition moyenne que le produit à analyser),

—homogène,

—de préparation simple,

—de forme appropriée au système d'analyse.

En activation, la séquence d'analyse est alors la suivante:

1—pesée de l'échantillon, 2—introduction en face de la source de neutrons, 3—irradiation pendant un temps défini, 4—refoulement vers un détecteur et refroidissement pendant un temps défini, 5—comptage pendant un temps défini, 6—éjection. Il peut y avoir plusieurs

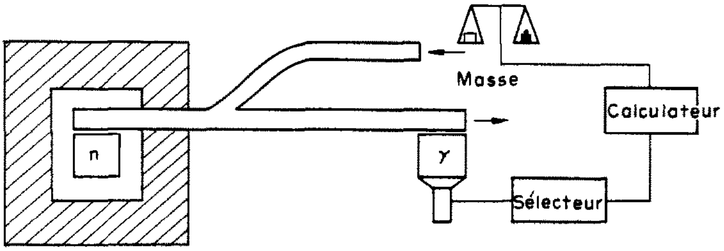


Fig. 1 Principe de l'analyse discrète.

comptages après des temps de refroidissement croissants afin d'éliminer les interférences dues à des périodes courtes. Cette séquence peut être répétée dans le cas des périodes très courtes, le comptage pouvant même être effectué en position d'irradiation (activation cyclique).[17] L'échantillon est habituellement véhiculé au moyen d'un système de transfert pneumatique, ce qui donne une grande souplesse d'installation.[18] Des dispositifs de rotation de l'échantillon autour de son axe à l'irradiation et au comptage peuvent compenser son hétérogénéité.[19]

Analyse en continu[20] (Fig. 2)

L'analyse par activation possède certaines qualités (en particulier la pénétration des rayonnements utilisés et la non-destruction de l'échantillon), qui permettent d'envisager de faire les dosages en continu. Ainsi, il n'y a plus de problème d'échantillonnage, l'ensemble de la production est analysé et on se rapproche autant que possible d'une véritable mesure en ligne. Le système de transfert est constitué par la bande transporteuse (solides) ou par la tuyauterie (liquides) qui fait défiler continuellement le produit en face de la source de neutrons puis en face du détecteur. Le débit du produit, ainsi que les volumes de la cellule d'irradiation, de celle de comptage et de la liaison entre les deux, doivent être optimisés en fonction des périodes des radioisotopes formés:[21] une diminution du débit crée une perte de comptage par augmentation du temps de refroidissement mais une augmentation du débit diminue le temps d'irradiation. La mesure des gamma prompts de capture ou de diffusion inélastique permet de s'affranchir du débit et fournit une réponse instantanée.

Dans le cas des solides, le débit de matière est facilement obtenu (si l'humidité est constante) par une bascule liée à la bande dont la vitesse est par ailleurs mesurée. Il est par contre difficile de maintenir des géométries constantes à l'irradiation et au comptage; de plus, ces géométries sont peu favorables et les sources de neutrons doivent être intenses.

Dans le cas des liquides, le débit de matière est fourni par un débitmètre et par une jauge de densité mais sa mesure est souvent délicate. Un débit minimum est nécessaire pour maintenir les suspensions. Par contre, les géométries sont bien stables et assez favorables pour envisager l'emploi de sources isotopiques.

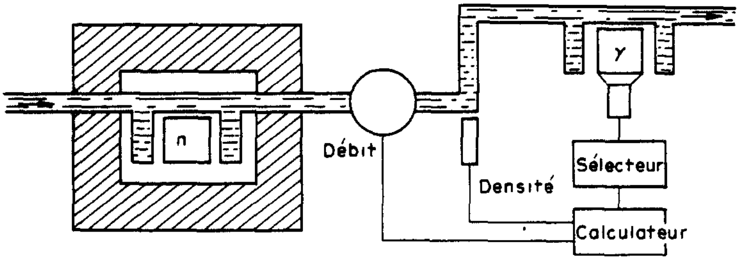


Fig. 2. Principe de l'analyse en continu.

Analyse par recirculation (Fig. 3)

Cette méthode est intermédiaire entre les deux précédentes. En effet, il y a prélèvement d'un échantillon mais l'analyse est ensuite continue et de plus cyclique. Une partie du produit à analyser est admise dans une boucle puis est recyclée plusieurs fois entre la source de neutrons et le détecteur avant d'être éjectée. Ainsi l'activité induite augmente à chaque cycle et on peut se contenter d'une source isotopique. De plus, on peut calculer le circuit

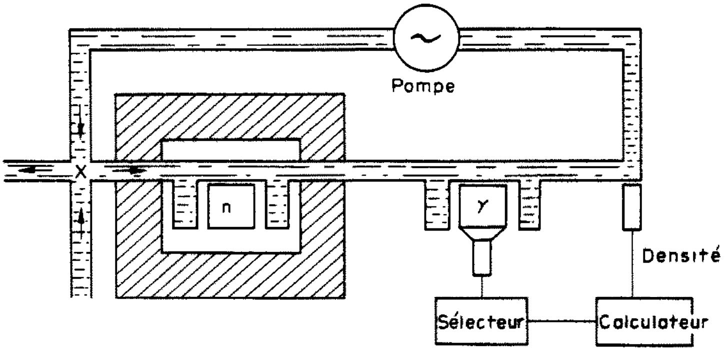


Fig. 3. Principe de l'analyse par recirculation.

de façon que l'activité atteigne un équilibre indépendant du débit, ce qui est intéressant pour les suspensions.[22]

Comparaison des échantillonnages

Le tableau 3 indique quelles sont les méthodes d'échantillonnages les mieux adaptées. On voit que, si l'analyse en continu constitue probablement l'avenir:

—l'analyse discrète se contente de systèmes de transfert simples, polyvalents et disponibles sur le marché.

—l'analyse par recirculation semble surtout intéressante pour les suspensions.

Tableau 3. Comparaison des échantillonnages

	discret	continu	recirculation
Sensibilité	bonne	faible* moyenne†	bonne
Précision	bonne	moyenne	bonne
Volume d'échantillon	quelques cm^3	pas d'échantillon	1 dm^3
Automatisation de la contreréaction	possible	simple	facile
Souplesse d'installation	bonne	moyenne	moyenne
Frais d'investissement	à partir de 35.000 FF	élevés* moyens†	moyens

* Pour les solides.
† Pour les liquides.

ADAPTATION DU TRANSFERT EN FONCTION DE L'ETALONNAGE

Conditions de l'étalonnage

On a vu qu'une méthode industrielle d'analyse devait permettre un réétalonnage commode. On va donc comparer l'activité induite dans l'échantillon avec celle induite dans un ou plusieurs étalons (droite d'étalonnage). Cependants ces étalons doivent répondre à certaines conditions:[23]

—avoir même forme et mêmes dimensions que l'échantillon,

—présenter des effets de matrice (autoprotection, autoabsorption), des temps morts et des blancs identiques à ceux de l'échantillon,

—être homogènes et contenir une quantité bien déterminée de l'élément à doser.

Les étalons doivent être ensuite irradiés et comptés dans des conditions si possible identiques (ou tout au moins bien définies par rapport) à celles des échantillons (géométries d'irradiation et de comptage, temps d'irradiation, de refroidissement et de comptage, flux de neutrons, efficacité du détecteur, étalonnage du sélecteur). Ceci est facile avec les sources isotopiques qui fournissent un flux stable. Nous allons décrire les dispositifs utilisables avec les générateurs de neutrons pour corriger les variations de flux.

Utilisation d'un moniteur

Echantillon et étalon sont irradiés successivement, chacun avec un moniteur (pastille de cuivre, compteur BF_3, activation de l'eau de refroidissement des cibles, ...).[24] On peut également utiliser un élément se retrouvant en teneur constante d'un échantillon à un autre (moniteur interne).[25] Cependant, exception faite de quelques montages particuliers,[26–28] ces corrections ne tiennent pas compte de la période du radioisotope utilisé pour le dosage.

Stabilisation du flux

Echantillon et étalon sont encore irradiés successivement mais on supprime la correction de flux en le stabilisant. Le principe consiste à asservir l'intensité du faisceau de deutérons frappant la cible en fonction du débit de neutrons mesuré par un détecteur. On peut agir sur l'extraction du courant d'ions, sur la déflexion d'une partie du faisceau ou bien par pulsation. Ce dernier procédé permet de conserver un impact constant sur la cible. La source d'ions est pulsée à fréquence fixe mais le taux de travail peut varier entre 10 et 55%.[29] On peut ainsi obtenir un débit de 2.10^{10} n/s ± 0,5% pendant 9 h avec une cible tritiée.

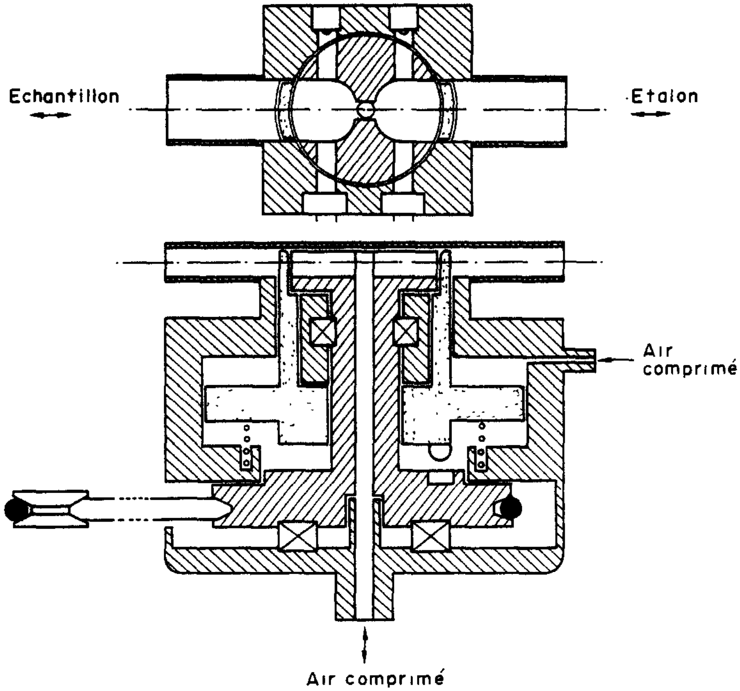


Fig. 4. Station pour irradiation simultanée de l'échantillon et d'un étalon avec rotations autour de leur axe et de l'axe de la cible.[34]

Irradiation simultanée

Echantillon et étalon sont irradiés simultanément. Cela exige un double système de transfert et en particulier une double station d'irradiation. De plus, on ne peut doser qu'un seul élément dans l'échantillon (sauf si on utilise un étalon multiélément[30]) et, si la période utilisée pour le dosage est longue, il faut de nombreux étalons.

Echantillon et étalon peuvent être irradiés l'un derrière l'autre par rapport à la cible[31] mais la détermination du rapport de flux entre les deux positions est parfois délicate. Si échantillon et étalon sont irradiés l'un à côté de l'autre, leur volume est plus faible et il est nécessaire de les faire tourner autour de l'axe de la cible;[32] il en résulte des stations d'irradiation assez délicates[33,34] mais fournissant une grande précision (Fig. 4).

Comparaison des contrôles de flux pour générateur de neutrons

Le tableau 4 montre que:

—pour les installations industrielles destinées à doser plusieurs éléments, la stabilisation est le système le plus simple,

—en laboratoire industriel, l'irradiation simultanée donne la meilleure précision.

Tableau 4. Comparaison des contrôles de flux pour générateur de neutrons

	Moniteur	Stabilisation	Irradiation simultanée
Sensibilité	bonne	moyenne	bonne
Précision	faible	moyenne	bonne
Automatisation de l'analyse	facile	simple	facile
Frais d'investissement	25.000 FF	40.000 FF	50.000 FF

ADAPTATION DU DETECTEUR

Deux types de détecteurs sont disponibles en spectrométrie gamma: les scintillateurs NaI(Tl) et les semi-conducteurs Ge(Li). Le tableau 5 permet de comparer leurs qualités respectives. En fait, on se rend compte que, si les semi-conducteurs sont utiles en laboratoire afin de déterminer la possibilité d'un dosage (étude des interférences),[35] les scintillateurs sont actuellement les seuls à être employés dans l'industrie du fait de:

—leur plus grande efficacité (possibilité de se contenter de flux plus faibles, de temps d'irradiation et de comptage plus brefs),

—leur plus grande robustesse (pas de refroidissement à l'azote liquide).

Tableau 5. Comparaison des détecteurs

	scintillateur	semi-conducteur
Efficacité	quelques %	quelques ‰
Résolution	quelques %	quelques ‰
Robustesse	bonne	moyenne
Frais d'investissement	10.000 FF	60.000 FF

L'utilisation de deux détecteurs montés en coïncidence est intéressante lorsque le radioisotope utilisé pour le dosage est émetteur de positrons (exemple: dosage du cuivre en présence de silicium).

ADAPTATION DU TRAITEMENT DES INFORMATIONS

Utilisation d'un ou de plusieurs sélecteurs monocanaux

Lorsque le radioisotope utilisé pour le dosage est le seul émetteur gamma (dans la zone d'énergie choisie et après le temps de refroidissement choisi), on peut se contenter d'un sélecteur monocanal dont la fenêtre est centrée sur le photopic. Les impulsions recueillies pendant le temps de comptage sont envoyées dans une échelle et on a (Fig. 5):

$$\frac{m}{M} = \frac{n - B}{N - B}$$

avec:

m et M: masses de l'élément à doser dans l'échantillon et dans l'étalon,
n et N: nombres d'impulsions comptées pour l'échantillon et pour l'étalon.
B: bruit de fond pour le même temps de comptage (ou blanc).

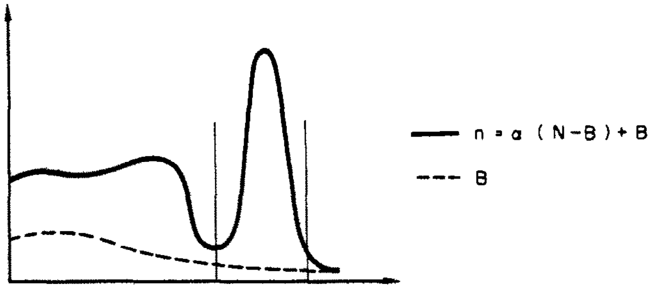


Fig. 5. Utilisation d'un monocanal sans refroidissement.

Lorsque le comptage du radioisotope utilisé pour le dosage est perturbé par un seul autre radioisotope à période plus longue, on peut encore se contenter d'un sélecteur monocanal et faire deux comptages successifs. On a (Fig. 6):

$$\frac{m}{M} = \frac{k}{(k - k')} \left\{ \frac{n_1 - B_1 - k'(n_2 - B_2)}{N_1 - B_1} \right\}$$

avec:

$$k = \frac{N_1 - B_1}{N_2 - B_2}$$

et

$$k' = \frac{N'_1 - B_1}{N'_2 - B_2}$$

m et M: masses de l'élément à doser dans l'échantillon et dans l'étalon,
n, N et N': nombres d'impulsions comptées pour l'échantillon, pour l'étalon de l'élément à doser et pour l'étalon de l'élément interférant.
B: bruit de fond pour le même temps de comptage (ou blanc),
1 et 2: indices correspondant aux deux comptages successifs.

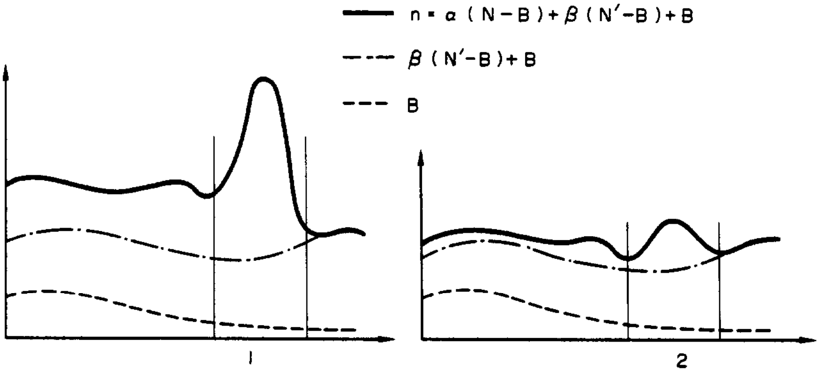


Fig. 6. Utilisation d'un monocanal avec refroidissement.

Lorsque le comptage du radioisotope utilisé pour le dosage est perturbé par un seul autre radioisotope produisant un photopic plus énergétique, on peut utiliser un seul comptage avec deux monocanaux centrés sur chacun des photopics. On a (Fig. 7):

$$\frac{m}{M} = \frac{n_1 - B_1 - k(n_2 - B_2)}{N_1 - B_1}$$

avec:

$$k = \frac{N'_1 - B_1}{N'_2 - B_2}$$

m et M: masses de l'élément à doser dans l'échantillon et dans l'étalon,
n, N et N': nombres d'impulsions comptées pour l'échantillon, pour l'étalon de l'élément à doser et pour l'étalon de l'élément interférant,
B: bruit de fond pour le même temps de comptage (ou blanc),
1 et 2: indices correspondant aux deux canaux d'énergies croissantes.

On peut encore combiner plusieurs sélecteurs monocanaux avec déclenchement de plusieurs comptages après des temps de refroidissement croissants, de façon à obtenir autant de mesures de l'activité de l'échantillon qu'il y a d'éléments interférants. Il en résulte des

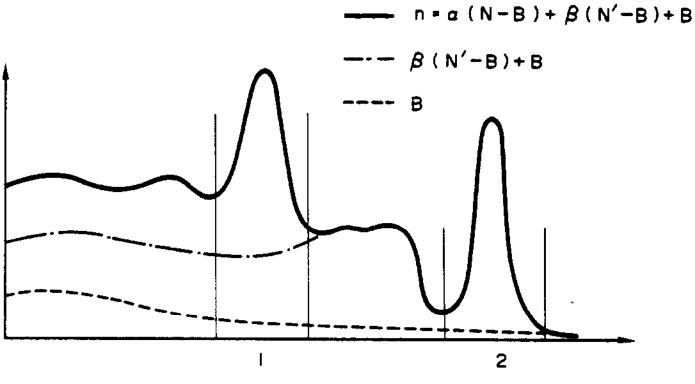


Fig. 7 Utilisation de deux monocanaux sans refroidissement.

programmateurs de transfert assez complexes mais le traitement des informations reste toujours assez simple pour être effectué en ligne par un très petit calculateur. L'utilisation de plusieurs temps de refroidissement allonge le temps de réponse mais il est souvent possible d'imbriquer les séquences de façon à ne pas trop diminuer le débit d'analyses.

Utilisation d'un sélecteur multicanal

Dès que les spectres obtenus sont un peu complexes, il est indispensable de les analyser plus finement au moyen d'un sélecteur multicanal. Chaque pic peut être mesuré séparément[36] mais il est préférable de traiter globalement l'ensemble des informations contenues dans tous les canaux par la méthode des moindres carrés. Celle-ci reconstitue le spectre de l'échantillon à partir des spectres des étalons de chacun des éléments constituants et les quantités de ces derniers dans l'échantillon se déduisent des coefficients de pondération.[37]

Cependant, la résolution d'un tel système d'équations linéaires nécessite un calculateur possédant une mémoire déjà assez importante, de l'ordre de 8 à 12 k mots de 20 bits. La mise en ligne de ce dernier exige une interface assurant le couplage entre multicanal et calculateur et un téléimprimeur pour commander et contrôler le calculateur puis sortir les résultats. Par contre, le même calculateur peut aussi être utilisé en guise de sélecteur multicanal[38] et de programmateur de transfert.

Cette méthode n'impose qu'un seul comptage et est donc très rapide. Bien que cela ne semble pas avoir été exploité il pourrait être intéressant d'ajouter la discrimination par la période à celle par l'énergie et d'appliquer les moindres carrés à la surface spectrale donnant l'amplitude en fonction de l'énergie et du temps, c'est-à-dire à un ensemble de spectres obtenus à intervalles réguliers sur un nombre plus faible de canaux.

Corrections de dérive et de temps mort

Le résultat du traitement des informations n'est exact qu'en l'absence de dérives du gain et du zéro et que si on tient compte des pertes dues au temps mort (qu'un comptage en temps actif ne peut entièrement compenser lorsque les périodes sont courtes).

Lorsqu'on utilise un petit calculateur, les dérives et le temps mort sont généralement corrigés par des circuits électroniques.[39–41] Par contre, un calculateur moyen permet d'opérer ces corrections par le calcul.[42,43]

Les calculateurs peuvent effectuer d'autres corrections: différence de conditions opératoires entre échantillon et étalon, calcul de la teneur à partir de la masse....

Tableau 6. Comparaison des méthodes de traitement des informations

	Monocanal	Multicanal*
Résolution	faible	bonne
Débit de matière analysée	bon*–moyen†	bon
Temps de réponse	court*–moyen†	court
Automatisation de l'analyse	simple*–facile†	facile
Robustesse	bonne	moyenne
Frais d'investissement	50.000 FF*	300.000 FF

* Un seul comptage.
† Plusieurs comptages successifs.

Comparaison des méthodes de traitement des informations

Le tableau 6 montre que:

—le monocanal n'est utilisable que dans les cas très simples et impose plusieurs comptages successifs avec imbrication des séquences dès que plusieurs radioisotopes sont simultanément en présence,

—le multicanal est la solution polyvalente mais aussi la plus coûteuse.

Le résultat est habituellement imprimé sous forme numérique. Afin d'automatiser la contreréaction et de permettre un contrôle en boucle, il peut être transmis sous cette forme à un calculateur ou bien transformé en signal analogique sous forme d'une tension ou d'un courant.

PRINCIPALES APPLICATIONS (Tableaux 1 et 7)

Dosage de l'oxygène

Cette application est certainement la plus importante. Elle intéresse surtout la métallurgie. La réaction utilisée donne une remarquable sensibilité mais nécessite l'emploi d'un générateur de neutrons. La période de ^{16}N permet une réponse rapide et l'énergie des gamma émis autorise l'emploi d'un monocanal.

Nous allons décrire brièvement une installation mise en place dans une aciérie L.D. belge, au pied même des convertisseurs.[44,45] Un convertisseur a une charge de 200 tonnes et une élaboration dure 20 mn. On effectue deux prélèvements par élaboration au moyen d'une lingotière plongeante. Le prélèvement est envoyé dès refroidissement dans une salle de préparation où un tour spécial permet de découper en 1,5 mn un disque de hauteur 9 mm et de diamètre 26 mm (poids = 36 g). Puis l'échantillon est placé dans un système de transfert à section rectangulaire en même temps qu'un étalon et leurs déplacements sont pris en charge par un programmateur: irradiation simultanée (l'un derrière l'autre par rapport à la cible) pendant 5 s, refoulement (chacun vers un scintillateur) en 2 s, comptage simultané pendant 20 s. Le résultat est imprimé en μg d'oxygène moins de 3 mn après l'arrivée du prélèvement.

Plusieurs autres installations fonctionnent selon des principes très voisins.[33,46] Par ailleurs, des essais ont montré la possibilite de doser l'eau et le sel dans le pétrole brut.[47]

Dosage de l'azote

Ce dosage est important pour les industries alimentaires. La réaction utilisée nécessite encore l'emploi d'un générateur de neutrons. Les teneurs élevées permettent une réponse rapide mais l'énergie des gamma émis par ^{13}N oblige à faire un traitement assez complexe des informations pour éliminer les interférences.

Une installation pour le dosage simultané de N, P, K et Ca est en début d'exploitation en U.R.S.S.[48] Elle doit fournir 500 dosages par journée de 8 h. On dispose donc de 50 s par échantillon et le système de transfert doit permettre de compter un échantillon pendant qu'un autre se fait irradier. L'échantillon est placé dans une capsule de 60 cm^3, elle-même placée dans un furet. Les déplacements sont commandés par un calculateur: enregistrement du numéro d'ordre et de la masse d'échantillon lors de l'introduction du furet, envoi du furet face contre cible (transfert de 3 s), commande de l'irradiation pour une durée de 47 s (avec stabilisation du flux et rotation du furet autour de l'axe de la cible), envoi en station de décapsulage, envoi de la capsule en station de stockage (disparition des activités parasites dues à l'oxygène et au sodium), envoi en face d'un premier scintillateur 6

Tableau 7. Comparaison de quelques applications industrielles

Elément matrice	Oxygène acier	Azote (et P, K, Ca) aliments	Fluor eau	Silicium minerais de fer en suspension
Radioisotope utilisé	^{16}N	^{13}N	^{19}O	^{28}Al
Source de neutrons	D–T, pompé	D–T, pompé	D–T, pompé	^{238}Pu–Be
Echantillonnage	discret	discret	continu	recirculation
Etalonnage	irradiation simultanée	stabilisation du flux	irradiation simultanée	source isotopique
Détecteur	scintillateur	scintillateur	scintillateur	scintillateur
Traitement des informations	monocanal	monocanal + multicanal	monocanal	monocanal
Date lère installation	1966*	1972*	essais	1970†
Nombre d'installations en service	2	1	—	2
Autres installations similaires	oui	oui (N seulement)	—	non
Précision relative	2%	10%	< 10%	2%
Temps de réponse	< 1 mn	22 mn	continu	6 mn
Nombre de dosages en 8 h	300	500	continu	50
Prix d'un dosage	3,2 FF (1969)[1]	5 FF (1972)	--	0,45 $ (1971)[53]

* Fabricant: SAMES (France).

† Fabricant: Nuclear Chicago (U.S.A.).

mn après le début de l'irradiation pour un comptage de 47 s sur 200 canaux entre 0,1 et 3,5 MeV (activités dues à ^{13}N, ^{30}P, ^{28}Al et ^{38}K principalement), envoi dans une deuxième station de stockage, envoi en face d'un second scintillateur 20 mn après le début de l'irradiation pour un comptage de 47 s avec un monocanal (activités dues à ^{38}K et ^{44}K), éjection de la capsule. Le calculateur détermine les teneurs en N, P et K à partir du premier comptage par la méthode des moindres carrés puis calcule la teneur en Ca à partir du second comptage, après soustraction de l'influence de K.

Il existe également d'autres installations ne dosant que l'azote.[49]

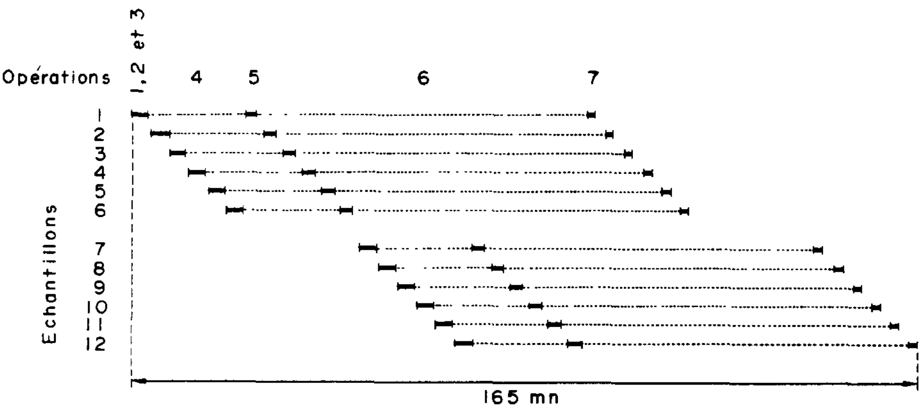
Dosage du fluor

Des essais ont été effectués pour doser en continu le fluor dans l'eau potable en utilisant la formation de ^{19}O.[50] L'eau circule avec un débit de 224 cm^3/mn, pénètre dans une cellule d'irradiation de volume 72 cm^3 en face d'un générateur (cellule à double courant, ce qui permet un étalonnage continu), puis dans une canalisation de liaison de volume 580 cm^3, puis dans une cellule de comptage de volume 72 cm^3 en face d'un scintillateur.

Dans les mines, le dosage rapide du fluor dans la fluorite a été réalisé en utilisant la formation de ^{16}N au moyen d'une source isotopique.[51,52] Ainsi, l'oxygène n'interfère pas et le comptage peut être effectué dans les mêmes conditions que pour le dosage de l'oxygène.

Dosage du silicium

Ce dosage est surtout intéressant dans les mines. La réaction produisant ^{28}Al a une sensibilité qui permet de se contenter d'une source isotopique. La station d'irradiation doit



Opération	Nature	Durée, mn
1	Irradiation	0,5
2	Refroidissement oxygéne	1,5
3	Comptage Si+Fe (1,78 MeV)	1
4	Refroidissement silicium	21
5	Comptage Al+Fe (1,02 MeV)	2
6	Refroidissement aluminium	70
7	Comptage fer (0,85 MeV)	1

Fig. 8 Imbrication des séquences pour le dosage de Fe, Si et Al dans des minerais de fer avec trois monocanaux.[54] (Reprinted by permission of the copyright holders.)

être entourée de cadmium pour éviter une interférence due à l'activation de l'aluminium par les neutrons thermiques.

Quelques installations sont à présent exploitées en laverie de minerais de fer.[53] L'échantillon étant sous forme de suspension, on a adopté la méthode par recirculation. Entre deux échantillons, la boucle est parcourue par de l'eau. L'échantillon (1 dm^3) est injecté jusqu'à remplir complètement la boucle (500 cm^3). Puis il circule avec un débit de l'ordre de 4 dm^3/mn autour d'une source ^{238}Pu–Be et autour d'un scintillateur couplé à un monocanal. La densité est mesurée au moyen d'une jauge gamma. Six minutes après l'injection, l'échantillon est éjecté, le résultat est imprimé en % de $Si\ O_2$ et le circuit est rincé.

Des essais de dosage au moyen d'un générateur de neutrons et de trois comptages successifs avec sélecteur monocanal ont montré par ailleurs qu'il était possible de doser Fe, Si et Al dans 85 échantillons de minerais de fer par 24 h (Fig. 8).[54] Une autre installation permet de doser Si et Al dans la bauxite.[55]

Il faut enfin signaler la commercialisation en Finlande d'un système permettant de doser Si, Cr et Al dans des concentrés de chrome.[56] L'échantillon (420 cm^3) est irradié par une source ^{241}Am–Be. Puis, après transfert, les activités dues à ^{28}Al, ^{52}V et ^{27}Mg sont enregistrées par trois monocanaux.

CONCLUSIONS

Les quelques exemples d'application cités plus haut montrent que les progrès des sources de neutrons et des systèmes de transfert ont d'ores et déjà permis à l'analyse par activation neutronique de s'adapter aux conditions industrielles dans la mesure où l'analyse porte sur un prélèvement.[44,53] On a même vu que le dosage simultané de plusieurs éléments est possible depuis peu grâce à la mise en ligne de calculateurs appliquant les moindres carrés.[48]

Cependant, comme pour les autres méthodes industrielles, l'avenir est probablement constitué par l'analyse en continu et, malgré quelques essais,[50,57] de nombreux progrès restent à faire.

Il importe, en effet, de ne pas oublier que l'activation neutronique vient en concurrence avec beaucoup d'autres techniques;[58] son adoption dépend donc non seulement du problème analytique particulier à résoudre, mais aussi de l'état de développement des autres techniques au moment où il faut résoudre ce problème.

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Summary—After a statement of the main requirements for an analytical system to be suitable for use in industry, a detailed examination is made of the response of each part of an activation installation (choice of neutron source and detector, transfer system for standards and samples, data handling) to these requirements. Several applications already established in industry are mentioned (determination of oxygen, nitrogen, fluorine, silicon). Some continuous analyses are also mentioned.

Zusammenfassung—Nach Darstellung der Hauptanforderungen, die an ein analytisches System zu stellen sind, damit es in der Industrie nützlich eingesetzt werden kann, werden alle Teile einer Aktivierungsapparatur (Neutronenquelle, Detektor, Standard- und Proben-Manipulation, Datenverarbeitung) eingehend daraufhin untersucht, wie weit sie diese Anforderungen erfüllen. Einige in der Industrie bereits eingerichtete Anwendungen werden erwähnt (Bestimmung von Sauerstoff, Stickstoff, Fluor, Silicium). Einige kontinuierliche Analysen werden ebenfalls erwähnt.

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SPECTROPHOTOMETRIC DETERMINATION OF DISSOLVED OXYGEN WITH TRIS(4,7-DIHYDROXY-1,10-PHENANTHROLINE)IRON(II)

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Summary—Tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) reacts rapidly and quantitatively with dissolved oxygen in alkaline aqueous solution. In ammoniacal solution, the reaction is accompanied by the disappearance of the intense red colour of the iron(II) compound, which gives way to the pale gray, slightly-dissociated ion tris(4,7-dihydroxy-1,10-phenanthroline)iron(III). By measurement of the absorbance of a solution containing the ferrous compound before and after the injection of an oxygen-containing solution, the concentration of dissolved oxygen in the sample can be accurately determined in the range 1–20 ppm.

4,7-Dihydroxy-1,10-phenanthroline was first prepared by Snyder and Freier,[1] and was used by Schilt, Smith and Heimbuch[2] as a reagent for the spectrophotometric determination of iron in strongly alkaline media. Improvements in the synthesis of 4,7-dihydroxy-1,10-phenanthroline were made by Poe,[3] who also found that the iron(II) compound of 4,7-dihydroxy-1,10-phenanthroline is a remarkably strong reducing agent, the formal reduction potential in $1M$ sodium hydroxide being $-0{\cdot}11$ V. In the present paper we report on the reaction of the iron(II) compound and oxygen.

EXPERIMENTAL

Reagents

A stock solution of 4,7-dihydroxy-1,10-phenanthroline (Hach Chemical Company, Ames, Iowa 50010, U.S.A.), $6 \times 10^{-4}M$, was prepared by dissolving 0·15 g of the hydrochloride in 1 litre of a buffer $2{\cdot}0M$ in ammonia and $0{\cdot}1M$ in ammonium chloride, stored in a Machlett burette under nitrogen.

A solution of iron(II) was prepared by dissolving 3·35 g of ferrous ammonium sulphate, 1·5 g of tartaric acid, and 1 ml of concentrated ammonia solution in 15 ml of water. The solution was stored in a serum bottle covered with a rubber septum. The commercial nitrogen used contained a significant amount of oxygen; this oxygen was removed by bubbling the nitrogen through vanadium(II) sulphate solution stored over zinc analgam,[4] then through alkaline permanganate [to remove hydrogen sulphide formed in the vanadium(II) tower], and finally through water

Apparatus

An all-glass flow-through cell system was constructed for use with a Beckman DU spectrophotometer, Fig. 1 A cell holder was altered to accept a 1·00 cm cell with side-arm, the cell being inserted into the bottom of the holder (Fig. 1, inset). The two glass tubes rising from the sample compartment were painted black and were inserted through two holes in a strip of black latex rubber which covered the compartment and blocked out light from the room. Four ball-and-socket joints were included in the apparatus to permit movement of the cell in and out of the light-path. Flexible rubber or synthetic tubing could not be used because they are permeable to oxygen. A rubber septum was used as a sample-injection port and a Teflon-coated magnetic stirring bar was used to circulate the liquid through the system. The Teflon coating slowly released oxygen into the solution.

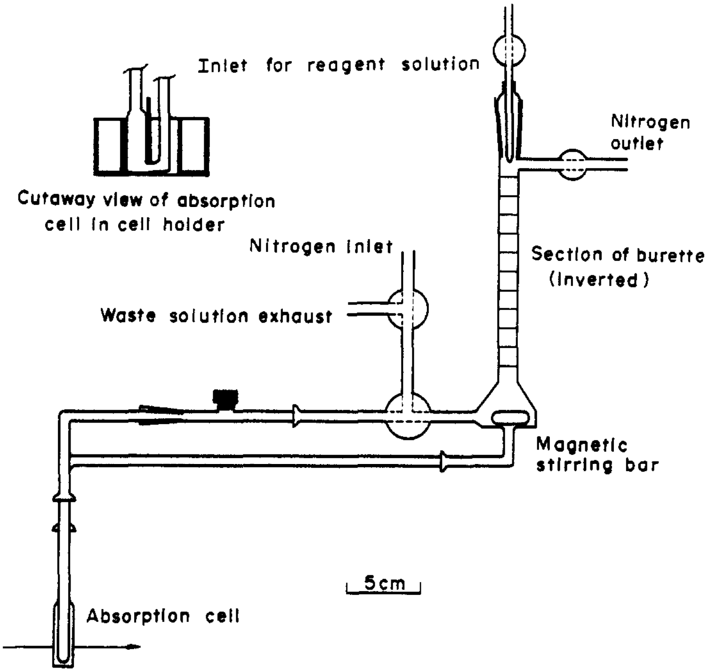

Fig. 1. Flow-through cell system.

causing a steady decrease in absorbance during use; this effect was eliminated by soaking the stirring bar in alkaline sodium hydrosulphite solution for a week or two before placing it in the apparatus. A glass-covered stirring bar introduced so much suspended silica from wear on the glass vessel that it had to be rejected. The calibrated portion of the apparatus was a section of a 50 ml burette, inverted. The volume of the apparatus when filled to the zero mark on the burette was determined. The total volume of solution circulating in the system, original solution plus sample, could thus be determined. The reagent solution inlet was fitted with a short section of Tygon tubing, which formed an air-tight seal when the tip of the Machlett burette was inserted for filling the apparatus.

Absorption spectra were obtained on a Cary 14 recording spectrophotometer.

Procedure

The flow-through cell system was purged by passage of nitrogen for 30 min and was then filled with the phenanthroline solution. Enough iron(II) solution (~4 μl) was injected into the system through the rubber septum to bring the absorbance at 520 nm to 0·7–0·8. A measured volume of the sample was injected through the septum from a 1 ml tuberculin syringe. After the system had come to equilibrium (about 15 min) the absorbance was measured. After several samples had been injected, enough ammoniacal sodium hydrosulphite solution (5 g/100 ml) was injected from a 50 μl syringe to bring the absorbance back to 0·7–0·8. Within a few minutes the system was ready to use for more determinations.

RESULTS AND DISCUSSION

Ferrous iron reacts with 4,7-dihydroxy-1,10-phenanthroline in alkaline solution to form an intensely red compound in which the ratio of iron to phenanthroline is 1:3.[2] The ferrous compound is easily oxidized to a gray-black iron(III) compound which is stable indefinitely in 0·2–4*M* ammonia solution, and in general in the pH range 8·5–12. At higher pH this gray-black compound is converted into an amber compound. By application of the method of continuous variations[5] it was established that in the gray-black iron(III) compound three molecules of phenanthroline are combined with one iron(III) ion and that

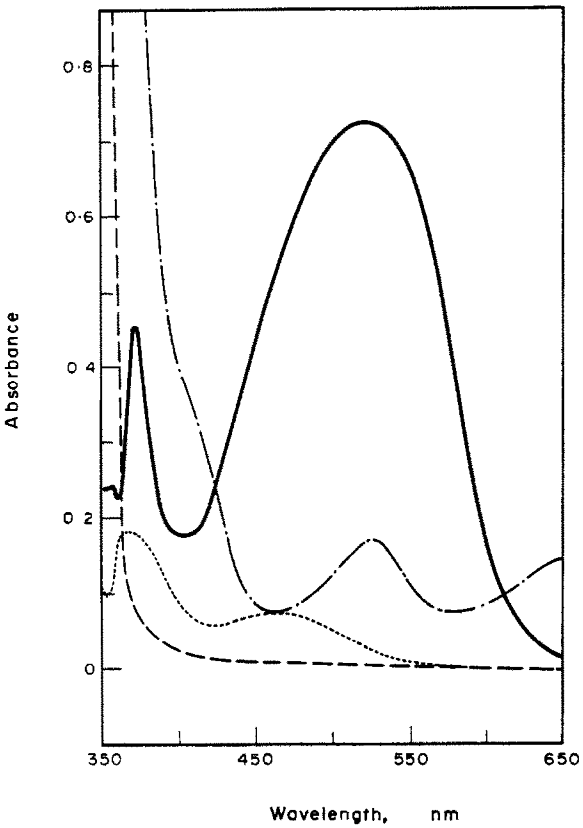

Fig. 2. Absorption spectra of the iron(II) and iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline.
—— Tris(4,7-dihydroxy-1,10-phenanthroline)iron(II), 4·89 × $10^{-5}M$. ..... Bis(4,7-dihydroxy-1,10-phenanthroline)iron(III), 4·89 × $10^{-5}M$. -·-·- Tris(4,7-dihydroxy-1,10-phenanthroline)iron(III), 5·0 × $10^{-5}M$. ----- 4,7-Dihydroxy-1,10-phenanthroline, 4·0 × $10^{-4}M$.

in the amber iron(III) compound two molecules of phenanthroline are combined with one iron(III) ion.

The absorption spectra of the iron(II) and iron(III) compounds between 350 and 650 nm are shown in Fig. 2. The wavelength of maximum absorbance of the iron(II) compound, 520 nm, and molar absorptivity, $\epsilon = 1{\cdot}48 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$, were the same as reported earlier by Schilt and co-workers.[2] These workers showed that the molar absorptivity of the iron(II) compound is independent of the concentration of alkali; in the present study this was shown to be true also for ammonia buffers as dilute as 0·2*M* ammonia–0·1*M* ammonium chloride (pH = 9·7). The molar absorptivity in all solutions agreed with the reported value. At 520 nm the absorbance of the iron(III) compound in ammonia solution is constant over the pH range 8·5–12 (Fig. 3), $\epsilon = 3{\cdot}30 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. At higher pH values the absorbance of the iron(III) compound decreases owing to the formation of the amber iron(III) compound.

A solution 2*M* in ammonia and 0·1*M* in ammonium chloride was chosen as the medium for the reagent because both the oxidized and reduced forms of the iron–phenanthroline

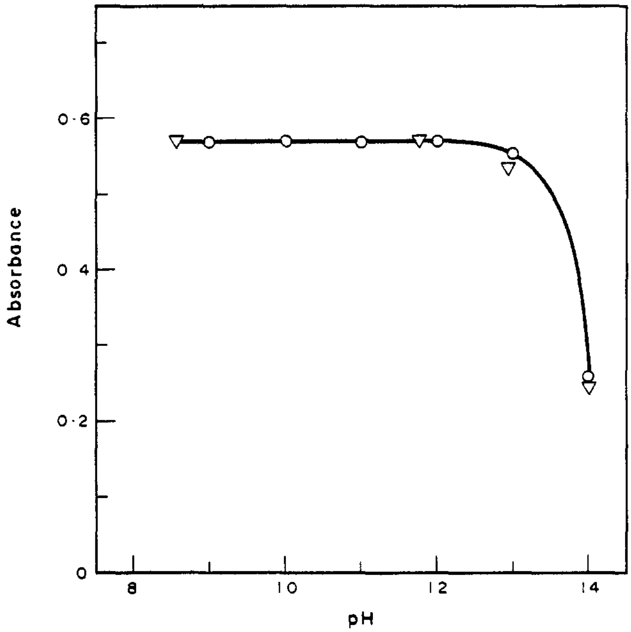

Fig. 3. Absorbance of Tris(4,7-dihydroxy-1,10-phenanthroline)iron(III) as a function of pH.
○ Absorbance measured on the same day as solutions were prepared.
△ Absorbance measured two weeks after solutions were prepared.

compound are stable in it and the molar absorptivities reproducible. Injection of a concentrated solution of ferrous ammonium sulphate into the solution containing the organic ligand resulted in the formation of a dense, gelatinous precipitate which could not be redissolved. Addition of tartrate to the solution prevented such precipitation. It was inferred from reference (2) that the amount of tartrate added would not interfere with the formation of Tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) and this proved true.

Absorbance values measured after injection of successive portions of water in equilibrium with air into the flow-through cell system charged as described above, are reported in Fig. 4. The measured absorbances were corrected for dilution by means of the relation $A_c = A_m(V_m/V_0)$, where A_c is the corrected absorbance, A_m the absorbance measured, V_m the volume at the time of measurement, and V_0 the initial volume.

The corrected absorbance decreased linearly with the amount of oxygen added, until the absorbance became very low, slightly high readings then being obtained for A_c because the reaction is considerably slower in this region. No further change in A_c occurred on addition of excess of oxygen. The intersection of the two straight-line portions of the curve marked the equivalence point in the titration of the reagent with oxygen. This point, as calculated from the absorbance data and the molar absorptivities of the iron(II) and (gray) iron(III) compounds, occurred when one molecule of oxygen had been added per four iron(II) compound oxidized:

$$4\mathrm{Fe(diOHphen)_3}^{2+} + \mathrm{O_2} + 2\mathrm{H_2O} = 4\mathrm{Fe(diOHphen)_3}^{3+} + 4\mathrm{OH}^-.$$

It was assumed that the absorbances of the iron(II) and iron(III) species were additive.

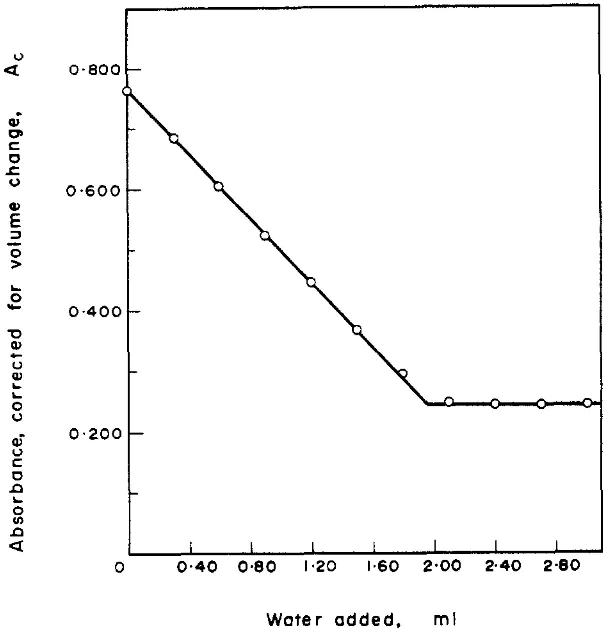

Fig. 4. Absorbance as a function of oxygen added as a solution in water in equilibrium with air. Absorbance corrected for volume change resulting from addition of liquid sample. Temperature, 26·5° Initial volume, 40·6 ml. Absorbance measured at 520 nm.

This ratio of reactants was confirmed as follows. The change in concentration of the iron(II) compound is given by:

$$\Delta[\mathrm{Fe(II)}] = (A_{c,1} - A_{c,2})/(\epsilon_{\mathrm{Fe(II)}} - \epsilon_{\mathrm{Fe(III)}})$$

Very little iron(III) was present initially, and the results in Fig. 4 give $\Delta[\mathrm{Fe(II)}] = 4{\cdot}55 \times 10^{-5} M$; the initial volume was 40·6 ml, so $1{\cdot}85 \times 10^{-6}$ mole of iron(II) was oxidized. The concentration of oxygen in the water used (air-saturated at 26·5°, 744 mmHg) was determined by using the azide modification of the standard Winkler method[6] and found to be 7·60 ppm. The break-point occurred at 1·96 ml of water added and corresponded to $0{\cdot}456 \times 10^{-6}$ mole of oxygen. Thus, 3·98 (a good approximation to 4) moles of iron(II) compound reacted per mole of oxygen added.

In using the system for the determination of oxygen, the oxygen concentration in ppm is given by

$$O_2 = \frac{(A_{m,1} V_{m,1} - A_{m,2} V_{m,2}) \times 32{\cdot}0 \times 10^3}{4 \times 11{\cdot}5 \times 10^3 \times V_s}$$
$$= \frac{0{\cdot}696\,(A_{m,1} V_{m,1} - A_{m,2} V_{m,2})}{V_s}\ \mathrm{ppm}$$

where $A_{m,1}$ and $A_{m,2}$ are the absorbances measured before and after addition of a volume of sample V_s ml.

The effects of iron (ferrous and ferric) in the sample were determined. Ferric iron (20 ppm) caused no significant interference. Ferrous iron did interfere significantly. On a sample containing 20 ppm of iron(II) the spectrophotometric method gave 3·72 ppm O_2;

the standard Winkler method, azide modification, gave 4·94 ppm O_2; the distilled water used to prepare the solution contained 7·99 ppm O_2 before the addition of the iron as ferrous sulphate.

Table 1. Comparison of spectrophotometric method with standard Winkler method, azide modification[6]

	Oxygen, *ppm* Spectrophotometric method	Winkler method
Distilled water,	7·54	7·53
air-saturated at	7·43	7·54
26·3°, 736 mmHg	7·55	7·57
Lake LaVerne water, 5°	12·21	12·10
	11·86	12·52
	11·75	12·02
		11·96
Ames Water Works		
Non-aerated water	−0·54	0·00
	−0·57	0·00
Aerated water	6·61	6·94
	6·44	7·02
		7·01
		6·93
Finished water	7·23	7·97
	7·53	

The method was compared with the standard Winkler method, azide modification, for the determination of dissolved oxygen in distilled water, water from Lake LaVerne (on the ISU campus), and water from the Ames Municipal Water Works (Table 1). Excellent agreement was obtained on distilled water and water from Lake LaVerne. The negative values obtained for the non-aerated water from Ames Water Works is a result of ferrous iron in the water as it comes from the wells. The discrepancy of about 0·5 ppm between the results by the proposed and the standard method for the aerated (but otherwise untreated) water is undoubtedly caused by ferrous iron still present. The discrepancy found for the finished water is left unexplained; curiously it is just about equal to the residual chlorine present.

No attempt was made to determine the effects of possible interferences other than iron. However, mild oxidizing agents, which interfere in the Winkler method[6–8] and in a more sensitive method using indigo carmine,[9,10] may be assumed to interfere. The accuracy of the method in the absence of interferences is good, being limited only by the accuracy with which the sample is measured and by the accuracy of the spectrophotometric measurement, the latter yielding the greater errors. Very small volumes of sample are required (less than 1 ml for water in equilibrium with air), and in this respect the method is superior to the Winkler method, which requires samples of the order of 200–300 ml.

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Zusammenfassung—Tris-(4,7-dihydroxy-1,10-phenanthrolin)eisen(II) reagiert mit gelöstem Sauerstoff in alkalischer wäßriger Lösung rasch und quantitativ. In ammoniakalischer Lösung ist die Reaktion vom Verschwinden der intensiv roten Farbe der Eisen(II)Verbindung begleitet; diese macht dem blaßgrauen, schwach dissoziierten Ion Tris(4,7-dihydroxy-1,10-phenanthrolin)eisen(III) Platz. Mißt man die Extinktion einer Lösung, die die Eisen(II)-Verbindung enthält, vor und nach Zugabe einer sauerstoffhaltigen Losung, dann kann die Konzentration von gelöstem Sauerstoff in der Probe zwischen 1 und 20 ppm genau bestimmt werden.

Résumé—Le tris(4,7-dihydroxy 1,10-phénanthroline)fer (II) réagit rapidement et quantitativement avec l'oxygène dissous en solution aqueuse alcaline. En solution ammoniacale, la réaction est accompagnée par la disparition de la coloration rouge intense du composé du fer(II), qui fait place à l'ion légèrement dissocié tris (4,7-dihydroxy 1,10-phénanthroline)fer(III) gris pâle. En mesurant l'absorption d'une solution contenant le composé ferreux avant et après l'injection d'une solution contenant de l'oxygène, la concentration de l'oxygène dissous dans l'échantillon peut être déterminée avec précision dans le domaine 1–20 ppm.

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POLAROGRAPHIC INDICATION OF THE END-POINT IN CHELOMETRIC TITRATIONS WITH TRIETHYLENETETRAMINEHEXA-ACETIC ACID

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Summary—The application of d.c. and square-wave polarographic measurements for the indication of the end-point in titrations with triethylenetetraminehexa-acetic acid (TTHA) has been studied. TTHA has ten co-ordinating groups and forms complexes with metal to ligand ratios of either 1:1 or 2:1, depending on the metal and experimental conditions. The shape of the titration curves, determined by the dependence of the limiting current (peak current of the square-wave polarographic curve) or of the half-wave potential (peak potential) on the amount of TTHA added indicates the composition of the complex formed in the titration. The composition of this complex as determined from the studied titration curves agrees with that predicted by theory. Titrations with polarographic indication of the end-point were also applied for direct titrations of binary mixtures of metal ions. The resulting titration curves indicated the existence of mixed dinuclear complexes and also the kinetic factors involved in the reactions between two different metal ions and TTHA.

In the study of chelometric titrations great interest has been taken recently in the use of titrants forming dinuclear complexes. A typical reagent is triethylenetetraminehexa-acetic acid (TTHA or H_6X) introduced as a titrant by Přibil.[1-4] Because this reagent forms mono- and dinuclear complexes of different stabilities, the composition of the resulting complex, formed at the end-point of the titration, depends on the nature of the metal ion to be titrated and on the experimental conditions of the titration e.g. concentration of hydrogen ions, nature of the buffer solution *etc.*

The theoretical problems connected with chelometric titrations with reagents forming mono- and dinuclear complexes were solved by Harju and Ringbom.[5] These authors used the concept of conditional stability constants,[6] where the extent of side-reactions is given by the side-reaction coefficients (α-coefficients),[6,7] and plotted the values of the conditional stability constants and of the pM values corresponding to the equivalence points, as functions of the hydrogen-ion concentration. These curves allow prediction of the course of the titrations under varying experimental conditions and thus distinguish whether a 1:1 or 2:1 metal to ligand complex is formed.

For experimental verification of their theoretical conclusions these authors used photometric titrations.

In the present paper, we show that the application of polarography for the same purposes has wider versatility and offers a simple way of distinguishing which type of complex is formed.

EXPERIMENTAL

Reagents

All solutions were prepared from *p.a.* chemicals TTHA solution (0·01*M*) was standardized by visual[1] and amperometric titration with standard zinc solution. The solutions of metal salts (0·01*M*) were standardized by EDTA titrations.

Apparatus

For the polarographic measurements Radelkis d.c. and square-wave polarographs were used. All values of half-wave potentials or peak potentials are referred to the SCE.

Procedure

Suitable buffer solution (0·1*M*, 7·0 ml), sodium perchlorate (7·0 ml) and (0·01*M*) solution metal salt (1·0 ml) were placed in the polarographic cell, and deaerated with nitrogen. Titrant (0·01*M*) was added stepwise from a micrometer syringe. (For square-wave polarography the concentrations of metal salt and titrant were both 0·001*M*.) After each addition of titrant the polarographic curve was recorded.

RESULTS AND DISCUSSION

Modes of polarographic indication of the end-point

When chelometric titrations are used to obtain information on the composition of the complex formed, either the reagent (L) or the metal (M) salt solution can be used as titrant. If the titrant is the reagent the titration curve can be derived by measuring one of the following parameters as a function of the amount of reagent added: (*a*) the limiting current of the metal ion i_{l_M}; (*b*) the limiting current of the complex $i_{l_{ML}}$; (*c*) the anodic limiting current of the reagent i_{l_L}; (*d*) the shift of the half-wave potential, $E_{1/2}$ for the metal ion; when square-wave polarography is used, the corresponding parameters are the peak-currents i_p or the shift of the peak potential, E_p. If metal salt solution is used as titrant, parameters (*a*), (*b*) and (*c*) are measured as functions of the amount of metal ion added.

Also, the hydrogen ions set free by the complex-formation can be titrated with sodium hydroxide solution, the height of the hydrogen wave being measured,[8] but this can only be used with neutral, unbuffered media.

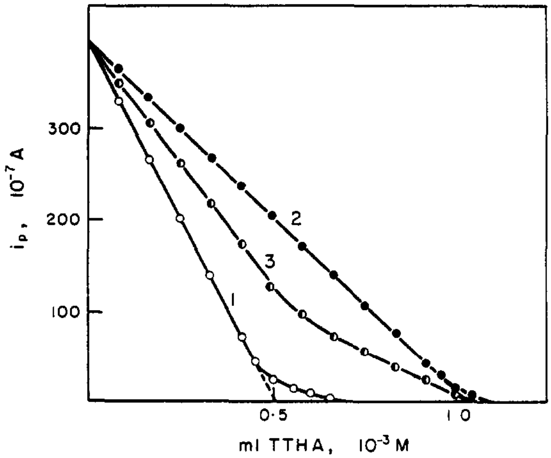

Fig. 1. Titration of cadmium (II) with TTHA and square-wave polarographic indication: dependence of the peak current, i_p, on the amount of TTHA added.
1—Electrolyte 0·05*M* NaClO and 0·05*M* NH /NH$_4$Cl buffer solution. *2*—Electrolyte 0·05*M* NaClO$_4$ and 0·05*M* acetate buffer solution, pH 4·2. *3*—Electrolyte 0·05*M* NH$_3$. Concentration of cadmium (II) in all cases 6·6 × 10^{-5}*M*.

Not all these types of titration can be applied generally—a suitable type should be chosen for any particular titration. In the following sections typical examples are presented.

Titration of cadmium

The reduction of cadmium (II) at the DME is reversible and therefore the application of square-wave polarography is advantageous. Because the cadmium–TTHA complex yields no peak in square-wave polarography, titration type (*a*) is recommended. Figure 1 shows i_{pCd} as a function of the amount of added TTHA for ammonia-ammonium chloride and acetate buffers and ammoniacal medium. These titration curves show the formation of a 1:1 cadmium-TTHA complex at pH 4 and 11 and a 2:1 complex at pH 8·4. These results agree with the theoretical considerations published by Harju and Ringbom.[5] The non-linear titration curve for ammoniacal medium (curve 3) is due to the tendency to form a 2:1 complex when the metal is present in excess relative to TTHA (beginning of the titration).

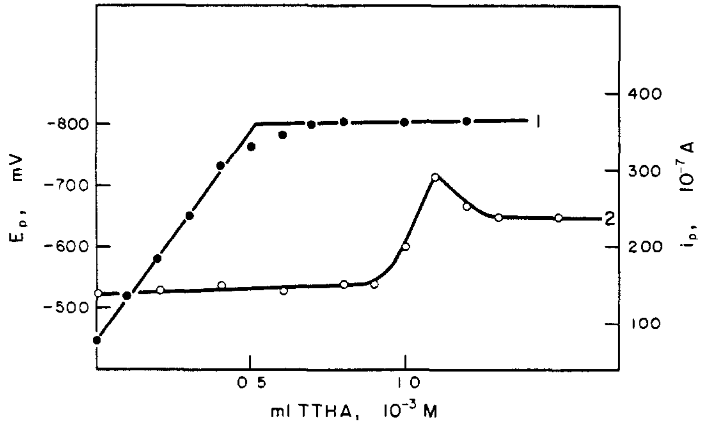

Fig. 2. Titration of lead (II) with TTHA and square-wave polarographic indication. *1*—Dependence of the peak potential, E_p, on the amount of TTHA added; electrolyte 0·05*M* $NaClO_4$ and 0·05*M* acetate buffer solution, pH 4·4. *2*—Dependence of the peak current, i_p, on the amount of TTHA added: electrolyte 0·05*M* $NaClO_4$ and 0·05*M* NaOH. Concentration of lead (II) in all cases 6·6 × 10^{-5}*M*.

Titration of lead

This is an example of titration type (*d*). The polarographic wave or the square-wave peak corresponding to the reduction of lead (II) is strongly shifted to more negative potentials when TTHA is added stepwise to lead (II) in slightly acidic media. When all the lead is complexed, the half-wave potential (or the peak potential) remains constant and thus a titration curve with a sharp end-point is obtained. Curve 1 in Fig. 2 shows the titration of lead (II) with TTHA in acetate buffer, pH 4·4, with square-wave polarographic indication of the end-point. The end-point indicates formation of 2:1 complex in agreement with Harju and Ringbom.[5]

If lead is titrated with TTHA in alkaline medium (0·05*M* sodium hydroxide with square-wave polarographic indication, the change of peak current, should be recorded [type (*a*), curve 2 in Fig. 2]. This curve, though not recommended for analytical application, allows the end-point to be read with sufficient accuracy to distinguish which type of complex is formed. The formation of the 1 : 1 complex in alkaline medium, again agrees with the theoretical data.[5]

Titration of copper

Because of the irreversibility of reduction of copper(II) at the DME, d.c. polarography is advantageous for the copper(II) titration with TTHA. Either $i_{l_{Cu}}$ or $i_{l_{ML}}$ can be followed. The titration curves presented in Fig. 3 correspond to the titration of copper (II) in acetate buffer at pH 4·7. Under these conditions $E_{1/2}$ for copper(II) is $-0{\cdot}03$ V and that for the complex $-0{\cdot}26$ V. Titration curves of this type are obtained from pH 2·5 to 8·0; these results verify the existence of the 2 : 1 copper–TTHA complex under the given conditions, as follows from the conditional stability constants.[5]

Similar titration curves are obtained for ammonia–ammonium chloride, but a 1 : 1 complex is formed as predicted.[5]

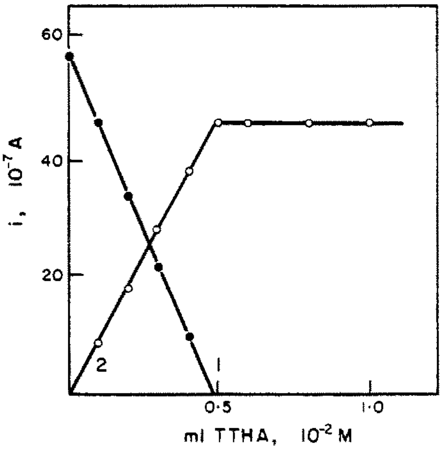

Fig. 3. Titration of copper (II) with TTHA and d.c. polarographic indication: dependence of the limiting current, *i*, on the amount of TTHA added.
Electrolyte 0·05*M* NaClO$_4$ and 0·05*M* acetate buffer solution, pH 4·7, concentration of copper (II) $6{\cdot}6 \times 10^{-4}$*M*. *1*—Decrease of the height of the wave of free Cu^{2+} ions. 2—Increase of the height of the wave of the 2 : 1 Cu–TTHA complex.

Titration of calcium, lanthanum and thorium

Here the titration is of type (*c*); TTHA (as do other reagents related to EDTA) yields a well-developed d.c. polarographic anodic wave or square-wave polarographic peak at potentials close to 0·0 V. The $E_{1/2}$ and E_p values depend on the pH of the electrolyte and are +0·06 V in acetate buffer solution at pH 5·1.

Calcium can be titrated directly at pH 6–10, the end-point being indicated by the appearance of the anodic wave or the square-wave polarographic peak corresponding to the oxidation of free TTHA. In all cases only a 1 : 1 complex is observed, as expected.[5]

Lanthanum (II) can also be titrated directly with TTHA, at pH up to 6. In alkaline media, the titrand is TTHA in a proper buffer and the titrant is lanthanum (II). In this case the end-point is indicated by decrease in the limiting current of the d.c. polarographic wave or the peak current of the square-wave polarographic peak corresponding to the oxidation of free TTHA. Again only a 1 : 1 complex is formed, as follows from the theoretical data.[5]

Thorium (IV) can also be titrated, but direct titration is possible only in acidic solutions, the 1:1 complex being formal.

Titration of indium

Titration of indium(III) is also an example of the titration type (*a*) but only at pH 2·7, when i_{In} for the indium (III) wave ($E_{1/2} = -0{\cdot}55$ V at pH 2·5) is a linear function of the amount of TTHA added, the end-point being when $i_{\text{In}} = 0$. This curve indicates the formation of only the 1 : 1 complex. At higher pH values (pH 2·7–5·5) the titration curve is more complex. Under these conditions the decrease of i_{In} is not linear during the titration and a new wave with more negative half-wave potential ($E_{1/2} = -0{\cdot}74$ V at pH 3·6) appears. The limiting current of this new wave increases with amount of TTHA added, reaches a maximum when half of the indium has been titrated and then decreases. At the end-point both limiting currents are zero (Fig. 4).

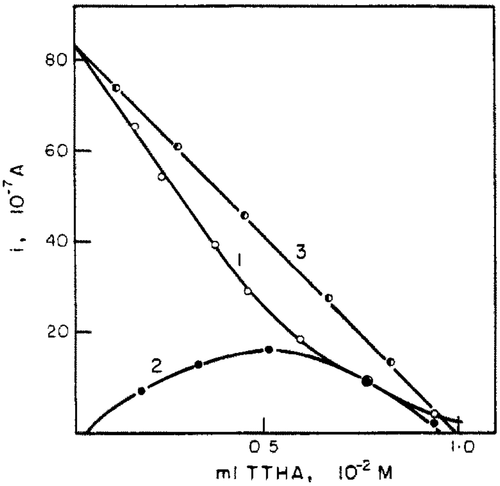

Fig. 4. Titration of indium (III) with TTHA and d.c. polarographic indication: dependence of the limiting current, *i*, on the amount of added TTHA.
Electrolyte 0·05*M* $NaClO_4$ and 0·05*M* monochloroacetate buffer solution, pH 3·6, concentration of indium(III) 6·6 × 10^{-4}*M*. *1*—Decrease of the height of the indium(III) wave. *2*—Changes of the height of the wave of the 2 : 1 indium-TTHA complex. *3*—Sum of the heights of both waves.

In a study published elsewhere[9] it has been proved that the second wave corresponds to the reduction of indium(III) from the 2:1 indium-TTHA complex. The titration curves thus indicate the simultaneous existence of both 1 : 1 and 2 : 1 indium-TTHA complexes during the titration in the pH interval from 2·7 to 5·5.

Titration of mixtures of metals

The results presented above lead to the proposal that polarography may be an important tool for the examination of the titration mechanism when a mixture of two metals is titrated. The advantage arises mainly when both metal ions yield well-separated polarographic waves. In the following sections it is shown that under the conditions where the titrant is able to form mono- and dinuclear complexes, the resulting titration curves are in many cases affected by the formation of mixed dinuclear complexes.

Titration of a mixture of copper(II) and nickel(II)

The changes in the concentrations of copper(II) and nickel(II) ions in mixtures when titrated with TTHA can easily be measured polarographically. In acetate buffer solution, pH 4·7, the $E_{1/2}$ value of copper(II) is $-0{\cdot}03$ V, that of nickel(II) is $-1{\cdot}10$ V, the $E_{1/2}$ value of the 2:1 Cu-TTHA complex is $-0{\cdot}26$ V and the nickel complex yields no polarographic wave. When, under the given conditions, nickel(II) and copper(II) are titrated separately by technique (*a*) the position of the end-points indicates in both cases the formation of the 2:1 complex in accordance with the conditional stability constants[5] (see Fig. 3). On the other hand the titration curves of the mixture of these ions have the shape shown in Fig. 5. Curve 1 in Fig. 5 shows the simultaneous decrease of the concentration of free copper(II) and nickel(II) ions from the start of the titration. During the titration a new wave is recorded, the height of which increases from the start of the titration and reaches its maximum height at the end-point (curve 2). The $E_{1/2}$ value of this new wave has the value $-0{\cdot}24$ V. The end-point of the titration corresponds to the consumption of one mole of TTHA per mole of nickel and mole of copper. The shape of the titration curve does not depend on time—when a series of solutions corresponding to different points of the titration curve is prepared and these solutions are polarographed after 2 hr, curves practically identical to those in Fig. 5 are observed. Since the conditional stability constants of the 2:1 copper and nickel-TTHA complexes are $10^{10{\cdot}5}$ and $10^{11{\cdot}2}$ respectively at pH 5·0, it can be presumed that both metal ions are titrated simultaneously.

Titration of a mixture of cadmium(II) and nickel(II)

The half-wave potentials of the waves of cadmium(II) and nickel(II) in ammoniacal medium are sufficiently separated for the titration with TTHA to be performed by method (*a*). The titration of cadmium(II) itself in ammoniacal medium indicates the formation of the 1:1 complex (see Fig. 1), while the titration of nickel(II) under the same conditions indicates the formation of the 2:1 complex. Titration of a equimolar mixture of nickel(II) and cadmium(II) gives curves such as those in Fig. 6 (curves 1–3). These curves show that

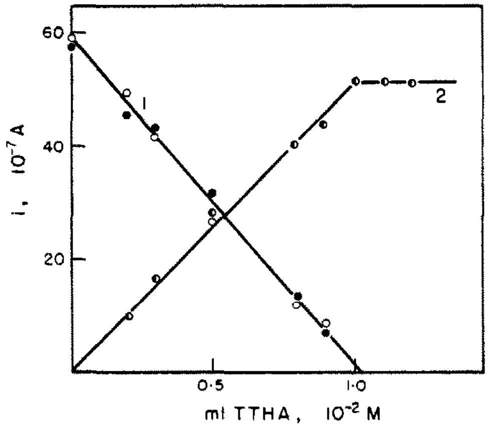

Fig. 5. Titration of a mixture of copper(II) and nickel(II) with TTHA, d.c. polarographic indication, dependence of the limiting current on the amount of TTHA added.
Electrolyte 0·05*M* $NaClO_4$ and 0·05*M* acetate buffer solution, pH 4·7, concentration of copper(II) and nickel(II) $6{\cdot}6 \times 10^{-4}M$ each. *1*—Decrease of the heights of the copper(II) and nickel(II) waves. *2*—Increase of the height of the 2:1 copper(II) complex wave.

the concentrations of both metal ions decrease from the beginning of the titration. During the course of this titration a new wave is observed with half-wave potential more negative than that of nickel(II). The half-wave potential of this wave changes with time, a constant value of −1·10 V being observed after 200 min. Also the concentrations of free nickel(II) and cadmium(II) ions change with time during the titration. Therefore a series of solutions corresponding to different points of the titration curve was prepared and these solutions were polarographed after 200 min. Under these conditions the titration curves have the shapes shown in Fig. 6, curves 4, 5 and 6. In the work of Neubauer and Kopanica[10] it was proposed that the wave with $E_{1/2}$ value −1·10 V (curves 3 and 6, Fig. 6) corresponds to the reduction of the mixed dinuclear complex Cd-TTHA-Ni.

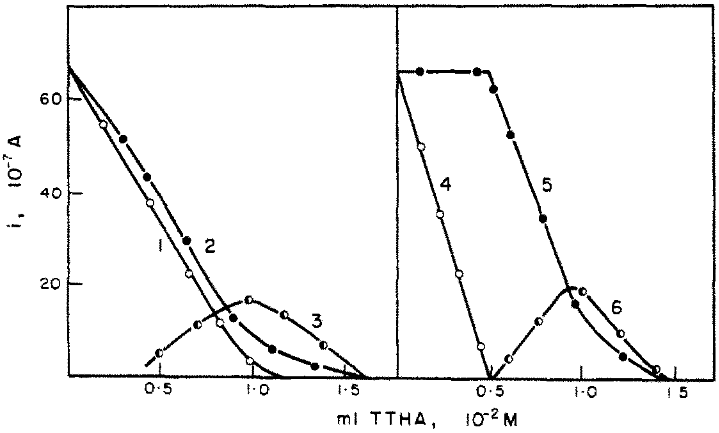

Fig 6 Titration of a mixture of cadmium(II) and nickel(II) with TTHA. d.c. polarographic indication.
Electrolyte 0·05M NaClO$_4$ and 0·05M NH$_3$, concentration of cadmium(II) and nickel(II) 6·6 × $10^{-4}M$ each *1–3*—Normal titration; *1*—decrease of the wave of Ni^{2+} ions; *2*—decrease of the wave of Cd^{2+} ions; *3*—variation of the wave of the mixed dinuclear complex. *4–6*—"Slow" titration, experimental data recorded 200 min after mixing; *4*—decrease of the wave of Ni^{2+} ions, *5*—decrease of the wave of Cd^{2+} ions; *6*—height of the wave of the mixed dinuclear complex.

The mechanism of the titration can be interpreted as follows. In the titration carried out with stepwise addition of the titrant both complexes are formed simultaneously, the mixed dinuclear complex being formed in maximum amount when the system reaches a 1 : 1 : 1 molar ratio of Ni : Cd : TTHA, and end-point detection for the sum of nickel + cadmium is not accurate. In a "slow" titration, first the 2:1 nickel complex is formed (sharp end-point) and when in the next step the 1 : 1 cadmium complex starts to form the interaction between both complexes (which have practically identical conditional stability constants, ~ 10^{13} at pH 11) leads to a partial formation of the mixed dinuclear complex (the end-point corresponding to the titration of cadmium can be read with sufficient accuracy).

Titration of a mixture of indium and nickel

The half-wave potentials of indium(III) and nickel(II) waves are well separated even in acidic media and this mixture can be titrated by technique (*a*). The nickel(II)–TTHA complexes yield no polarographic waves and, as mentioned above, none of the In–TTHA complexes is polarographically active below pH 2·7. The titration of the mixture of indium

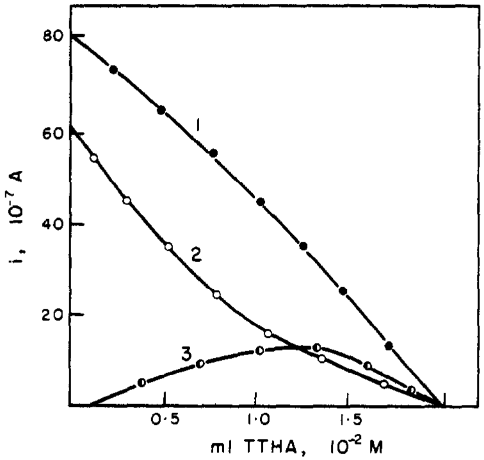

Fig. 7. Titration of a mixture of indium(III) and nickel(II) with TTHA. d.c. polarographic indication.

Electrolyte 0·05*M* $NaClO_4$ and 0·05*M* formic acid, sodium formate buffer solution, pH 2·4, concentration of indium(III) 6·6 × 10^{-4}*M*, concentration of nickel(II) 13·2 × 10^{-4}*M*, experimental data recorded 50 hr after mixing. *1*—Decrease of the height of the wave of nickel(II). *2*—Decrease of the height of the wave of indium(III). *3*—Change in the wave-height of the mixed dinuclear complex.

(III) and nickel(II) at pH less than 2·7 should therefore be expressed by two curves indicating the decrease of the concentration of non-complexed metal ions during the titration. Experiment, however, results in the titration curves shown in Fig. 7. To obtain these curves solutions corresponding to different points of the titration curve were prepared and measured 50 hr after mixing (formic acid/sodium formate buffer solution, pH 2·4) because non-reproducible results are obtained when the titrant is added stepwise. The third wave which appears during the titration (Fig. 7, curve 3) has, under the given conditions, an $E_{1/2}$ value of −0·76 V and corresponds to the reduction of indium(III) from the mixed dinuclear complex indium–TTHA–nickel as verified by Huyen and Kopanica.[11] The end-point corresponds to the titration of the sum of indium and nickel by formation of the 1 : 1 indium and the 2 : 1 nickel complexes, and the course of the titration curves indicates the existence of the mixed dinuclear complex during the titration.

CONCLUSION

The results presented in this work show that polarographic techniques can be used for the detection of the end-point in chelometric titrations with TTHA. Because polarographic measurements can be performed in acidic, neutral or alkaline media, the titrations can be realized at any concentration of hydrogen ions in the supporting electrolyte. This fact is very advantageous for the study of the composition of the complex formed in the titration, where the titrant is able to form mono- and polynuclear complexes. Titrations with polarographic indication of the end-point are therefore superior to spectrophotometric titrations carried out in the presence of metallochromic indicators. When the polarographic techniques are used, the dependence of various polarographic parameters on the amount of added titrant can be measured and thus any metal (even if not polarographically active) can be titrated. The compositions of the resulting complexes (as obtained in the experiments described) agree very well with the theoretical data based on the concept of conditional stability constants.[5–7]

Polarographic methods for detection of the end-point can also be applied to direct titrations of two-component mixtures of metal ions. Under these conditions the polarographic data lead to verification of the existence of mixed dinuclear complexes during the titrations and further to the establishment of the kinetic effects which play an important role in systems containing two metal ions and the reagent TTHA.[12]

These polarographic techniques may in some cases be applied to practical analysis. For the determination of small concentration of metal ions ($10^{-5}M$), titrations with square-wave polarographic detection of the end-point are very useful. Under these conditions all titrations of type (*a*) yield titration curves with sharp end-points (see Fig. 1). The titration of lead(II) in acetate buffer solution is particularly interesting, since the shift of the peak potential of lead(II) ions during the titration with TTHA is so pronounced that a titration curve suitable for analytical use is obtained. The titrations of mixtures of metals cannot be utilized for practical analysis, but are of great value for establishment of the reaction mechanism.

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Zusammenfassung—Gleichstrom- und square wave-Polarographie wurden dazu verwendet, den Endpunkt bei Titrationen mit Triäthylentatraminhexaessigsäure (TTHA) anzuzeigen. TTHA hat zehn koordinationsfähige Gruppen und bildet mit Metallen Komplexe mit Metall:Ligand-Verhältnissen von 1:1 oder 2:1 je nach Metall und Versuchsbedingungen. Die Form der Titrationskurven, die bestimmt wird durch die Abhängigkeit des Grenzstroms (Spitzenstroms der square wave-Polarographie) oder Halbstufenpotentials (spitzenpotentials) von der zugegebenen Menge TTHA gibt einen Hinweis auf die Zusammensetzung des bei der Titration gebildeten Komplexes. Die Zusammensetzung dieses Komplexes, wie man sie aus den untersuchten Titrationskurven erhält, stimmt mit der theoretisch vorhergesagten überein. Titrationen mit polarographisch angezeigtem Endpunkt wurden auch zur direkten Titration binärer Gemische von Metallionen benutzt. Die erhaltenen Titrationskurven zeigten die Existenz gemischter zweikerniger Komplexe an und gaben Hinweise auf die kinetischen Faktoren, die bei Reaktionen zwischen zwei verschiedenen Metallionen und TTHA eine Rolle spielen.

Résumé—On a étudié l'application des mesures polarographiques en courant continu et onde carree à l'indication du point de fin de dosage dans les titrages avec l'acide triéthylènetétraminohexacetique (TTHA). Le TTHA a dix groupes coordinants et forme des complexes avec des rapports métal-coordinat de 1:1 ou 2:1, dépendant du métal etdes conditions expérimentales. L'allure des courbes de titrage, déterminée par la dépendance du courant limitant (courant de pic de la courbe polarographique à onde carrée) ou du potentiel de demi-vague (pic de potentiel) par rapport à la

quantité de TTHA ajoutée indique la composition du complexe formé dans le titrage. La composition de ce complexe, telle qu'elle a été déterminée à partir des courbes de titrage étudiées. est en accord avec celle prévue par la théorie. On a aussi appliqué les titrages avec indication polarographique du point final aux titrages directs de mélanges binaires d'ions métalliques. Les courbes de titrage résultantes indiquent l'existence de complexes dinucléaires mixtes et aussi les facteurs cinétiques mis en jeu dans les réactions entre deux ions métalliques différents et le TTHA.

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SIMULTANEOUS NEUTRON-ACTIVATION DETERMINATION OF SELENIUM AND MERCURY IN BIOLOGICAL SAMPLES BY VOLATILIZATION

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Summary—A method is described for the determination of selenium together with mercury in biological samples by neutron-activation analysis based on quantitative volatilization of both elements. The technique originally developed for mercury, based on pyrolysis with filtration of undesirable impurities and selective trapping from the gas phase, is now extended to selenium. The radionuclides ^{197}Hg and ^{75}Se, from one sample, are trapped separately and counted in a well-type NaI(Tl) detector and γ-spectrometer for maximum sensitivity. The method has been tested by comparative analyses and analyses of standard biological materials, and gives good results. It is simple and is especially effective in studies of the interaction of mercury and selenium in biological systems: a positive correlation for these elements was found for human tissues.

In studies of the role of mercury in the environment, particularly the toxicological aspects, it is becoming increasingly important to determine also the selenium content of the sample. This is a consequence of the findings of Parizek and co-workers[1,2] on the protective, or in certain circumstances, the potentiating effect of selenium compounds on the toxicity of mercury, and of recent analytical observations of a significant positive correlation between mercury and selenium contents in tuna tissue by Ganther *et al.*[3] and in seals and whales by Koeman *et al.*[4]

Neutron-activation analysis is one of the most reliable analytical methods for both mercury and selenium. Although a number of recent papers have described non-destructive activation techniques for selenium[5–7] and mercury,[8] by high-resolution Ge(Li)-detector gamma spectrometry, sensitivities are in general inadequate for most environmental samples. Thus ^{197}Hg (65 hr) and ^{75}Se (120 d) radioisotopes produced by neutron irradiation in a reactor, must be separated after wet destruction, for measurement with an NaI(Tl) detector and γ-spectrometer.

Taking advantage of its volatility, we have quickly and quantitatively separated mercury from irradiated biological samples by pyrolysis.[9] The gaseous products are burnt in oxygen on a hot platinum gauze, passed through a hot silver-coated filter to absorb other volatile radionuclides (notably ^{82}Br), and mercury is trapped on a selenium-impregnated paper from the gas phase, to give a very pure ^{197}Hg spectrum. In the original report[10] we noted high yields of ^{75}Se in the intermediate trap, which offered a promising technique for determining selenium. The same general approach for both elements has since been developed by Rook *et al.*[11,12] However, there the high-temperature ignition in oxygen (800–1000°), was followed not by a physical separation by filtration, but by counting on a high-resolution Ge(Li)-detector to resolve the mercury and selenium γ-ray peaks from those of other radionuclides, with consequent loss of sensitivity or tediously long counting periods (particularly for ^{75}Se). When bromine is abundant in the sample, a separate chemical separation of ^{82}Br must be introduced[11] to permit determination of the mercury, which itself (^{197m}Hg) interferes with the measurement of the most intense ^{75}Se peak at 136 keV.

The purpose of the present paper is to show that both pyrolysis and heating at intermediate temperatures (600–700°) cause biological samples to lose quantitatively not only mercury but also selenium, which can be trapped separately in sufficiently high purity to allow measurement on the highly-efficient well-type NaI(Tl) crystal and γ-spectrometer. ^{197}Hg caught on selenium-impregnated paper is sufficiently pure to be counted immediately, while 120-day ^{75}Se, trapped on granular soda-lime, is cooled for up to 20 days before counting, to allow ^{82}Br to decay. The general advantage of this approach is that a rapid quantitative separation is achieved by physicochemical processes not requiring any chemical manipulation, while the filtration and trapping provide selectivity to allow the use of the most efficient γ-counting apparatus.

EXPERIMENTAL

Apparatus

The apparatus has already been described.[9] The packing of the first filter, contained in a silica tube fitted with B14 cone and socket, has, however, now been modified (Fig. 1). Half of the silvered quartz wool is replaced by a loose packing of about 1·5 g of granular soda-lime at the upstream end, held in place by a thin layer of quartz wool. In practice, no significant activity has been found on the silvered wool after ignition.

The three furnaces, surrounding the ignition tube, the soda-lime–silvered-wool filter, and the selenium-impregnated paper, were uninsulated ceramic annuli, bored longitudinally with holes containing a spiral Kanthal winding and controlled by "Variacs". As before, the temperatures of the furnaces around the soda-lime filter and selenium-impregnated paper were maintained at 350° and 100° respectively.

About 20 sets of apparatus are currently in use; after use they are cleaned by soaking in nitric acid (1 + 1) followed by washing and igniting at 800° (with the exception of the Pyrex section).

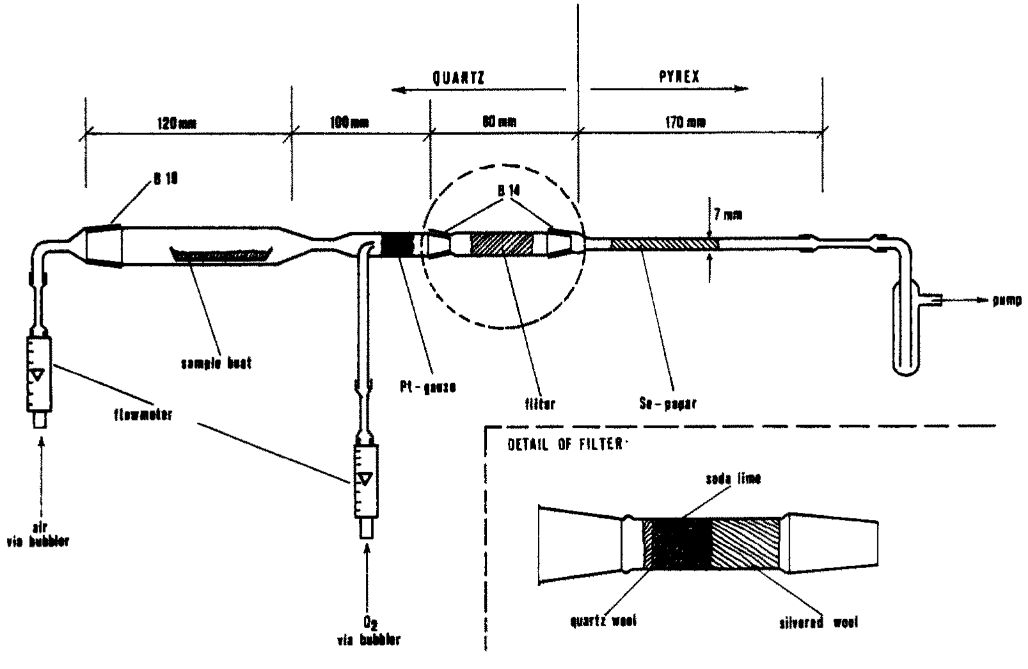

Fig. 1. Apparatus for volatilization and trapping of selenium and mercury from biological samples (furnaces not shown).

Reagents and standards

Mercuric chloride and selenium dioxide, analytical grade.

Soda-lime, granular.

Silver-coated quartz wool and selenium-impregnated paper prepared as before.[9]

A stock solution of mercury (1·0 mg/ml in 0·2*M* hydrochloric acid) was diluted as required, to provide a working solution for 5 μg/g standards, of which 50–100 mg were weighed into 2 mm bore polythene tubing and sealed in. After irradiation the outside of the tube was cleaned in an organic solvent bath, then in *aqua regia*, and folded into the bottom of a counting vial, with identical geometry to the selenium paper from the sample. One day after the end of the irradiation the contribution of impurities in the polythene to the ^{197}Hg γ-spectrum was negligible

About 50 mg of a 1·0 mg/ml solution of selenium in 0·2*M* nitric acid were weighed into narrow quartz tubes and sealed in. After irradiation the tubes were opened and the contents transferred with several washings of acidified selenium carrier solution to a 10 ml volumetric flask. A 1 ml aliquot was transferred to the counting vial for measurement; about 0·5 ml of water was added to make the volume equal to that of the soda-lime.

Ignition procedure

The sample is pyrolysed in a stream of air with oxygen-assisted catalytic combustion of the gaseous products on a hot platinum gauze. The selenium and other volatile elements are absorbed on the first filter, while mercury passes through to be absorbed on the selenium-impregnated paper. The alternative direct combustion in oxygen can lead to uncontrolled rises in temperature with volatilization of undesirable elements. (Gorsuch[13] showed that for wet oxidations, heavy charring, *i.e.*, reducing conditions, favours the volatilization of selenium.) After gases have ceased to be evolved (at about 400°), the temperature of the sample, measured by a thermocouple between the furnace and ignition tube, is raised to 650–700° and held there for 10 min. After the furnaces have been switched off, the three sections are dismantled and the selenium paper roll, with trapped ^{197}Hg, is pushed out into a 5 ml counting vial. The soda-lime and first quartz wool packing are also transferred to a counting vial.

Before ignition two small pads of quartz wool are inserted, one on each side of the sample boat; the upstream one prevents any back-diffusion, while the downstream one traps any particles of sample or ash which might be carried by the gas stream and contaminate the first filter. As before, 3 or 4 drops of a carrier solution ([Hg^{2+}] 1 mg/ml) are spotted on the sample before ignition, *i.e.*, 30–40 μg of mercury, but no selenium carrier was found necessary (mercury also acts as a carrier for selenium).[12]

Irradiation

Samples were irradiated in sealed precleaned silica ampoules, with mercury and selenium standards taped alongside, in the rotating rack of the Institute's TRIGA Mark II reactor at a flux of 2 × 10^{10} n/mm^2/sec. A 20 hr irradiation provided ample sensitivity for all mercury determinations, and also for selenium in most samples of moderate weight ($\geqslant$0·5 g). After irradiation the ampoules were frozen in liquid nitrogen, then opened at the neck, and the contents transferred to the combustion boat. For some samples it was convenient to clean the outside of the ampoules thoroughly, to open or crush them frozen, and to heat sample and ampoule together in the combustion tube.

Counting

Both ^{197}Hg and ^{75}Se activities were measured in a 3 × 3 in. NaI(Tl) well-type crystal detector connected to a γ-spectrometer (TMC 256- or 400-channel analyser). Apart from the general advantages of higher efficiency and lower sensitivity to geometrical effects, this type of crystal has a special advantage for ^{75}Se measurements, as pointed out by Steinnes[14] The 0·40 MeV sum peak obtained has a much higher counting efficiency, and the background in this region is rather low. This situation is demonstrated in Table 1 for a 1 ml ^{75}Se source counted in a 3 × 3 in. well crystal, a 3 × 3 in. flat-top crystal and a 3·3% efficient Ge(Li) detector. The integral peak count-rates are normalized to a value of 100 for the 0·40-MeV sum peak.

Since the 265 keV peak must normally be used for measurement of ^{75}Se with a Ge(Li) detector unless a complete radiochemical separation has been performed, it can be seen that even for a large, say 10% efficient, Ge(Li) crystal, the sensitivity is at least an order of magnitude lower than for the NaI(Tl) well-type crystal.

RESULTS AND DISCUSSION

The method has been thoroughly tested for mercury already, therfore we concern ourselves mainly with the modification of the method for selenium.

Table 1. Relative count rates for various peaks of ^{75}Se (1 ml source) with different detectors

Detector	Relative peak count-rate 121 *keV*	136 *keV*	265 *keV*	280 *keV*	401 *keV*
Ge(Li) 3·3% efficient	2·3	7·1	2·8	1·2	0·6
3 × 3 in. NaI(Tl) well-type	20		23		100
3 × 3 in. NaI(Tl) flat-top*	17		17		5·2

* Actually 3 × 3 in. well-type with source at surface.

It is well known that dry-ashing of biological samples results in large or total loss of selenium, and that combustion train techniques can be used for organo-selenium compounds. Thus we would expect selenium to be totally volatilized from biological samples on pyrolysis and heating, since it is believed to occur mainly in the form of selenium-containing amino-acids and their derivatives, or in proteins.

Some authors have reported losses of selenium during growth,[15] drying[16,17] and storage[18] of certain plant materials; since this problem is even more acute for mercury, only fresh samples should be irradiated, if possible, with the minimum of pretreatment, handling and storage.

Preliminary tracer experiments

Tracer experiments must be interpreted cautiously, owing to differences in the chemical bonding of the tracer and the element in the sample; additionally, even if the tracer can be incorporated equivalently *in vivo* or *in vitro*, the measurement does not take into account structural alterations produced by neutron and gamma bombardment. For example, it has been stated that moderate reactor irradiation converts organo-mercury compounds into inorganic mercury species.[19] Some preliminary experiments with ^{75}Se tracer were therefore made to investigate its volatility.

While Se(IV) was not appreciably volatile from acid or alkali alone at 500°, the yield increased to about 50% when the tracer was spotted onto dried grass and then pyrolysed.

Next, a goldfish kept in a tank of water to which a few μCi of ^{75}Se had been added was sacrificed and a homogenate of the organs prepared. On pyrolysis for only 5 min, the fraction of ^{75}Se left in the ash varied from 15 to 10% at temperatures of 500–600°, with recoveries of 60–80% on the silver-coated quartz wool filter. This was encouraging, but also indicated that silver wool was not completely effective in absorbing volatile selenium compounds. Since we had successfully used[20] a combined soda-lime–silvered-wool filter for the determination of mercury in samples which had high sulphur content or evolved halogen acids, and since volatile selenium is probably present as SeO_2 after passage through the hot platinum gauze in the presence of oxygen, we decided to try this as a trapping agent. A 5-min ignition of the goldfish sample at 650° then gave recoveries of over 90% on the soda-lime, the balance being found in the ash.

Comparative analyses

A procedure consisting of pyrolysis, followed by ignition at 650° for 10 min was then tested more rigorously.

A homogenized freeze-dried tuna sample was prepared and irradiated along with a selenium standard, and allowed to "cool" for over a month (mainly to facilitate non-

Table 2. Effect of ignition temperature in selenium recovery

Final temperature, °C	400	500	600	700	800
Se found, *ppm*	3·90	4·03	4·73	4·92	4·89

Se found by non-destructive Ge(Li) spectrometry = 4·78 ppm.
Se found by destructive radiochemical separation = 4·82 ppm

destructive analysis). Aliquots of the sample (250 mg) were analysed by the procedure described, but with use of different final temperatures to see the effect on the recovery of selenium. In addition, the sample was analysed by two other methods: by non-destructive γ-ray spectrometry with a Ge(Li) detector, and by a radiochemical method[14] involving wet ashing, distillation of the bromide and precipitation of elemental selenium. The results are shown in Table 2.

It is clear that the method gives results in excellent agreement with those from the other analyses, and that above 600° a plateau is observed which indicates that all the selenium is volatilized at this temperature.

A series of samples consisting of IAEA fish solubles, fresh trout muscle, and trout liver, were analysed by both the proposed volatilization technique and the radiochemical method. The results were in good agreement, and for the 11 samples can be expressed as

$$\frac{\text{Se found by volatilization method}}{\text{Se found by radiochemical separation}} = 0{\cdot}99$$

with a standard deviation of 0·06. The selenium contents ranged from 0·4 to 7 ppm.

Analysis of standard materials

The NBS standard material, Bovine Liver SRM 1577, was analysed 6 times by the proposed method, and found to contain 1·11 ± 0·05 ppm of selnium. This is in excellent agreement with the certified value of 1·1 ± 0·1 ppm. The mercury content of this material was found to be 16·0 ± 1·0 ng/g, as compared with the certified value of 16 ng/g.

Bowen's kale standard was also analysed for selenium and a value of 0·11 ± 0·008 ppm ($n = 6$) obtained, in good agreement with the reported average of 0·12 ppm.[21]

Other applications

The method is now in use in our laboratory in connection with projects on the uptake and fate of mercury in the environment.

We have found the enormous uptake and retention of mercury in the thyroid of persons highly exposed to inorganic mercury, which we have previously reported,[22] to be paralleled by increased selenium contents. This example of the simultaneous determination of mercury and selenium is shown in Table 3. A similar trend was observed for other organs. These results will be reported in detail elsewhere.

Table 3. Hg and Se contents (in *ppm* on fresh-weight of sample) of thyroid from persons exposed in varying degree to inorganic mercury

Subject	O.R	A.Z	M.B.	K.F.	F.M	B.P.	T.A
Hg	0·3	0·08	0·11	0·98	7·8	26·5	101
Se	0·45	0·43	0·44	1·0	3·2	12·3	41

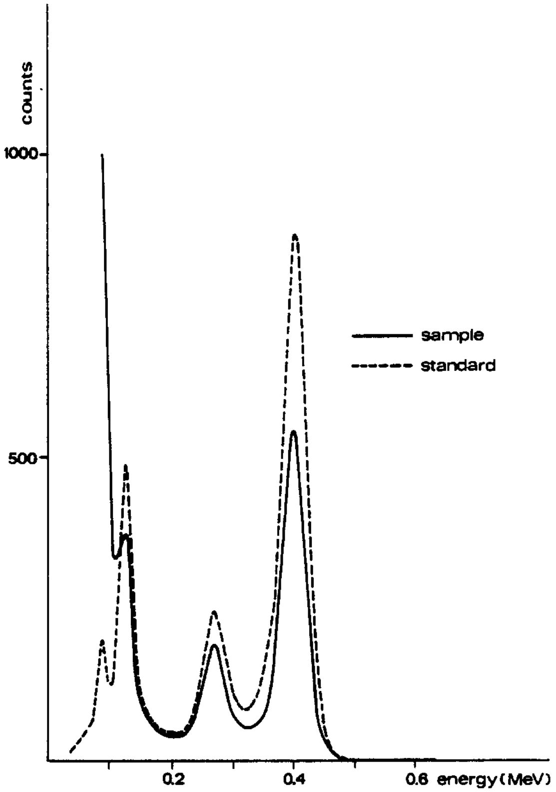

Fig. 2. ^{75}Se γ-spectra of material in soda-lime trap from 0·5 g of Bowen's kale. 3 × 3 in. NaI(Tl) well crystal, 40 min count, and ^{75}Se standard.

Accuracy and sensitivity

The accuracy and precision of the technique for selenium (and mercury) has been demonstrated by the comparative analyses and the analyses of standard materials.

With many samples, the soda-lime trap also contains some ^{32}P activity. An example of a high ^{32}P/^{75}Se ratio is shown in the γ-spectrum of ^{75}Se from a sample of Bowen's kale in Fig. 2. The bremsstrahlung rise at the low-energy end of the spectrum does not affect the estimation of the 0·40 MeV sum peak, even for such low selenium levels. The well crystal, 2 in. deep and 1 in. in diameter, was fitted with a plastic liner, and found to give better results than an unlined crystal of smaller well dimensions.

The well crystal was shown to be relatively insensitive to small changes in the volume and density of the standard or sample. The reliability of comparing ^{75}Se from the samples absorbed on soda-lime with an aqueous standard of the same volume was also checked directly by dissolving the soda-lime in nitric acid and measuring against an equal volume of standard. The results were unchanged.

The ^{82}Br activity (36-hr half-life) co-absorbed with ^{75}Se on the soda-lime makes immediate measurement with the NaI(Tl) detector difficult or impossible for many samples (26·4-hr ^{76}As has also been observed in a few cases). Since ^{75}Se has a long half-life (120 days).

the soda-lime can be kept for up to 20 days, depending on the bromine content, to allow ^{82}Br to decay, without loss of sensitivity. Most samples can be measured after 7–10 days. If a result is urgently required, a Ge(Li) detector may be used with the limitations mentioned, or a simple chemical separation step such as precipitation of silver bromide may be performed.

As regards sensitivity, ^{75}Se obtained by irradiation as described contributes about 1000 counts/min per μg to the 0·4 MeV sum peak. Thus selenium contents of the order of 0·05 ppm are easily measured without excessively long counting periods. The sensitivity is naturally increased by higher neutron doses.

For the range of biological samples studied, the volatilization of selenium was complete under the conditions used, but the possibility still exists of exceptions to this.

In conclusion, apart from the inherent simplicity of the volatilization principle, its extension to selenium is of particular importance since it allows, under identical sampling and analytical conditions, determination of two elements which appear to have important biological interactions.

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Zusammenfassung—Es wird ein Verfahren beschrieben. Selen zusammen mit Quecksilber in biologischen Proben durch Neutronenaktivierungsanalyse zu bestimmen. wobei beide Elemente quantitativ verflüchtigt werden. Das ursprünglich für Quecksilber entwickelte Verfahren der Pyrolyse mit Filtration unerwünschter Verunreinigungen und selektivem Auffangen aus der Gasphase wird jetzt auf Selen ausgedehnt. Die Radionuklide ^{197}Hg und ^{75}Se von einer Probe werden getrennt aufgefangen und, um die höchste Empfindlichkeit zu erzielen, in einem NaJ(Tl)-Detektor vom Bohrlochtyp und einem γ-Spektrometer gezählt. Das Verfahren wurde durch Vergleichsanalysen und Analysen von biologischem Standardmaterial getestet; es gibt gute Ergebnisse. Es ist einfach und besonders nützlich bei Untersuchungen der Wechselwirkung von Quecksilber und Selen in biologischen Systemen; in menschlichem Gewebe wurde eine positive Korrelation zwischen diesen Elementen gefunden.

Résumé—On décrit une méthode pour le dosage du sélénium conjointement au mercure dans les échantillons biologiques par analyse par activation de neutrons basée sur la volatilisation quantitative des deux éléments. La techniqu initialement développée pour le mercure. basée sur la pyrolyse avec filtration des impuretés indésirables et captage sélectif de la phase gazeuse. est maintenant étendue au sélénium. Les radionuclides ^{197}Hg et ^{75}Se, d'un échantillon, sont captés séparément dans un détecteur NaI(Tl) du type puits et un spectromètre γ pour la sensibilité maximale. La méthode a été essayée par des analyses comparatives et des analyses de produits biologiques étalons, et donne de bons résultats. Elle est simple et particulièrement efficace dans les études de l'interaction du mercure et du sélénium dans des systèmes biologiques; on a trouvé une corrélation positive pour ces éléments pour des tissus humains.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM AND ITS APPLICATION TO NIOBIUM-STABILIZED STAINLESS STEEL

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Niobium is added to certain types of stainless steel as a stabilizer against the phenomenon known as "weld decay" or "intercrystalline corrosion", but the amount added must be carefully controlled. Elwell and Wood[1] and Cockbill[2] have reviewed the methods used for the spectrophotometric determination of niobium in steels. The most widely used methods involve the use of hydrogen peroxide, thiocyanate and pyrogallol. Niobium has also been determined as a reduced molybdoniobic heteropoly acid blue.[3] During recent years several chromogenic reagents have received much attention. Thus 4-(2-pyridylazo)resorcinol,[4] 1-(2-pyridylazo)resorcinol,[5] sulphochlorophenol-S,[6] Xylenol Orange,[7] Bromopyrogallol Red,[8] Arsenazo-I,[9] *etc.* have been suggested as reagents for niobium.

Tannin reacts with a number of cations and anions and is generally used to flocculate certain hydrous oxides, the precipitate so obtained usually being ignited to the oxide. It has been observed that a mixture of tannin and thioglycollic acid produces a yellow-orange colour with a niobium solution and that the reaction could be utilized as a sensitive spectrophotometric method for the determination of niobium in niobium-stabilized stainless steels and other types of steels containing relatively low amounts of niobium.

EXPERIMENTAL

Reagents

Standard niobium solution (1 *mg/ml*). Fuse 0·1431 g of pure Nb_2O_5 with 2 g of potassium pyrosulphate in a silica crucible and after cooling take up the cake with 10 ml of 40% tartaric acid solution by warming. Transfer the solution into a 100 ml standard flask and make up to volume with distilled water.

Standard niobium solution (0·05 *mg/ml*). Pipette out 25 ml of the 1 mg/ml solution into a 250 ml beaker and add dilute ammonia solution (1 + 1) drop by drop to adjust the pH of the solution to 7–7·5. Transfer the solution quantitatively into a 500 ml standard flask and dilute to volume with distilled water.

Tannic acid–thioglycollic acid mixture. Mix equal volumes of 5% w/v tannic acid and 10% v/v thioglycollic acid solutions. Filter the solution and store it in an amber glass bottle. Prepare fresh every week.

Acetate buffer, pH 4. Dissolve 25 g of sodium acetate trihydrate and 57·5 ml of glacial acetic acid in 1 litre of distilled water.

Cupferron wash-solution. Dissolve 1 g of cupferron in 1 litre of distilled water and add 1 ml of thioglycollic acid. Prepare daily and filter before use.

Table 1. Weight of sample for analysis.

Niobium content, %	Weight of sample, *g*
0·1	5
0·5	2
1·0	1
1·5	0·5

Procedure

Dissolve a suitable weight of sample (according to Table 1) in 60–70 ml of dilute sulphuric acid (1 + 3) by warming. Oxidize with a few drops of nitric acid and heat to fumes. Cool and take up the mass with dilute hydrochloric acid. Filter off the silica, wash and ignite it, treat it with hydrofluoric and sulphuric acids, fuse the residue with potassium pyrosulphate, dissolve the product and add it to the main solution. Adjust the hydrochloric acid concentration to 10–15% v/v. Add 20 ml of thioglycollic acid, cool the solution to below 15° and add freshly

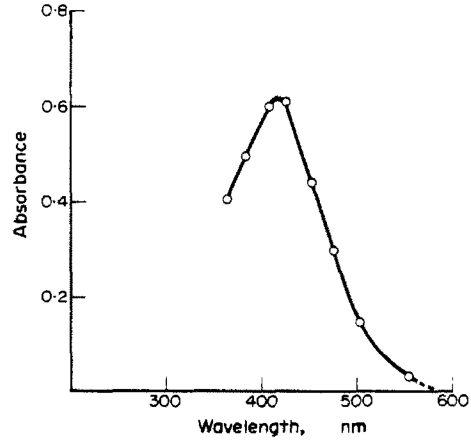

Fig. 1. Absorption spectrum of niobium–tannin–thioglycollic acid complex.

prepared 2% cupferron solution drop by drop with constant stirring until the precipitation of niobium is complete and a precipitate of iron begins to appear. Add 1 ml of cupferron solution in excess and some filter-paper pulp and stir for 2–3 min to coagulate the precipitate. Filter off on Whatman No. 41 paper and wash the precipitate several times with cupferron wash-solution. Carefully ignite the precipitate in a large silica crucible and fuse the ignited residue with potassium pyrosulphate. Cool and take up the cake by warming with 10 ml of 5% tartaric acid solution and transfer the solution into a 250 ml beaker, neutralize it with dilute ammonia solution (1 + 1) as described above, transfer the solution to a 250 ml standard flask and dilute to volume with distilled water

Pipette 10 ml of the solution into a 50-ml volumetric flask, add 10 ml of tannic acid–thioglycollic acid mixture, 20–25 ml of acetate buffer, mix well and dilute to volume with distilled water. After 10–15 min measure the absorbance at 420 nm.

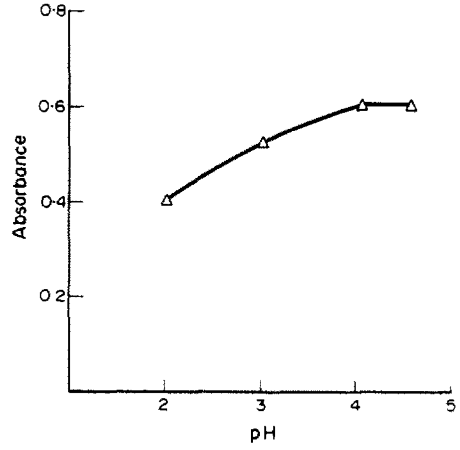

Fig. 2. Effect of pH on the absorbance of the complex.

RESULTS AND DISCUSSION

Spectroscopic data

The absorption spectrum of a 5 ppm niobium solution at pH 4 was recorded between 350 and 550 nm (Fig. 1). The complex has its absorbance maximum at 410–420 nm and 420 nm was chosen for all measurements. The dependance of the absorbance on pH is shown in Fig. 2. The maximum appears at pH 4–4·5. A calibration curve showed that Beer's law is obeyed over the range 0·2–10 ppm niobium. The upper limit can be extended by working with lower pH, *e.g.*, to 40 ppm at pH 2·5.

The stability of the colour depends on the niobium concentration and the pH at which the colour is developed. The colour developed with a 5 ppm niobium solution at pH 4–4·5 is stable for more than 1 hr whereas with

10 ppm solution at pH 4·5 the colour decreases rapidly because of coagulation, but at pH 4 is also stable for more than 1 hr Thus all measurements were made at pH 4

Effect of diverse ions

Tantalum up to 10 ppm may be tolerated Tungsten does not interfere but titanium even at the 0·2 ppm level interferes The interference due to Cu, Ni, Cr, Mo, V, Co *etc.* can be eliminated by prior separation of niobium with cupferron in presence of thioglycollic acid. Iron does not interfere.

Effect of sequestering agents

Complexing anions such as fluoride and EDTA seriously interfere Excess of chloride, sulphate or nitrate has no effect but nitrite interferes. Large excess of hydrogen peroxide or phosphate cannot be tolerated. Oxalate and citrate above 1 mg ml suppress the colour Tartaric acid up to 2–3 mg/ml does not interfere, but higher concentrations slightly decrease the absorbance, so the tartaric acid concentration should be kept fixed.

PRACTICAL APPLICATIONS

Niobium-stabilized stainless-steels generally contain 0·2–1·2% niobium. For such samples the preliminary separation of niobium with controlled addition of cupferron in presence of thioglycollic acid is faster. Other methods, *e.g.*, tartrate hydrolysis, tannin separation or sulphurous acid hydrolysis may also be adopted, but the present method is less time-consuming.

Typical results for niobium in standard niobium-stabilized stainless-steel samples are shown in Table 2. Determination of niobium in synthetic samples containing 0·5–5·0 mg of Nb gave recoveries of 99–100·4%.

Table 2. Determination of niobium

Sample	General composition, %	Nb, % Reported	Nb, % Found
BCS 261	C—0·083, Si—0·39, Mn—0·66, Ni—13·08, Cr—17·20, Mo—0·03, Cu—0·06, V—0·03, W—0·04	0·71	0·70 0·70
BCS 261 1	C—0·09, Si—0·05, Cr—17·4, Ni—13·1, Ta—0·006, Mo—0·11, Cu—0·12, Co—0·05	0·91	0·88 0·90
Jap-655-2	Mn—0·15, Si—0·50, Cr—18·5, Ni—11·5, Cu—0·05, Ta—0·03, Mo—0·05	0·60	0·60 0·62

Acknowledgements—Our thanks are due to Dr. A. N. Choudhury, Chief Chemist and Dr. N. R. Sen Gupta, Senior Chemist, Geological Survey of India, Calcutta for their co-operation and help. Our thanks are also due to the General Superintendent, Durgapur Steel Plant, for according permission to publish the paper.

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Summary—A spectrophotometric method is described for the determination of niobium by means of its reaction with tannin and thioglycollic acid. The yellow-orange colour developed with the reagent mixture at pH 4 is measured at 410–420 nm and obeys Beer's law between 0·5 and 10 ppm niobium. The method is suitable for the determination of niobium in niobium-stabilized stainless steel and other types of steels containing niobium, but a prior separation of niobium is necessary. Titanium interferes even in traces.

Zusammenfassung—Ein spektrophotometrisches Verfahren zur Bestimmung von Niob mit Hilfe seiner Reakton mit Tannin und Thioglycolsäure wird beschrieben. Die bei pH 4 mit dem Reagentiengemisch entwickelte orangegelbe Farbe wird bei 410–420 nm gemessen; sie befolgt zwischen 0,5 und 10 ppm Niob das Beersche Gesetz. Das Verfahren ist zur Bestimmung von Niob in mit Niob passiviertem rostfreiem Stahl und anderen Niob enthaltenden Stahlsorten geeignet; das Niob muß jedoch vorher abgetrennt werden. Titan stört selbst in Spuren.

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EFFECT OF CHLORIDE IONS ON THE BEHAVIOUR OF THE ORION COPPER(II) ION-SELECTIVE ELECTRODE

(*Received* 21 *January* 1974. *Accepted* 25 *February* 1974)

A common type of interference experienced with solid-state ion-selective electrodes occurs when the interferent interacts with the solid surface to form a film of another insoluble material.[1] Thus even a slow leakage of chloride ions from a saturated calomel reference electrode ruins the performance of an Orion 94-29A copper(II) ion-selective electrode and makes its usual shiny surface dull. Chloride ions also complex with copper(II) ions, and for this reason Johansson and Edström[2] used a $2M$ potassium nitrate bridge solution to investigate the surface parameters of this Orion electrode. However, chloride ions frequently occur in the solutions being measured and the present study relates to their influence on the copper(II) ion-selective electrode.

EXPERIMENTAL

An Orion 94-29A copper(II) ion-selective electrode was used in conjunction with either a Corning (No. 476109) ceramic-plug type calomel reference electrode containing $4M$ potassium chloride, or an Orion (No. 92-02) double-junction reference electrode with an outer 10% potassium nitrate filler. The potentials of such cells were recorded with either an Orion 801, or a Corning 101, digital pH-meter, to ±0·1 mV. All solutions (20 ml) were stirred and equilibrated to 25 ± 0·1 before the potential measurement and the electrodes were thoroughly washed in demineralized water between changes of test solutions.

Additional studies on mixed copper sulphide/silver sulphide membranes were made with pressed discs of well-washed, intimately mixed precipitates of copper sulphide and silver sulphide. These precipitates were obtained by adding freshly prepared $0{\cdot}1M$ sodium sulphide (250 ml) to a stirred solution composed of $0{\cdot}1M$ copper nitrate (100 ml) and $0{\cdot}1M$ silver nitrate (200 ml). The precipitates were filtered off, washed well and dried in the dark at 110. 1 g samples were pressed into discs at about 10^4 psi.

Photomicrographs of pressed discs were taken with a Vickers microscope with a Polaroid camera attachment.

Summary—A spectrophotometric method is described for the determination of niobium by means of its reaction with tannin and thioglycollic acid. The yellow-orange colour developed with the reagent mixture at pH 4 is measured at 410–420 nm and obeys Beer's law between 0·5 and 10 ppm niobium. The method is suitable for the determination of niobium in niobium-stabilized stainless steel and other types of steels containing niobium, but a prior separation of niobium is necessary. Titanium interferes even in traces.

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Photomicrographs of pressed discs were taken with a Vickers microscope with a Polaroid camera attachment.

RESULTS AND DISCUSSION

Before each calibration, the Orion 94-29A copper electrode, with shiny surface, was soaked for 24 hr in 1*M* copper nitrate. Despite low chloride-ion leakage from the Corning reference electrode (0·01 ml/hr), attempts to obtain a stable calibration of the conditioned copper electrode failed when it was coupled with the Corning calomel reference electrode, owing to slow potential drift in a negative direction. The leakage rate reported above would give an increase of about 2×10^{-3} mole l^{-1} hr^{-1} in the chloride ion concentration in the calibration solution The sensing surface of the electrode, which became black, was restored by lightly polishing with "Crocus" emery cloth (Behr Manning, New York), for a few minutes This treatment regularly restored the shiny appearance as well as the normal e.m.f. response in standard copper nitrate solutions when the electrode was coupled with an Orion (No. 92-02) double-junction reference electrode (curve A, Fig. 1).

Calibration response times when the Orion (No. 92-02) double-junction reference electrode was used were of the order of minutes and the surface remained shiny even after repeated transfers between various standard copper solutions In some runs several air bubbles accumulated on the sensor surface but these had no serious effect on the potential responses.

Effect of added chloride ions

The steady potential recorded for the copper electrode against the Orion double-junction reference electrode in a stirred 0 1*M* copper nitrate solution fell dramatically from +224·7 mV to +120 mV in 10 min after addition of saturated potassium chloride solution (0·1 ml) to the calibration solution (20 ml). This fall was considerably greater than that which could arise from any lowering of copper(II) ion concentration by the 0·02*M* concentration of chloride ions in the solution and can only be attributed to changes in the sensing surface of the electrode. However, after washing and placing in fresh 0·1*M* copper nitrate, the copper electrode, the sensor surface of which had become a dull black, gave a steady response of +262 mV for over 15 min when coupled with the double-junction electrode, thus suggesting an unexpectedly high copper(II) ion concentration (curve A, Fig. 1) or possibly a low chloride concentration (curve B, Fig. 1). Polishing about half of the dull electrode surface area in the manner described above led to a potential (in a fresh 0·1*M* copper nitrate solution) which changed steadily from an initial +255 mV to +232·4 mV in 35 min The remaining dull surface area was then polished and the potential recorded for 0·1*M* copper nitrate was +224·1 mV within 2 min, and altered to only +224·7 mV even after standing (coupled to the double-junction electrode) for 16 hr in the 0·1*M* copper nitrate. The cycle of chloride-induced failure and surface-restoration by polishing was repeated many times with differences of only a few millivolts being recorded at each recalibration stage

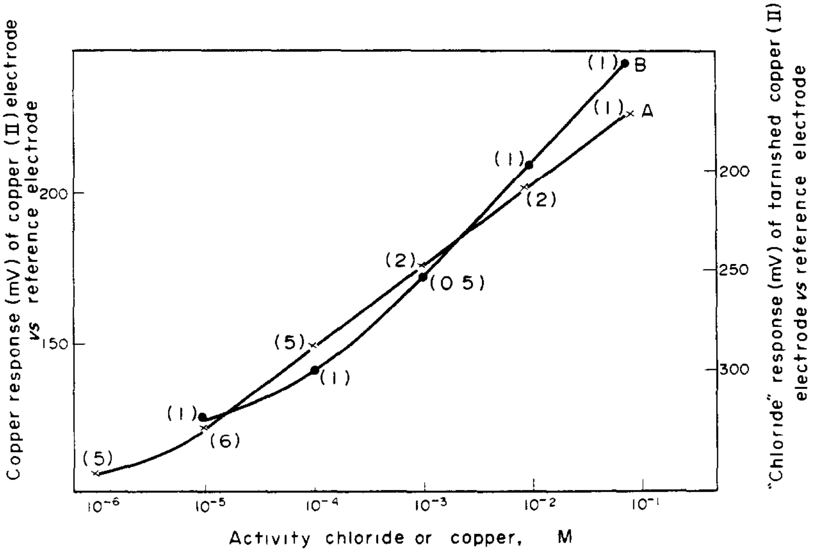

Fig. 1 Calibrations of an Orion 94-29A copper(II) electrode against an Orion double-junction reference electrode

A Copper response of copper(II) electrode *vs* standard copper solutions B. "Chloride" response of tarnished copper(II) electrode *vs* standard chloride solutions [Numbers in parentheses on the plots refer to static time-responses (min)]

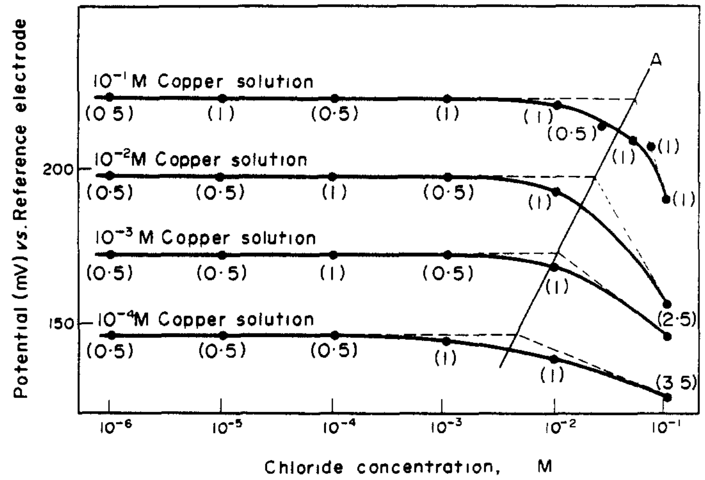

Fig. 2. Potential responses of an Orion 94-29A copper(II) electrode to copper(II) ions in the presence of various concentrations of chloride ions. [Numbers in parentheses on the plots refer to static time-responses (min).]

Potential responses of the copper electrode *vs.* the double-junction reference electrode were measured for a set of solutions containing copper(II) ions and chloride ions (Fig. 2). The electrode was polished between being immersed in each of the different solutions. The copper(II) ion response was not affected until the chloride ion concentration approximated to that of the copper(II) ion and so presumably when copper(II) chloro-complexes became significant in concentration.

Nature of the surface interferent

Anion interference at the sensing surface of heavy metal sulphide/silver sulphide electrodes has been claimed[3] to arise in a manner which in the present instance amounts to

$$Ag_2S(s) + Cu^{2+}_{aq} + 2Cl^-_{aq} \rightleftharpoons CuS(s) + 2AgCl(s) \tag{1}$$

In order to maintain the stability of the sensor, this reaction demands[3,4] that

$$\log[Cu^{2+}] + 2\log[Cl^-] < \log\frac{K_{S_{CuS}}(K_{S_{AgCl}})^2}{K_{S_{Ag_2S}}} = -5{\cdot}80 \tag{2}$$

otherwise a thin film of copper sulphide/silver chloride can be expected to be deposited on the sensing surface of the electrode. In these circumstances, the impaired copper(II) ion electrode ought to function as a chloride-sensitive electrode as indeed is the case here (curve B, Fig. 1). The chloride-ion calibration slope departs from the expected value of 59·2 mV per decade, possibly owing to the imperfect quality of the silver chloride layer.

Although curve B in Fig. 1 shows that the electrode responds to chloride ions, the picture is not the simple one depicted by equations (1) and (2), for these demand that $\log[Cu^{2+}] + 2\log[Cl^-]$ should be a constant governed by the relevant solubility products. Instead, the line connecting the points of equal contribution of $[Cu^{2+}]$ and $[Cl^-]$ [Fig. 2 (line A)] corresponds to the more complicated relation

$$\log[Cu^{2+}] - 2{\cdot}8\log[Cl^-] = 2{\cdot}7 \tag{3}$$

suggesting that other factors such as the formation of copper(II) chloro-complexes may be involved.

It was not physically possible to obtain infrared reflectances, or photomicrographs, of the ion-selective electrode surface. However, the sensor disc of the Orion 94-29 copper(II) ion-selective electrode, and presumably also of the later 94-29A model, comprises copper and silver sulphides although in unknown proportions.[1,3] Hence, as a compromise measure, simulated sensor discs were pressed at about 10^4 psi from 1 : 1 molar mixtures of copper sulphide and silver sulphide.

Photomicrographs of the disc surfaces before and after soaking in 0·1*M* copper nitrate (20 ml) with added 10% potassium chloride solution (0·1 ml) are quite different (Figs. 3a and 3b). Their "restoration" following polishing is also evident (Fig. 3c).

Bands in the 400 cm^{-1} region are to be expected for copper(II) chloro-complexes, but reflectance measurements of the shiny, dull, or repolished disc surfaces gave no infrared patterns. Resort was therefore made to an examination of the freshly cast discs after grinding and pressing into 1–5 mg% potassium bromide discs but again without success. Even this finely ground material (about 500 mg), after stirring in saturated potassium chloride solutions, and thereby producing more of the interferent material, showed no significant infrared character in potassium bromide matrices. The presence of a substantial level of copper(II) chloro-complexes could not therefore be established as the cause of the interference.

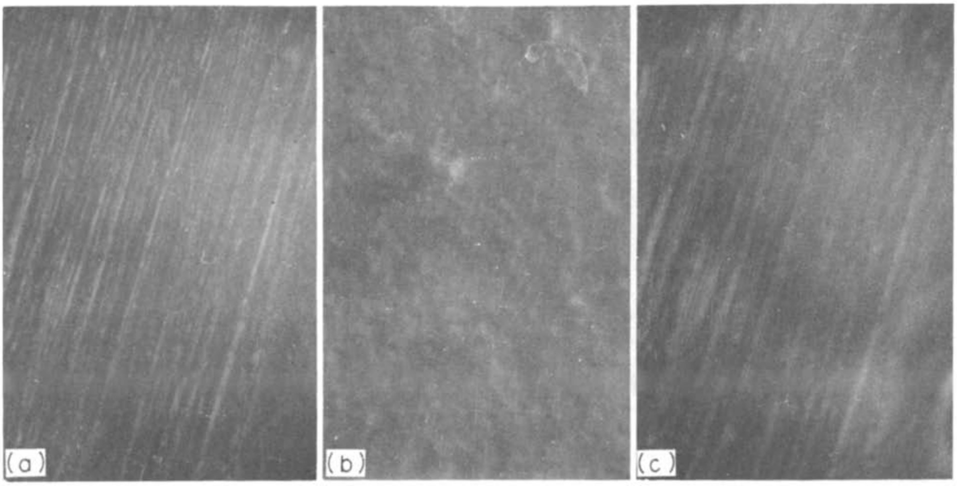

Fig. 3. Photomicrographs (× 200) showing the surfaces of a silver sulphide/copper sulphide pressed disc.
a. Freshly pressed disc. b. Disc after tarnishing by soaking in 0·1*M* copper nitrate (20 ml) with added 10% potassium chloride solution (0·1 ml). c. Surface of tarnished disc (b) after polishing with "Crocus" emery cloth.

Considerable difficulty was, however, experienced in achieving finely ground disc material. This is quite significant. One of the many stringent requirements[1-5] of solid-state electrode sensor membranes is good abrasive strength. Except for their electrical properties, quantitative information on physical properties of these solid-state sensors is sparse.[5,6] Although these discs of 1:1 molar constitution possessed excellent anti-scratch character, they shattered under test in an Avery hardness penetration rig.

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Summary—The normal shiny surface of a copper(II) ion-selective electrode tarnishes when exposed to chloride ions. Polishing with fine emery cloth easily removes this dull surface layer and fully restores the proper potential response characteristics of the electrode. No such loss of character is evident with a non-chloride based reference electrode except in the presence of added chloride ions. The electrode also seems less affected in premixed solutions of copper(II) and chloride, the chloride ions then being largely bound as copper(II) chloro-complexes.

Zusammenfassung—Die normalerweise glänzende Oberfläche einer ionenselektiven Kupfer(II)-Elektrode wird in Gegenwart von Chloridionen trübe. Polieren mit feinem Schmirgelleinen entfernt diese stumpfe Oberflächenschicht leicht und stellt das richtige Potentialansprechverhalten der Elektrode in vollem Umfang wieder her. Mit einer chloridfreien Bezugselektrode tritt das beschriebene Verhalten nicht auf, außer man gibt Chloridionen zu. Auch in vorher gemischten Lösungen von Kupfer(II) und Chlorid scheint die Elektrode weniger beeinträchtigt zu werden, da die Chloridionen dann weitgehend als Kupfer(II)-Chlorokomplexe gebunden sind.

Résumé—La surface brillante normale de l'électrode spécifique de l'ion cuivre(II) se ternit quand elle est exposée aux ions chlorure. Le polissage avec une toile émeri fine élimine aisément cette couche de surface terne et restaure pleinement les caractéristiques de réponse de potentiel convenables de l'électrode. Aucune telle perte de qualité n'est évidente avec une électrode de référence non basée sur le chlorure sauf en la présence d'ions chlorure ajoutés. L'électrode semble aussi moins altérée dans des solutions prémélangées de cuivre(II) et de chlorure, les ions chlorure étant alors essentiellement liés à l'état de chloro-complexes du cuivre(II).

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MOLECULAR-WEIGHT FRACTIONATION OF POLYSTYRENE BY ZONE-MELTING CHROMATOGRAPHY*

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Summary—Polystyrene can be fractionated by zone-melting chromatography on a solid column of durene. The polymer solute moves in the same direction as the heated zone. The higher the molecular weight of the polymer the slower it moves. Experiments with model mixtures of monodisperse polystyrenes of average molecular weight 6×10^2–2×10^5 indicate that a polymer fraction can be separated in 90% purity from fractions with molecular weights higher or lower by one order of magnitude. Polystyrene samples of various molecular weight distributions, after processing on durene columns, gave several fractions having significantly narrower dispersions than that of the starting polymer, in terms of gel-permeation chromatography.

Several experiments have been reported on molecular-weight fractionation of synthetic polymers by means of fractional solidification.[1–3] Although the separations were not particularly effective or reproducible, the technique seemed to be promising.

As we have been successful in the separation of metal chelates by zone-melting chromatography (ZMC), using a new apparatus which was constructed in our laboratory,[4] we decided to try it for molecular-weight fractionation of synthetic high polymers. Features of our apparatus are that a column as long as 120 cm can be treated and that the molten zone length is held constant at 5·0 ± 0·2 mm during a prolonged operation time.

This paper presents the results for application of our apparatus to the fractionation of polystyrene.

EXPERIMENTAL

Materials

Monodisperse standard samples of polystyrene were obtained from the Pressure Chemical Co., U.S.A., the average molecular weights being $6·0 \times 10^2$, $2·1 \times 10^3$, $4·0 \times 10^3$, $1·0 \times 10^4$, $2·04 \times 10^4$ and $2·0 \times 10^5$, and $\bar{M}_w/\bar{M}_n$ ratio (weight-average m.w. to number-average m.w.) of each sample was less than 1·10 according to the manufacturer's specification sheets.

"Coloured" polystyrene was prepared by introducing a chromophoric group into the monodisperse standard samples according to the following procedure. Polystyrene was nitrated with nitric acid in acetic anhydride,[5] the degree of nitration being about 20% (average of one nitro-substitution per five structure units). The nitro-derivative was reduced with sodium dithionite in dimethylformamide to give an amino-derivative,[6] which was diazotized and subsequently coupled with *N,N*-dimethyl-2,4-dimethoxyaniline, to afford a red polymer. The visible absorption spectrum of this polymer had λ_{max} at 430 nm $l.mole^{-1}.cm^{-1}$, ϵ being about $1·6 \times 10^3$, $l.mole^{-1}.cm^{-1}$ (where the mole is of the repeating unit of the polymer). Coloured polymers of three different molecular weights, $6·0 \times 10^2$, $2·04 \times 10^4$ and $2·0 \times 10^5$, were thus prepared.

Polydisperse samples were those obtained by bulk polymerization according to a standard procedure, and purified by precipitation from methanol four times. Two kinds of sample, $\bar{M}_w$ $2·36 \times 10^4$ and $1·60 \times 10^4$, were used.

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ZMC procedure

Preparation of the column and manipulation of the apparatus were done as described in the previous papers.[4-7] The column was a Pyrex glass tube 4 mm in bore and up to 50 cm long. During ZMC, the zone-length was maintained at 5·0 ± 0·2 mm and the glass tube travelled at the rate of 27 mm/hr while rotating on its axis at 6 rpm.

After a specified number of zone passes (n), the column was cut into pieces 5 or 10 mm long, and a sample from each piece was weighed and then dissolved in an appropriate solvent. A sample containing the "coloured" polystyrene was dissolved directly in dimethylformamide and the polymer concentration determined spectrophotometrically at 430 nm. A sample from polystyrene (solute)–durene (solvent) systems, was dissolved in tetrahydrofuran after most of the durene had been sublimed off at 65° under reduced pressure, and was analysed for the polymer by dual-wavelength spectrophotometry at the key bands of 261·8 and 280·7 nm on a Hitachi 356 Two-Wavelength Double Beam Spectrophotometer.[8]

Measurement of molecular-weight distribution (MWD).

The MWD of polystyrene in each ZMC fraction was determined by gel-permeation chromatography (GPC) on a Toyo Soda HLC-801 High Speed Liquid Chromatograph, using three serial combinations of two 60-cm columns packed with styrene–divinylbenzene co-polymer beads with various controlled pore-sizes. Tetrahydrofuran was used as eluent. The number of theoretical plates on each combination of these columns was found to be about 12000 when acetone was used as a sample. The calibration function between the elution count number and the molecular weight of polystyrene was computed for each combination of GPC columns, to give a polynomial of the eleventh order which gives a good fit to the elution data for the six kinds of monodisperse standards.

The molecular-weight averages were tentatively calculated from the elution curves by the strip method: the elution curve was divided into small strips and, using the calibration polynomial, the number-average molecular weight, $\bar{M}_n$, and the weight-average molecular weight, $\bar{M}_w$, were calculated according to the equations

$$\bar{M}_n = \sum_i m_i \Big/ \sum_i (m_i/M_i)$$

and

$$\bar{M}_w = \sum_i (m_i \,.\, M_i)$$

where m_i and M_i were the weight-fraction and the molecular weight of the ith fraction, respectively.

Numerical computation was carried out by use of FACOM 230–60 in the Computer Centre of Kyushu University.

Corrections for peak broadening or instrument spread[9,10] were ignored because the absolute MWD was not the object of the investigation and because such peak-broadening effects would probably cancel in comparison of relative MWDs measured on the same instrument under the same conditions.

Determination of the distribution coefficient

The distribution coefficient in the ZMC process was determined according to Sorensen.[11] For this purpose, an apparatus for single-stage zone-melting was constructed; the molten zone length was controlled at 5·0 ± 0·2 mm by employing a heating compartment interposed between two cooling compartments and separated from them by double partitions. The compartments are heated or cooled with hot or cold air blasts as in the multi-zone apparatus.[4]

RESULTS AND DISCUSSION

Selection of solid solvents

GPC measurements on the coloured polystyrene showed no indication of the presence of lower molecular-weight fractions, suggesting that the sequence of reactions by which the chromophore was introduced caused very little cleavage of the polymer chain. ZMC experiments with a single solute on durene or naphthalene columns showed that the coloured polymers gave distribution curves indistinguishable from those of the parent polystyrenes.

Thus the three kinds of coloured polymers were useful as visible indicators for selecting suitable solid solvents. The following organic compounds were tested, the m.p. being given in parentheses: 2,6-dimethylnaphthalene (108°), durene (80°), 2,3-dimethylnaphthalene

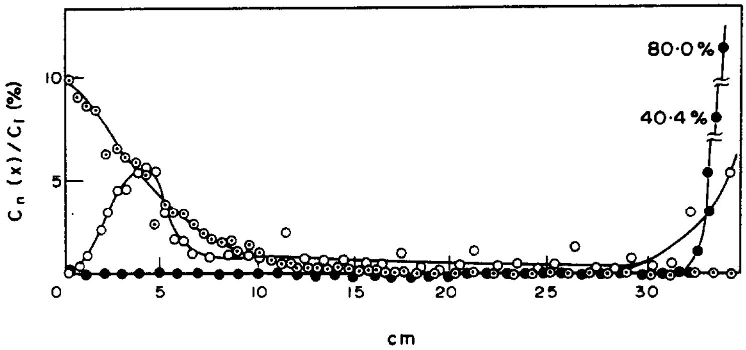

Fig. 1. Concentration profiles of $\overline{M}$ 6·0 × 10^2 polystyrene on some column materials. ○; biphenyl, $n = 20, C_i = 1{\cdot}4 \times 10^{-4}$ mole/g. ●; durene, $n = 10, C_i = 2{\cdot}3 \times 10^{-4}$ mole/g. ⊙; 2-methoxynaphthalene, $n = 30, C_i = 1{\cdot}2 \times 10^{-4}$ mole/g.

(102°), naphthalene (80°), biphenyl (70°), naphthodioxan (83°), phenanthrene (101°), benzylacetophenone (72°), acenaphthene (95°), fluorene (116°), 9,10-dihydroanthracene (109°), hexaethylbenzene (127°), 2-methoxynaphthalene (72°), 1,4-dimethoxynaphthalene (87°), 2,3-dimethoxynaphthalene (115°), phenyl benzoate (70°), *p*-diethoxybenzene (71°), and 2,5-diphenyloxazole (71°).

The ZMC distribution band of the "coloured" solute moved to various extents on solid solvent columns, depending upon the kind of solvent used; the solvents are listed above in decreasing order of band-shift. For example, on a durene column, the coloured polymer of $\overline{M}$ 600 was completely swept to the bottom end of the column after 10 zone passes. With a biphenyl column, however, it gave a chromatographic peak at 4 cm from the top, and with a 2-methoxynaphthalene column the solute remained at the starting position even after 30 zone passes (Fig. 1).

The coloured sample of $\overline{M}$ 2·04 × 10^4 gave a peak at 3 cm from the top of a durene column after 20 zone passes, whereas on a naphthalene column, the solute remained at the top end after the same number of zone passes, and an additional 10 zone passes caused only a slight movement towards the bottom. With a 2-methoxynaphthalene column, the solute was spread over the top 8 cm even after 30 zone passes (Fig. 2).

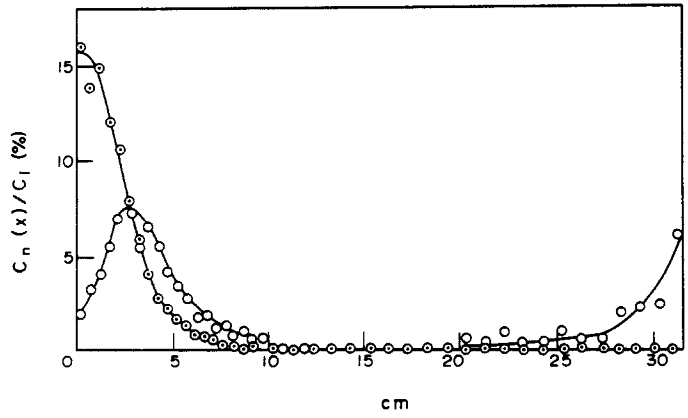

Fig. 2. Concentration profiles of $\overline{M}$ 2·04 × 10^4 polystyrene on some column materials. ○; durene, $n = 20, C_i = 0{\cdot}8 \times 10^{-4}$ mole/g. ⊙; 2-methoxynaphthalene, $n = 30, C_i = 3{\cdot}0 \times 10^{-4}$ mole/g.

Although the chemical structures of the column materials were found to affect strongly the ZMC behaviour of polystyrene, no clear correlation was found which would permit prediction of an optimal solvent material. Of the solvents studied, durene seemed the best because it gave a proper rate of movement of the ZMC band and its m.p. was convenient.

Distribution coefficient of monodisperse polystyrene

In order to correlate peak movement with molecular weight of the polymer, distribution coefficients were determined for six kinds of monodisperse standard polystyrenes on durene columns.

The relationship between log $\bar{M}$ and distribution coefficient, k, can be expressed by $k = 0{\cdot}24 \log \bar{M} - 0{\cdot}33$, and the correlation coefficient, r, is 0·966. The result shows that the distribution coefficient apparently increases with increased molecular weight of polystyrene, as observed in the benzene–polystyrene system.[2]

The distribution coefficient was also dependent upon the polymer concentration. Measurements on the polymers of $\bar{M}$ $2{\cdot}04 \times 10^4$ and $6{\cdot}0 \times 10^2$ at a certain range of initial concentrations, C_i, showed that the distribution coefficient increased slightly with C_i, the relationships being:

$$\bar{M} = 6{\cdot}0 \times 10^2 \text{ polymer,} \quad k = 0{\cdot}013 \times 10^4\, C_i + 0{\cdot}21;\ (r = 0{\cdot}80)$$
$$\bar{M} = 2{\cdot}04 \times 10^4 \text{ polymer,} \quad k = 0{\cdot}018 \times 10^4\, C_i + 0{\cdot}58;\ (r = 0{\cdot}94)$$

The results can be interpreted as meaning that the higher the polymer concentration, the more likely the entanglement of polymer chains at the crystal-growth front at the liquid–solid interface.

ZMC experiments with a single solute of standard polystyrene

In order to furnish reference data for ZMC separation of the polydisperse polymers on durene columns, single-solute operations were carried out, on the six kinds of monodisperse polysterene of $\bar{M}$ $6{\cdot}0 \times 10^2$–$2{\cdot}0 \times 10^5$.

After 10 zone passes, the sample of $\bar{M}$ $6{\cdot}0 \times 10^2$ was completely swept into the last 6 cm of a 33-cm column, and that of $\bar{M}$ $2{\cdot}1 \times 10^3$ into the last 5·5 cm of a 29·5-cm column. The polymer of $\bar{M}$ $4{\cdot}0 \times 10^3$ was also mainly shifted to the bottom, although it tailed over 22 cm of a 34-cm column. The peak for the $\bar{M}$ $1{\cdot}0 \times 10^4$ sample appeared at about 6 cm from the column top after 10 zone passes, and in the case of $\bar{M}$ $2{\cdot}04 \times 10^4$, the peak moved only 2·3 cm from the top even after 20 zone passes. The sample of $\bar{M}$ $2{\cdot}0 \times 10^5$, the highest molecular weight investigated, showed the peak at 8 mm, only two zone-lengths, below the column top after 20 zone passes, and the peak moved 2 cm more after 30 zone passes. Typical concentration profiles from these experiments are shown in Fig. 3.

The effective distribution coefficients estimated from the observed peak position in the ZMC experiments[12] were $k = 0{\cdot}43$, 0·81 and 0·94 for the samples of $\bar{M}$ $1{\cdot}0 \times 10^4$, $2{\cdot}04 \times 10^4$ and $2{\cdot}0 \times 10^5$, respectively. These values are in fair agreement with those obtained by the Sorensen method, if the dependence of k on C_i is taken into consideration. The result shows that the peak position on the solute concentration profile in ZMC can be predicted if the distribution coefficient of the solute is known, as in the case of other chromatographic techniques.

ZMC experiments with binary and ternary mixtures of standard polystyrenes

The above-mentioned relationship between the distribution coefficient and molecular weight of polystyrene, suggested that a polydisperse polystyrene might be fractionated by

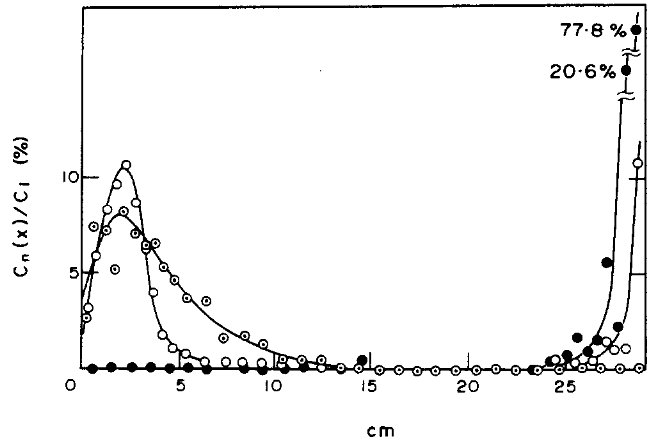

Fig. 3. Concentration profiles of the various monodisperse polystyrenes on durene columns. ●; $\bar{M}$ 2·1 × 10^3, n = 10. ○; $\bar{M}$ 204 × 10^4, n = 20. ⊙; $\bar{M}$ 2·0 × 10^5, n = 50.

ZMC, and this was tested on model mixtures of the monodisperse standard polymers: (*a*) $\bar{M}$ 6·0 × 10^2 and 2·04 × 10^4, (*b*) $\bar{M}$ 2·1 × 10^3 and 2·04 × 10^4, (*c*) $\bar{M}$ 6·0 × 10^2 and 2·1 × 10^3, (*d*) $\bar{M}$ 6·0 × 10^2 and 2·0 × 10^5 and (*e*) $\bar{M}$ 4·0 × 10^3, 2·04 × 10^4 and 2·0 × 10^5.

The typical behaviour of the solute during ZMC is shown in Fig. 4, which illustrates the GPC profile of the fractions from the top, middle and bottom portions of the column after 3 zone passes for mixture (*c*). Peaks A and B correspond to the $\bar{M}$ 2·1 × 10^3 and 6·0 × 10^2 polymers, respectively. If it is assumed that the peak areas are proportional to the weight fractions of the two components, the top portion consists of 71% $\bar{M}$ 2·1 × 10^3 and 29% $\bar{M}$ 6·0 × 10^2, while the bottom portion consists of 9% $\bar{M}$ 2·1 × 10^3 and 91% $\bar{M}$ 6·0 ± 10^2. Thus, it is seen that considerable separation can be attained after only 3 zone passes.

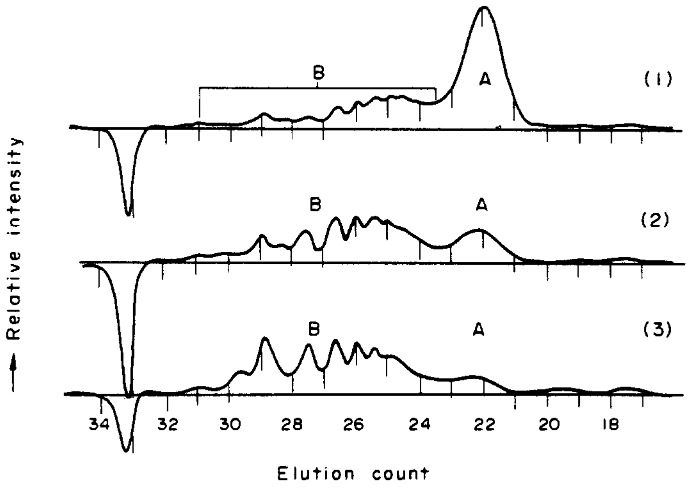

Fig. 4. Gel-permeation chromatograms of the fractions obtained after ZMC on a 1 : 1 mixture of $\bar{M}$ 2·1 × 10^3 and 6·0 × 10^2 polymers. n = 3. C = 11·8 × 10^{-4} mole/g. L = 32·0 cm. Curves (1), (2) and (3) indicate the fractions from the column top, mid-point and bottom, respectively. Zones *A* and *B* correspond to the $\bar{M}$ 2·1 × 10^3 and 6·0 × 10^2 polymers, respectively.

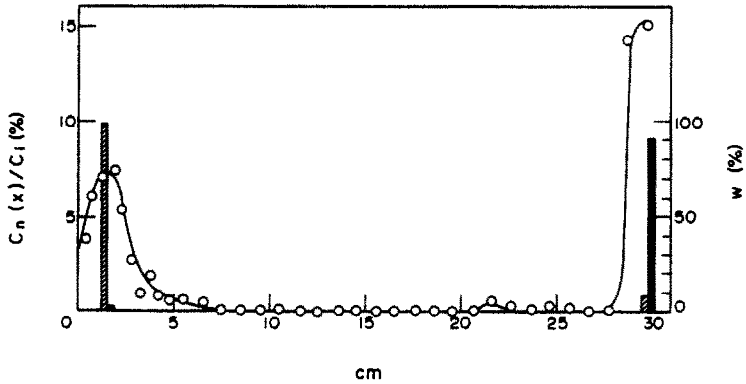

Fig. 5. Concentration profile and weight fractions of the component polymers after 20 zone passes on a 1 : 1 mixture of monodisperse polymers. O——O; relative polymer concentration. $C_n(x)/C_i$ (%). ▨, ■; weight fractions, w (%), of $\bar{M}$ 2·04 × 10^4 and 2·1 × 10^3 polymers, respectively. ZMC on a durene column 30·0 cm long and C_i = 7·4 × 10^{-4} mole/g.

After ZMC of each mixture for a given number of zone passes, the concentration distribution of the polymers along the column was determined by dual wavelength spectrophotometry, and the molecular weight distributions of some representative fractions were determined by GPC.

From the results of both measurements, it was found that the mixtures were satisfactorily separated into their components if the molecular weights differed by more than a factor of ten.

Representative results are shown in Figs. 5, 6 and 7. Each circle in the figures shows the ratio of the total concentration at that position to that of the initial charge and the lines connecting the circles show the general trend of the concentration profiles. The histograms indicate the percentage of each component of the solute in the given fraction.

Figure 5 shows the distribution of sample (*b*) after 20 zone passes. Chromatographic separation in this system seems quite satisfactory. The two peak positions in the concentration profile are found to be identical to the corresponding peak positions observed in the single-solute ZMC experiments, indicating that there is no co-operative interaction between the two solutes.

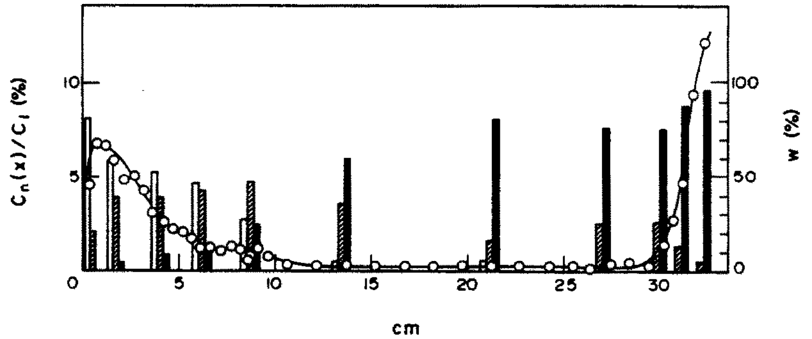

Fig. 6. Concentration profile and weight fractions of the component polymers after 30 zone passes on a 1 : 1 : 1 ternary mixture of monodisperse polymers. O——O; relative polymer concentration, $C_n(x)/C_i$ (%). □, ▨, ■; weight fractions, w (%), of $\bar{M}$ 2·0 × 10^5, 2·0 × 10^4 and 4·0 × 10^3 polymers, respectively. ZMC on a durene column 32·5 cm long and C_i = 16·2 × 10^{-4} mole/g.

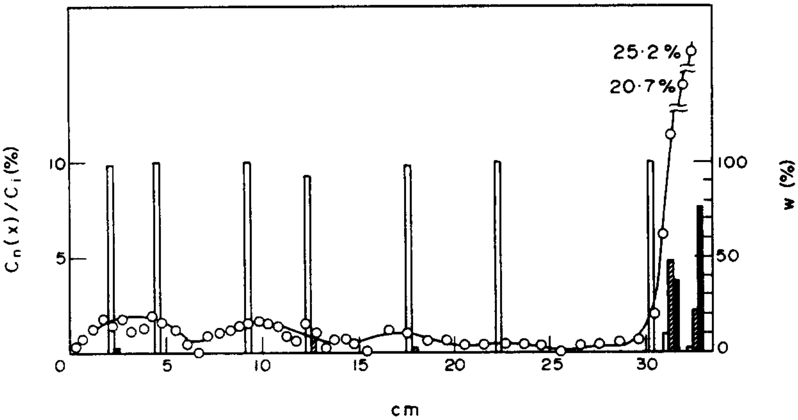

Fig. 7. Concentration profile and weight fractions of the component polymers after 50 zone passes on a 1:1:1 ternary mixture of monodisperse polymers. Symbols as for Fig. 6. ZMC on a durene column 33·0 cm long and $C_i = 13{\cdot}5 \times 10^{-4}$ mole/g.

The distributions of sample (*e*) after 30 and 50 passes are shown in Figs. 6 and 7, respectively. Comparison of the two figures indicates that in ZMC fractionation of polymers on a column of limited length, it is important to select a proper number of zone passes, depending upon the molecular weight range of the polymer solutes.

ZMC experiments with polydisperse polystyrene

On the basis of these results, ZMC fractionation was applied to two kinds of polydisperse polystyrene, one with $\bar{M} = 1{\cdot}6 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1{\cdot}79$, and the other with $\bar{M} = 2{\cdot}36 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2{\cdot}09$. The top, middle and bottom fractions from the columns were analysed by GPC for molecular weight distribution, which was conveniently expressed by the $\bar{M}_w/\bar{M}_n$ value. The results are summarized in Table 1.

It was found that the average molecular weight of the top fraction was higher than that of the bottom fraction by a factor of 2·0–2·3. The polydispersity of each fraction was also found to decrease in comparison with that of the starting material. The $\bar{M}_w/\bar{M}_n$ ratio of the top fraction was in the range 1·2–1·4, and that of the bottom fraction was 1·4–1·7. These values are more satisfactory than those obtained by the preparative GPC process,[13] in which $\bar{M}_w/\bar{M}_n$ values were reported as 1·2–1·4 for the best fractionated samples, and up to 3·0 or more for lower molecular-weight fractions; however, a different method of determination was used.

Further fractionation of monodisperse polystyrene by ZMC

As it was found that ZMC was very effective in molecular-weight fractionation of polydisperse polystyrene, the technique was applied to further fractionation of commercially available monodisperse polystyrene. Three samples of monodisperse polystyrene were fractionated by ZMC. The results of the GPC measurements are summarized in Table 1, which indicates that the average molecular weight of the top and bottom fractions after ZMC became higher and lower than that of the starting materials. The $\bar{M}_w/\bar{M}_n$ values of the top and bottom fractions after 10 zone passes on the polymer of $\bar{M} = 2{\cdot}04 \times 10^4$ were found to be 1·047 and 1·044, respectively, which are lower than that of the starting material, $\bar{M}_w/\bar{M}_n = 1{\cdot}053$ (estimated by the same GPC procedure). Similar results were

Table 1. M_w* and $\bar{M}_w/\bar{M}$ * ratios of the fractions at various points on a column after ZMC molecular-weight fractionation of polydisperse and monodisperse polystyrenes

Dispersity	Polymer sample $\bar{M}_w$* and $(\bar{M}_w/\bar{M}_n)$*	n	M_w* and $(M_w/M\ )$* of the fractions after ZMC Top	Mid-point	Bottom
Polydisperse					
	$1{\cdot}60 \times 10^4$ (1·79)	10	$2{\cdot}25 \times 10^4$ (1·27)	$1{\cdot}66 \times 10^4$ (1·22)	$9{\cdot}5 \times 10^3$ (1·68)
	$1{\cdot}60 \times 10^4$ (1·79)	40	$2{\cdot}24 \times 10^4$ (1·18)	$1{\cdot}84 \times 10^4$ (1·18)	$1{\cdot}13 \times 10^4$ (1·42)
	$2{\cdot}36 \times 10^4$ (2·09)	40	$2{\cdot}51 \times 10^4$ (1·38)	$2{\cdot}32 \times 10^4$ (1·28)	$1{\cdot}09 \times 10^4$ (1·47)
Monodisperse					
	$1{\cdot}85 \times 10^4$† (1·053)	10	$1{\cdot}96 \times 10^4$ (1·047)	$1{\cdot}76 \times 10^4$ (1·045)	$1{\cdot}71 \times 10^4$ (1·044)
	$4{\cdot}00 \times 10^3$ (1·12)	10	$4{\cdot}20 \times 10^3$ (1·09)	— —	$3{\cdot}80 \times 10^3$ (1·13)
	$2{\cdot}10 \times 10^3$ (1·21)	3	$2{\cdot}40 \times 10^3$ (1·06)	$2{\cdot}20 \times 10^3$ (1·08)	$2{\cdot}00 \times 10^3$ (1·09)

* Each value is calculated from the GPC curve.

† According to the manufacturer's sheet, $\bar{M} = 2{\cdot}04 \times 10^4$.

obtained for the other two polymers. Thus the ZMC technique is found to increase the monodispersity of monodisperse polystyrene. Although the present process was applied to about 10 mg of the sample on a column of 4·0 mm in diameter, a limitation imposed by the dimensions of our apparatus, the process could perhaps be extended to the preparative scale if columns of larger diameter could be treated.

Acknowledgements—The authors are grateful to Mr. H. Sakomura, Director of Research Laboratory of Toyo Soda Co., for his generosity in the use of a GPC apparatus. The authors also wish to thank Dr. Y. Hatate, Department of Applied Chemistry, Kyushu University, for his helpful advice in FORTRAN programming to compute MWD from GPC curves. Financial support for this work was given by the Ministry of Education, Japanese Government, to whom the authors are thankful.

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Zusammenfassung—Polystyrol kann durch Zonenschmelzchromatographie an einer Säule von festem Durol fraktioniert werden. Das gelöste Polymere wandert in dieselbe Richtung wie die geheizte Zone. Je höher das Molekulargewicht des Polymeren ist, desto langsamer wandert es. Versuche mit Modellgemischen aus monodispersen Polystyrolen vom mittleren Molekulargewicht $6 \cdot 10^2$–$2 \cdot 10^5$ zeigen, daß man eine Polymerenfraktion mit 90% Reinheit von Fraktionen trennen kann, deren Molekulargewichte eine Größenordnung höher oder niedriger liegen. Nach der Behandlung an Durolsäulen gaben Polystyrolproben verschiedener Molekulargewichtsverteilungen mehrere Fraktionen, die im Sinne der Gelpermeationschromatographie wesentlich engere Verteilungen hatten als die des Ausgangs-Polymeren.

Résumé—Le polystyrène peut être fractionné par chromatographie de fusion de zone sur une colonne solide de durène. Le soluté de polymère se déplace dans la même direction que la zone chauffée. Le polymère se meut d'autant plus lentement que son poids moléculaire est plus élevé. Des expériences avec des mélanges modèles de polystyrènes monodispersés de poids moléculaire moyen $6 \times 10^2 - 2 \times 10^5$ indiquent qu'une fraction de polymère peut être séparée à 90% de pureté de fractions avec des poids moléculaires d'un ordre de grandeur plus élevé ou plus bas. Des échantillons de polystyrène de diverses répartitions de poids moléculaires, après traitement sur colonnes de durène, ont donné plusieurs fractions ayant des dispersions notablement plus étroites que celles du polymère de départ, par rapport à la chromatographie de perméation de gel.

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PERFORMANCE CHARACTERISTICS OF ANALYTICAL METHODS—IV*

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Summary—Sources of systematic errors in analytical results are discussed, and suggestions are made for the investigation and reporting of such errors when characterizing the performances of analytical methods. The four types of error considered arise from: (1) blank determinations, (2) calibration, (3) differences in the efficiencies with which different forms of the determinand are measured, and (4) interferences. The comparison of results with accepted values of standard samples or with the results obtained by standard methods is also discussed.

Analytical results are subject to random and systematic errors, the general natures of which have been discussed in Part II, where the estimation of random errors was considered, and suggestions for defining relevant performance-characteristics were made. In the present Part, systematic errors are similarly discussed, and it is useful briefly to restate the definition of systematic error (bias) given in Part II. The mean of n repeated analytical results on the same sample approaches a definite value, μ, as n is increased indefinitely (an important proviso is given in Part II). When the value of μ differs from the true value, τ, the results are said to be subject to a systematic error of magnitude B where $B = \mu - \tau$.

SOURCES OF SYSTEMATIC ERROR (BIAS)

Four sources of bias in analytical results may generally be distinguished though not all are necessarily present for a particular method.

(1) The results of blank determinations may be biased.

(2) The calibration (used to convert from analytical response to concentration†) may be biased.

(3) The analytical method may be such that different responses are obtained for equal concentrations of different forms of the determinand.

(4) Substances other than the determinand in the sample may cause bias, *i.e.*, interference may occur.

These sources of bias are considered in turn in the following sections. In addition, a final section discusses the overall bias of analytical results.

Blank determination

For any method of analysis, the direct analytical result, C'_S for the concentration of determinand in a sample may be regarded as made up of three components (assuming that no interfering substances are present in the original sample).

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* Part III-*Talanta*, 1973, **20**, 725.

† For simplicity, throughout this paper, analytical results are spoken of as in units of concentration; the arguments apply equally if other units (*e.g.*, mass, volume) are used.

(1) The concentration of determinand in the original sample, C_S.

(2) The determinand (and possibly interfering substances) may be introduced into the sample during analysis (*e.g.*, from reagents, contamination). This will result in the apparent determinand concentration in the sample being increased by an amount C_R.

(3) Constituents of the sample matrix present in essentially constant amounts in each sample may also give an analytical response equivalent to a determinand concentration, C_M. For example, when certain methods are used to analyse water samples, the analytical response may be affected by water itself. It is rather arbitrary to distinguish this effect from interference, but it is useful in the present context and should not cause problems. Thus $C'_S = C_S + C_R + C_M$.

The analyst wishes to determine C_S, and thus it is generally necessary to make a special determination to estimate $C_R + C_M$. This determination is commonly termed "*the blank determination*", and this term is used throughout this series. Subtraction* of the blank, C_B, from the result for the sample, C'_S, then gives the value for C_S, *i.e.*,

$$C_B = C_R + C_M$$
$$C_S = C'_S - C_B$$

Of course, not all methods require a blank, but it is normally essential for the wide range of methods used in trace analysis. It is also important to note that, as defined here, a blank determination is not intended merely to measure the determinand present in any reagents. Two sources of bias can affect the result for the blank.

Differences between blank and sample procedures. Clearly, if the result for the blank is to be unbiased, the determination should be subject to all the effects (*e.g.*, contamination) that apply to samples. Thus, the blank should generally be analysed by exactly the same procedure as that used for samples. This simple and obvious conclusion is worth stating because it appears often to be ignored. Of course, situations arise where it is impracticable or not essential to analyse blanks and samples identically, but such situations generally require experimental confirmation. It is also important to bear in mind that the magnitudes of effects such as contamination are likely to vary markedly from time to time, and from one laboratory to another. Thus, even though one worker finds that a "short-cut" analytical procedure for the blank is satisfactory, this is by no means necessarily true.

These simple ideas cannot be quantified to allow definition of a numerical performance-characteristic. Nevertheless, they are important in assessing the suitability of an analytical method. It is generally desirable to regard as suspect the accuracy of a method using different procedures for the blank and samples—at least until any effect of such differences has been experimentally assessed.

Determinand content of the blank sample. The considerations above imply that, in principle, the blank determination best consists of the analysis of a special sample of the material of which normal samples are composed, and which contains a negligible concentration of the determinand. Sometimes this principle is easily applied, *e.g.*, demineralized water is often used for the blank when samples of water are to be analysed. In other applications, *e.g.*, analysis of complex alloys, it may be impracticable to apply the principle. For the latter applications, the consequent differences between sample and blank procedures should be regarded as suggested in the preceding section. For the methods that use a spe-

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* The most accurate and/or convenient method of making the blank correction may, in practice, differ from one method to another. This is not considered here as it is unimportant for the purposes of this paper.

cial sample for the blank, an additional source of bias arises, *i.e.*, the determinand content of the blank sample.

Thus with the same notation as before, and letting C_D = determinand concentration in the blank sample:

$$C'_S = C_S + C_R + C_M$$

$$C_B = C_D + C_R + C_M$$

$$C_S = C'_S - C_B + C_D$$

so that C_D must be known if results for C_S are to be known to be unbiased. Again, this simple and well-known conclusion is worth restating because it seems often not to be applied.

As before, these ideas do not lead to a definition of a numerical performance-characteristic, but they emphasize that methods should clearly state how the determinand concentration in the blank sample is to be measured with sufficient accuracy.

Calibration

Various terms are used to denote the relationship between the analytical response, R, and the concentration of determinand in the sample, C_S, that is used to determine C_S from the measured response. Calibration curve is used by ISO[2] in its recommendations for the format of analytical methods, while IUPAC[3] uses analytical curve. Standard curve and working curve are also commonly employed. In a penetrating analysis of the basic considerations involved in the relationship between response and concentration, Kaiser[4] proposes that both the terms—calibration curve and analytical curve—are required. He suggests that the former be used to denote the curve produced when determining the response equivalent to known concentrations of the determinand, and that the latter denote the curve used to obtain the concentrations in samples from their measured responses. With the existing range of usage, and the lack of agreement of international bodies, there seems little point in arguing here for one or other of the terms. Calibration curve is preferred by the author (purely on the grounds that the term suggests the use), and is used throughout this series.

Many analytical methods do not explicitly use a calibration curve, but employ a multiplicative factor to convert responses into concentrations *e.g.*, in gravimetric analysis. The use of such factors is, however, essentially the same as the use of a calibration curve of the form $C_S = kR$. Other methods use instruments that give direct read-out of concentrations, but calibration of the instrument scales is then a first requisite, so a calibration curve, is, in effect, involved. With these differences in practical details of calibration, it is more useful to speak of calibration functions rather than curves, the term function denoting the mathematical form of the relationship between concentration and response. Factors affecting the accuracy of the calibration functions are considered in the next two sections.

Nature of the calibration function. The nature of the calibration function can have important effects on factors of practical importance, *e.g.*, the ease and accuracy with which the function can be completely defined experimentally. For example, functions of the form $C_S = a + bR$ are easier to define accurately than those of the form $C_S = a + bR + cR^2$. Kaiser[4] has recently emphasized the importance of using linear calibration functions in trace analysis, and, when necessary, of transforming one or both of the variables, C_S and

R, so that linearity is achieved. Thus, when using ion-selective electrodes, calibration functions of the Nernst form are commonly used so that log C_S rather than C_S is directly related to the analytical response (in mV):

$$\log C_S = a + bR.$$

The importance of the calibration function requires that it be regarded as a performance-characteristic of an analytical method, as suggested by Kaiser and Specker[5] and Gottschalk.[6] Further, by quoting the numerical values of the constants in the function, the sensitivity of the method is also completely defined, but this aspect will be dealt with in Part V. Thus, using a spectrophotometric method as an example, one would quote:

$$\text{Calibration function: } C\,(\text{mg/l.}) = 0.62A \ (A = \text{absorbance}).$$

Experimental determination of the calibration function. The points made under "*Differences between blank and sample procedures*" apply equally to differences between the procedures used in analysing samples and in determining the calibration function. Two other aspects should also be considered.

(1) Experimental determination of the constants of a calibration function leads only to estimates which will, in general, differ from the true values because of the random errors of the measurements. The magnitudes of the resultant errors in analytical results for samples will depend on the precision of measurements, the number and concentrations of the standards used in defining the calibration, and the concentrations of the samples. In principle, these errors arising from the calibration can be made as small as desired by sufficient replication of the calibration measurements. For this reason, the random error of the calibration is best not regarded as a performance-characteristic, particularly since an estimate of the error can be readily derived from the quoted values for the precision of analytical results (see Part II[1]).

(2) The standards used to determine the calibration function should be such that the latter is not appreciably biased. In other words, the concentrations of determinand in the standards must be known with inappreciable bias *and* a given concentration of determinand in a standard should give the same analytical response as the same concentration in a sample. It is usually possible to observe both these conditions when fluids are analysed, but great care may be needed for solids. When solids are used the concentrations assigned to standards may need to be determined by an independent method, and, in addition, physical factors, *e.g.*, particle-size of the material, may affect the analytical response for a given concentration of the determinand. Again, there appears to be no convenient means of summarizing these ideas as a performance-characteristic, but they must be borne in mind when considering the suitabilities of analytical methods for particular purposes.

Analytical response to different forms of the determinand

The determinand in samples may often be present in a number of different chemical and/or physical forms. If the method is to give unbiased results, each of these forms must be determined with equal efficiency, *i.e.*, the analytical response for a given concentration of determinand must be independent of its form. For example, if the determinand in samples of river water were total iron, a suitable analytical method would have to determine dissolved and undissolved materials, ferrous and ferric forms, complexes and chelates of iron with a variety of ligands, *etc.* Similar situations occur for many other determinands and types of sample.

A related aspect is the frequent need to determine only certain specified forms of a substance when other forms of the same substance are present. For example, it is often necessary to determine only dissolved orthophosphate in samples of natural waters when other phosphates (*e.g.*, undissolved orthophosphates, condensed inorganic phosphates) are also present.

It is clearly essential that evidence bearing on the ability of a method selectively to determine all forms of the determinand be obtained and presented when characterizing analytical methods. However, it is difficult to see how such information can be usefully summarized so as to provide a numerical performance-characteristic of value. Further, there is the additional problem that, in many types of sample, not all the forms of the determinand may be known, and even if this knowledge exists it may be impossible to obtain known amounts of certain forms so that direct tests of the method's ability to determine them are impossible. Notwithstanding such problems, these points should be borne in mind when considering the suitability of analytical methods for particular applications. Indirect but relevant information can often be obtained by comparing results obtained for the same sample(s) by different methods (see below—"*Overall bias of results*").

Selectivity and specificity

The terms selectivity and specificity have been used by many authors, though often in different senses and with no precise quantitative definition. The general concepts embodied in such terms are usually that a selective/specific method responds primarily/only to the determinand, and is little/not affected by other substances. Kaiser[4] has recently discussed these concepts in detail, and has suggested precise, mathematically-formulated definitions for both selectivity and specificity. Kaiser's approach* basically quantifies the overall response of methods to all substances other than the determinand so that one arrives at two numbers characterizing the selectivity and specificity of an analytical method. In principle, therefore, the selectivities and specificities of different methods can be quantitatively compared. At first sight, it might appear that such numerical definitions would form ideal performance-characteristics, but the writer believes that this is not so for the purposes with which this series is concerned.

As defined in Part I,[7] the performance-characteristics of interest in this series are those of importance in assessing the suitability of a method for any given purpose. It is of little direct help to the practising analyst to know quantitatively that one method is more selective/specific (in the sense of the preceding paragraph) than another. He needs to know the effects of particular concentrations of other substances on particular concentrations of the determinand. It is difficult to obtain, and space-consuming to communicate, such information, but an approach describing the integrated effects of particular concentrations of a large number of substances is impracticable. On this basis, it is concluded that the information of primary interest for this series must be based on the numerical description of the effects (interference) of individual substances. Some remarks and suggestions on this approach are given below, the treatment being given in some detail not because of any originality but because this vital analytical topic often seems to be accorded scant and/or ambiguous attention.

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* The approach is completely general, but certain assumptions are required for its application to be practicable. These assumptions are, in practice, not always valid; this aspect is not considered here because, as will be seen, the approach is considered unsuitable for the purposes of this series.

Meaning of the term "interference". Surprisingly, there appears to be no universally-accepted definition of the commonly-used term "*interference*". Some authors use an implicit or explicit definition that an interfering species is one that causes a systematic error greater than some arbitrarily-chosen magnitude (*e.g.*, 1% or 5% of the determinand concentration). Betteridge[8] has even suggested different values for the allowable error for different analytical techniques. Kirkbright[9] has suggested that an interfering species be regarded as one that causes a systematic error greater than twice the standard deviation of measurements. Other authors *e.g.*,[10,11] have proposed that interference be defined simply as systematic error (of any magnitude). Finally, there have been suggestions[12,13] that the term interference should also include increased random errors caused by substances other than the determinand. Some short discussion of these different ideas is desirable as a basis for the definition of interference proposed in this Part.

The author has already argued[11] against the type of definition proposed by Betteridge,[8] the main disadvantages of which can be summarized as follows. First, the choice of the size of error deemed to constitute interference is quite arbitrary, and likely to lead to confusion. Second, a substance having an effect which depends on its concentration and/or that of the determinand might well have to be considered simultaneously as an interfering *and* a non-interfering substance! Third, no account is taken of the random experimental errors of the tests.

Kirkbright's[9] approach, though introducing consideration of random errors, also has several weaknesses. First, the choice of twice the standard deviation is arbitrary, and takes no account of errors of the second kind.[13] Second, as with the preceding approach problems arise when a given substance does not cause a constant effect. Third, the decision on whether a substance is said to interfere is governed by the magnitude of the random experimental error. Thus, different laboratories testing the same method could well reach opposite conclusions; indeed, the same worker could reach different conclusions depending only on the degree of replication of his measurements.

The suggestion[12,13] that interference should comprise both systematic error and also increased random error has much to recommend it, but on balance the author prefers not to use one term to include two different types of error, the interpretation and practical import of which differ markedly. Further, it seems to be rare for a substance to cause increased random error without causing any systematic error. Thus, there does not appear to be an important need to extend the usual concept of interference to include random error, particularly since any analyst should check the precision he achieves with his own samples. Of course, information on the effects of other substances on the precision of analytical results is of value in characterizing the performance of analytical methods. In the author's opinion, it would be better to include such information as supplementary data relevant to precision (see Part II[1]). On this basis, the following definition of an interfering substance is proposed.

> *Definition*: An interfering substance for an analytical method is one that causes systematic error (of any magnitude) in the analytical results for at least one concentration of the determinand within the range* of the method.

As has been pointed out,[11] this definition implies that no substance can be considered as not interfering; this is so, because the random errors of experimental results prevent proof

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* A proposed definition of the concentration range of a method is given in Part III.[14]

that a substance causes no interference. However, this rather rigid approach need cause no problems provided the results of interference tests are properly described and interpreted. The proposed definition has the additional advantage that it tends to focus attention on the magnitude of interference effects.

Experimental estimation of interference effects. It is unnecessary to discuss the many physical and chemical mechanisms responsible for interference; textbooks dealing with particular analytical techniques should be consulted for such information. For present purposes, it suffices to emphasize that the magnitude of interference caused by a substance often depends in a non-linear manner on the concentrations of that substance and the determinand. An additional complication is that the effect of one substance may also depend on the concentrations of other substances. Of course, in developing methods of analysis steps are usually taken to minimize interference, but it is seldom the case that such measures eliminate the need to estimate residual interference effects. Thus, the experimental design of tests to estimate interference should be generally based on the idea that the nature of interference effects is not simple. This idea itself makes it difficult to describe completely general designs, but a few guide-lines seem useful, and are outlined below. Other authors have also discussed this aspect for spectrophotometric,[9] gravimetric,[15] and potentiometric[16] methods, and Maurice and Buijs[13] have proposed a general experimental design for any analytical technique. A complete, quantitative check of interference would usually involve an extremely large amount of time and effort, and this is seldom available. Emphasis is, therefore, placed in the following on what can reasonably be regarded as the minimum number of interference tests.

Interference effects may depend on the concentration of the determinand, and it is, therefore, suggested that the effect of any substance should be estimated for at least two concentrations of the determinand.* The upper and lower concentrations of interest are generally most suitable if only two concentrations are tested (see also Part III[14]). If the results from these tests show that the effects of a substance differ markedly at the two concentrations, further tests at intermediate concentrations of the determinand are indicated.

It is much more difficult to decide questions such as the concentrations and combinations of other substances to be tested. *As a minimum*, it is suggested that each substance of interest should be tested alone at a concentration rather greater than maximum expected in samples, but three disadvantages of this approach should be noted.

(1) The effects of greater concentrations of the substances are not determined, so the validity of extending the use of the method to other types of sample may not be known. This is not a crucial disadvantage, and if desired can easily be remedied by additional tests.

(2) The effects of some substances may be greater when they are present in smaller concentrations. Knowledge of the physical and chemical mechanisms of interference operative in the particular method will often help to decide for which substances tests should be made at smaller concentrations. Again, when in doubt, there is no difficulty, in principle, in testing the effects of at least two concentrations of any substance.

(3) The effects of other substances on the interference caused by a particular substance are not defined. Again, detailed knowledge of the method will often help to decide when

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* It is assumed that the concentrations of the determinand and other substances can be varied at will. When this is not practicable, useful tests of interference may not be possible, and even greater importance then attaches to comparative analyses of samples by different analytical methods (see below—"*Overall bias of results*"). Further, when making the tests, it is obviously important that the substances to be tested contain negligible amounts of the determinand or that a correction for their determinand content is made.

such interactions are likely to exist, and thus suggest combinations of substances to be tested. In addition, it will often be of value to test the effects of combinations of many substances such that the compositions of typical samples are simulated.

Given these considerations, there remains the question of how the tests should be organized. The interference effect is estimated by the difference between the results obtained in the presence and absence of a particular substance. In any experiment, the power for detecting statistically significant effects improves as the random error of the measurements decreases. Thus, as results are generally subject to within- and between-batch errors,[1] the most powerful design is to estimate interference effects from tests within one batch so that a typical design would be as indicated in Table 1. The results from the tests should be recorded with the finest discrimination achievable with the measuring system; premature rounding-off of results should be avoided.

Table 1. Experimental design for one batch of interference tests

Other substance	Concentration of other substance	Concentration of determinand C_0	C_1
–($j = 0$)	—	S_{00}	S_{10}
X($j = 1$)	C_X	S_{01}	S_{11}
Y($j = 2$)	C_Y	S_{02}	S_{12}
Z($j = 3$)	C_Z	S_{03}	S_{13}
W($j = 4$)	C_W	S_{04}	S_{14}

S_{ij} denotes a sample with determinand at concentration C_i and the jth other substance present at a defined concentration.
$j = 0$ corresponding to no other added substance.

Other batches of similar design would be analysed until all the other substances at all concentrations and combinations of interest had been tested. Clearly, more than one determination for each S_{ij} can be made if it is required to reduce the random error of the mean result for each S_{ij} or if it is required to check the effects of the other substances on precision.[13] Duplicate analyses seem generally suitable for interference tests; in addition to giving some reduction in the random errors of the mean results, duplicates also provide an internal estimate of those errors.

Interpretation and reporting of results on interference. The estimate of the effect of the jth substance at the ith concentration of the determinand is clearly given by the difference $\bar{D}_{ij}$ where $\bar{D}_{ij} = (\bar{R}_{ij} - \bar{R}_{i0})$ and $\bar{R}_{ij}$ represents the mean analytical result (in concentration units) for the sample S_{ij} (see Table 1). These differences are the primary experimental estimates of the interference effects, and it is therefore strongly urged[17] that the individual differences be reported together with their confidence limits (at a defined confidence level) for each value of i*. Table 2 gives an example of a suitable format for presenting the results.

This method of presenting the results allows rapid examination to identify those substances causing statistically significant effects, *i.e.*, those for which $(|\bar{D}_{0j}| - L_0|) > 0$ and/or $(|\bar{D}_{1j}| - |L_1|) > 0$. The effects of such substances are directly recorded, may easily be converted into relative effects if desired, and may also be easily assessed at other confidence levels. Further, the table also clearly records the results for any substances having effects which may just not have achieved statistical significance. There are certainly other ways in which the results of interference tests can be quoted, but the one above seems to meet

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* The precision of analytical results is assumed here to depend on the concentration of determinand but to be unaffected by the presence of the other substances.

Table 2. Example of reporting results on interference

Substance	Concentration of substance	Estimated effect* of substance for determinand concentrations of C_0	C_1
X	C_X	$\bar{D}_{01}$	$\bar{D}_{11}$
Y	C_Y	$\bar{D}_{02}$	$\bar{D}_{12}$
Z	C_Z	$\bar{D}_{03}$	$\bar{D}_{13}$
W	C_W	$\bar{D}_{04}$	$\bar{D}_{14}$

* The results in the table have p% confidence limits of L_0 and L_1 for determinand concentrations of C_0 and C_1, respectively.

generally-important requirements, and is recommended. Of course, some transformations of these primary results may also be of particular interest, *e.g.*, calculation of selectivity coefficients for ion-selective electrodes.[16] Such results can also easily be given when desired, but it is suggested that they should not replace the primary experimental results.

Many publications use summarizing statements in quoting the results of interference tests,' *e.g.*, "the substances tested had no significant effect", "the substances tested caused effects less than 5%", *etc.* Such statements not only conceal the primary experimental estimates but also are often incapable of unambiguous and quantitative interpretation; such summaries should, therefore, be avoided.

For any analysts not familiar with the statistical aspects involved in calculating the confidence limits required for Table 2, they may be obtained as follows, assuming that precision is not affected by the other substances, that m replicate analyses are made for each sample, that n other substances are tested, and that the normal distribution adequately describes the random errors of results.

(*i*) Estimate the variance, V_{ij}, for each sample from its m results.

$$V_{ij} = \left[\left(\sum_k R_{ijk}^2\right) - \left(\sum_k R_{ijk}\right)^2 \Big/ m\right] \Big/ (m - 1)$$

where the subscript k refers to the kth replicate result of a sample.

(*ii*) Combine all estimates of variance for a given determinand concentration, C_i, to obtain a pooled estimate of variance, V_i, for each value of i.

$$V_i = \left(\sum_j V_{ij}\right) \Big/ (n + 1)$$

N.B., when $m = 2$,

$$V_i = \left(\sum_j \Delta_{ij}^2\right) \Big/ 2(n + 1)$$

where Δ_{ij} is the difference between the two results for the sample S_{ij}.

(*iii*) The confidence limits, L_i, for the differences $\bar{D}_{ij}$ for each value of i are given by:

$$L_i = t\sqrt{2V_i/m},$$

where t = Student's-t for the desired confidence level and $(n + 1)(m - 1)$ degrees of freedom, *e.g.*, $t = 2{\cdot}45$ for the 95% confidence level and $n = 5$ and $m = 2$.

DEFINITION OF PERFORMANCE-CHARACTERISTICS FOR INTERFERENCE

In the preceding considerations, it was concluded that concepts of overall performance such as selectivity and specificity are of little value for the purposes of this series. In the author's opinion, the result of each interference test and its associated confidence limit (for a specified confidence level) are best regarded jointly as a performance-characteristic of an analytical method. There seems to be no useful way of summarizing all the individual performance-characteristics relating to interference except by tabulation, *e.g.*, as in Table 2. However, this question of summary is taken up again in Part V where suggestions are made for methods of summarizing all performance-characteristics of analytical methods.

Overall bias of results

The emphasis of the preceding discussion is on the assessment and estimation of particular sources of bias, but it is clear that not all possible sources can be individually and conclusively investigated. This does not decrease the need for such investigations when they can be made, but it does raise the need for another type of bias investigation that is commonly used, *i.e.*, the comparison of results obtained on certain samples by the method under evaluation with the results for the same samples by other methods of analysis.

Ideally, one would, of course, compare results obtained by the method of interest with the true values for the samples, but these values are generally unknown.* Nevertheless, one can sometimes resort either to standard samples with accepted concentrations of the determinand or to standard methods that are accepted as capable of giving results free of bias. The use of such standards should, in general, be subject to the proviso that they have no obvious sources of bias, and this is not always so. Comparative analyses of this type can be of great value, and the results of such tests should be regarded as performance-characteristics provided they are interpreted and quoted on a quantitative and unambiguous basis. These aspects are considered below.

Experimental design. The samples (standard or otherwise) used for the tests should satisfy certain conditions whenever possible, *e.g.*, they should have satisfactorily small degrees of heterogeneity, they should cover the range of interest of determinand concentration, *etc.* Such conditions are well understood and need no discussion here.

Several factors should be considered when choosing the experimental design itself. First, better estimates of bias and/or of their statistical significances can sometimes be obtained for a given number of analyses by pooling results from more than one sample. Such pooling is, however, valid only under certain conditions that may often not be satisfied in tests of bias. It will often be worthwhile to obtain statistical advice on this question, but unless there are compelling *a priori* reasons or experimental evidence otherwise, it seems to the author safer not to pool results from different samples. On this basis, it is suggested that the estimate of bias for a particular sample should be obtained solely from the results for that sample.

The number of replicate analyses made for each sample should, ideally, be chosen so that the tests have sufficient power to detect bias of the magnitude of interest. This aspect is discussed in textbooks on statistics (*e.g.*, ref. 19), but the available time and effort will

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* Indeed, Eisenhart[18] in discussing the concept "true value" concludes that it can be defined only as the mean result of many replicate analyses using *an agreed method* for determining its value. When such methods are not available, comparative analyses by different methods may still be of great interest, but the results cannot be used to conclude that the results of a particular method are biased with respect to the true value. Thus, attention is restricted in this Part to comparisons where standard samples or analytical methods are available.

often govern the achievable degree of replication. From the dependence of the numerical value of t (see below) on the number of replicates, it is generally desirable to make at least three (and preferably more) analyses of each sample by each method. When results are subject to appreciable between-batch as well as within-batch variability (see Part II[1]), it is generally better to achieve the chosen number of analyses of each sample by analysing one portion in each of that number of batches. As before, results should be recorded with the finest discrimination achievable, and premature rounding-off should be avoided.

INTERPRETATION AND REPORTING OF RESULTS

Case 1. *Comparison with standard samples*

Let n samples, S_i ($i = 1$–n), of accepted concentrations, C_i, be analysed, m_i results being obtained for the ith sample, and the jth ($j = 1$–m_i) result for the ith sample being denoted by r_{ij}. Then the experimental estimate of bias, B_i, for the ith sample is given by:

$$B_i = \left(\sum_j r_{ij}/m_i\right) - C_i.$$

The confidence limits, L_i, for B_i are given by:

$$L_i = t\,.\,s_i/\sqrt{m_i}$$

where

$$s_i = \sqrt{\frac{\left(\sum_j r_{ij}^2\right) - \left(\sum_j r_{ij}\right)^2 \Big/ m_i}{m_i - 1}}$$

and t = Student's-t for $(m_i - 1)$ degrees of freedom and the chosen confidence level, *e.g.*, $t = 4{\cdot}30$ for the 95% confidence level and $m_i = 3$.

These calculations summarize the experimental evidence for bias; their results can be summarized in several ways, and a suggested method is shown in Table 3, the appropriate description and numerical values, respectively, being entered in the first and last four columns.

Table 3. Example of summarizing results of tests of overall bias

Standard sample	Accepted concentration	Mean result by method under evaluation	Number of analyses	Observed bias*
S_1	C_1	$\sum r_{1j}/m_1$	m_1	$B_1 \pm L_1$
S_2	C_2	$\sum r_{2j}/m_2$	m_2	$B_2 \pm L_2$
S_3	C_3	$\sum r_{3j}/m_3$	m_3	$B_3 \pm L_3$
S_4	C_4	$\sum r_{4j}/m_4$	m_4	$B_4 \pm L_4$

* The p% confidence limits for the bias are also quoted.

Case 2. *Comparison with results by a standard method*

In this case, the samples must be analysed by the standard method as well as the method being evaluated. The same notation as before can be used with M_i denoting the number of analyses of the ith sample by the standard method and R_{ij} denoting results from that method. If it is known that the precision achieved with both methods is approximately the same, it is desirable that $m_i = M_i$. Otherwise, it is useful to make $m_i/M_i \sim s_i^2/S_i^2$, where S_i = estimated standard deviation for the ith sample when the standard method is used.

The experimental estimate of bias, B_i, for the ith sample is given by:

$$B_i = \left(\sum_j r_{ij}/m_i\right) - \left(\sum_j R_{ij}/M_i\right),$$

and the confidence limits, L_i, for B_i are given by:

$$L_i = t\sqrt{\frac{s_i^2}{m_i} + \frac{S_i^2}{M_i}}$$

where

$$S_i = \sqrt{\frac{\left(\sum_j R_{ij}^2\right) - \left(\sum_j R_{ij}\right)^2 \Big/ M_i}{M_i - 1}}$$

and t = Student's-t for v_i degrees of freedom and the chosen confidence level, v_i being given by

$$v_i \approx \frac{[V_i(r) + V_i(R)]^2}{\dfrac{[V_i(r)]^2}{m_i - 1} + \dfrac{[V_i(R)]^2}{M_i - 1}}$$

$$V_i(r) = s_i^2/m_i$$

$$V_i(R) = S_i^2/M_i.$$

This derivation of L_i is based on the idea that the precisions obtained with the two methods are not equal.[20] Some simplification is possible if the assumption of equal precision is justified; details are given in statistical texts, but the approach given above is generally recommended.[20]

The results from such tests can be summarized as in Table 3 with the replacement of the first two columns by entries giving the mean result and number of analyses for each sample by the standard method.

DEFINITION OF A PERFORMANCE-CHARACTERISTIC

As in the case of interference tests it is considered best to regard the result for bias (*i.e.*, $B_i \pm L_i$) for each sample as an individual performance-characteristic. Again, the only valid method of summarizing such information is by tabulation, *e.g.*, as in Table 3, but this question of summary is further considered in Part V.

CONCLUSIONS

Numerous sources of bias may affect the accuracy of analytical results, and all need careful assessment when considering the suitability of an analytical method for a particular purpose. Many of these sources cannot be usefully quantified, but it is suggested that the following should be regarded as performance-characteristics for which numerical values should be quoted when describing the capabilities of methods: calibration function, bias caused by substances (individually or in combination) other than the determinand, and bias of results with respect to the accepted concentrations of standard samples or to the results from other methods accepted as giving unbiased results.

Part V of this series will deal with the remaining characteristics of interest (*e.g.*, sensitivity, time, cost, robustness), and consider how overall summaries of performance-characteristics can usefully be provided.

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Zusammenfassung—Systematische Fehlerquellen in analytischen Ergebnissen werden diskutiert. Es werden Vorschläge gemacht, wie man bei der Kennzeichnung der Leistungsfähigkeit analytischer Methoden vorgehen sollte, um solche Fehler zu finden und mitzuteilen. Die vier in Betracht gezogenen Fehlertypen rühren von: (1) Blindbestimmungen; (2) der Eichung; (3) unterschiedlicher Erfassung verschiedener Formen des zu bestimmenden Stoffes bei der Messung; (4) Störungen. Auch der Vergleich der Ergebnisse mit allgemein anerkannten Werten von Standards oder mit Ergebnissen, die mit Standardmethoden erhalten wurden, wird diskutiert.

Résumé—On discute de sources d'erreurs systématiques dans les résultats analytiques et fait des suggestions pour la recherche et le mode d'exposition de telles erreurs lors de la caractérisation des possibilités de méthodes analytiques. Les quatre types d'erreur considérés proviennent de: (1) déterminations de témoin, (2) étalonnage, (3) différences dans les efficacités avec lesquelles les différentes formes du produit à déterminer sont mesurées, et (4) interférences. On discute aussi de la comparaison des résultats avec des valeurs admises d'échantillons de référence ou avec les résultats obtenus par des méthodes normalisées.

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RAPID COULOMETRIC METHOD FOR THE KJELDAHL DETERMINATION OF NITROGEN

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Summary—A rapid coulometric method for the Kjeldahl determination of nitrogen is described. The samples are digested by means of the Tecator AB digestion system which permits forty samples to be digested at the same time. The digestion products are diluted to 75 ml and 1 ml is coulometrically titrated in 1–2 min: 20–30 determinations can be performed per hour. For substances containing nitrogen in the per cent range the relative standard deviations for eight different substances were 0·1–1%.

Many efforts have been made to modify the classical Kjeldahl method. Bradstreet[1] has published an excellent book on this subject. Most of the improvements suggested deal with the digestion procedure. In fact a proper choice of the temperature and digestion medium has resulted in shorter digestion times and higher recoveries. Furthermore, elimination of the time-consuming distillation of ammonia reduces the time for a complete nitrogen analysis.

Christian and Jung[2] showed that coulometric titration could be applied directly to the Kjeldahl digestion mixture. Using Christian and Jung's principles, Cedergren and Johansson[3] developed a cell for the rapid coulometric titration of ammonia with electrogenerated hypobromite. They showed that hypobromite could be generated quantitatively at a platinum gauze working-electrode even for currents as large as 200 mA. This method involves an automatic potentiometric titration in which the end-point of the titration corresponds to a known excess of hypobromite.

Another means of eliminating the distillation step has been offered by the development of the ammonia-selective electrode. Bremner and Tabataboi[4] compared the conventional Kjeldahl procedure using the distillation–titration technique with a modified procedure using the ammonia electrode and stated that the electrode method showed good agreement with the earlier method and that the recovery of ammonia was good. The main drawback with this method is that mercury cannot be used as a catalyst during the digestion procedure because it forms complexes with ammonia. Mercury is generally considered to be the best of the catalysts used in the Kjeldahl method. The *Orion Research Newsletter*[5] compared the time required when using the ammonia-selective electrode with the time required in the conventional method. It was stated that the electrode method is capable of completing about ten analyses per hour provided there are six electrodes available.

The Technicon AutoAnalyzer is a rapid continuous-flow device for automatically digesting nitrogen-containing samples and mixing the digest with phenol and hypochlorite in alkaline solution to transform the ammonia into indophenol blue in amounts proportional to the nitrogen present. Various modifications of the Technicon apparatus have been reported[6,7] and comparisons of precision with the conventional Kjeldahl method and micro-Kjeldahl method have also been reported.[8,9] The accuracy of the Technicon method is not as good as that of the standard Kjeldahl procedure.

The present work was undertaken in order to shorten the time for an analysis by the coulometric method described above.[2] Experience with this method in our laboratory over several years has shown that the critical step is the digestion procedure, as incompletely digested organic substance can adhere to the walls of the container and consume titrant in the subsequent titration. A suitable design of digestion system (Tecator AB) has eliminated this problem.

EXPERIMENTAL

Apparatus

A temperature-regulated aluminium block provided with 40 holes for digestion tubes (Tecator AB, Helsingborg, Sweden, model 40) was used. The tubes could be lowered into the block (2) simultaneously by means of a stand (3) as shown in Fig. 1. The temperature controller and timer (1) could be set between 50 and 400°. After an equilibration time of 1·5 hr the temperature was constant to within 3°. The digestion tubes, see Fig. 2, had a volume mark for 75 ml.

The titration system consisted of an LKB 16300 Coulometric Analyzer [(6) in Fig. 1], and a cell (5) with a rotating platinum electrode (LKB 16369). The indicating electrode system consisted of a combined platinum electrode and an Ag/AgCl electrode (Metrohm EA 217-A). The working electrode of the generating electrode system was a platinum gauze, 10 cm^2 in area, which was fastened to the axle of a small d.c. motor with a silver–graphite sliding contact. The auxiliary electrode was a platinum wire (0·5 cm^2 surface area) inside a glass tube with a sintered-glass disc to separate it from the sample compartment. This tube was filled with buffer solution. A combined glass electrode, Metrohm EA 125 U, also dipped into the sample compartment. It was connected to a pH-meter [(4) in Fig. 1]. A microburette with a fine capillary was inserted into one of the female joints of the titration cell. It was filled with 50% potassium hydroxide solution.

The cell was filled with 30 ml of a buffer, 1·5 *M* in potassium bromide and 0·075 *M* in sodium tetraborate, adjusted to pH 8·60 ± 0·05 with 2 *M* sulphuric acid. Hypobromite can be generated quantitatively at a platinum anode in this medium with a high current density, up to 20 mA/cm^2 for the electrode used. The hypobromite oxidizes ammonia to nitrogen:

$$3\,\mathrm{BrO^-} + 2\,\mathrm{NH_3} \rightarrow \mathrm{N_2} + 3\,\mathrm{Br^-} + 3\,\mathrm{H_2O} \tag{1}$$

The indicating electrode senses the excess of hypobromite according to

$$E = E' + \frac{RT}{2F}\ln\frac{a_{\mathrm{BrO^-}}}{a_{\mathrm{Br^-}}\cdot a_{\mathrm{OH^-}}^2}. \tag{2}$$

The potential of the indicating electrode system is compared with a voltage from a potentiometer in the coulometric analyser. The difference obtained is amplified and used to produce a current through the generating electrode pair. The electrolysis current is thus proportional to the deviation from the preset potential, resulting in a rapid titration at the start. An electronic integrator in the analyser records the quantity of electricity. It can be read to 2 μC, corresponding to 6×10^{-12} mole of ammonia.

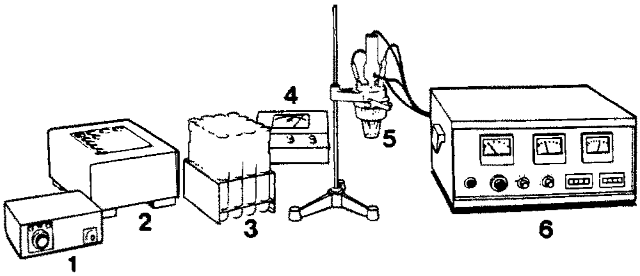

Fig. 1. Experimental arrangement. (1) Temperature controller and timer. (2) Temperature regulated aluminium block. (3) Stand for digestion tubes. (4) pH-meter. (5) Titration cell. (6) Coulometric analyser.

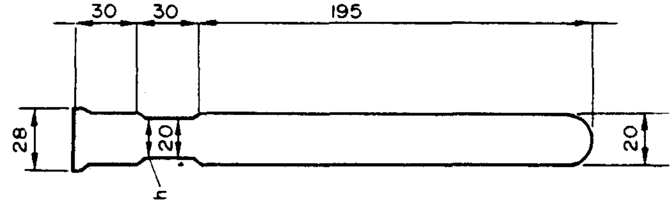

Fig. 2. Digestion tube. (h) Volume mark for 75 ml. Dimensions in mm.

Procedure

Samples were weighed or pipetted into the digestion tubes followed by 1·30 g of purified potassium sulphate, 40 mg of mercuric oxide and 1·00 ml of conc. sulphuric acid. The potassium sulphate was freed from ammonium salts by making an aqueous slurry alkaline and evaporating it to dryness. The tubes were lowered into the aluminium block which, for solid samples, was set to 370° and were digested for 45–90 min depending on the type of sample. When ready, the digestion tubes were removed from the heater, and when they had cooled down somewhat, distilled water was added to the mark, 75 ml. Rubber stoppers were inserted and the contents were mixed. An aliquot, usually 1·00 ml, of the contents of a tube was transferred to the titration cell with an Oxford pipetter. The cell had previously been filled with buffer and pretitrated to the end-point. When the sample was added, the pH of the buffer decreased and it was restored to 8·60 ± 0·05 with a small amount of potassium hydroxide solution from the burette. The analyser was then switched into the titration mode and the sample was titrated, which required 1–2 min. The integrator was read and a new sample was taken from the next digestion tube. Up to 15 samples could be analysed in succession before the buffer solution in the titration cell needed to be replaced. The pretitration is made with the same instrumental setting and it therefore results in an overtitration. This is advantageous because the reaction rate between the impurities in the medium and the hypobromite is increased for higher concentrations of the reagent. After a few seconds, 1 ml of a standard solution containing 1 μmole of ammonium chloride is added and titrated, thus restoring the hypobromite to a value corresponding to the preset potential. This pretitration procedure takes about 2 min.

RESULTS AND DISCUSSION

The titration

After the end-point has been reached the indicating electrode system follows equation (2). Before the end-point, hypobromite will react with ammonia and the potential decreases as the reaction proceeds. When most of the hypobromite has reacted, equation (2) is not necessarily valid as other redox species in the solution can contribute to the redox potential. The rate of the reaction with ammonia increases as the hypobromite concentration is increased, resulting in a more rapid attainment of a steady electrode potential. It was found that the attainment of equilibrium was slow even at the inflexion point of the asymmetrical titration curve. At about $10^{-5}M$ excess of hypobromite, a stable electrode potential was obtained almost immediately. Concentrated solutions of hypobromite are known[10] to be unstable. Separate experiments were made to estimate the stability of $10^{-5}M$ hypobromite, and showed that the concentration decreased by about $10^{-7}M$ per min. If an ammonia sample is titrated within 2 min, then assuming that the hypobromite concentration is constant, this source of error corresponds to a positive error of 0·002 μmole. As the titration times in practice are shorter and the hypobromite concentration is much lower before the end-point, this error can be neglected provided no waiting periods are allowed. About $10^{-5}M$ excess of hypobromite thus represents an optimum, giving rapid reactions and sufficiently stable reagents.

The single most important source of error is contamination by gaseous substances such as ammonia, amines, *etc.* from the atmosphere. A rapid titration will reduce this error. The cell used was not completely gas-tight and a drift of 0·003–0·008 μmole/min resulted. This figure can be increased by a factor of 100 or more if a cigarette is smoked in the room.

By strictly avoiding smoke and other sources of contamination a low and reproducible drift could be obtained.

Ammonium chloride standard solutions were titrated and for 1-μmole samples delivered with a precision μl-syringe a relative standard deviation of less than 0·2% was obtained. The titration time was 1–2 min. This shows that the titration procedure is very reproducible and that the contamination from the atmosphere can be controlled. The higher standard deviations reported below are mainly due to the volumetric device.

Determinations

Table 1 shows the results obtained with the procedure described. Each sample was digested, diluted to 75 ml, and mixed. A 1·00-ml aliquot was taken and titrated and then between 3 and 7 more aliquots from the same digestion tube were dealt with. The reported results are thus means of several titrations and the standard deviations refer to the titration only. The large standard deviation depends mainly on the volumetric device, which had been selected so that the speed of analysis had high priority. The multiple titrations were made in order to determine the standard deviation. In normal use only a single titration is necessary as long as the present precision is acceptable. If higher precision is necessary another volumetric vessel should be selected at the cost of taking a longer time for the determination.

The reported values have been corrected for a blank of 1·5 μmole of nitrogen (N). A blank was digested in the same way as the samples, diluted, and titrated. As only a very small amount of ammonia, 0·02 μmole, was to be titrated, the gain of the amplifier was increased. The blank was also determined potentiometrically by noting the potential change of the indicating electrode system. By generating a very small amount of reagent and noting the corresponding potential change a blank value can be evaluated. This latter procedure is simpler and more precise.

The values found, which are obtained from a purely electrical calibration of the instrument, are slightly higher than those calculated on the assumption that pure chemicals were

Table 1. Results for the determination of nitrogen in organic compounds

Substance	Taken		Digestion time, *min*	Temp., °*C*	Found, *μmole N*	Rel. std. deviation, %	No. of detns.
	mg	*μmole N*					
Phenacetin	13·215	73·7	80	370	73·8	1·2	4
	13·047	72·8			72·4	0·1	3
Nicotinic acid	12·954	105·2	90	390	106·0	0·2	7
	8·738	71·0	90		71·6	0·4	4
	13·932	113·2	60		114·2	0·4	4
Imidazole	3·480	102·2	45	370	102·6	1·2	4
	4·364	128·2	50	350	128·6	0·3	3
Methionine	14·854	99·2	50	350	100·3	1·2	3
L-Asparagine	6·379	85·0	50	350	85·6	0·3	4
Cystine	9·831	81·8	90	380	82·5	0·4	4
Glycine	6·020	80·2	30	380	80·7	0·1	4
S-Carboxymethyl-L-cysteine	10·890	60·8	90	370	60·8	0·6	6

used. As has been mentioned, contamination from the air can cause consumption of reagent. For the titration times used, 1–2 min, a separate determination of the absorption of contaminants showed that this source of error contributes the equivalent of about 0·01 μmole of nitrogen. As only 1/75 of the sample is titrated, this will be responsible for 0·5–1 μmole of nitrogen (N). Since this contribution is fairly reproducible and easy to measure, a correction of the values reported in Table 1 is justified. Such a correction can be made by subtracting 0·5–1 from "μmole found" in the Table.

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Zusammenfassung—Es wird eine schnelle coulometrische Methode für die Kjeldahl-Bestimmung von Stickstoff beschrieben. Die Proben werden mittels des Tecator AB Auflösungssystem, welches gleichzeitig 40 Proben erfassen kann, in Lösung gebracht. Die Auflösungsprodukte werden auf 75 ml verdünnt, und 1 ml davon wird coulometrisch in 1–2 min titriert: Es können 20–30 Bestimmungen pro Stunde durchgeführt werden. Die relative Standardabseichungen für acht verschiedene Verbindungen die je mehrere Prozente Stickstoff enthielten lagen zwischen 0,1 und 1%.

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ANALYTICAL STUDY OF THE PHOSPHORESCENCE OF PYRIMIDINE DERIVATIVES IN FROZEN AQUEOUS SOLUTION*

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Summary—Phosphorescence excitation and emission spectra, phosphorescence lifetimes, phosphorimetric analytical curves and limits of detection were determined at 77 K in 10/90 v/v methanol/water solution for seven pyrimidine derivatives. The effect of pH on the phosphorescence intensity indicated an improvement of the sensitivity of the method in basic medium (pH $\simeq$ 11). Low limits of detection, between 10^{-5} and $10^{-8}M$, were obtained. The effect of sodium iodide on the phosphorescence efficiency led to heavy-atom enhancement factors ranging from 1·1 to 9·6, depending on the molecular structure and the pH conditions.

Pyrimidine derivatives have an important role because of their presence in natural macromolecules and of their significant application in biochemistry and clinical chemistry. A number of spectroscopic fluorescence and phosphorescence studies have already been devoted to them.[1–13] However, surprisingly, few analytical techniques have been described for their determination at low concentration. Most of these techniques are based on gas chromatography,[14,15] thin-layer chromatography[16,17] and cation-exchange chromatography,[18,19] and they are mainly oriented towards the separation of pyrimidine derivatives from purines and other biological molecules.

Some of the pyrimidine derivatives have been considered as relatively weak phosphorescent compounds.[2,3,20,21] However, recent instrumental progress in phosphorimetry has permitted the improvement of limits of detection, and the use of predominantly aqueous snowed matrices, suitable for the study of pyrimidine derivatives, has now become possible.[22–25] Purines,[25] cytosine, cytidine and its nucleotides[26] have already been successfully determined by phosphorimetry. In the present paper, we wish to apply a pH-controlled phosphorimetry technique to the quantitative analysis of pyrimidine derivatives and to show the influence of the heavy-atom effect on the study of the interactions of these compounds in frozen solution.

EXPERIMENTAL

Apparatus

Phosphorescence excitation and emission spectra were obtained on an Aminco-Bowman spectrophotofluorometer (SPF) equipped with an Aminco-Keirs phosphoroscope attachment. The 150–W xenon arc-lamp was powered by an Aminco xenon-lamp power supply (Model 422–818). The RCA-1P28 multiplier phototube was powered by a Keithley Model 244 high voltage supply. Phosphorescence intensities were measured with a low-noise nanoammeter.[27]

A rotating capillary tube, approximately 0·9 mm i.d. and 5 mm o.d. made from T21 Suprasil quartz capillary tubing (Amersil Inc., Hillside, N.J.) was used as the sample cell, under the conditions previously described.[22,23,25] All phosphorescence measurements were performed at 77 K.

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Phosphorescence lifetimes were measured by recording the nanoammeter output as a function of time, after complete termination of the exciting radiation by a guillotine-type shutter.

Reagents

Pyrimidine derivatives. 2-Aminopyrimidine, 4,6-dihydroxypyrimidine, 4-amino-2,6-dihydroxypyrimidine, 2,6-dichloropyrimidine, 2,4-dithiopyrimidine, 2-thio-4,6-dioxypyrimidine and 2-thio-6-aminouracil were obtained commercially and used without further purification.

Solvents. Methanol "spectroquality grade" and demineralized water.

Procedure

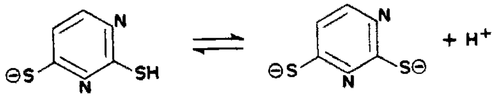
Stock solutions of pyrimidine derivatives (concentrations 10^{-4}–10^{-3}M) were prepared in neutral, acidic (~0·05*M* hydrochloric acid, pH ~2), and basic (~0·2*M* sodium hydroxide, pH ~11) 10:90 v/v mixtures of methanol and water. Analytical curves were obtained from measurements on basic (~0·01*M* sodium hydroxide) solutions prepared by successive dilutions. Phosphorescence signal *vs.* pH measurements were performed by adding microquantities of 0·1*M* sodium hydroxide to acidic stock solutions of the compounds, measuring the pH at room temperature and immediately taking the phosphorescence signal intensity from the nanoammeter output. For all pH values, phosphorescence measurements were taken in duplicate or triplicate. Reproducibility of the phosphorescence signals was found to be within 5% for all the solutions used. Heavy-atom effect studies were performed by preparing acidic (pH 2) or basic (pH 11) solutions of pyrimidine derivatives (concentrations about 10^{-4} *M*) in 10/90 v/v methanol–water mixture with or without addition of sodium iodide.

RESULTS AND DISCUSSION

Phosphorescence properties

Phosphorescence excitation and emission wavelengths of seven pyrimidine derivatives are given in Table 1. All phosphorescence spectra were obtained at 77 K in neutral, acidic and basic 10/90 v/v methanol–water solutions. Upon acidification, small or medium shifts in the excitation spectra peak wavelength were observed, although no noticeable change was apparent in the shape of the excitation spectra. No significant shift of the emission maximum took place, except in the case of 2-aminopyrimidine for which there was a relatively large blue-shift (about 2400 cm^{-1}).

In basic solution, several changes in the shape and peak wavelength of the excitation and emission phosphorescence spectra occurred, depending on the compound. For the dihydroxypyrimidine derivatives, blue-shifts of about 1300 cm^{-1} in the excitation maximum were observed. In the case of 2,4-dithiopyrimidine, a dramatic pH-dependent change in the phosphorescence spectra was observed: in moderately basic solution (0·01*M* sodium hydroxide), an additional phosphorescence emission band appeared on short-wavelength excitation, while in strongly basic medium (0·2*M* sodium hydroxide), only one emission band was apparent, whatever the excitation wavelength (Table 1). Moreover, very large blue-shifts (in the range 2900–3700 cm^{-1}) in both the excitation and emission peak wavelengths were noted for this alkaline solution. We attributed these various changes to the formation in moderately basic solution of singly and doubly charged anions of 2,4-dithiopyrimidine, which would emit from energetically-different triplet states [see equilibrium (1)]. In strongly basic solution, the equilibrium (1) would be shifted towards the formation of the doubly charged anion, resulting in the marked blue-shift of the excitation and emission wavelengths, and the appearance of only one emission band.



(1)

Phosphorescence lifetime values greater than 0·5 sec (Table 1) indicate that the excited triplet state of pyrimidine derivatives is of π,π^* type, in agreement with other literature data.[21] However, shorter lifetimes are exhibited by 2,6-dichloropyrimidine and sulphur-containing pyrimidine derivatives. This strongly suggests that the introduction of a chlorine or sulphur atom in pyrimidine derivatives enhances or perturbs the probability of the

Table 1. Phosphorescence spectral characteristics and lifetimes of pyrimidine derivatives in neutral, acidic and basic 10:90 v/v methanol–water solutions at 77 K.[a]

	Peak wavelengths,[b] *nm*						
	Acidic solution[c]		Neutral solution		Basic solution[d]		
Compound	Excitation maxima[e]	Emission maxima	Excitation maxima[e]	Emission maxima	Excitation maxima[e]	Emission maxima	Lifetimes[f] *sec*
2-aminopyrimidine	312	426	308	393	310	399	1·9,[g] 1·3, 2·1[h]
4,6-dihydroxypyrimidine	290	424	316	425	302	416	2·3, 1·0[h]
4-amino-2,6-dihydroxypyrimidine	245, $\underline{314}$	410	243, $\underline{316}$	405	255, $\underline{303}$	408	1·1[h]
2,6-dichloropyrimidine	280	420	—	—	286	410	≤0·5[i]
2,4-dithiopyrimidine	—	—	330, $\underline{366}$	477	$\underline{276}$, 322[j] (295), 370	420[j] 420, 450	≤0·5[i]
2-thio-4,6-dioxypyrimidine	283, $\underline{354}$	448	(280), $\underline{345}$	441	290	442	≤0·5[i]
2-thio-6-aminouracil[k]	290	417	295	420	285	412	≤0·5[i]

[a] Concentrations approximately 10^{-5}–$10^{-3}M$, depending on the compounds.

[b] Peak wavelength error ±5 nm.

[c] Approximately $5 \times 10^{-2}M$ HCl.

[d] Approximately $1 \times 10^{-2}M$ NaOH, except when otherwise noted.

[e] When necessary, wavelength of the main peak is underlined—wavelengths of shoulders are given in parentheses.

[f] Lifetimes measured in neutral solution, unless otherwise noted. Precision of the lifetime values ±5%.

[g] Lifetime measured in acidic solution.

[h] Lifetime measured in basic solution.

[i] Value not accurately determined, owing to the limiting factor of the response time of the recorder.

[j] In 0·2*M* NaOH.

[k] In acidic solution, this compound was progressively photodecomposed under the conditions for phosphorescence spectra measurement.

singlet–triplet intersystem crossing transition, as had been previously observed in the case of purine derivatives.[12,25]

Quantitative analytical studies

In order to evaluate optimal pH conditions for the quantitative analysis of pyrimidine derivatives, the pH effect on the phosphorescence intensity was studied in two typical cases. Phosphorescence intensity *vs.* pH curves in 10/90 v/v methanol–water mixture at 77 K are shown for 2-aminopyrimidine and 2-thio-6-aminouracil in Fig. 1.

In the case of 2-aminopyrimidine, a 2·5-fold increase of phosphorescence intensity is observed in the pH 3·5–5 region, followed by a plateau region at pH 5·5–11. The estimated p*K* value of 4·05 is slightly larger than the literature value of 3·54 determined by a conventional method.[28] The sigmoidal shape of the phosphorescence titration curve of 2-aminopyrimidine indicates the absence of molecular aggregation.[26]

On the contrary, the phosphorescence titration curve of 2-thio-6-aminouracil is characterized by a larger increase of phosphorescence intensity (about 25-fold increase) in the pH region 7–10·5, followed by a smaller decrease as the solution becomes more basic. The anomalous peak which results at a pH value of about 11·0 might be due to molecular aggregates of 2-thio-6-aminouracil similar to those observed in the case of cytosine and cytidine.[26]

Because of the higher phosphorescence intensity observed in basic medium, the quantitative determination of pyrimidine derivatives was undertaken at a constant pH of 11, except for 2,6-dichloropyrimidine, for which a large heavy-atom effect—described in the next section—made use of an acidic sodium iodide solution more suitable. All pyrimidine

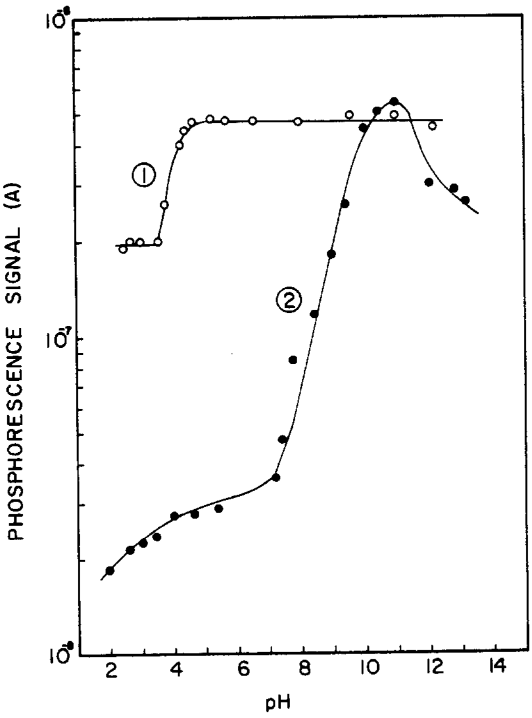


Fig. 1. Phosphorescence signal as function of pH in 10/90 v/v methanol–water solution at 77 K. Curve 1: 2-aminopyrimidine ($2{\cdot}5 \times 10^{-4}M$). Curve 2: 2-thio-6-aminouracil ($1{\cdot}4 \times 10^{-4}M$). Phosphorescence intensity measured at excitation and emission wavelength maxima.

Table 2. Phosphorimetric properties of pyrimidine derivatives[a]

Compound	Concentration range, for near linearity,[b] M	Slope of linear portion	Limit of detection[c], M
2-aminopyrimidine	10^4	1·03	2×10^{-8}
4,6-dihydroxypyrimidine	10^3	1·00	$1{\cdot}5 \times 10^{-6}$
4-amino-2,6 dihydroxypyrimidine	10^3	0·97	1×10^{-5}
2,6-dichloropyrimidine	—[d]	—[d]	$\sim 1 \times 10^{-5d}$
2,4-dithiopyrimidine	10^4	0·88	$1{\cdot}5 \times 10^{-8c}$
2-thio-6-aminouracil	10^4	0·96	$1{\cdot}4 \times 10^{-7}$

[a] In basic 10:90 v/v methanol–water solution (0·01M NaOH), unless otherwise noted.

[b] Near linearity means region over which slope of analytical curve is within 1% of the values designated in column 3.

[c] Limit of detection is defined as the concentration giving a phosphorescence signal (located on the linear part of the analytical curve) two times greater than the background noise. The background signal was subtracted from the observed signal value.

[d] Value of the detection limit was estimated in 0·05M HCl in 10:90 v/v methanol–water solution that was 0.1M in NaI.

[e] Analytical curve obtained for 0·2M NaOH solution.

derivatives were found to have analytically useful phosphorescence signals. Characteristics of the phosphorescence analytical curves are given in Table 2. Slopes of the analytical curves are close to unity as expected, and the ranges of linearity are large (10^3–10^4 concentration units). Limits of detection, which range between 10^{-8} and $10^{-5}M$, are satisfactory.

Heavy-atom effect

Phosphorescence excitation and emission maxima of pyrimidine derivatives are practically unchanged in a medium of 0·1M in sodium bromide. Heavy-atom enhancement factors determined at the wavelength maximum are given in Table 3.

It is of interest to note that values of heavy-atom enhancement factors are close to unity for basic solutions, while larger values, ranging from 1·5 to 9·6, depending on the compound, are observed for acidic media. That the heavy-atom effects are larger for acidic media might be attributed to stronger interactions between pyrimidine-derivative cations—the predominant species at pH 2—and iodide ions, resulting in an increase in

Table 3. Heavy-atom effect of sodium iodide on phosphorescence intensity of pyrimidine derivatives in frozen matrix[a] at 77 K

Compound	Heavy-atom enhancement factor[b], I_p^{NaI}/I_p	
	pH 2	pH 11
2-aminopyrimidine	$1{\cdot}8_5$	1·1
4,6-dihydroxypyrimidine	$1{\cdot}5_5$	1·1
4-amino-2,6-dihydroxypyrimidine	1·9	1·4
2,6-dichloropyrimidine	9·6	1·1
2-thio-4,6-dioxypyrimidine	1·1	1·1
2-thio-6-aminouracil	—[c]	1·0

[a] Methanol/water (10:90 v/v) as solvent; 0·1M in NaI.

[b] Enhancement factor calculated from the ratio of the phosphorescence intensity (at maximum wavelength) in methanol–water–sodium iodide solution (I_p^{NaI}) and in methanol–water (I_p) with equal concentrations of pyrimidine derivative (about $1{\cdot}5 \times 10^{-4}M$).

[c] Thio-6-aminouracil is photodecomposed under these conditions.

the rate of intersystem-crossing between the excited singlet and triplet state in acidic medium. That the 2,6-dichloropyrimidine exhibits a dramatically larger increase of the heavy-atom enhancement factor (9·6 in acidic medium *vs.* 1·1 in alkaline medium) may be explained by the existence of a strongly localized charge on its cation (due to the electron-withdrawing effect of chlorine substituents), which would interact more powerfully with iodide ions in acidic medium. We had already demonstrated the occurrence of similar interactions leading to an anomalous heavy-atom effect in the case of cytidine.[26] Although it is not yet possible to predict such large heavy-atom enhancement factors, it is necessary to take into consideration their analytical usefulness for the phosphorescence study of pyrimidine derivatives.

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Zusammenfassung—Phosphoreszenzanregungs- und -emissionsspektren, Phosphoreszenzlebensdauern, phosphorimetrische Eichkurven und Nachweisgrenzen wurden für sieben Pyrimidinderivate bei 77°K in Methanol—Wasser 10:90 v/v bestimmt. Der pH-Einfluß auf die Phosphoreszenzintensität weist auf eine höhere Empfindlichkeit der Methode in basischem Medium (pH $\simeq$ 11) hin. Nachweisgrenzen zwischen 10^{-5} und $10^{-8}M$ wurden erhalten. Der Einfluß von Natriumjodid auf die Phosphoreszenzausbeute ergab Schweratom-Verstärkungsfaktoren zwischen 1,1 and 9,6 je nach Molekülstruktur und pH-Wert.

Résumé—On a déterminé les spectres d'excitation et d'émission de phosphorescence, les durées d'existence de la phosphorescence, les courbes analytiques phosphorimétriques et les limites de détection à 77 K en solution 10/90 v/v méthanol/eau pour sept dérivés de la pyrimidine. L'influence du pH sur l'intensité de phosphorescence indique une amélioration de la sensibilité de la méthode en milieu basique (pH $\simeq$ 11). On a obtenu de basses limites de détection, entre 10^{-5} et $10^{-8}M$. L'influence de l'iodure de sodium sur l'efficacité de phosphorescence mène à des facteurs d'exaltation d'atome lourd allant de 1,1 à 9,6, suivant la structure moléculaire et les conditions de pH.

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ENHANCED CAPACITY OF CHITOSAN FOR TRANSITION-METAL IONS IN SULPHATE–SULPHURIC ACID SOLUTIONS

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Summary—Batch measurements have shown that the collection yields of chitosan for chromium(III), iron(III), nickel, copper(II), zinc and mercury(II) from sulphuric acid solutions are higher when the solutions contain ammonium sulphate, or when chitosan conditioned in ammonium sulphate is used, particularly at pH 3·0 and 5·0. The contrary is verified for the oxy-anions vanadate, chromate and molybdate. Manganese is never collected. At pH 1·0 no collection occurs. A procedure for recycling chromatographic columns includes fixation of Cu or Ni from a sulphate solution at pH 3–5 on sulphate-conditioned chitosan, and elution with 0·1*M* sulphuric acid/0·1*M* ammonium sulphate at pH 1·0; the presence of sulphate in the eluent obviates the detrimental effect of sulphuric acid on the next cycle. Sulphate is the favoured counter-ion of the chelated cations and its action produces shorter chromatographic bands. The interaction of sulphate with chitosan is discussed in terms of crystallinity and steric distribution of the protonated amino-groups in the polymer. Data on the new diethylaminohydroxypropylcellulose are included.

Chitosan powder treated with copper sulphate shows more numerous and sharper X-ray diffraction bands than untreated chitosan.[1,2] A comparison of the X-ray patterns for chitosan treated with chlorides and sulphates gives the impression that the sulphate anion is partially responsible for the increased degree of crystallinity of the treated polymer. On the other hand, it is known that chitosan forms an insoluble sulphate.[1,3]

Chitosan has seldom been used in sulphuric acid or sulphate media. Chitosan bonded with silver and zinc ions was used to collect traces of cyanide from 0·44*M* ammonium sulphate solutions.[4]

An investigation of the treatment of chitosan with concentrated sulphuric acid (90% w/w) has shown that it is depolymerized to give a sticky mass.[5] However, at lower acidity ($<0{\cdot}1M$ sulphuric acid) chitosan is not dissolved or degraded by sulphuric acid. Because even small amounts of sulphate induce structure modifications in chitosan, we expect that chitosan previously conditioned in sulphate media might show enhanced capacity for transition metal ions.

EXPERIMENTAL

Instrumentation

A Perkin–Elmer 305 atomic-absorption spectrometer equipped with a three-slot air–acetylene burner, with the hot graphite atomizer HGA-70 and with the Hitachi Perkin–Elmer 56 Recorder was used. Normally the determinations were carried out by flame AAS, but vanadium and molybdenum required the use of the HGA-70. The experimental conditions were those suggested by the pertinent literature and previous work.

Solutions

For the batch measurements 5 ml of each reference solution were added to 5 ml of 1*M* ammonium sulphate, if desired, and after addition of about 35 ml of water, the pH was adjusted to the desired value with sulphuric acid or ammonia and the solutions were diluted accurately to 50 ml so that they were 0·5 m*M* with respect to the metal and about 0·1*M* with respect to ammonium sulphate. The solutions were shaken with 200 mg of polymer powder in a Dubnoff bath at 25° and aliquots were taken for analysis after 1 and 12 hr. The reference 5m*M* solutions were prepared from $Cr_2(SO_4)_3$, $K_2Cr_2O_7$, $MnSO_4 . H_2O$, $FeCl_3 . 4H_2O$, $NiSO_4 . 6H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $HgCl_2$, $Na_3VO_4.12H_2O$, $Na_2MoO_4.2H_2O$ and standardized appropriately.

Chitosan conditioning

Chitosan (5 g) was introduced into about 400 ml of a solution 0·1*M* in both sulphuric acid and ammonium sulphate. After 4 hr stirring, the polymer was washed with water till neutral. For some measurements the polymer was similarly conditioned with ammonium sulphate alone.

Columns

Chitosan was supplied by the Kypro Co., P.O. Box 239, Haverford, Pennsylvania 19041, U.S.A. The large columns used were 1 × 24 cm and contained 6 g of 1-mm grains of chitosan. The small columns were 0·6 × 15 cm and contained 3 g of 100–200 mesh chitosan powder.

DEAHP-cellulose

Samples of DEAHP-cellulose with various nitrogen contents were kindly supplied by R. Noreika, Polytechnic Institute of Kaunas, Kaunas, SSSR. The preparation of this cellulose has recently been reported.[1,6]

RESULTS AND DISCUSSION

Cations

Table 1 shows that at pH 3·0 in the absence of ammonium sulphate, sulphuric acid conditioned chitosan is less efficient than chitosan as a collecting agent; 0·1*M* ammonium sulphate at pH 3·0 enhances collection of manganese on free chitosan, but sulphate-conditioned chitosan does not collect manganese. The chitosan functions more efficiently if conditioned with ammonium sulphate alone. For instance, while chitosan collected 71% of the Ni added, the sulphuric acid conditioned chitosan collected only 30%, but the chitosan conditioned with both sulphuric acid and ammonium sulphate collected 78%. Collection

Table 1. Collection of metal ions on 200 mg of chitosan. Expressed as fraction (%) extracted from 50 ml of 0·5m*M* solution

pH	Conditioning	$(NH_4)_2SO_4$	Time, *hr*	Cr^{3+}	Mn^{2+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Hg^{2+}
3·0	none	absent	1	53	0	72	70	95	7	100
			12	93	15	74	71	100	22	100
	0·1*M* H_2SO_4	absent	1	28	15	18	28	68	9	89
			12	36	10	13	30	79	15	89
	none	0·1*M*	1	58	22	94	83	100	57	100
			12	95	23	100	88	100	63	100
	0·1*M* H_2SO_4	0·1*M*	1	36	0	25	25	35	23	91
	+0·1*M* $(NH_4)_2SO_4$		12	84	0	20	78	76	58	86
	0·1*M* $(NH_4)_2SO_4$	0·1*M*	1	70	7	96	90	96	63	90
			12	95	0	95	90	100	73	90
5·0	none	absent	1	85	0	—	76	100	30	100
			12	86	13		85	100	58	100
	0·1*M* H_2SO_4	absent	1	32	10	—	37	81	12	95
			12	76	0		55	80	30	93
	none	0·1*M*	1	74	12	—	80	100	70	100
			12	93	12		80	100	88	100
	0·1*M* H_2SO_4	0·1*M*	1	78	10	—	78	100	61	90
	+0·1*M* $(NH_4)_2SO_4$		12	90	10		86	100	71	90
	0·1*M* $(NH_4)_2SO_4$	0·1*M*	1	95	5	—	95	100	90	90
			12	90	3		95	100	96	90

is slightly more efficient at pH 5·0. Sulphuric acid at pH 1·0 prevents collection of the transition metal ions on chitosan and conditioned chitosan.

The sulphate ions form electrostatic bonds with the protonated amino-groups of the polymer: the general reaction mechanisms are those of the protonation of weak bases.[7] The structure parameters of chitosan are not known, but on the basis of those for the parent polymer chitin[1,8–10] (which is not perfectly crystalline) the minimum distance between two nitrogen atoms is at least 8 Å in the *bc* plane of the orthorombic cell described by Carlstrom.[11] Therefore, assuming that the N–H–O–S–O–H–N group has a 109° angle with interatomic distances N–H 1·034 Å O–H 1·029 and S–O 1·432, the two nitrogen atoms would lie ∼ 5·5 Å apart. Thus, it seems that an H_2SO_4 molecule cannot bridge two amino-groups without altering the form of the macromolecule.

Chitosan conditioned in sulphuric acid would probably carry $-NH_3^+\,{}^-SO_4H$ groups, while chitosan conditioned in a mixture of sulphuric acid and ammonium sulphate, or in ammonium sulphate alone, would probably carry $-NH_3^+\,{}^-SO_4NH_4$ groups.

The metal cations can be regarded as polybasic Lewis acids capable of reaction with several basic entities (including nitrogen and oxygen), the number of which is related to the co-ordination number of the metal cation. The hydrated copper ion is a Lewis acid which competes with sulphate and bisulphate acids for the electron pairs of nitrogen atoms in chitosan:

$$-NH_3^+\,{}^-SO_4NH_4 + Cu^{2+} = -NH_2 \rightarrow Cu^{2+} + NH_4^+\,{}^-HSO_4.$$

The complexation of the cation is also due to a contribution of the $-OH$ groups.

The enhancement of the chitosan capacity in sulphate solutions should therefore be regarded as a phenomenon originated by a novel crystallinity induced in the polymer by sulphate, and favoured by the availability of sulphate.

Oxy-anions

Table 2 reports the collection of three oxy-anions on chitosan, conditioned chitosan and DEAHP cellulose at various pH values. The trend with pH is the same as for the cations, except that the presence of sulphate depresses the degree of collection to a certain extent, especially at pH 5·0. The method worked out for the determination of vanadium in sea-water[12] is based on these results and takes advantage of the maximum yield at pH 3·0 for collection, and minimum yield at pH 1·0 for elution with sulphuric acid.

The better values for chitosan conditioned with sulphuric acid indicate that the polymer in this case behaves as an anion-exchanger:

$$-NH_2 + H^+ + HSO_4^- = -NH_3^+\,{}^-SO_4H \text{ (conditioning)}$$

$$-NH_3^+\,{}^-SO_4H + \text{oxy-anion}^{n-} = -NH_3^+\text{oxy-anion}^{n-} + SO_4H^- \text{ (anion-exchange)}$$

As Table 2 shows, whenever the sulphate concentration is high, the amount of the oxy-anion collected is lowered, in accordance with the second equilibrium.

Chromatographic experiments

In order to take advantage of the batch measurements reported above, for inorganic chromatography, the following points have been experimentally verified:

(*a*) a metal ion can be retained in a narrower band if the polymer has been conditioned with sulphate:

Table 2. Metal oxy-anion collection on 200 mg of chitosan. Expressed as fraction (%) extracted from 50 ml of 0·5m*M* solutions at various pH values

pH	Time, *hr*	Ammonium sulphate absent VO_4^{3-}	CrO_4^{2-}	MoO_4^{2-}	Ammonium sulphate 0·1*M* VO_4^{3-}	CrO_4^{2-}	MoO_4^{2-}
Chitosan, free base							
1·0	1	5	0	0	12	18	0
	12	12	0	0	23	18	0
3·0	1	89	88	67	78	34	6
	12	93	90	67	84	46	17
5·0	1	50	36	18	78	18	0
	12	70	38	27	82	25	10
Chitosan conditioned in 0·1*M* H_2SO_4					Chitosan, conditioned in 0·1*M* H_2SO_4 + 0·1*M* $(NH_4)_2SO_4$		
1·0	1	0	12	10	0	17	15
	12	0	12	12	0	17	0
3·0	1	95	91	100	75	17	85
	12	100	95	100	60	20	85
5·0	1	100	92	100	30	28	30
	12	100	93	100	20	35	0
DEAHP-cellulose, 4·9% nitrogen							
1·0	1	10	15	0			
	12	15	10	0			
3·0	1	92	100	100			
	12	88	100	100			
5·0	1	93	90	87			
	12	83	90	91			
DEAHP-cellulose, 0·4% nitrogen							
1·0	1	0	5	0			
	12	0	4	0			
3·0	1	94	92	48			
	12	100	90	38			
5·0	1	94	29	65			
	12	87	32	66			

(*b*) the sulphate anion is necessarily involved in the collection;

(*c*) a metal ion can be eluted from chitosan with sulphate–sulphuric acid at pH 1·0 and the column can be recycled by taking advantage of the fact that the presence of sulphate compensates for the depression of the collection yield by the sulphuric acid.

For the first point, 1 × 24 cm columns were prepared with 6 g of chitosan, or sulphate-conditioned chitosan, then 20 ml of 0·05*M* copper chloride or sulphate were passed through and 150 ml of water added for washing. The band-heights before and after washing were measured on the basis of the blue colour; the amounts of sulphate or chloride were determined as $BaSO_4$ or AgCl by standard methods. It was found that the shortest bands (6 cm) appeared in the sulphate-treated chitosan columns, while the washing with water produced a broadening of the band down to the bottom of the column in the case of absence of sulphate. As Table 3 shows, the best retention (no band-broadening) is when sulphate accompanies copper, while the sulphate present in the conditioned column ensures minimum band length. Moreover, it can be seen that 90% of the sulphate added with the copper is retained in the column, against 76% of the chloride. When sulphate and chloride are together, the chloride is completely washed out. This is the reverse of the common rules for anion-exchangers and stresses the particular physico-chemical requirements of chitosan.

Table 3. Anion release from a 6-g, 1 × 24 cm chitosan column (1-mm grain-size) treated with 20 ml of 0·05*M* copper solution, and washing with 150 ml of water

	$CuCl_2$	$CuCl_2$ $(NH_4)_2SO_4$	$CuCl_2$	$CuSO_4$
Column conditioning	none	none	ammonium sulphate	none
Copper band height, *cm*				
before washing	12	12	6	12
after washing	24	12	18	12
Eluate pH	8	8	8	8
Ratio $\frac{\text{anion in column}}{\text{anion in eluate}}$	3·297	0·099	0·087	9·000
		chloride		sulphate

The smaller columns were used to define the optimum conditions for recycling. Copper and nickel can be eluted with 0·1*M* sulphuric acid, but the polymer would no longer be suitable for the next collection because the elution would correspond to a sulphuric acid conditioning. However, the results in Table 1 indicate that a mixture of sulphuric acid and ammonium sulphate is suitable for elution and is not detrimental for the next cycle.

Through the columns of sulphate-conditioned chitosan were passed 100 ml of 0·1*M* ammonium sulphate at pH 5·5 containing 5 μmole of copper or nickel. After washing with 15 ml of water, elution was performed with 10 ml of 0·1*M* ammonium sulphate and sulphuric acid, at pH 1·0, in 2-ml fractions; after a further washing with 15 ml of water, the column was reconditioned with 0·1*M* ammonium sulphate adjusted to pH 10·0 with ammonia, until the pH of the effluent was 5·5. From the yields reported in Table 4 and the shapes of the elution curves, it can be said that the columns work quite satisfactorily under the said conditions for at least 20 cycles.

DEAHP-cellulose

The general trend for the DEAHP-cellulose samples is that the higher the nitrogen content, the higher the degree of collection. The good collection efficiency of DEAHP cellulose was expected[1] on the basis of its nitrogen content, which is higher than in all the other modified celluloses so far produced; however other factors must be taken into account to explain why nickel is not collected. The DEAHP-cellulose samples, except the one with 0·4% N, become violet upon collection of copper; however the presence of large amounts

Table 4. Recovery of metal ions during recycling of a chitosan column with ammonium sulphate, ammonium sulphate–sulphuric acid, ammonium sulphate–ammonia. Fraction of the total amount of 5 μmole

Cycle	Copper, %	Nickel, %	Cycle	Copper, %	Nickel, %
1	93	104	11	90	104
2	98	94	12	105	93
3	97	97	13	89	98
4	102	94	14	99	97
5	96	96	15	95	102
6	99	103	16	102	96
7	89	100	17	80	97
8	109	92	18	92	93
9	97	92	19	100	101
10	102	95	20	103	99

Table 5. Metal ion collection on 200 mg of DEAHP-cellulose. Expressed as fraction (%) extracted from 50 ml of 0·5m*M* solutions at various pH values.

pH	Time, *hr*	Cr^{3+}	Mn^{2+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Hg^{2+}
DEAHP-cellulose, 4·9% nitrogen								
1·0	1	0	10	0	0	0	5	0
	12	0	10	0	0	0	0	0
3·0	1	80	15	70	0	95	30	68
	12	80	10	50	0	100	30	86
5·0	1	75	20		0	100	70	79
	12	85	65		0	100	50	98
DEAHP-cellulose, 3·3% nitrogen								
1·0	1	3	4	5	3	10	0	0
	12	0	0	3	5	5	0	0
3·0	1	68	10	100	0	55	12	51
	12	87	18	95	8	71	8	75
5·0	1	70	4		4	83	20	55
	12	91	10		12	92	15	35
DEAHP-cellulose, 2·6% nitrogen								
1·0	1	7	0	0	0	0	0	0
	12	0	0	0	0	0	0	0
3·0	1	63	7	97	20	68	30	50
	12	60	0	100	0	56	30	75
5·0	1	93	15		10	97	23	49
	12	75	0		0	100	18	68
DEAHP-cellulose, 0·4% nitrogen								
1·0	1	0	12	0	10	0	10	0
	12	0	14	0	5	0	0	0
3·0	1	12	12	24	5	5	16	20
	12	10	9	53	5	7	0	10
5·0	1	72	26		27	75	45	39
	12	68	47		10	80	45	57
Natural cellulose								
1·0	1	4	2	2	2	6	0	0
	12	0	0	0	8	4	0	0
3·0	1	3	5	75	0	9	0	0
	12	0	3	65	6	12	0	0
5·0	1	16	8		5	13	0	0
	12	16	2		6	14	2	0

of other salts, and 0·1*M* ammonium sulphate, prevents the collection of copper. Results are in Table 5.

CONCLUSIONS

For the first time, chitosan columns have been operated and recycled with sulphuric acid solutions; this offers a new procedure for elution of copper, which has so far been performed with organic complexing agents, such as 1,10-phenanthroline and EDTA.[13]

Ammonium sulphate seems to induce a new crystallinity in chitosan and makes it better able to interact with most transition metal ions in acidic media. Sulphate is preferred to chloride as the counter-ion for the sorbed cations.

The new DEAHP-cellulose is superior to DE-cellulose mainly because of its higher nitrogen content, but the collection ability of chitosan is unsurpassed, because it can collect transition metal ions in the presence of large amounts of salts, whereas substituted celluloses can not.

The non-collection of manganese by chitosan in sulphate media makes feasible a rapid and sharp separation of copper and nickel from manganese.[14]

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Zusammenfassung—Diskontinuierliche Messungen haben gezeigt, daß die Sammelausbeute von Chitosan für Chrom(III), Eisen(III), Nickel, Kupfer(II), Zink und Quecksilber(II) aus schwefelsaurer Lösung größer wird, wenn die Lösungen Ammoniumsulfat enthalten, oder wenn mit Ammoniumsulfat vorbehandeltes Chitosan verwendet wird, besonders bei pH 3,0 und 5,0. Das Gegenteil ist der Fall bei den Oxyanionen Vanadat, Chromat und Molybdat. Mangan wird nie gesammelt. Bei pH 1,0 findet keine Sammlung statt. In einer Vorschrift zur cyclischen Verwendung chromatographischer Säulen wird Cu oder Ni aus sulfathaltiger Lösung bei pH 3–5 an sulfatbehandeltem Chitosan fixiert und dann mit 0,1*M* Schwefelsäure/0,1*M* Ammoniumsulfat bei pH 1,0 eluiert; die Gegenwart von Sulfat im Elutionsmittel vermeidet den schädlichen Effekt von Schwefelsäure für den nächsten Cyclus. Sulfat wird von den als Chelat gebundenen Kationen als Gegenion bevorzugt; daher bewirkt es kürzere chromatographische Banden. Die Wechselwirkung von Sulfat mit Chitosan wird im Hinblick auf den Kristallinitätsgrad und die räumliche Verteilung der protonierten Aminogruppen in dem Polymeren diskutiert. Daten für die neue Diäthylaminohydroxypropylcellulose werden ebenfalls angegeben.

Résumé—Des mesures discontinues ont montré que les rendements de fixation du chitosane pour les chrome(III), Ser(III), nickel, cuivre(II), zinc et mercure(II), à partir de solutions d'acide sulfurique sont plus élevés quand les solutions contiennent du sulfate d'ammonium, ou quand on utilise du chitosane conditionné en sulfate d'ammonium, particulièrement à pH 3,0 et 5,0. Le contraire est vérifié par les oxy-anions vanadate, chromate et molybdate. Le manganèse n'est jamais concentré. A pH 1,0 la fixation n'a pas lieu. Une technique pour le recyclage des colonnes chromatographiques comprend la fixation de Cu ou Ni à partir d'une solution de sulfate à pH 3–5 sur du chitosane conditionné au sulfate, et l'élution par l'acide sulfurique 0,1*M*/sulfate d'ammonium 0,1*M* à pH 1,0; la présence de sulfate dans l'éluant évite l'effet nuisible de l'acide sulfurique sur le cycle suivant. Le sulfate est l'ion opposé privilégié des cations chélatés et son action produit des bandes chromatographiques plus courtes. On discute de l'interaction du sulfate avec le chitosane en fonction de la cristallinité et de la répartition stérique des groupes aminés protonés dans le polymère. Des données sur la nouvelle diéthylaminohydroxypropylcellulose sont incluses.

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ATOMIC-EMISSION SPECTROMETRY WITH AN INDUCTION-COUPLED HIGH-FREQUENCY PLASMA SOURCE

COMPARISON WITH THE INERT-GAS SHIELDED PREMIXED NITROUS OXIDE–ACETYLENE FLAME FOR MULTI-ELEMENT ANALYSIS

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Summary—The performance for trace analysis in solution by atomic-emission spectrometry from a 36-MHz induction-coupled radiofrequency plasma atom-cell is predicted from a simple model and compared with the corresponding characteristics of an inert-gas shielded nitrous oxide–acetylene flame. A longer linear calibration range is predicted for the plasma source owing to the greater freedom from self-absorption under optimum operating conditions, and the long residence time of analyte species confers freedom from solute vaporization interferences. The predictions are verified experimentally and the advantages of the use of the plasma source are demonstrated in the analysis of aluminium alloys for copper, iron, magnesium, manganese, titanium and zinc.

A number of recent publications have been concerned with the use of induction-coupled radiofrequency plasma sources for atomic spectrometry.[1–11] Some of these papers have outlined the possible advantages of these sources compared to the flame cell[1,4,6,8,9] and also as atom cells for simultaneous multi-element analysis.[2,5,7,9] Recent work in this laboratory has been concerned with the use of an inductively-coupled radiofrequency plasma source for detection by emission spectrometry of elements having principal resonance lines which lie at short wavelengths and are difficult to excite in flame cells.[10,11] During the course of this work, however, we have had occasion to examine several other aspects of the radiofrequency plasma and to compare its suitability with the premixed nitrous oxide–acetylene flame as a source for trace analysis by emission spectrometry, particularly with regard to its application in simultaneous multi-element analysis.

This paper outlines some factors which would be expected to lead to different performances for the plasma and flame with aqueous samples with respect to sensitivity, selectivity and linear calibration range and illustrates that many of these effects are observed in practice.

EXPERIMENTAL

Apparatus

The Radyne model H30/P plasma generator and torch design employed have been described in an earlier paper.[10] The argon plasma was supplied with aqueous sample solution from a conventional adjustable indirect nebulizer (Perkin Elmer Corp., Norwalk, Connecticut, U.S.A.) and the expansion chamber of a Techtron AA4 spectrometer. No desolvation of the aerosol was employed.

Flame-emission studies were undertaken with a nitrogen-shielded premixed nitrous oxide–acetylene flame supported at a 50-mm slot burner (Beckman-RIIC Ltd., Glenrothes, Scotland) viewed end-on and supplied with aqueous sample solution from the same nebulizer and expansion chamber.

A Techtron AA4 flame spectrometer was used for both plasma and flame studies. In both cases, the radiation from the centre of the tail-flame of the plasma or flame was focused onto the entrance slit of the monochromator by a 62·5-mm focal-length fused silica lens and the radiation was modulated at 285 Hz by a rotating sector in synchronization with the a.c. amplification of the spectrometer.

Reagents

A stock solution containing 20000 ppm of calcium was prepared by dissolving analytical reagent grade calcium carbonate (50·0 g) in 6*M* hydrochloric acid (*ca* 200 ml) and diluting to 1 litre with distilled water. Stock solutions containing 20000 ppm of copper and zinc were prepared by dissolving analytical reagent grade copper(II) chloride dihydrate (53·7 g) and zinc sulphate heptahydrate (88·0 g) in distilled water and diluting to 1 litre.

Stock solutions containing 1000 ppm of zinc (zinc sulphate), titanium [titanium(IV) chloride], manganese [manganese(II) chloride], magnesium (magnesium chloride), iron [iron(II) ammonium sulphate] and copper [copper(II) chloride] were prepared from the analytical-grade reagents specified in brackets.

Plasma operating conditions

The plasma was operated with an injector-gas flow-rate of 3·0 l./min with a sample-uptake rate variable over the range 0·1–0·6 ml/min. The coolant-gas flow-rate was 15 l./min. The emission from the section of plasma between 20 and 30 mm above the top of the work coil was viewed.

Flame operating conditions

The nitrous oxide flow-rate to the burner was maintained at 6·6 l./min; the sample-uptake rate was variable between 2 and 6 ml/min. The acetylene flow-rate was adjustable over the range 3·0–4·0 l./min. The burner height was adjusted so that the emission observed was from a section of flame, 10 mm high, in the interconal zone just above the top of the primary reaction zone. The nitrogen shield-gas flow-rate was 15 l./min.

Dissolution of aluminium alloy samples

Aluminium alloy samples (2·5 g) were dissolved in 6*M* hydrochloric acid (75 ml); hydrogen peroxide (10 vol., 40 ml) was added and the solutions were boiled until dissolution was complete. The solutions were then evaporated till crystallization began and then were cooled. The residue was redissolved in hot distilled water to which 5 ml of concentrated nitric acid had been added; these solutions were cooled, transferred to 250-ml volumetric flasks and diluted to volume with water.

Standards for the preparation of calibration surves for copper, iron, magnesium, manganese, titanium and zinc were prepared by appropriate dilution of the stock solutions of the salts of these metals. To each of these solutions sufficient aluminium chloride solution, prepared from spectroscopically pure aluminium metal in a manner similar to that used to prepare the samples, was added so that each solution contained *ca* 1% w/v aluminium upon dilution.

RESULTS AND DISCUSSION

In order to facilitate the prediction of comparative performance of flame and plasma atom-cells as emission sources it is helpful to construct a simple ideal model of both cells (Fig. 1). A semi-quantitative comparison may be obtained for plasma and flame atom-cells in which the following assumptions are made.

1. The injector gas in which the sample is introducted into the plasma may be equated in function with the combined fuel and oxidant gases supplied to support the flame.
2. The coolant gas employed for the plasma has a similar function to the shield gas used with the flame and does not play a significant part in sustaining the discharge or carrying the sample.
3. All gases enter the atom-cell at constant velocity and with laminar flow.
4. The velocity of the gas stream and analyte species is the same.
5. All energy is supplied initially in the plasma core and the flame primary reaction zone.
6. Sample desolvation and vaporization occur in or slightly above the core of the plasma or the primary reaction zone of the flame before the sample passes into the gas volume viewed by the detector.
7. In the plasma, argon accelerates instantaneously upon entering the core and then travels through the tail-flame with uniform velocity.

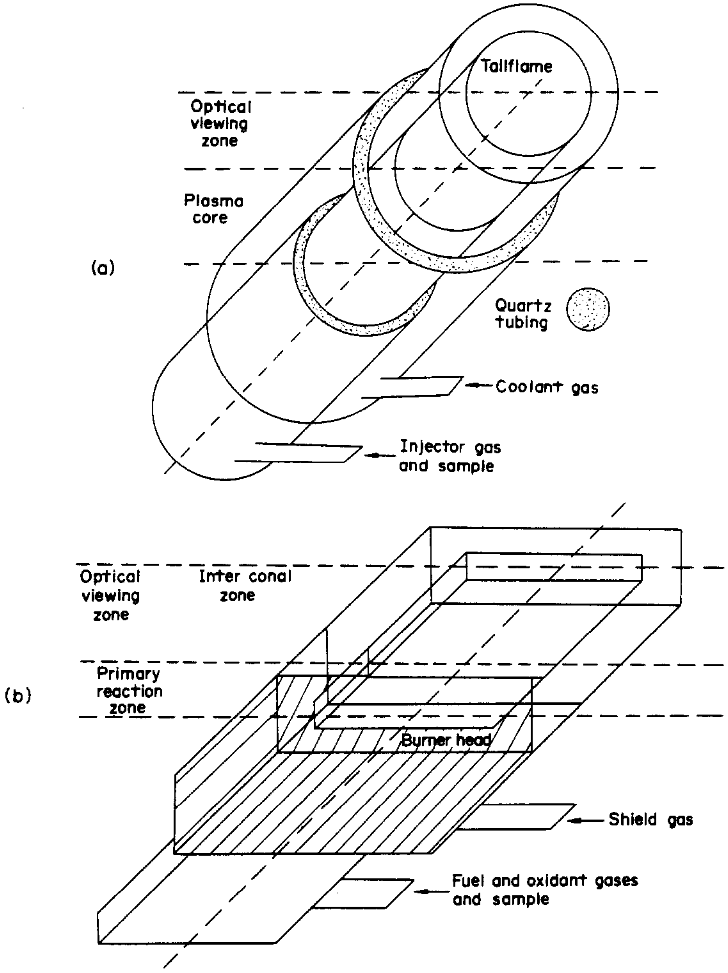

Fig. 1. Diagrammatic representation of ideal plasma and flame models: (*a*) plasma; (*b*) flame.

8. In the flame, gas molecules accelerate uniformly through the primary reaction zone and then move with uniform velocity through the viewing (interconal) zone.
9. The temperature and the flame expansion on combustion are the principal factors which affect changes in flame gas velocity once the flame gases have entered the combustion zone.

Most of these assumptions are necessary in order that the systems can be subjected to a simple physical interpretation and may only be valid for a first approximation. The last assumption is valid if the effects of intermolecular and interatomic reactions within the flame or plasma, and the small corrections to allow for the buoyancy of the hot gases in air and frictional effects at the outer layers, are all neglected.

Figure 2 shows the observed and assumed temperature profiles of the plasma system. The temperature shown is that measured by Johnson[12] for the axial channel of a 2-kW 36-MHz induction-coupled radiofrequency plasma. The assumed temperature of the

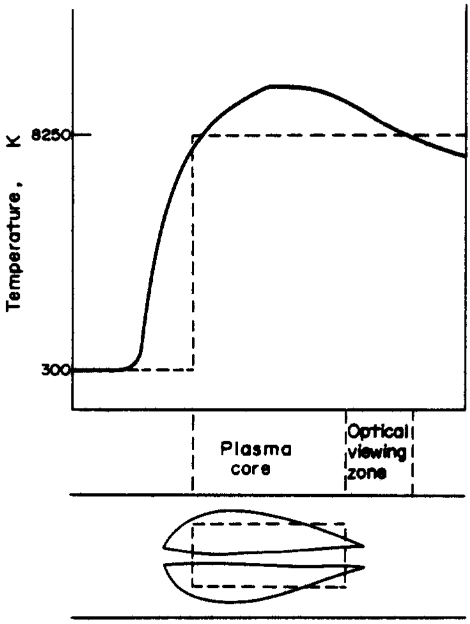

Fig. 2. Observed and assumed temperature profiles for central axis of-radiofrequency plasma. Observed profile shown as solid line and assumed profile as broken line.

plasma was taken to be 8250 K in the zone of observation. This temperature was estimated from the observed degrees of ionization of calcium and zinc in the tail-flame, by using the Saha equation. The observed and assumed shapes of the plasma core are shown in the lower half of Fig. 2.

Figure 3 shows the temperature profile in the shielded nitrous oxide–acetylene flame. The temperature profile of the interconal zone is based upon measurements made in this

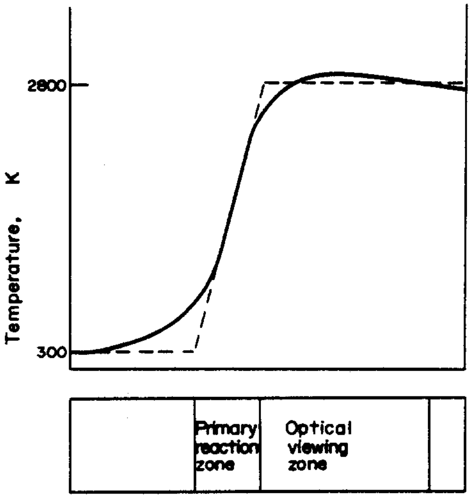

Fig. 3. Observed and assumed temperature profiles in the nitrogen-shielded nitrous oxide–acetylene flame. Observed profile shown as solid line and assumed profile as broken line.

Table 1. Typical operating conditions for the radiofrequency induction-coupled plasma and premixed nitrogen-shielded nitrous oxide–acetylene flame

Parameter	Plasma	Flame
Fuel-gas flow-rate, *l./min*		3·3
Injector-gas flow-rate, *l./min*	3·0	
Oxidant-gas flow-rate, *l./min*		6·6
Coolant-gas flow-rate, *l./min*	15	
Shield-gas flow-rate, *l./min*		15
Sample-uptake rate, Q_s, *ml/min*	1·5	4·2
Nebulizer efficiency, ψ	0·01	0·1
Path-length of cell, L, *mm*	20	50
Width of burner, b, *mm*		0·4
Height of reaction zone, h_r, *mm*	25	0·1
Height of viewing zone, *mm*	10	10
Surface area of core	22 cm^2	50 mm^2
Volume of core	8 cm^3	2 mm^3
Mean gas density, ρ, *g/l.*	1·78	0·96
Mean specific heat of gas, C_p, $J.g^{-1}.deg^{-1}$	0·524	1·35
Flame expansion factor	1·0	1·667
Ambient temperature, T_0, K	300	300
Flame temperature, T, K	8250	2800
Maximum temperature, T_{max}, K	9000	3000

laboratory[13] and on consideration of the temperature profile through the primary reaction zone made by Jenkins and Sugden.[14]

Typical operating conditions for the plasma and flame are shown in Table 1; these conditions were used throughout the following comparison.

Self-absorption and its effect on calibration curves in atomic-emission spectrometry with the two cells

The particle density, N_A, of an analyte element introduced into the atom-cells can be calculated from

$$N_A = \frac{Q_s \psi}{Q_G \gamma} \frac{T_0}{T} \frac{A}{M_A} C_A. \tag{1}$$

In equation (1) Q_G is the volume of flame or plasma gas entering the atom-cell per second at an ambient temperature T_0, ψ is the nebulizer efficiency, A is Avogadro's number, Q_s is the sample-uptake rate, M_A is the atomic weight of the analyte element A, T is the mean flame temperature, γ is the molar flame expansion factor and C_A is the concentration of A in aqueous solution.

For the purpose of comparison of the two atom-cells, the line emission observed for the calcium atom and ion at 422·67 and 393·37 nm respectively, zinc at 213·86 nm and copper at 327·40 nm will be considered.

The particle densities of elements calculated from equation (1) give the total particle density of *all* species of that element so that to determine the particle densities of the individual species, the free-atom fraction and the degree of ionization must be measured or calculated. Few data are available concerning the free-atom fraction of these species in the radiofrequency plasma, although consideration of the dissociation energies of their oxide and hydroxide species suggests that an assumption of unity for the free-atom fraction is

Table 2. Particle densities of analyte atoms in the plasma and flame atom-cells and the Doppler half-width and oscillator strength of the lines of the atoms considered

Species	λ *nm*	M_A	f	Particle density m^{-3} Plasma	Flame	Doppler half-width *nm* Plasma	Flame
Ca(I)	422·67	40·1	1·75	$6{\cdot}8 \times 10^{15}$	$8{\cdot}2 \times 10^{15}$	0·0043	0·0025
Ca(II)	393·37	40·1	0·69	$2{\cdot}1 \times 10^{15}$	$5{\cdot}4 \times 10^{15}$	0·0040	0·0024
Cu(I)	327·40	63·5	0·16	$8{\cdot}6 \times 10^{14}$	$8{\cdot}6 \times 10^{15}$	0·0027	0·0016
Zn(I)	213·86	65·4	1·2	$1{\cdot}6 \times 10^{15}$	$1{\cdot}3 \times 10^{16}$	0·0017	0·0010

realistic. With values of 104, 95 and 65 kcal/mole for the dissociation energy of CaOH, CuO and ZnO respectively, we calculate a value of unity for the free-atom fraction of each element, assuming a partial pressure of 10^{-6} atm for the oxide species and a temperature of 8000 K. We may not assume a value of unity for the free-atom fractions of these elements in the nitrous oxide–acetylene flame, however, as lower values have been found by several workers.[15–17] For the purposes of our calculations we will assume values of 0·33, 0·33 and 0·50 for the free-atom fractions of calcium, copper and zinc respectively.

In the radiofrequency plasma, the degrees of ionization of calcium and zinc were measured to be 0·75 and 0·1 respectively from the observed intensities of the atom and ion lines, assuming a temperature of 8250 K.* The degree of ionization of copper under these conditions, calculated from the Saha equation, is 0·5. In the plasma the higher free-electron density (*ca* $10^{20}/\text{m}^3$)[9,12,14,18,19] is so much greater than the analyte particle density that the degree of ionization remains practically constant at all analyte concentrations studied. In the nitrous oxide–acetylene flame the degree of ionization of calcium has been calculated[20] to be 0·43, by using the Saha equation and assuming a partial pressure of 10^{-6} atm for the analyte atoms. The measured degree of ionization of calcium in this flame has been reported to be 0·43,[21] and 0·38,[22] and for this calculation we have assumed a figure of 0·4. The calculated degree of ionization for zinc in this flame is less than 0·01 and may be neglected, while that of copper is only *ca* 0·03, and this has also been neglected. The degree of ionization for each element in the flame refers to that for a 1-ppm solution; no allowance has been made here for any variation in degree of ionization with analyte concentration.

Table 2 shows the calculated particle densities of these species when a solution containing 1 ppm of analyte element is nebulized into both the plasma and flame operated under the conditions shown in Table 1, the wavelength of the line of the species considered, the oscillator strength and the Doppler half-widths of these lines calculated assuming a plasma temperature of 8250 K and a flame temperature of 2800 K.

The absorption of effect coefficient at the line centre, K_ν, for the analyte element at the line considered can be calculated from equation (2):

$$K_\nu = \frac{\lambda^2}{\Delta\lambda_D}\left|\frac{\ln 2}{\pi}\right|^{1/2}\frac{e^2}{2m\epsilon_0 c}N_A f. \tag{2}$$

In this equation, e is the electronic charge, m is the mass of the electron, c is the velocity of light, $\Delta\lambda_D$ is the Doppler half-width, f is the oscillator strength, ϵ_0 is the permitivity of free space and N_A is the particle density in the ground state.

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* Atomic and ionic partition functions were taken from C. W. Allen, *Astrophysical Quantities*, 2nd Ed., Athlone Press, London, 1966.

Table 3. Absorption coefficients of analyte atoms in the plasma and flame atom-cells

Species	λ *nm*	Plasma		Flame	
		K_ν, m^{-1}	$K_\nu L$	K_ν, m^{-1}	$K_\nu L$
Ca(I)	422·67	0·408	0·00408	8·41	0·210
Ca(II)	393·37	0·450	0·00450	2·06	0·051
Cu(I)	327·40	0·046	0·00046	0·79	0·020
Zn(I)	213·86	0·406	0·00406	5·80	0·145

The values of K_ν and $K_\nu L$ computed for the plasma and flame at the particle densities obtained from equation (1) and assuming that the radiation is viewed from the centre of the atom-cell, are shown in Table 3.

From the values of $K_\nu L$ obtained for these lines it is possible to construct theoretical calibration curves by using the relationship:

$$I_{obs} = I_{em}(1 - \exp[-K_\nu L])/K_\nu \tag{3}$$

where I_{em} is defined by the Einstein–Boltzmann equation:

$$I_{em} = \frac{N_A}{u}\frac{2\pi e^2 h}{\epsilon_0 m}\frac{g_k f}{\lambda^3}\exp[-E_k/kT] \tag{4}$$

where u is the partition function of the atom or ion, h is Planck's constant, g_k is the statistical weighting factor of the upper state involved in the transition, E_k is the energy of the upper state and k is the Boltzmann constant. Curves obtained for the four lines considered are shown in Fig. 4. The intensity represented for the plasma is the intensity emitted per unit volume relative to the intensity emitted per unit volume in a flame, at the limit where the absorption coefficient, K_ν, becomes equal to that of a black body at the wavelength concerned. It is quite apparent from these curves that at high solution concentration, the radiofrequency plasma exhibits a more extended linear working range than that attainable

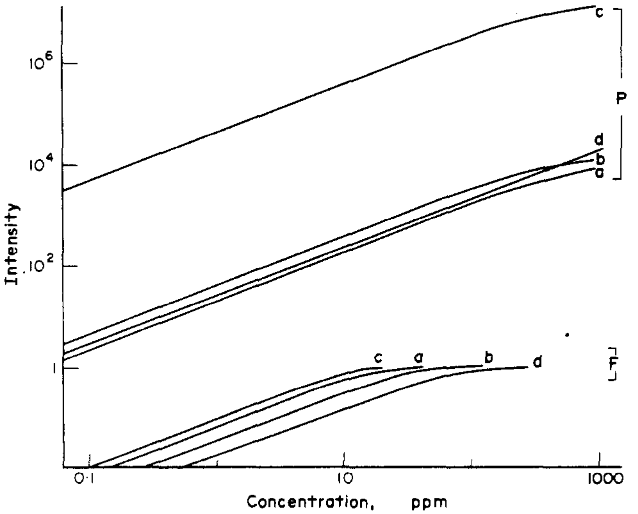

Fig. 4. Growth curves calculated for plasma [P] and flame [F] cells for elements considered: (*a*) calcium at 422·67 nm; (*b*) calcium at 393·37 nm; (*c*) zinc at 213·86 nm; (*d*) copper at 327·40 nm.

with the flame. In the plasma, the linearity of the Ca(I) line at 422·67 nm, the Ca(II) line at 393·37 nm and the Zn(I) line at 213·86 nm are predicted to be almost identical, as the value of $K_\nu L$ for each line is similar. As the absolute emitted intensity at any line is very much greater in the plasma than in a flame, the potential sensitivity of the technique is much higher and the linear range should also be extended to lower absorbances (*i.e.*, concentrations).

A second advantage of the plasma system is that as the absolute emitted intensity is very much higher than that obtained with a flame, it is possible to reduce the sample-uptake rate of the nebulizer system and still maintain adequate signal intensity. This reduces the particle density in the plasma and hence reduces the value of K_ν. This, therefore, offers a very simple way of extending the linear range obtained at high concentrations in the plasma, with minimal sacrifice in sensitivity.

Residence times of analyte species in the atom cells

One of the advantages claimed for the radiofrequency plasma system is that the residence time of an analyte particle in the discharge and tail-flame is long compared to that in a flame or arc excitation-cell.[4] For the plasma system used in the present work, if it can be assumed that the linear velocity of analyte particles and carrier-gas atoms is the same, then the residence time of analyte particles will be the same as that for the gas atoms or molecules.

The linear velocity of gas through the entrance port into the plasma is given by equation (5).

$$v_0 = \frac{4Q_G}{\pi L^2}, \qquad (5)$$

where L is the path-length of the cell (*i.e.*, the diameter of the tail-flame), Q_G is the flow-rate of gas at ambient temperature and v_0 is the linear velocity of the gas up the plasma tube.

The corresponding equation from the flame is:

$$v_0 = \frac{Q_G}{bL}, \qquad (6)$$

where L is now the burner-slot length and b the burner-slot width. Solving these equations for the operating conditions in Table 1 gives the linear gas velocity as 0·16 m/sec into the plasma and 8·25 m/sec into the flame. After passing into the plasma core or primary reaction zone of the flame, the gases expand, and their linear velocity, v_T, after leaving the reaction zone is given by

$$v_T = v_0 \gamma \frac{T}{T_0}, \qquad (7)$$

where γ is the molar flame expansion factor.

Solving this equation for the plasma and flame gives linear velocities of 4·4 and 130 m/sec respectively.

The residence time, t_r, of analyte particles in the reaction zone can be calculated from

$$t_r = \frac{h_t}{v_{av}}, \qquad (8)$$

where h_t is the thickness of the reaction zone and v_{av} is the average linear velocity through the reaction zone. For the plasma it is assumed that the average velocity through the plasma core is 4·4 m/sec and for the flame it is assumed that the average velocity through the primary reaction zone is 70 m/sec. The calculated residence times are 5·7 msec for the plasma and 1·5 μsec for the flame.

If it is assumed that the emission intensity viewed is that from a 10-mm high section above the top of the plasma core or primary reaction zone, the residence time of analyte in the viewing zone (t_v) can be calculated from

$$t_v = \frac{1}{100\, v_T}. \tag{9}$$

The residence time for an analyte particle in the plasma tail-flame is therefore 2·3 msec, compared to 77 μsec in the flame.

The plasma system can be readily seen to retain the analyte atom in the volume viewed for a much longer period than the flame. It can therefore undergo many more collisions to effect excitation during its residence, compared to the number experienced in the flame. As the lifetime of the excited atom is typically a few nanoseconds, it is apparent that the atom can go through the cycle of excitation and emission about thirty times in the plasma tail-flame compared to once in the flame. The additional advantage of the longer residence time is that for samples with a low rate of vaporization, complete vaporization may be possible during their residence in the plasma, whereas complete vaporization may not be attained in the nitrous oxide–acetylene flame.

Energy of the atom-cells

The rate of supply of energy to the plasma, assuming totally efficient coupling, is 4 kW. For the flame, the rate of supply of energy W_{in} can be calculated, assuming unit efficiency, from

$$W_{in} = \frac{Q_f\, \Delta H_f}{V}, \tag{10}$$

where Q_f is the flow-rate of the fuel gas, V is the molar volume, and ΔH_f is the heat of reaction of the gas oxidation process in this equation.

For the nitrous oxide–acetylene flame reaction

$$2N_2O + C_2H_2 \rightarrow 2N_2 + 2CO + H_2,$$

the heat of reaction is 179 kcal/mole; for the gas flow-rates used this corresponds to a power of 1·8 kW.

Thermal energy

The thermal energy, E_T, available in the atom-cell can be calculated from

$$E_T = m_g C_p (T_{max} - T_0), \tag{11}$$

where C_p is the specific heat of the gas at constant pressure, T_{max} is the maximum temperature experienced by the bulk of the gas and m_g is the mass of gas in the atom-cell. The mass of gas in the atom-cell at any instant is related to the product of the density of the gas, ρ, and the flow rate, Q_G, so substitution into equation (11) gives for the thermal power (W_T):

$$W_T = \rho Q_G C_p (T_{max} - T_0). \tag{12}$$

When this equation is solved for the plasma, a thermal power of 400 W for the argon gas is obtained. For the flame an average density and specific heat must be assumed (as not all the flame molecules are identical). The average density of the flame gas shown in Table 1 was calculated for the average molecular weight of flame gases of 21·67 reported by Taylor.[23] The specific heat of the flame gases was also calculated from this molecular weight, assuming a diatomic flame gas and ideality of the flame species. The thermal power for the flame is calculated in this way to be 580 W.

The maximum thermal energy (J_T) which can be transferred to analyte particles in the primary reaction zone or plasma core, assuming 100% efficiency, can be calculated from

$$J_T = W_T t_r. \tag{13}$$

For the plasma this energy is 2·3 J and for the flame 0·001 J.

Background emission from atom-cells

In the plasma system, the principal contribution to the background continuum emission is most probably from the bremsstrahlung radiation. In bremsstrahlung radiation, the acceleration of charged particles takes place *via* the Coulomb field of other charged particles and the major part of the radiation is due to electron-ion collisions and, since the initial and final stages are continuous, the bremsstrahlung radiation is also continuous. The bremsstrahlung radiation at any angular frequency, ω, in the plasma can be calculated[24] from equation (14).

$$W_B \, d\omega = \frac{16}{3\pi}\left(\frac{2\pi}{m^3kT}\right)^{1/2}\left(\frac{e^2}{4\pi\epsilon_0 c}\right)^3 N_e N_i Z^2 \mu \left(\ln\frac{b_{max}}{b_{min}}\right)\exp\left(\frac{-h\omega}{2\pi kT}\right) d\omega. \tag{14}$$

In this equation, N_e is the electron density, N_i is the ion density, Z is the atomic number, μ is the refractive index of the plasma and b_{max} and b_{min} represent the maximum and minimum impact parameters respectively.

If this equation is integrated over all frequencies then the total bremsstrahlung radiation is given by equation (15).

$$W_B = \frac{32\pi}{3}\left(\frac{2\pi kT}{3m^3}\right)^{1/2}\left(\frac{e^2}{4\pi\epsilon_0 c}\right)^3 \frac{N_e N_i Z^2 \mu}{h} G_{ff}(T). \tag{15}$$

$G_{ff}(T)$ is the Gaunt factor at a temperature T, averaged over both electron velocity and frequency. For a plasma with a core temperature of 9000 K and an electron density of $2 \times 10^{21}/\text{m}^3$, taking both the Gaunt factor and the refractive index to be unity, the total bremsstrahlung radiation for a plasma core volume of 8 cm^3 will be *ca* 175 W.

As the plasma is immersed in a steady magnetic field it radiates as a consequence of the acceleration of charges in their orbital motions around the magnetic lines of induction. This emission is primarily from the free electrons and is termed the cyclotron radiation. Although the particles are free, the spectrum is a type of line spectrum composed of frequencies which are harmonics of the cyclotron frequency. For relativistic particles, the radiation becomes truly continuous and is termed synchrotron radiation.

The ratio of the bremsstrahlung to cyclotron radiation is given by equation (16):

$$\frac{W_B}{W_{cy}} = 2\left(\frac{\omega_p}{\omega_{cy}}\right)^2 \left(\frac{Z^2 R_y}{3\pi kT}\right)^{1/2} G_{ff}(T). \tag{16}$$

In this equation R_y is the Rydberg constant, ω_p is the angular frequency of the plasma defined by

$$\omega_p = 2\pi e\left(\frac{N_e}{\epsilon_0 m}\right)^{1/2}, \tag{17}$$

and ω_{cy} is the cyclotron frequency defined by

$$\omega_{cy} = \frac{eB}{m}, \tag{18}$$

where B is the magnetic flux density of the magnetic field maintained around the plasma.[24]

The cyclotron radiation will only be significant if the cyclotron angular frequency is significant compared to the plasma angular frequency. For this plasma core, the plasma angular frequency is $2{\cdot}6 \times 10^{12}$ rad/sec while the cyclotron angular frequency is governed by the magnetic field strength. For a flux density of typically *ca* 3 mT (millitesla) in the centre of the induction coil, the cyclotron angular frequency will be $5{\cdot}3 \times 10^8$ rad/sec. Thus the radiated cyclotron power from the plasma core is typically *ca* 1 μW. This means that the observed background continuum from free electrons in the plasma should closely represent principally the bremsstrahlung power spectrum, *i.e.*, the cyclotron radiation is negligible.

The background radiation from the plasma can only approach the black-body frequency distribution if there is a complete thermal and radiative equilibrium throughout the plasma. This situation is approached only in very dense plasmas such as those found in stellar interiors. If the induction-coupled radiofrequency plasma behaved as an ideal black body, then it would have to radiate much more power than it could sustain.

Figure 5 shows the variation with wavelength of the observed background continuum from the plasma after correction for the variation in photomultiplier response with wavelength (*a*). This is compared with the theoretical variation with wavelength of the bremsstrahlung radiation (*b*) and that of the black-body radiation (*c*). The wavelength variation of the bremsstrahlung radiation has been calculated for a unit volume of plasma in local thermodynamic equilibrium at a temperature of 8250 K for a unit angular frequency distribution and is shown relative to the peak emission taken as 100. The black-body spectrum has been calculated for a unit volume of an ideal black body of unit emissivity in total thermodynamic equilibrium at a temperature of 8250 K for a unit wavelength interval and is shown relative to its peak emission taken as 100. In Fig. 5 the relative intensity scale for curves (*a*), (*b*) and (*c*) is different. Theory predicts that the black-body radiation should be some 3000-fold more intense than the bremsstrahlung radiation. The shape and intensity of the observed spectrum (*a*) therefore suggests that the observed background is composed principally of the bremsstrahlung radiation.

In the flame, background continuum radiation due to free electrons is almost negligible. The total bremsstrahlung radiation from a flame is typically less than a microwatt and the cyclotron radiation is absent as there is no local magnetic field. The major contributor

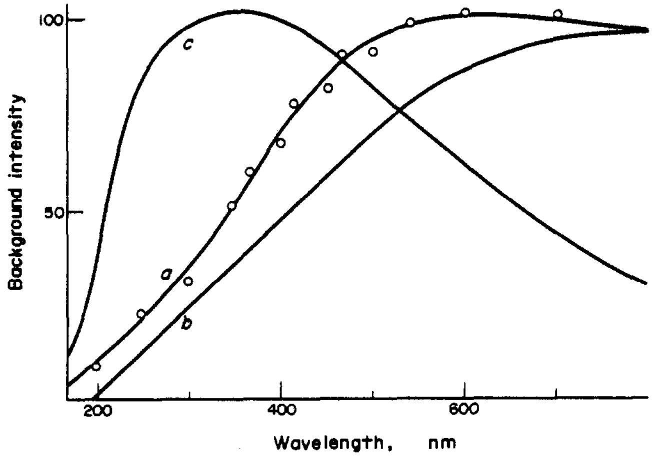

Fig. 5. Comparison of observed and predicted background emission spectra from plasma for bremsstrahlung and black-body radiation: (*a*) observed background spectrum; (*b*) predicted bremsstrahlung background spectrum; (*c*) predicted black-body spectrum at 8250 K.

to the background in the flame is the black-body radiation, which is typically of the order of a few milliwatts.

In both the plasma and flame, the emission spectra of species in the tail-flame are observed superimposed upon the continuum background. For the plasma system, the only species present are argon and water; the latter is decomposed principally to atomic hydrogen and atomic oxygen in the plasma. A typical background scan of the plasma at minimal electronic gain over the wavelength range 200–700 nm is shown in Fig. 6. Only a few intense argon lines around 420 nm and the intense H_α and H_β lines are observed, with no

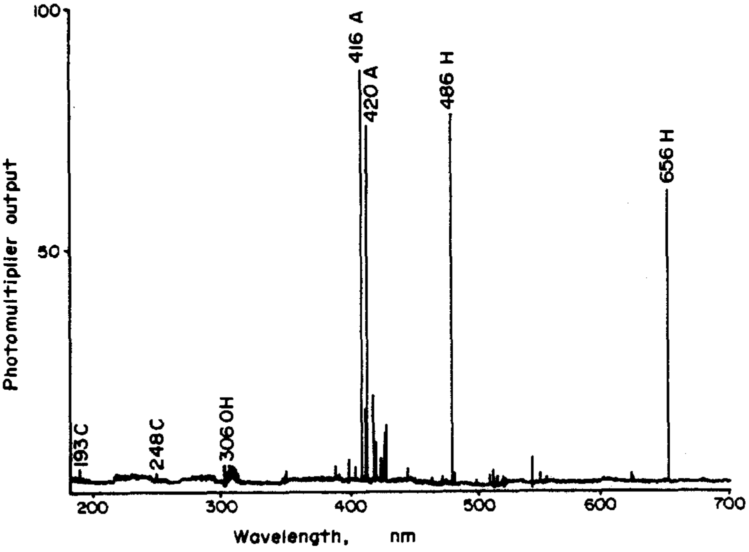

Fig. 6. Background emission spectrum observed from plasma at minimal electronic gain over the wavelength range 185–700 nm.

appreciable OH band system. Carbon lines at 193 and 248 nm, due to impurities in the argon, are also observed. In the flame there are several intense band emission systems due to CH, OH, C_2 and CO which greatly complicate the background spectrum.[25]

PRACTICAL OBSERVATIONS

Effect of sample-uptake rate on calibration curves

Figure 7 shows the effect of variation in the sample-uptake rate in the radiofrequency plasma upon the calibration curves obtained for calcium at 393·37 nm. The effects for calcium at 422·67 nm and zinc at 213·86 nm are similar. At low sample-uptake rates, the particle density, and hence optical density, is low; the linear range is therefore extended to higher solution concentrations, compared with the range obtained with high sample-uptake rates. The observed emitted intensity at each line is, of course, reduced at low sample uptake rates, as the particle density is lower. The detection limit does not deteriorate at low sample-uptake rates to the same extent as the signal attenuation predicted from the reduction of particle density. This is probably due to the fact that less solvent is transferred to the discharge at low sample-uptake rates so that there is less impedance mismatch between the resonance circuit of the oscillator valve and the plasma discharge. Also, it is to be expected that the plasma temperature will increase at low sample-uptake rates as there is less solvent in the discharge to absorb the applied power. This effect can be observed (a plot of temperature vs. uptake rate is linear, with negative slope) and it appears that the decrease in plasma tail-flame temperature is directly proportional to the rate of introduction of solvent.

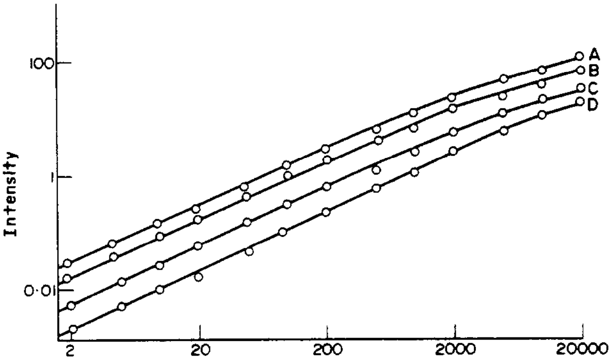

Fig. 7. Effect of sample-uptake rate on calibration graphs in the radiofrequency plasma for calcium at 393·37 nm. Uptake rates (ml/min): A—4·5, B—3·2; C—1·5; D—0·8.

In the nitrous oxide–acetylene flame a similar increase in linear range at low sample-uptake rates is observed for the calibration curves of calcium and copper (Fig. 8). With the nebulizer used, in which no auxiliary oxidant support inlet was available, less variation in sample-uptake rate is possible, however, without greatly affecting the pressure of the nitrous oxide carrier-gas, which in turn alters the flame conditions.

The advantage of the radiofrequency plasma is that the observed linear range of the calibration curves may be made to extend over five or six orders of magnitude (*e.g.*, for zinc) while for the flame under the conditions employed the maximum observed was three orders of magnitude.

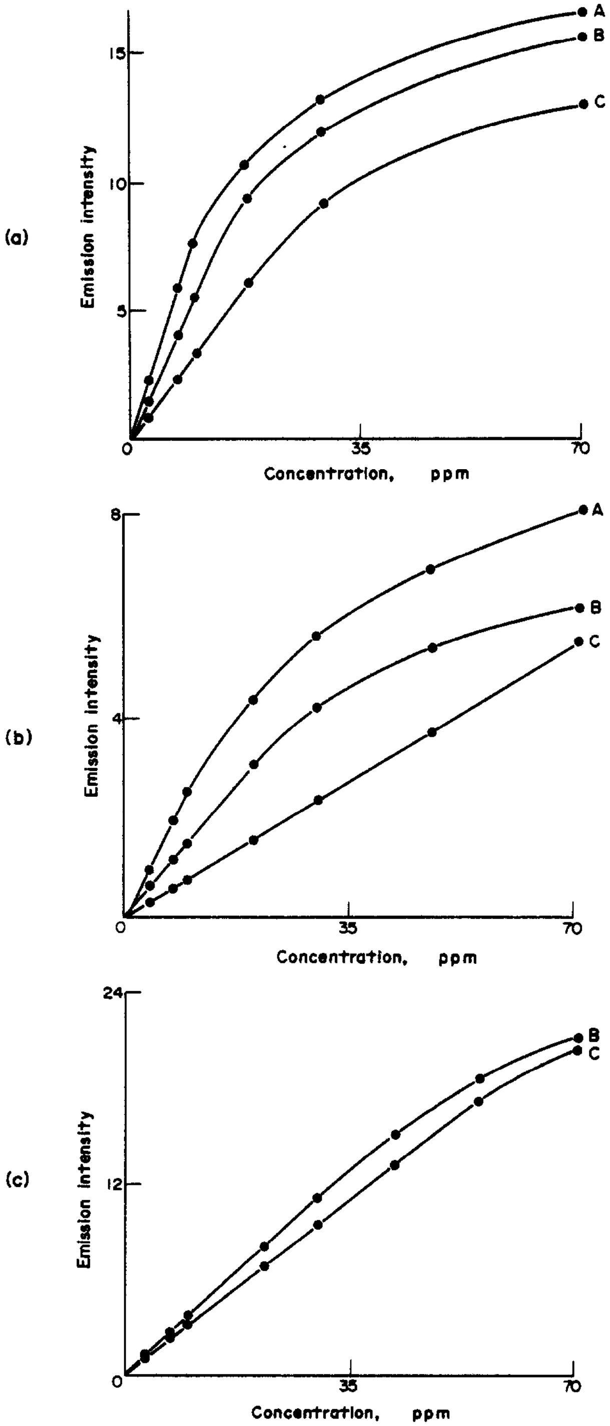

Fig. 8. Effect of sample-uptake rate on calibration graphs in nitrous oxide–acetylene flame for (*a*) calcium at 422·67 nm; (*b*) calcium at 393·37 nm; (*c*) copper at 327·40 nm. Uptake rates (ml/min): A—6·0; B—4·5; C—3·0.

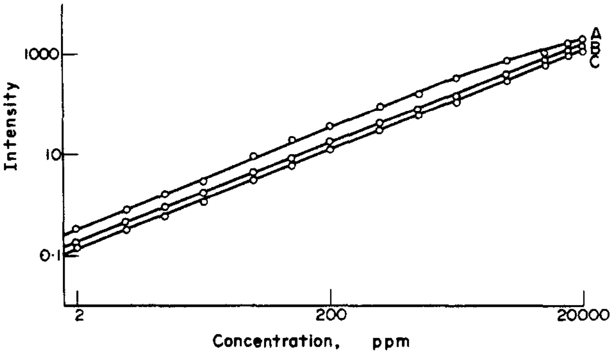

Fig. 9. Calibration curves obtained in the radiofrequency plasma by using different plasma-gas flow-rates for calcium at 422·67 nm. Flow-rates (l./min): A—0; B—4; C—6.

Effect of gas flow-rates on calibration curves

In the plasma system employed the carrier-gas flow (or injector-gas flow) is optimized to produce the maximum efficiency of sample transfer to the atom-cell. With most plasma systems it is possible to dilute the atomic concentration in the cell by introducing a second gas, the plasma gas. Figure 9 shows the observed calcium calibration curves obtained for various plasma-gas flow-rates. The curves for the 393·37-nm calcium line and 213·86-nm zinc line are similar. The increase in linear range observed at high concentration may be attributed to the reduction in the particle density of analyte when the plasma-gas flow is used. Use of the plasma-gas flow, however, reduces the temperature of the tail-flame; the Doppler half-width is then reduced, so the absorption coefficient increases slightly and the full effect of decreased self-absorption due to the reduction in particle density may not be observed. Where the sample-uptake rate is reduced to lessen particle density, and therefore self-absorption, the converse is true and as the particle density is reduced the plasma temperature rises.

In the nitrous oxide–acetylene flame, the oxidant-gas flow was optimized to give the maximum sample transport to the flame and the acetylene flow-rate adjusted to maximize the emission signal from the element concerned. With the burner system employed in this work it was not possible to reduce the particle density by introducing an inert gas or additional oxidant into the flame. No dilution of the atomic concentration was therefore possible except by changing the flame-gas flow-rates and this may adversely affect the sample-transfer efficiency by increase in the mean droplet diameter at the nebulizer.

Effect of height of observation

In simultaneous or sequential multi-element analysis, the height at which the analytical signal is observed must be chosen as a compromise between the optimal heights for the different elements to be analysed. In general, in both atom-cells, the temperature decreases high in the tail-flame and entrainment of air beings to occur, so the sensitivity attainable is usually greatest low in the tail-flame.

It is common practice to view near the primary reaction zone or core of the flame or plasma to obtain greatest sensitivity for an element in the sample which is difficult to excite or is present at a concentration near its detection limit, or both. For other elements which are present at high concentration or are more easily excited, however, this frequently means that an intense emission signal is obtained on the non-linear portion of their calibration curves. If sample dilution and two or more time-consuming nebulization stages are to be avoided, therefore, it is useful to ensure that the greatest linear working range is available simultaneously for all elements to be determined. It is in this respect that the radiofrequency plasma can be best exploited.

Analysis of aluminium alloys

Plasma-emission spectrometry. The plasma was operated under the conditions shown in Table 1. Solutions of B.C.S. aluminium samples and standard solutions were introduced into the plasma at a sample-uptake rate of 1·5 ml/min and different elements were determined sequentially in the same solution without dilution. Titanium was determined at 365·35 nm, iron at 371·99 nm, manganese at 403·07 nm, zinc at 213·86 nm, copper at 327·40 nm and magnesium at 285·21 nm. A slit width of 25 μm (spectral bandpass of 0·08 nm) was employed throughout.

Flame-emission spectrometry. The nitrous oxide–acetylene flame was operated under the conditions of Table 1. The acetylene flow-rate was adjusted to maximize the signal obtained for titanium. The solutions were introduced directly into the flame and analysed for titanium, manganese and iron at the same lines as those employed for the plasma. Because of the non-linearity of the calibration curves for magnesium and copper at these lines, appropriate dilutions were made before these metals were determined. Insufficient sensitivity was obtained in the flame for zinc to be determined in three of the aluminium samples, and zinc was detectable but could not be determined with adequate precision in the fourth sample.

The results of these analyses are shown in Table 4. Each value shown is the mean of six results obtained by each technique; the values are compared with the B.C.S. certificate values in each case. There appears to be no significant discrepancy between the results except where dilutions of the stock solution were necessary (for magnesium and copper) owing to the restricted linear range when the nitrous oxide–acetylene flame was employed. The results obtained for titanium by flame-emission spectrometry are somewhat high; this may be due to the fact that no ionization suppressant was added to the standard titanium solutions or to the aluminium samples.

The precision of the results obtained by plasma-emission spectrometry was typically of the order of 5% over the whole concentration range. At low levels of analyte, therefore, the precision obtained in the plasma method is comparable with the independent analysis, but at high levels it is less precise. The precision obtained with the flame-emission technique was not as good as with the plasma-emission technique; typically about 10% relative standard deviation was obtained in the results. This is probably due to the high concentration of aluminium (*ca* 1%) in the solution, which tended to cause clogging of the burner slot. At lower dilutions this is greatly reduced, but a dilution error is then introduced.

Aluminium was added to the standard solutions principally to eliminate possible matrix effects in the flame caused by the high concentration of aluminium present. With the plasma, no significant effects of this type were observed and the results obtained for the determination of chromium without addition of aluminium to the standard solution in one sample (B.C.S. 263/1) was 0·25% by the plasma emission method, compared with a certificate value of 0·24%.

The results shown in Table 4 for the analysis of aluminium alloy samples by both plasma- and flame-emission spectrometry demonstrate the utility of the wide con-

Table 4. Analysis of aluminium alloys by plasma and flame emission

		Content, %		
Element	Certificate value	Plasma	Flame	
		B.C.S. 181/1		
Cu	3·99 ± 0·02	3·97 ± 0·08	3·8 ± 0·4	[a]
Fe	0·36 ± 0·01	0·36 ± 0·01	0·34 ± 0·04	
Mg	1·42 ± 0·03	1·41 ± 0·04	1·4 ± 0·1	[b]
Mn	0·10 ± 0·01	0·10 ± 0·01	0·09 ± 0·01	
Ti	0·14 ± 0·01	0·14 ± 0·01	0·18 ± 0·04	
Zn	0·02 ± 0·01	0·02 ± 0·01	[c]	
		B.C.S. 216/2		
Cu	4·56 ± 0·01	4·54 ± 0·10	4·3 ± 0·3	[a]
Fe	0·28 ± 0·01	0·28 ± 0·01	0·27 ± 0·03	
Mg	0·75 ± 0·01	0·75 ± 0·03	0·90 ± 0·04	[b]
Mn	0·71 ± 0·01	0·70 ± 0·01	0·71 ± 0·04	
Ti	0·037 ± 0·001	0·037 ± 0·003	0·04 ± 0·02	
Zn	0·20 ± 0·01	0·20 ± 0·02	[c]	
		B.C.S. 263/1		
Cu	0·09 ± 0·01	0·10 ± 0·01	0·10 ± 0·02	
Fe	0·35 ± 0·01	0·33 ± 0·02	0·34 ± 0·03	
Mg	4·92 ± 0·05	4·94 ± 0·11	4·6 ± 0·3	[b]
Mn	0·36 ± 0·01	0·36 ± 0·01	0·35 ± 0·05	
Ti	0·038 ± 0·001	0·037 ± 0·004	0·04 ± 0·02	
Zn	0·05 ± 0·01	0·05 ± 0·01	[c]	
		B.C.S. 300		
Cu	1·28 ± 0·02	1·27 ± 0·04	1·4 ± 0·1	[a]
Fe	0·30 ± 0·01	0·30 ± 0·01	0·29 ± 0·02	
Mg	2·76 ± 0·03	2·78 ± 0·09	2·9 ± 0·1	[b]
Mn	0·41 ± 0·01	0·41 ± 0·01	0·41 ± 0·02	
Ti	0·15 ± 0·01	0·16 ± 0·01	0·18 ± 0·06	
Zn	5·98 ± 0·04	5·94 ± 0·15	[d]	

All analyses were performed on a solution containing 1 g of alloy in 100 ml of solution, by plasma-emission spectrometry. These solutions were also used for flame-emission spectrometry except as indicated by:

[a] 0·1 g of alloy per 100 ml of solution.
[b] 0·01 g of alloy per 100 ml of solution.
[c] Not detected.
[d] Not determined.

centration ranges for each element over which linear calibration is obtained with the high-frequency plasma source. Thus whereas all the analytical results shown in Table 4 for plasma-emission spectrometry were obtained at a single dilution (1 g of alloy/100 ml), in the corresponding analysis by flame-emission spectrometry several dilutions were required for each sample in order to effect the determination of five elements.

CONCLUSIONS

Although the induction-coupled radiofrequency plasmas used for spectrochemical analysis by other workers[1–9] have employed widely differing conditions, they are to a certain extent similar in their general properties. The temperatures in or just above the plasma core reported for some of these plasmas[1,6,9] lie in the range 8000–9000 K and these temperatures are in general agreement with those calculated[18,26] or measured[12,18,19,27] by plasma physicists. Thus, when our simple ideal model is applied to these other plasmas,

Table 5. Comparison of the particle density and residence times in different plasma systems

Parameter	This work	Ref. 1	Ref. 2, 28, 29	Ref. 3, 4	Ref. 5, 6	Ref. 7	Ref. 8	Ref. 9
Plasma-gas flow, *l./min*	3	5	18	0·9	2·5	3·5	1·7	2
Sample-uptake rate, *ml/min*	1·5*	2·5*	2·5*	0·12†	0·6†	0·2†	0·8†	1·5†
Particle density,‡ $10^{15}/m^3$	1·6	1·6	0·44	12	62	15	12	190
Residence time in core,§ *msec*	5·7	4·8	1·9	10	1·7	6·8	31	4·8
Residence time in viewing zone,‖ *msec*	2·3	1·4	0·4	4·3	0·7	2·0	3·1	1·9

* Indirect nebulizer used, efficiency assumed = 0·01.

† Ultrasonic nebulizer used, efficiency assumed = 0·8.

‡ Calculated for a solution containing 1 ppm of zinc, assuming core diameter is *ca* 1 mm less than the internal diameter of inner (plasma) tube.

§ Calculated from heights of core given by different workers, usually 25–25 mm. Veillon and Margoshes[8] assume core extends to bottom of viewing zone, *i.e.*, 100 mm.

‖ Calculated assuming emission is viewed over a 10-mm section of the tail-flame.

we can assume to a first approximation that the same temperature distribution as that which we observed also occurs in these plasmas.

The residence time of analyte atoms in the plasma core and a 10-mm section of the tail-flame, and the particle density obtained by the introduction of an aqueous solution containing 1 ppm of zinc into the plasma systems described by Greenfield *et al.*,[1,2,28,29] Fassel *et al.*,[3–6] Hoare and Mostyn,[7] Veillon and Margoshes[8] and Boumans and de Boer,[9] calculated by using the simple model, are compared in Table 5 with those values obtained for the plasma source used in this work. In the plasma used by Wendt and Fassel,[3,4] the coolant flow was more than twenty times greater than the combined plasma and injector gas flows, so for this plasma our initial assumption is almost certainly invalidated and the values calculated for this plasma are likely to be higher than the actual values. In the plasma of Veillon and Margoshes,[8] the emission was viewed at a height of 100 mm above the top of the work coil and our simple ideal model is no longer strictly applicable at such a great distance from the core.

Table 5 shows that there is a large difference in the particle densities obtained in each plasma system, but there is a general similarity in the atom residence times. The average time that an analyte atom spends in the plasma core is calculated to be generally *ca* 4·5 msec. and *ca* 1·5 msec in a 10-mm viewing zone of the tail-flame. These residence times are very much greater than those attainable with flames, arcs or sparks and this represents a considerable advantage for plasma excitation cells, as explained earlier, when sensitivity and freedom from solute vaporization interferences are considered.

The detection limits quoted for plasma-emission spectrometry reported by various workers[1,3,6,7,9] are generally lower than those reported for flame-emission spectrometry[1,6] and these detection limits have been progressively improved with improvements in instrument design. The detection limit is principally a function of particle density, residence time, source stability and detection optics and elecronics. In general, we can say that the detection limit will be lower in plasmas which permit attainment of a high particle density or long residence time. Thus the detection limits quoted by Boumans and de Boer[9] reflect the higher particle density and long residence time of their plasma. It is difficult to determine the relative stability of different plasma systems, but it seems likely that where the sample is introduced *via* ultrasonic nebulization followed by desolvation of the sample, the plasma discharge will be more stable than when an indirect nebulizer is used. In the latter case, a comparatively large volume of water is introduced into the discharge with the sample and this may cause instability.

For many elements the plasma system is predicted to exhibit a much extended concentration range for linear calibration curves, compared to the flame. With the plasma used in this work the upper limit of the linear calibration range was generally observed at a concentration about one order of magnitude greater than that predicted from our considerations based on the simple ideal model used. In the model, it is implied that the analyte atoms are distributed homogeneously throughout the plasma core. This is not true for any real plasma system, as the plasma in continually expanding outwards presents an aerodynamic barrier to the entrance of analyte particles into the core. At the frequencies used to generate most plasmas (20–60 MHz) the plasma has a cooler axial channel (see Fig. 2) and the analyte atoms are forced to travel either through this central hole or around the edges of the plasma. In the plasma systems used by Greenfield *et al.*, [1,2,28,29] Fassel *et al.*[3–6] and Boumans and de Boer[9] the sample is forced into the central axis by the geometry of the torch tubes and a higher linear velocity of the injector gas so that a large proportion of the analyte is injected into the central channel of the discharge. In the plasma used in this work, however, no such effort was made to force the sample into the central axis, so it is likely that a much greater proportion of the sample passes around the edges of the discharge than in the plasmas used by other workers. This would have the effect of reducing the average path-length of the radiation before it leaves the cell and hence cause a reduction in the effects of self-absorption and give rise to a greater extension of the observed linear range at high solution concentration than predicted.

In order to perform multi-element analysis for solution samples at a single dilution it is important to ensure that the technique employed permits greatest linear working range for each element and that these ranges overlap so that samples containing the analyte elements at widely differing concentration ratios may be accepted. The suggestion is sometimes made that the use of a weaker emission (or absorption) line in atomic spectrometry permits the extension of the linear range to higher concentrations of the element concerned, so that overlap with the linear calibration ranges of other elements present in the sample solution is achieved to facilitate analysis of samples of considerably different composition without the need to resort to the use of different dilutions. Thus when analysing the aluminium alloys for magnesium by flame-emission spectrometry we could have avoided the dilution step by choosing a non-resonance line (*e.g.*, 383·83 nm) or an ion line (*e.g.*, 279·55 nm) which may give a linear calibration curve over the concentration range of magnesium in the sample solutions (*i.e.*, 75–500 ppm). With copper in these samples, however, where the concentration range of analyte in solution is 5–500 ppm, this approach would not be applicable at a single dilution. Use of a weaker emission line (*e.g.*, 330·80 or 319·41 nm) would permit the determination of copper at high concentrations in the sample solution without dilution, but it is unlikely that there would be sufficient sensitivity to permit analysis of the low copper-content solutions. To avoid dilution of the sample solution, therefore, it would be necessary in this case to use at least two emission lines for the determination of copper.

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Zusammenfassung—Die Leistungsfähigkeit der Spurenanalyse in Lösung durch Atomemissionsspektrometrie mit einer 36 MHz-induktionsgekoppelten Radiofrequenz-Plasmaatomzelle wird anhand eines einfachen Modells vorhergesagt und mit den entsprechenden Eigenschaften einer mit Inertgas abgeschirmten Distickstoffoxid-Acetylen-Flamme verglichen. Es wird für die Plasmaquelle ein längerer linearer Eichbereich vorausgesagt, da die Quelle unter optimalen Arbeitsbedingungen eher von Selbstabsorption frei ist. Die lange Verweilzeit der zu analysierenden Spezies befreit von Störungen durch Verflüchtigung gelöster Stoffe. Die Voraussagen werden im Versuch bestätigt; die Vorteile der Plasmaquelle werden bei der Analyse von Aluminimulegierungen auf Kupfer, Eisen, Magnesium, Mangan, Titan und Zink sichtbar gemacht.

Résumé—On prévoit les possibilités pour l'analyse de traces en solution par spectrométrie d'émission atomique d'une cellule à plasma d'atomes de radiofréquence 36 MHz couplée par induction à partir d'un modèle simple et les compare avec les caractéristiques correspondantes d'une flamme protoxyde d'azote—acétylène protégée par un gaz inerte. On prévoit un domaine d'étalonnage linéaire plus long pour la source de plasma à cause de la plus grande indépendance *vis-à-vis* de la self-absorption dans des conditions opératoires optimales, et le long temps de séjour de l'espèce à analyser confère l'indépendance *vis-à-vis* d'interférences dues à la vaporisation du soluté. Les prévisions sont vérifiées expérimentalement et l'on démontre les avantages de l'emploi de la source de plasma dans l'analyse d'alliages d'aluminium pour les cuivre, fer, magnésium, manganèse, titane et zinc.

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GRAPHIC DETERMINATION OF EQUIVALENCE VOLUMES IN POTENTIOMETRIC TITRATIONS OF MIXTURES OF WEAK ACIDS—I

TWO MONOBASIC ACIDS

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Summary—A titration method for analysis of binary mixtures of weak acids is given. The equivalence volumes of the individual acids can be determined graphically from only two titration points. However, use of more than two points gives a more accurate result. Mixtures of acetic acid with ascorbic acid, hydroxyacetic and monochloroacetic (Δ log $K^{\mathrm{H}}_{\mathrm{HA}}$ = 0·5–1·9) are titrated with an error of approximately 0·5–2·5% in all three cases.

A mixture of two acids can be analysed by titrating them potentiometrically with a strong base. Plotting the measured pH *vs.* the added volume of standard base, V, usually gives a curve with two potential jumps. The equivalence points of the stronger and the weaker acid respectively lie at the inflexion points of the first and second potential jumps. Such an analysis will succeed only if the potential jumps obtained are separate and large enough. The stability constants of the acids, $K^{\mathrm{H}}_{\mathrm{HA}}$, should be less than 10^7 and $\Delta \log K^{\mathrm{H}}_{\mathrm{HA}}$ larger than 4. This method of analysis presupposes that the equivalence point of the stronger acid is the starting point for titration of the weaker acid. If the difference in the stability constants of the acids is not large enough some of the weaker acid will have been titrated during the final stage of titration of the stronger acid. This results in a decrease in the height and a small displacement of the position of the first potential jump, which no longer represents the equivalence volume of the stronger acid alone. In a case like this only the sum of the acids can be determined from the second potential jump. If the stability constants of the acids lie close to each other only one jump in the titration curve can be obtained. This is also the case when two strong acids are titrated.

If $\Delta \log K^{\mathrm{H}}_{\mathrm{HA}}$ is larger than 4, the whole titration can be considered to consist of two separate titrations. Both equivalence points can be located by using the same wide selection of methods as when titrating just one acid. If the two acids cannot be titrated separately, special methods should be used, *e.g.*, Gran plots[1] as developed by Ingman and Still[2] and Johansson.[3] Ingman and Still have formulated a mathematical equation describing the titration of a weak acid with a strong base. By introduction of the α-coefficient concept,[4] the competing side-reaction, *i.e.*, titration of the weaker acid, can be taken into account. A straight line can be obtained when plotting the equation as a function of the volume of added standard base V. The intersection of this line and the V-axis gives the equivalence volume of the stronger acid. As an example Ingman and Still give the titration of monochloroacetic acid in the presence of acetic acid, $\Delta \log K^{\mathrm{H}}_{\mathrm{HA}} \sim 1·9$. Johansson[3] gives a method of analysing a mixture of hydrochloric and acetic acids by means of two equations describing the titration in the acid and alkaline regions. When these equations are plotted as functions of V, two straight lines are obtained. The intersections of the lines with the V-axis in the acid and alkaline regions gives the equivalence volume of the hydrochloric acid and the sum of the acids respectively. These preliminary values can then be corrected by taking account of the dissociation of acetic acid.

In this paper a potentiometric titration method of analysing a mixture of two weak acids will be given. The equivalence volumes of the acids can be determined graphically by using only two titration points.

TITRATION OF TWO MONOBASIC WEAK ACIDS WITH A STRONG BASE

The acids to be titrated are denoted by HA_I and HA_{II}. HA_I is the stronger. The titration is performed with a strong base, *e.g.*, potassium hydroxide, with a concentration of C_{OH}. The initial concentrations of the acids are C_{HA_I} and $C_{HA_{II}}$ and the initial volume is V_O. The volume of added standard base is denoted by V, and V_{eq_I} and $V_{eq_{II}}$ are the equivalence volumes of the acids. In formulating the equation three assumptions are made.

(*a*) The law of mass action:

$$HA_I \rightleftharpoons H + A_I \qquad K^H_{HA_I} = \frac{[HA_I]}{\{H\}[A_I]} \tag{1}$$

$$HA_{II} \rightleftharpoons H + A_{II} \qquad K^H_{HA_{II}} = \frac{[HA_{II}]}{\{H\}[A_{II}]} \tag{2}$$

For convenience, charges are omitted. The constants $K^H_{HA_I}$ and $K^H_{HA_{II}}$ are mixed stability constants, hydrogen-ion activities being used instead of concentrations. The relationship between activity and concentration is expressed by

$$\{G\} = f_G[G] \tag{3}$$

where f_G is the activity coefficient of the ion G.

(*b*) The following equations, defining the equivalence volume, are valid.

$$V_O C_{HA_I} = V_{eq_I} C_{OH} \tag{4}$$

$$V_O C_{HA_{II}} = V_{eq_{II}} C_{OH} \tag{5}$$

(c) The solution must be electrically neutral.

$$[H] + [K] = [OH] + [A_I] + [A_{II}] \tag{6}$$

The concentration of potassium ion can be expressed by

$$[K] = \frac{VC_{OH}}{V_O + V} \tag{7}$$

Equation (6) should also include concentrations of ions originating from the neutral salt added to adjust the ionic strength. The salt used for this purpose, potassium chloride, is completely dissociated, so the concentrations of the anion and cation are the same and cancel each other out in equation (6).

The total concentration of the acids HA_I and HA_{II} (irrespective of form) during the titration can be expressed as follows.

$$\frac{C_{HA_I}V_O}{V_O + V} = [HA_I] + [A_I] \tag{8}$$

$$\frac{C_{\mathrm{HA_{II}}}V_{\mathrm{O}}}{V_{\mathrm{O}} + V} = [\mathrm{HA_{II}}] + [\mathrm{A_{II}}] \tag{9}$$

Combining equations (8) and (9) with (1), (2), (4) and (5) gives $[\mathrm{A_I}]$ and $[\mathrm{A_{II}}]$:

$$[\mathrm{A_I}] = \frac{V_{\mathrm{eqI}}C_{\mathrm{OH}}}{(V_{\mathrm{O}} + V)(1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}})} \tag{10}$$

$$[\mathrm{A_{II}}] = \frac{V_{\mathrm{eqII}}C_{\mathrm{OH}}}{(V_{\mathrm{O}} + V)(1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_{II}}})} \tag{11}$$

Introduction of equations (7), (10) and (11) into (6) and rearranging, gives the equation:

$$\frac{V_{\mathrm{eqI}}}{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}}} + \frac{V_{\mathrm{eqII}}}{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_{II}}}} = \frac{V_{\mathrm{O}} + V}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}]) + V \tag{12}$$

If the second term on the left-hand side of (12) is neglected and this equation solved for $(V_{\mathrm{eqI}} - V)$, the equation given by Ingman and Still[2] for titration of one monobasic acid with a strong base, is obtained. If a mixture of three monobasic acids is titrated with a strong base, a term $V_{\mathrm{eqIII}}/(1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_{III}}})$, symbols V_{eqIII} and $K^{\mathrm{H}}_{\mathrm{HA_{III}}}$ being analogous to the ones already used, should be added on the left-hand side of equation (12). A similar equation for the titration of more than three monobasic acids can be formulated.

Equation (12) can be solved for V_{eqI}:

$$V_{\mathrm{eqI}} = (1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}})\left[\frac{(V_{\mathrm{O}} + V)}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}]) + V\right] - \frac{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}}}{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_{II}}}} \cdot V_{\mathrm{eqII}} \tag{13}$$

Every titration point in a potentiometric acid-base titration gives a value of V and pH. Since V_{O}, C_{OH}, $K^{\mathrm{H}}_{\mathrm{HA_I}}$ and $K^{\mathrm{H}}_{\mathrm{HA_{II}}}$ are known and constant, equation (13) can be rewritten as

$$V_{\mathrm{eqI}} = P_1 - Q_1V_{\mathrm{eqII}} \tag{14}$$

where

$$P_1 = (1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}})\left[\frac{(V_{\mathrm{O}} + V)}{C_{\mathrm{OH}}}([\mathrm{H}] - [\mathrm{OH}]) + V\right] \tag{15}$$

$$Q_1 = \frac{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_I}}}{1 + \{\mathrm{H}\}K^{\mathrm{H}}_{\mathrm{HA_{II}}}} \tag{16}$$

The values of P_1 and Q_1 can be calculated for every titration point. Equation (14) describes a straight line in the V_{eqI}, V_{eqII} plane. With two titration points, and hence two values of V and pH and two values of P_1 and Q_1, two different lines can be plotted in co-ordinates V_{eqI} and V_{eqII}. The point of intersection of these lines gives the desired values of V_{eqI} and V_{eqII}. If several titration points were used, all the lines plotted should, theoretically, intersect each other at the same point. An incorrect value of either or both of the constants, $K^{\mathrm{H}}_{\mathrm{HA_I}}$ and $K^{\mathrm{H}}_{\mathrm{HA_{II}}}$, will result in a certain dispersion of the point of intersection if several lines are plotted.

This titration method can be used when a mixture of acetic acid with monochloroacetic acid, hydroxyacetic acid or ascorbic acid (as the monobasic acid) is titrated with potassium hydroxide. The stability constants of these acids are determined by titrating them with 0·1004*M* potassium hydroxide at 25°, $\mu = 0{\cdot}1$ (KCl) and processing the data with a desk

Table 1. Titration of monochloroacetic, hydroxyacetic, ascorbic and acetic acid with 0·1004M KOH, $T = 25°$, $\mu = 0{\cdot}1$ (KCl), $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$

	Monochloroacetic acid		Hydroxyacetic acid		Ascorbic acid		Acetic acid	
Theoretical	V_{eq} = 6·29 ml		4·23 ml		5·24 ml		5·84 ml	
	V_0 = 51·38 ml		50·43 ml		52·06 ml		50·25 ml	
	V, *ml*	pH	*V*, *ml*	pH	*V*, *ml*	pH	*V*, *ml*	pH
	1·00	2·60	1·00	3·35	1·00	3·53	1·00	4·00
	1·50	2·67	1·50	3·54	1·50	3·73	1·50	4·20
	2·00	2·75	2·00	3·72	2·00	3·91	2·00	4·37
	2·50	2·83	2·50	3·91	2·50	4·08	2·50	4·53
	3·00	2·92	3·00	4·13	3·00	4·24	3·00	4·67
	3·50	3·03	3·50	4·42	3·50	4·42	3·50	4·82
	4·00	3·14	4·00	4·96	4·00	4·63	4·00	4·98
	4·50	3·28	4·10	5·20	4·50	4·91	4·50	5·17
	5·00	3·46	4·20	5·70	5·00	5·43	5·00	5·41
	5·50	3·71			5·20	6·09	5·20	5·54
	5·75	3·91					5·40	5·71
	6·00	4·25					5·60	5·96
	6·10	4·49						
	6·20	5·02						
Found	V_{eq} = 6·23 ml		4·24 ml		5·24 ml		5·87 ml	
	$\log K^{H}_{HA}$ = 2·726		3·719		4·100		4·649	

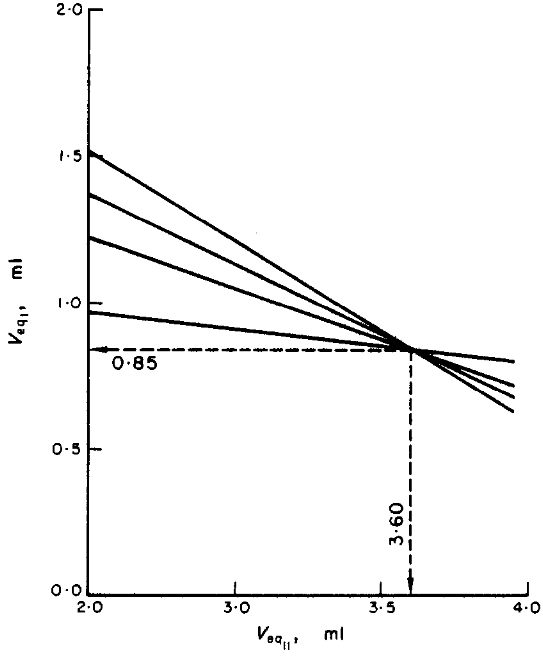

Fig. 1. Titration of a mixture of monochloroacetic acid and acetic acid [(*a*) in Table 2] with 0·1004 M KOH, $V_0 = 50{\cdot}52$ ml, $T = 25°$, $\mu = 0{\cdot}1$ (KCl), $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$. Theoretical values $V_{eq_I} = 0{\cdot}86$ ml and $V_{eq_{II}} = 3{\cdot}64$ ml.

calculator program described in the literature.[5] Titration data and results are given in Table 1.

Data obtained when titrating mixtures of different acids with different concentration ratios are given in Table 2. The method proposed is used to arrive at a graphical evaluation

Table 2. Titration of mixtures of acetic acid with monochloroacetic, hydroxyacetic and ascorbic acid. C_{OH} = 0·1004*M* KOH, T = 25°, μ = 0·1 (KCl), log f_H = −0·10 and log f_{OH} = −0·10

	Monochloroacetic acid (I) *and acetic acid* (II). $\Delta \log K^{H}_{HA}$ = 1·923					
	(*a*)		(*b*)		(*c*)	
Theoretical	V_0 = 50·32 ml		50·67 ml		50·99 ml	
	V_{eq_I} = 0·86 ml		2·54 ml		4·13 ml	
	$V_{eq_{II}}$ = 3·64 ml		3·84 ml		2·85 ml	
	V, *ml*	pH	V, *ml*	pH	V, *ml*	pH
	1·00	3·70	3·00	3·99	4·00	3·79
	2·00	4·35	4·00	4·48	5·00	4·39
	2·50	4·59	4·50	4·69	5·50	4·67
	3·00	4·83	5·10	4·97	6·00	4·96
		Error %		Error %		Error %
Found	V_{eq_I} = 0·85 ml	−1·2	2·50 ml	−1·6	4·09 ml	−1·0
	$V_{eq_{II}}$ = 3·60 ml	−1·1	3·87 ml	+0·8	2·89 ml	+1·4
	Hydroxyacetic acid (I) *and acetic acid* (II), $\Delta \log K^{H}_{HA}$ = 0·930					
	(*d*)		(*e*)		(*f*)	
Theoretical	V_0 = 50·65 ml		50·82 ml		50·79 ml	
	V_{eq_I} = 2·74 ml		4·03 ml		5·32 ml	
	$V_{eq_{II}}$ = 3·85 ml		4·79 ml		2·49 ml	
	V, *ml*	pH	V, *ml*	pH	V, *ml*	pH
	2·00	3·85	4·00	4·14	4·00	4·03
	3·00	4·20	5·00	4·40	5·00	4·31
	4·00	4·54	6·00	4·66	6·00	4·65
	5·00	4·91	7·00	4·96	7·00	5·13
		Error %		Error %		Error %
Found	V_{eq_I} = 2·75 ml	+0·4	3·96 ml	−1·7	5·33 ml	+0·2
	$V_{eq_{II}}$ = 3·74 ml	−2·9	4·86 ml	+1·5	2·48 ml	−0·4
	Ascorbic acid (I) *and acetic acid* (II), $\Delta \log K^{H}_{HA}$ = 0·549					
	(*g*)		(*h*)		(*i*)	
Theoretical	V_0 = 50·71 ml		51·00 ml		51·52 ml	
	V_{eq_I} = 1·31 ml		2·03 ml		3·53 ml	
	$V_{eq_{II}}$ = 4·39 ml		3·52 ml		2·88 ml	
	V, *ml*	pH	V, *ml*	pH	V, *ml*	pH
	2·00	4·26	1·00	3·80	2·00	4·00
	3·00	4·59	2·00	4·20	3·00	4·30
	3·50	4·75	3·00	4·54	4·00	4·60
	4·00	4·93	4·00	4·90	5·00	4·96
		Error %		Error %		Error %
Found	V_{eq_I} = 1·28 ml	−2·3	1·98 ml	−2·5	3·50 ml	−0·8
	$V_{eq_{II}}$ = 4·41 ml	+0·5	3·60 ml	+2·3	2·87 ml	−0·3

of the given data and the results obtained are also included in Table 2. Evaluation of data from titration (*a*) in Table 2 is shown in Fig. 1.

As can be seen in Fig. 1 the lines used to determine the equivalence volumes do not intersect at exactly the same point. The slight dispersion of the point of intersection is probably due to experimental errors in measuring V and pH, or to the values of stability constants given in Table 1 and used to calculate P_1 and Q_1 may be incorrect. It should be emphasized that a variation of even $\pm 0{\cdot}01$ log units in the value of the stability constants of the acids would give a dispersion of the point of intersection and a certain displacement of its position. The slope of the lines becomes more negative with increasing pH and approaches -1, as can be realized when studying the expression for the slope, *i.e.*, Q_1 [see equation (16)]. When acids with $\Delta \log K^{H}_{HA}$ greater than 1 are titrated, lines obtained from equation (14) can easily be plotted separately even if the difference in pH for the titration points used is as little as 0·2. If $\Delta \log K^{H}_{HA}$ is less than 0·5, lines based on titration points with ΔpH even larger than 0·2 would still lie quite near each other and it would be difficult to locate the point of intersection; small experimental errors or variations in the stability constants of the acids would then make the method less favourable.

From Table 2 it can be seen that the individual acids in the mixtures have been titrated with an error varying approximately between 0·5 and 2·5%. The difference between the accuracy obtained when acids with different $\Delta \log K^{H}_{HA}$ values or concentration ratios are titrated is not significant. Even ascorbic acid and acetic acid, $\Delta \log K^{H}_{HA} \sim 0{\cdot}5$, are titrated with a reasonable accuracy.

It should be emphasized that the calibration of the pH-meter is of importance and should be done every time in the same way as when determining the stability constants of the individual acids.

EXPERIMENTAL

Apparatus

A digital pH-meter (Orion Research 701, accurate to ±0·01 pH units) was used with a Beckman glass electrode (pH 0–14, factory-guaranteed) and a saturated calomel electrode. The pH-meter was standardized against 0·05*M* potassium phthalate (pH = 4·01 at 25°) and 0·01*M* borax (pH = 9·18 at 25°) was used as a secondary buffer. The activity coefficients f_H and f_{OH} were calculated from measured pH values in hydrochloric acid and potassium hydroxide solutions of known concentrations [ionic strength 0·1 (KCl) and temperature 25°] according to the equations $f_H = 10^{-pH}/[H]$ and $f_{OH} = 10^{(-14{\cdot}00+pH)}(1)/[OH]$. Values for $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$ were obtained.

Reagents

The potassium hydroxide solution was prepared from reagent grade "Titrisol" (Merck). All other chemicals were of Merck reagent grade. A Metrohm piston-burette (5 ml) was used and the initial volume was measured by means of a pipette. The titration beaker temperature was thermostatically controlled at 25·0 ± 0·1°. Weight-burettes were used to determine the initial concentrations of the acids from which the theoretical consumptions were calculated.

Procedure

The titrations were performed in the normal way and the titration solutions were continuously stirred with a magnetic stirrer.

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Zusammenfassung—Ein Titrationsverfahren zur Analyse binärer Gemische schwacher Säuren wird angegeben. Die Äquivalentvolumina der einzelnen Säuren können graphisch aus nur zwei Titrationspunkten bestimmt werden. Die Verwendung von mehr als zwei Punkten gibt jedoch ein genaueres Ergebnis. Gemische von Essigsäure mit Monochloressigsäure. Hydroxyessigsäure und Ascorbinsäure ($\Delta \log K^{H}_{HA}$ = 0,5–1,9) lassen sich mit einem Fehler von etwa 0,5–2,5% titrieren.

Résumé—On donne une méthode de titrage pour l'analyse de mélanges binaires d'acides faibles. Les volumes d'équivalence des acides définis peuvent être déterminés graphiquement à partir de seulement deux points de titrage. Toutefois, l'utilisation de plus de deux points donne un résultat plus précis. Des mélanges d'acide acétique avec les acides monochloracétique, hydroxyacétique et ascorbique ($\Delta \log K^{H}_{HA}$ = 0,5–1,9) sont titrés avec une erreur d'approximativement 0,5–2,5%.

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GRAPHIC DETERMINATION OF EQUIVALENCE VOLUMES IN POTENTIOMETRIC TITRATIONS OF MIXTURES OF WEAK ACIDS—II*

TITRATION OF A DIBASIC ACID AND DETERMINATION OF ITS TWO ACID SPECIES H_2A AND HA^-

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Summary—The method given in Part I is used to determine the mixed stability constants of a dibasic acid. Values of $\log K^{H}_{HA_2} = 2{\cdot}878$ and $\log K^{H}_{HA} = 4{\cdot}011$ for tartaric acid and 4·077 and 5·335 for succinic acid at $\mu = 0{\cdot}1$ and $T = 25°$ have been obtained. The method is also applied to titrations of these acids, the error obtained being about 0·5%, and to titrate a mixture of tartaric acid and potassium hydrogen tartrate with an error of 0·7–1·6%

An equation can be formulated to describe the titration of a dibasic acid with a strong base, *e.g.*, potassium hydroxide. The initial concentration of the acid is C_{H_2A} and the other symbols are the same as for equation (13) in Part I.[1] Three basic sets of equations are required.

(*a*) The law of mass action:

$$H_2A \rightleftharpoons H + HA \qquad K^{H}_{H_2A} = \frac{[H_2A]}{\{H\}[HA]} \tag{1}$$

$$HA \rightleftharpoons H + A \qquad K^{H}_{HA} = \frac{[HA]}{\{H\}[A]} \tag{2}$$

(*b*) Definition of V_{eq} (first dissociation stage):

$$V_O C_{H_2A} = V_{eq} C_{OH} \tag{3}$$

(*c*) The rule of electroneutrality:

$$[K] + [H] = [OH] + [HA] + 2[A] \tag{4}$$

The total concentration of the acid can be expressed by

$$\frac{C_{H_2A} V_O}{V_O + V} = [H_2A] + [HA] + [A] \tag{5}$$

By combination of equations (1), (2), (3) and (5), the following expressions for [HA] and [A] are obtained:

$$[HA] = \frac{V_{eq} C_{OH} \{H\} K^{H}_{HA}}{(V_O + V)(1 + \{H\}K^{H}_{HA} + \{H\}^2 K^{H}_{HA} K^{H}_{H_2A})} \tag{6}$$

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* Part I. *Talanta* 1974. **21**, 1167.

$$[A] = \frac{V_{eq}C_{OH}}{(V_O + V)(1 + \{H\}K^H_{HA} + \{H\}^2K^H_{HA}K^H_{H_2A})} \tag{7}$$

Equations (6) and (7) and the expression for $[K]$, equation (7) from Part I,[1] are inserted into equation (4), which after rearranging gives the equation

$$V_{eq} = \frac{(1 + \{H\}K^H_{HA} + \{H\}^2K^H_{HA}K^H_{H_2A})}{\{H\}K^H_{HA}}\left[\frac{(V_O + V)}{C_{OH}}([H] - [OH]) + V\right] - \frac{2V_{eq}}{\{H\}K^H_{HA}} \tag{8}$$

DETERMINATION OF THE STABILITY CONSTANTS OF A DIBASIC ACID

Equation (8) can be used to determine the stability constants of a weak dibasic acid by solving it for K^H_{HA}:

$$K^H_{HA} = \frac{2V_{eq} - \dfrac{V_O + V}{C_{OH}}([H] - [OH]) - V}{\{H\}\left[(1 + \{H\}K^H_{H_2A})\left[\dfrac{(V_O + V)}{C_{OH}}([H] - [OH]) + V\right] - V_{eq}\right]} \tag{9}$$

Equation (9) can be solved graphically in order to obtain K^H_{HA} and $K^H_{H_2A}$. Parameters V_{eq}, V_O and C_{OH} are constant for a particular titration and every titration point gives values of V and pH. By assuming different values for log $K^H_{H_2A}$ and calculating the corresponding log K^H_{HA}, a line valid for one titration point can be plotted in co-ordinates log $K^H_{H_2A}$ and log K^H_{HA}. Different titration points give different lines and their point of intersection gives the desired values of log $K^H_{H_2A}$ and log K^H_{HA}. Data obtained from titration of tartaric acid and succinic acid with potassium hydroxide are given in Table 1. In this work the pH values were measured with a Orion 801 digital pH-meter to ±0·001.

The graphic determination of stability constants of tartaric and succinic acid by the method is shown in Fig. 1. The data evaluated are those given in Table 1.

The value of stability constants obtained from Fig. 1, log $K^H_{H_2A} = 2{\cdot}878$ and log $K^H_{HA} = 4{\cdot}011$ for tartaric acid and 4·077 and 5·335 for succinic acid at $\mu = 0{\cdot}1$ and temperature 25°, agree satisfactorily with the values given in the literature,[2] 2·88 and 3·94, and 4·07 and 5·28 respectively at $\mu = 0{\cdot}2$ and 25°C.

When the values of the mixed stability constants obtained from Fig. 1 for succinic acid are calculated to be converted into thermodynamic constants at this temperature by the

Table 1. Titration of tartaric and succinic acids with 0·1008M KOH at $\mu = 0{\cdot}1$ (KCl), $T = 25°$, where $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$[1]

Tartaric acid $V_O = 50{\cdot}82$ ml $V_{eq} = 4{\cdot}986$ ml		Succinic acid $V_O = 51{\cdot}21$ ml $V_{eq} = 4{\cdot}331$ ml	
V, ml	pH	*V, ml*	pH
3·00	3·083	3·00	4·299
4·00	3·287	4·00	4·609
5·00	3·503	4·50	4·764
6·00	3·730	5·00	4·919
7·00	3·974	5·50	5·075
7·50	4·108	6·00	5·234

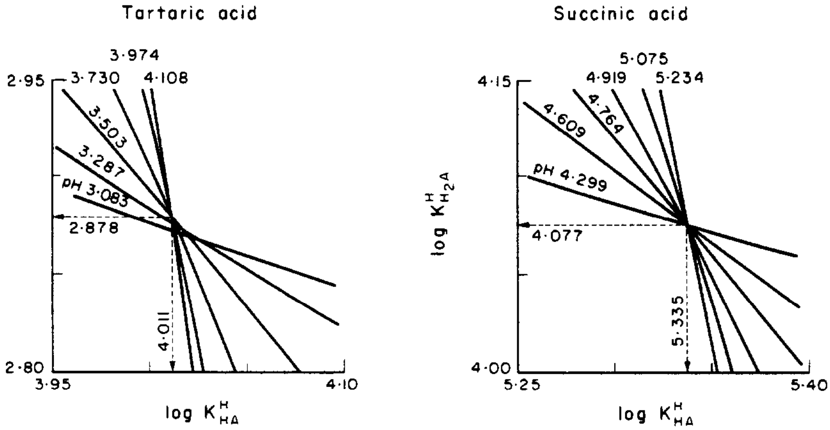

Fig. 1. Determination of stability constants of tartaric and succinic acid. Graphical evaluation of titration data from Table 1. $\mu = 0{\cdot}1$ (KCl), $T = 25^{\circ}$, $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$.

method given by Albert and Serjeant[3] the following values are obtained: $\log {}^{T}K^{H}_{H_2A} = 4{\cdot}188$ and $\log {}^{T}K^{H}_{HA} = 5{\cdot}667$. These thermodynamic constants agree well with the values 4·200 and 5·634 obtained by Albert and Serjeant.

In the titrations considered in Table 1 the solution has its maximum buffer capacity when the buffer regions corresponding to the two dissociation stages of the acid overlap each other. The pH of these solutions at their maximum buffer capacity is approximately $\frac{1}{2}(\log K^{H}_{H_2A} + \log K^{H}_{HA})$. As can be seen in Fig. 1 the lines representing titration points with pH within about $\pm 0{\cdot}3$ units of this value intersect each other at almost the same point. Only when lines with pH values outside this region are considered is a certain dispersion of the point of intersection apparent. When determining the stability constants of the acids by this method too much weight should not be attached to the lines representing points taken from a pH region of low buffer capacity.

TITRATION OF A DIBASIC ACID

Graphical interpretation similar to equation (13) in Part I[1] can also be made for equation (8). Each titration point gives the following equation:

$$V_{eq} = P_2 - Q_2 V_{eq} \tag{10}$$

where

$$P_2 = \frac{(1 + \{H\}K^{H}_{HA} + \{H\}^2 K^{H}_{HA} K^{H}_{H_2A})}{\{H\}K^{H}_{HA}} \left[\frac{(V_0 + V)}{C_{OH}} ([H] - [OH]) + V \right] \tag{11}$$

and

$$Q_2 = \frac{2}{\{H\}K^{H}_{HA}} \tag{12}$$

When lines from equation (10) are plotted in co-ordinates V_{eq} and V_{eq} they should theoretically intersect each other at the same point, lying on the line passing through the origin and having a slope of 1. The equivalence volume could be determined by using only one titration point, but because of experimental errors more than one point should be used. The usefulness of the method is shown in Fig. 2 where data from the titration of tartaric and

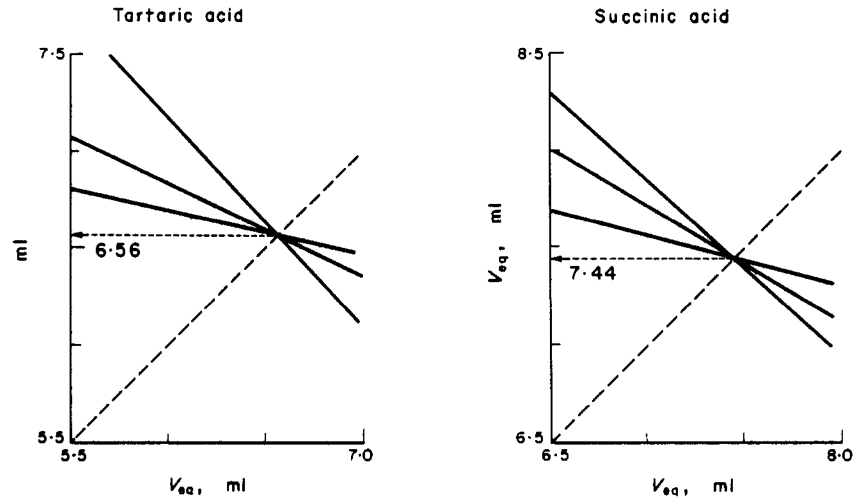

Fig. 2. Titration of tartaric and succinic acids. Graphical evaluation of titration data from Table 2.

succinic acids given in Table 2 are graphically evaluated. In calculation of the constants P_2 and Q_2 according to equations (11) and (12) the stability constant values obtained from Fig. 1 are used. The line passing through the origin and having a slope of 1 is drawn as a dotted line in Fig. 2. The results obtained and the titration errors are given in Table 2.

As can be seen in Fig. 2, lines plotted according to equation (10) intersect each other with moderate accuracy on the dotted line, and the equivalence volumes are determined with an error of 0·0–0·5%.

The fact that the lines should intersect each other on the dotted line increases the accuracy of the method appreciably compared with the determination of equivalence volumes of two weak acids where the dispersion of the point of intersection makes its location sometimes quite difficult.

Table 2. Titration of tartaric and succinic acids with 0·1008*M* KOH, log $K^{H}_{H_2A}$ = 2·878 and log K^{H}_{HA} = 4·011 for tartaric acid and 4·077 and 5·335 for succinic acid. $\mu = 0{\cdot}1$ (KCl), $T = 25°$, log $f_H = -0{\cdot}10$ and log $f_{OH} = -0{\cdot}10$

Tartaric acid				*Succinic acid*			
V_0 = 51·00 ml				52·06 ml			
Theoretical V_{eq} = 6·56 ml				7·40 ml			
V, ml	pH	P_2, *ml*	Q_2	*V, ml*	pH	P_2, *ml*	Q_2
4·00	3·069	8·057	0·229	6·00	4·448	9·372	0·259
6·00	3·394	9·719	0·483	8·00	4·809	11·883	0·596
8·00	3·741	13·615	1·074	9·00	4·991	14·185	0·906
			Error %				Error %
Found V_{eq} = 6·56 ml			0·0	V_{eq} = 7·44 ml			−0·5

DETERMINATION OF THE TWO ACID SPECIES H_2A AND HA^- OF A DIBASIC ACID

The titration of a mixture of H_2A and HA^- with a strong base, *e.g.*, potassium hydroxide, can be regarded as a special case of the titration of a dibasic acid. An equation similar to (8) can be formulated. The initial concentrations of the acid species are denoted by C_{H_2A} and C_{HA}. The basic equations are as follows.

(*a*) The law of mass action: equations (1) and (2) are valid.

(*b*) Definition of equivalence volumes:

$$V_O C_{H_2A} = V_{eq_I} C_{OH} \tag{13}$$

$$V_O C_{HA} = V_{eq_{II}} C_{OH} \tag{14}$$

(*c*) The rule of electroneutrality:

$$[M] + [K] + [H] = [OH] + [HA] + 2[A] \tag{15}$$

where M denotes the cation corresponding to the species HA^-. The concentration of the ion M can be expressed as

$$[M] = \frac{V_O C_{HA}}{V_O + V} \tag{16}$$

The following equation is valid during the titration:

$$\frac{V_O}{V_O + V}(C_{H_2A} + C_{HA}) = [H_2A] + [HA] + [A] \tag{17}$$

Combining equations (1), (2), (13), (14) and (17) gives:

$$[HA] = \frac{C_{OH}\{H\}K^H_{HA}}{(V_O + V)(1 + \{H\}K^H_{HA} + \{H\}^2 K^H_{HA} K^H_{H_2A})}(V_{eq_I} + V_{eq_{II}}) \tag{18}$$

$$[A] = \frac{C_{OH}}{(V_O + V)(1 + \{H\}K^H_{HA} + \{H\}^2 K^H_{HA} K^H_{H_2A})}(V_{eq_I} + V_{eq_{II}}) \tag{19}$$

After insertion of equation (7) from Part I[1] and equations (18), (19) and the combination of (16) and (14) in (15), and rearrangement, the following equation is obtained:

$$V_{eq_I} = \frac{(1 + \{H\}K^H_{HA} + \{H\}^2 K^H_{HA} K^H_{H_2A})}{2 + \{H\}K^H_{HA}}\left[\frac{(V_O + V)}{C_{OH}}([H] - [OH]) + V\right] - \frac{1 - \{H\}^2 K^H_{HA} K^H_{H_2A}}{2 + \{H\}K^H_{HA}} \cdot V_{eq_{II}} \tag{20}$$

Equation (20) can be interpreted graphically in the same way as equation (13) in Part I[1] and equation (8). Values of $K^H_{H_2A}$, K^H_{HA}, V_O and C_{OH} are known and every titration point gives V and pH. Equation (20) can be shortened to

$$V_{eq_I} = P_3 - Q_3 V_{eq_{II}} \tag{21}$$

where

$$P_3 = \frac{(1 + \{H\}K^H_{HA} + \{H\}^2 K^H_{HA} K^H_{H_2A})}{2 + \{H\}K^H_{HA}}\left[\frac{(V_O + V)}{C_{OH}}([H] - [OH]) + V\right] \tag{22}$$

Table 3. Titration of a mixture of tartaric acid and potassium hydrogen tartrate. $C_{OH} = 0{\cdot}1008M$ KOH, $V_O = 50{\cdot}82$ ml, $\log K^H_{H_2A} = 2{\cdot}878$, $\log K^H_{HA} = 4{\cdot}011$, $\mu = 0{\cdot}1$ (KCl), $T = 25°$, $\log f_H = -0{\cdot}10$ and $\log f_{OH} = -0{\cdot}10$. Theoretical $V_{eq_1} = 5{\cdot}37$ ml and $V_{eq_2} = 1{\cdot}29$ ml

V, ml	pH	P_3, *ml*	Q_3
3·00	3·095	4·918	−0·391
5·00	3·419	5·375	−0·021
7·00	3·763	5·670	+0·204
9·00	4·151	5·858	+0·353
			Error %
Found	$V_{eq_1} = 5{\cdot}41$ ml		+0·7
	$V_{eq_2} = 1{\cdot}27$ ml		−1·6

and

$$Q_3 = \frac{1 - \{H\}^2 K^H_{HA} K^H_{H_2A}}{2 + \{H\} K^H_{HA}} \tag{23}$$

In Table 3 are given data obtained when a mixture of tartaric acid and potassium hydrogen tartrate is titrated with potassium hydroxide. These data are graphically evaluated in Fig. 3 by using equation (21). The results obtained in Fig. 3 and the corresponding errors are given in Table 3. The values of the constants P_3 and Q_3 used when drawing the lines in Fig. 3 are also given in Table 3. When calculating these constants according to equations (22) and (23) the values for the acid stability constants obtained from Fig. 1 are used.

As can be seen from Fig. 3 the point of intersection of the lines has a certain dispersion, making its location a little difficult and several lines should be used in order to obtain the equivalence volumes with reasonable accuracy. The lines to be used should represent titra-

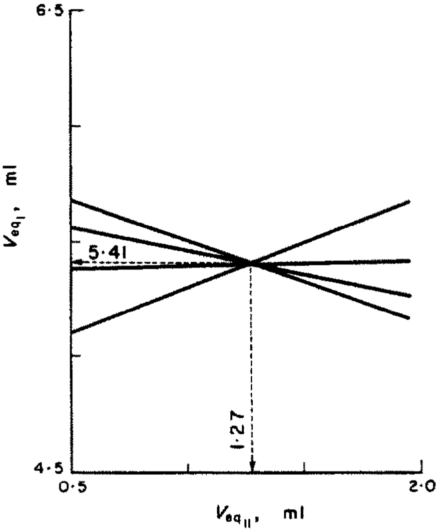

Fig. 3. Titration of a mixture of tartaric acid and potassium hydrogen tartrate. Graphical evaluation of titration data from Table 3.

tion points from the pH range recommended when determining the stability constants of the acid.

Considering the small value of $\Delta\log K \sim 1$ of tartaric acid, the titration error obtained, 0·7–1·6%, can be regarded as satisfactory. The method described can be used only if reliable values for the stability constants of the acid are available. This is a drawback but can be avoided by determining the constants in advance according to the method given earlier in this paper.

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Zusammenfassung—Das in Teil I angegebene Verfahren wird zur Bestimmung der gemischten Stabilitätskonstanten zweibasiger Säuren verwendet. Für Weinsäure wurde log $K^{H}_{H_2A}$ = 2,878 und log K^{H}_{HA} = 4,011 erhalten, für Bernsteinsäure 4,077 und 5,335, jeweils bei μ = 0,1 und T = 25°C. Das Verfahren wird auch zur Titration dieser Säuren verwendet, wobei der Fehler etwa 0,5% beträgt, sowie dazu, ein Gemisch von Weinsäure und Kaliumhydrogentartrat mit einem Fehler von 0,7–1,6% zu titrieren.

Résumé—La méthode donnée dans la première partie est utilisée pour déterminer les constantes de stabilité mixtes d'un acide dibasique. On a obtenu les valeurs de log $K^{H}_{H_2A}$ = 2,878 et log K^{H}_{HA} = 4,011 pour l'acide tartrique, et 4,077 et 5,335 pour l'acide succinique à μ = 0,1 et T = 25°C. La méthode est aussi appliquée aux titrages de ces acides, l'erreur obtenue étant d'environ 0,5%, et pour titrer un mélange d'acide tartrique et de tartrate acide de potassium avec une erreur de 0,7–1,6%.

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SELECTIVE SEPARATION OF INDIUM FROM ZINC, LEAD, GALLIUM AND MANY OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROHALIC ACID–ACETONE MEDIUM

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Summary—Indium can be separated from Zn, Pb(II), Ga, Ca, Be, Mg, Ti(IV), Mn(II), Fe(III), Al, U(VI), Na, Cu(II), Ni(II) and Co(II) by selective elution with 0·50*M* hydrochloric acid in 30% aqueous acetone from a column of AG50W-X8 cation-exchange resin, all the other elements being retained by the column. Lithium is included in the elements retained by the column when 0·35*M* hydrochloric acid in 45% aqueous acetone is used for eluting indium, but the elution of indium is slightly retarded. Ba, Sr, Zr, Hf, Th, Sc, Y, La and the lanthanides, Rb and Cs should also be retained according to their distribution coefficients. Cd, Bi(III), Au(III), Pt(IV), Pd(II), Rh(III), Mo(VI) and W(VI) can be eluted with 0·20*M* hydrobromic acid in 50% aqueous acetone before the elution of indium, and Ir(III), Ir(IV), As(III), As(V), Se(IV), Tl(III), Hg(II), Ge(IV), Sb(III) and Sb(V), though not investigated in detail, should accompany these elements. Relevant distribution coefficients and elution curves and results for analyses of synthetic mixtures of indium with other elements are presented.

Several methods have been described for the ion-exchange separation of indium from zinc, lead, gallium and other elements. A cation-exchange separation of indium from lead and cadmium has been developed from the fact that lead and cadmium complexes with EDTA are not stable at a pH of 0·8 and are adsorbed on a cation-exchange resin while the more stable indium complex passes through.[1] Kocheva *et al.*[2] have retained the indium–EDTA complex on Wofatit L150 anion-exchanger from EDTA in 0·1*M* hydrochloric acid, zinc and other elements being not adsorbed. Though the separation of indium from only a limited number of other elements has been investigated in EDTA solutions at low pH-values, many others can probably be separated, according to their known complex stabilities. Only elements such as Fe(III), Sc, Zr and Th, which also form very stable EDTA complexes, would tend to accompany indium. The major disadvantages of the methods above are that the presence of EDTA often complicates further work and that ion-exchange of EDTA complexes tends to give slow exchange rates and tailing, especially in the case of anion-exchange procedures.

Most other published methods describe the separation of indium from one or from a few other elements and they seem to be less selective than the method based on EDTA-complexes. Zagorchev *et al.*[3] have used 0·1*M* ammonium acetate at pH 3·65 to elute indium from Dowex 50W-X8 cation-exchange, zinc and cadmium being retained. The distribution coefficient of indium seems to be rather high under these conditions and elution is very prolonged. About 0·2*M* ammonium acetate improves the elution of indium without leading to premature appearance of zinc or cadmium according to our own work.[4]

Alimarin *et al.*[5] have adsorbed indium from ammonium carbonate solution at pH 10 on an anion-exchange resin, but zinc passes through. A cation-exchange method in which indium is eluted preferentially has also been described.[5] The methods are of limited applicability because many common elements are insoluble in the eluting agent.

An anion-exchange method using ammonia for the elution of Cd, Zn, Al and Ga, followed by the elution of indium with ammonium carbonate, lead with sodium hydroxide and iron with hydrochloric acid has been described by Eristavi *et al.*[6] Only about 1 mg of each element was used and the recoveries did not seem to be very accurate and tended to be low.

Bausova[7] has eluted indium from the Russian weakly basic EDE-10P anion-exchanger with 0·1*M* hydrobromic acid, lead and cadmium being retained. Distribution data by Andersen *et al.*[8] and quantitative work by Strelow *et al.*[9] suggest that a similar separation should be possible on Dowex 1-X8 or AG 1-X8.

Stancheva *et al.*[10] have adsorbed indium from 0·5*M* ammonium sulphate on weakly basic EDE-10P anion-exchanger, zinc passing through. From 0·3*M* ammonium sulphate that is 0·01*M* in sulphuric acid, zinc is retained by the strongly acidic KU-2 cation-exchanger, but indium is not. Mosheva *et al.*[11] have shown that indium can be eluted with ethylenediamine dihydrochloride from a Dowex 50 cation-exchanger, zinc being retained.

The systematic work of Kraus *et al.*[12] on distribution coefficients shows that indium is only relatively weakly retained by strongly basic anion-exchange resins such as Dowex 1–X10, Dowex 1-X8 and AG 1-X8, from hydrochloric acid solutions, even at the most favourable concentrations. Kraus *et al.*[13] have described a separation of indium from Al, Ga and Tl(III), eluting aluminium and indium successively with 7*M* hydrochloric acid from a Dowex 1 anion-exchanger. The separation between aluminium and indium is marginal and only small amounts of indium can be tolerated. Furthermore, the indium peak shows strong tailing. Some other elements accompany indium. Good separations are possible mainly from those elements which are more strongly adsorbed. Torko[14] has used 0·15*M* hydrochloric acid for the elution of indium from Dowex 1-X8 resin, while cadmium in retained, and Raby *et al.*[15] have eluted indium from the same resin with 0·5*M* hydrochloric acid containing 0·1% of hydroxylamine hydrochloride, while tin(II) is retained. A separation of indium from Fe(III), Al and Mn(II) on the strongly basic Wofatit L150 anion-exchanger has been described by Jentzsch *et al.*[16] The other elements are eluted with 4*M* hydrochloric acid, indium being retained. Tin accompanies indium when this element is eluted with 0·1*M* hydrochloric acid. Korkisch *et al.*[17] have separated indium from gallium and aluminium by anion-exchange in hydrochloric acid–organic solvent mixtures. The applicable distribution coefficients seem to be rather low, long columns (75 cm) have to be used, and recovery tests do not seem to give very accurate results.

The most useful among the procedures described for the separation of indium from other elements are probably those based on cation-exchange chromatography in aqueous hydrochloric acid. Klement *et al.*[18] suggested a concentration of 0·4*M* hydrochloric acid for the separation of indium from Pb, Cu, Zn, Fe and Ga. Unfortunately this was rather low and led to uncomfortably large elution volumes for indium (about 2000 ml). If 0·50*M* hydrochloric acid is used, the elution volumes are considerably reduced, while the other elements are still sufficiently retained. Cadmium, lithium and tin accompany indium, and the separation from sodium is not satisfactory.

In all the methods discussed above the separation of only a limited number of other elements from indium has been investigated in detail. A method capable of separating indium from most other elements of the periodic table in a relatively simple procedure does not seem to be available. Recent systematic surveys of distribution coefficients of elements in hydrochloric acid–acetone[19] and hydrobromic acid–acetone mixtures[20] used with AG50W-X8 cation-exchanger suggest that a very selective method for the separation of indium from other elements can be obtained by a combination of these two elution systems. It has been shown[21] that Cd, Bi(III), Au(III), Pt(IV), Pd(II), Rh(III), Mo(VI) and W(VI) can be separated from indium quantitatively by eluting these elements from a column of AG50W-X8 or AG50W-X4 cation-exchanger with 0·20*M* hydrobromic acid containing 50% of acetone. Indium and most other elements are retained by the column. The coefficients in hydrochloric acid–acetone[19] suggest that by use of 0·50*M* hydrochloric acid containing 30% of acetone, indium can be eluted and separated more effectively from Zn, Pb, Ga and the other cations still retained by the column than by use of aqueous hydrochloric acid alone. This separation therefore was investigated in detail by preparing relevant elution curves and analysing synthetic mixtures of known composition.

EXPERIMENTAL

Reagents and apparatus

Chemicals of analytical-reagent grade purity were used throughout. The resin was AG50W-X8 sulphonated polystyrene cation-exchanger (BIO.RAD Laboratories, Richmond, California). Resin of 200–400 mesh particle size was used for column work. Borosilicate glass tubes of 20 mm bore with fused-in glass sinters of No. 2 porosity, a burette tap at the bottom, and a B19 ground-glass joint at the top, were used as columns.

Atomic-absorption measurements were carried out with a Perkin-Elmer 303 atomic-absorption spectrometer and a Zeiss spectrophotometer was used for spectrophotometric measurements.

Distribution coefficients

An inspection of known distribution coefficients[19] reveals that the method of Klement *et al.*[18] can probably be extended to include the separation of many other elements from indium. The distribution coefficient for indium is 7·6 in 0·5*M* aqueous hydrochloric acid and 110 in 0·2*M* aqueous hydrochloric acid. By interpolation it should be about 15–20 in the 0·4*M* aqueous acid, the eluent concentration chosen by Klement for most of his separations of indium. This and the fact that he used resin of 20–50 mesh particle size, which in combination with the higher distribution coefficient will tend to give considerable peak broadening and tailing, probably explains the very large elution volume of 2000 ml he obtained for indium from a column containing 50 ml of Dowex 50 resin. Elution with 0·5*M* hydrochloric acid—used by Klement *et al.* only for the In–Cu pair—and use of a finer resin should give a considerably improved elution of indium without causing premature appearance of the other elements. The situation is even more favourable when hydrochloric acid–acetone mixtures are used for elution. The distribution coefficient for indium decreases from 7·6 to 3·6 when

Table 1. Relevant distribution coefficients in aqueous HCl and HCl–acetone mixtures

Element	0·5*M* HCl	0·5*M* HCl–30% acetone	0·35*M* HCl–45% acetone
Sn(IV)	6·3	2·7	3·8
In	7·6	3·6	7·6
Li	7·6	13·3	27·1
Na	13·9	26·4	56
Be	42·1	70	>200
Pb(II)	62	53	>60
Zn	64	55	48
Ga	245	1560	>2000
Cu(II)	64	90	>200
Co(II)	72	113	>200
Mn(II)	84	118	>200
Ni(II)	70	114	>200
U(VI)	58	92	>200
Mg	67	90	>200
Ca	131	220	>500
Fe(III)	205	228	>1000
Al	278	610	>1000
Ti(IV)	39·1	147	>200

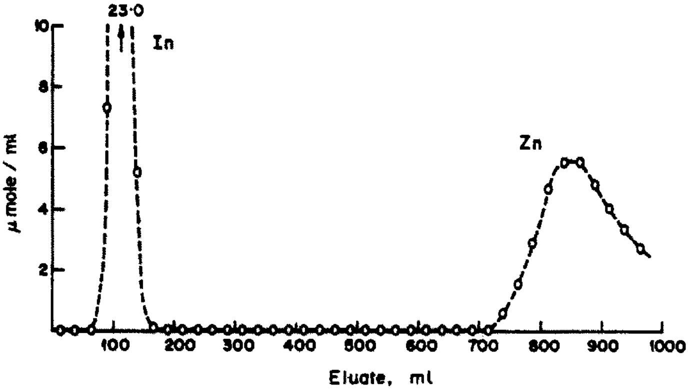

Fig. 1. Elution curve for In–Zn with 0·50*M* HCl–30% acetone. Column 60 ml (19 × 2·1 cm) of AG50W-X8 resin, 200–400 mesh. Flow-rate 2·5 ± 0·5 ml/min.

aqueous 0·5*M* hydrochloric acid is replaced by 0·5*M* hydrochloric acid containing 30% of acetone, while those of zinc and lead are only slightly decreased and those of all other elements increase substantially. Of those species which are retained on the column after elution of Cd, Bi(III) and others with 0·20*M* hydrobromic acid containing 50% of acetone,[21] tin(IV) appears to be the only one co-eluted with indium under all conditions. Some of the relevant distribution coefficients are presented in Table 1. The coefficients in 0·5*M* hydrochloric acid containing 30% of acetone and in 0·35*M* hydrochloric acid containing 45% of acetone were obtained by graphic interpolation from known values.[19] The coefficients for 0·5*M* aqueous hydrochloric acid are included for comparison.

Elution curves

From Table 1 it appears that a fast elution of indium combined with a good separation from all other species, except tin(IV) and lithium, can be obtained by eluting indium with 0·50*M* hydrochloric acid containing 30% of acetone. Elution curves for indium and the most critical and interesting other elements were therefore prepared.

A solution containing about 1 mmole of both indium and zinc in ~ 0·2*M* nitric acid containing 30% of acetone was passed through a column of 60 ml (20 g) of AG50W-X8 cation-exchange resin of 200–400 mesh particle size. The resin was in the hydrogen form and in water the resin column was about 19 cm in length and 2·1 cm in diameter. The column was equilibrated by passage of about 50 ml of 0·2*M* nitric acid containing 30% of acetone. The ions were washed onto the resin with 0·2*M* nitric acid containing 30% of acetone, and indium and zinc were eluted with 0·50*M* hydrochloric acid containing 30% of acetone. A flow-rate, of 2·5 ± 0·5 ml/min was maintained throughout, and 25-ml fractions were taken with an automatic fraction-collector. After removal of the excess of acid and acetone by evaporation, and the suitable dilution of the salts with 0·1*M* hydrochloric acid, the amounts of the elements in the fractions were determined by atomic-absorption spectrometry (Perkin-Elmer 303 instrument, acetylene–air flame, and the 304·6 and 213·8 nm lines for indium and zinc, respectively). The experimental elution curve is presented in Fig. 1.

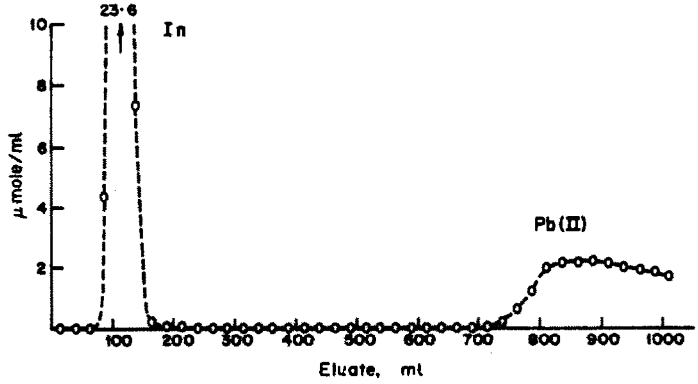

Fig. 2. Elution curve for In–Pb(II) with 0·50*M* HCl–30% acetone. Column, *etc*., as for Fig. 1.

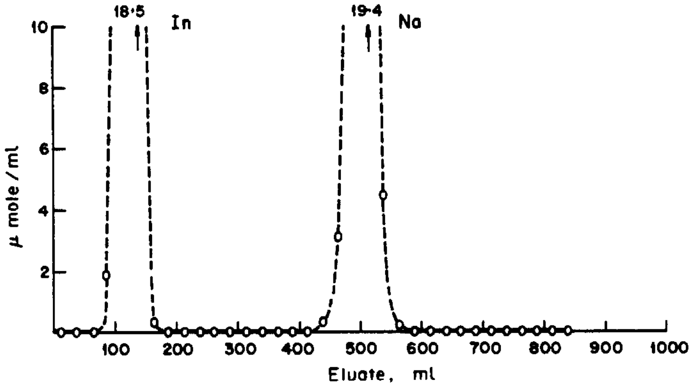

Fig. 3. Elution curve for In–Na with 0·50*M* HCl–30% acetone. Column, *etc.*, as for Fig. 1.

Figures 2 and 3 show similar elution curves for the In–Pb(II) and In–Na pairs. No Ga, Al, Fe(III), Cu(II), Co(II), Mn(II), Ni(II), U(VI), Mg or Ca could be detected in the first 1000 ml of eluate when elution experiments using the same conditions were carried out with 1-mmole amounts of these species present together with 1 mmole of indium. In the case of the In–Be pair the first traces of beryllium appeared when about 950 ml of eluate had been collected. Lithium appears later than indium, but there is some overlap of their elution peaks.

Figure 4 shows an elution curve for a mixture containing 1 mmole each of indium, lithium and zinc, with the same column dimensions as above, but elution with 0·35*M* hydrochloric acid containing 45% of acetone. The indium peak appears somewhat later when this eluent concentration is used but lithium is even more retarded and clearly separated. Figure 5 shows an example of an elution curve for Cd–In–Zn, using 350 ml of 0·20*M* hydrobromic acid containing 50% of acetone for the elution of cadmium, 300 ml of 0·50*M* hydrochloric acid containing 30% of acetone for the elution of indium and 250 ml of 0·50*M* hydrochloric acid containing 60% of acetone for the elution of zinc. In this case the elution was not continued until the next element had appeared, but was interrupted after complete elution of the first element had been achieved; a few more fractions were collected, and then the next eluent was used, thus imitating an actual analytical situation. The column and flow-rate were the same as for Fig. 1. A similar elution curve for a mixture containing 1 mmole each of bismuth, indium and lead is shown in Fig. 6, except that lead was eluted with 300 ml of 3·0*M* nitric acid.

Quantitative analysis of synthetic mixtures

Standard solutions containing known amounts of indium and one other element were measured out in sextuplicate and three pairs of these solutions were mixed and passed through a column containing 60 ml of AG50W-X8 cation-exchange resin of 200–400 mesh particle size. The three unmixed solutions of indium and of the other elements were retained as standards for comparison. The resin was in the hydrogen form and the columns were

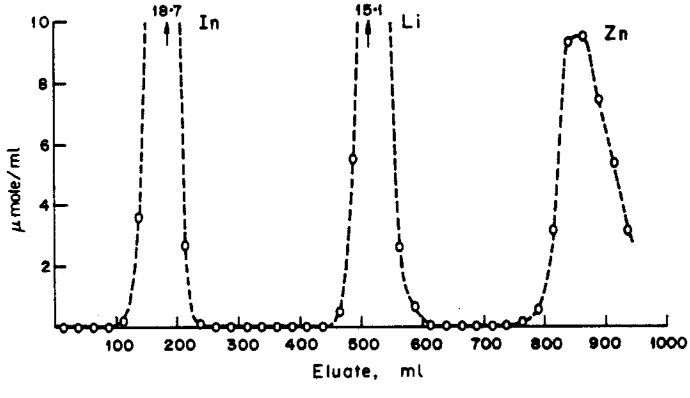

Fig. 4. Elution curve for In–Li–Zn with 0·35*M* HCl–45% acetone. Column, as for Fig. 1. Flow-rate 3·0 ± 0·5 ml/min.

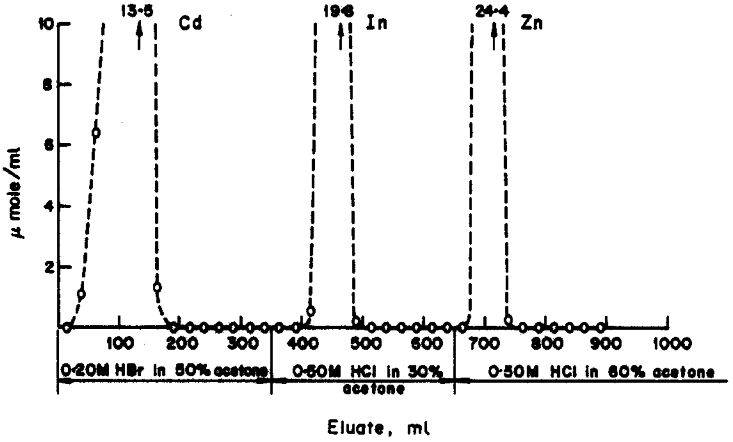

Fig. 5. Elution curve Cd–In–Zn. Column, *etc*., as for Fig. 4.

19 cm long and 2·1 cm in diameter. The columns had been equilibrated by passage of about 50 ml of 0·2*M* nitric acid containing 30% of acetone. The titanium standard solution was kept in 1*M* nitric acid containing 0·2% of hydrogen peroxide. All other standard solutions were made up in 0·2*M* nitric acid. The mixtures were about 0·2*M* in nitric acid and contained 30% of acetone when put onto the column. Titanium-containing mixtures were diluted accordingly. The ions were washed onto the resin with 0·1*M* nitric acid containing 30% of acetone. Indium was then eluted with 300 ml of 0·50*M* hydrochloric acid containing 30% of acetone. In the case of the In–Li pair 350 ml of 0·35*M* hydrochloric acid containing 45% of acetone were used for the elution of indium. The acetone was then washed from the column by passage of about 50 ml of 0·1*M* nitric acid. This effluent was discarded. The second element was then eluted, by use of 300 ml of 1·0*M* hydrochloric acid for Li and Na, 300 ml of 3·0*M* hydrochloric acid for Zn, Fe(III), Ca, Al, U(VI), Cu(II), Ni(II), Be, Mg and Ti(IV) and 300 ml of 3·0*M* nitric acid for Pb(II) and Ga. A flow-rate of 2·5 ± 0·5 ml/min was maintained throughout. The eluates were evaporated to dryness on the water-bath, organic material was destroyed when necessary by heating with perchloric and nitric acids, and the elements were determined by appropriate analytical methods. Determinations on the unmixed standards were carried out at the same time. The analytical results are presented in Table 2, and the methods used for determination are summed up in Table 3.

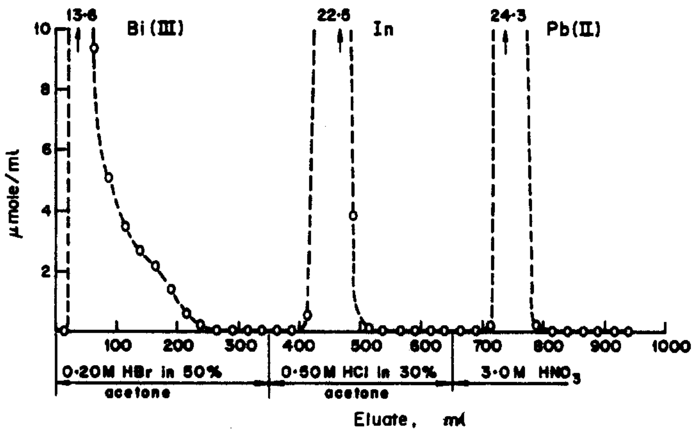

Fig. 6. Elution curve Bi(III)–In–Pb(II). Column, *etc*., as for Fig. 1.

Table 2. Results of analyses of synthetic mixtures*

Taken		Found	
In, *mg*	Other element, *mg*	In, *mg*	Other element, *mg*
102·9	Zn 68·50	102·9 ± 0·1	68·5$_1$ ± 0·02
1032·5	Zn 0·0647	1032·7 ± 0·6	0·064$_5$ ± 0·0004
0·1701	Zn 342·5	0·1703 ± 0·0006	342·5 ± 0·1
102·9†	Zn 68·50	102·9 ± 0·1	68·5$_0$ ± 0·03
106·0	Pb(II) 102·3	106·0 ± 0·1	102·2 ± 0·1
106·0	Ca 42·69	106·1 ± 0·1	42·7$_3$ ± 0·06
106·0	Mn(II) 55·08	106·0 ± 0·1	55·1$_1$ ± 0·05
108·4	Al 28·17	108·4 ± 0·1	28·1$_7$ ± 0·01
108·4	Fe(III) 60·57	108·4 ± 0·1	60·5$_9$ ± 0·03
108·4	U(VI) 238·6	108·4 ± 0·1	238·5 ± 0·1
107·7†	Li 14·15	107·7 ± 0·1	14·1$_4$ ± 0·02
107·7	Na 46·22	107·7 ± 0·1	46·2$_5$ ± 0·06
107·7	Ga 70·25	107·7 ± 0·1	70·2$_4$ ± 0·04
107·7	Cu(II) 64·17	107·6 ± 0·1	64·1$_6$ ± 0·05
107·7	Ni(II) 58·55	107·7 ± 0·1	58·5$_7$ ± 0·04
107·7	Co(II) 59·24	107·7 ± 0·1	59·2$_5$ ± 0·04
107·7	Be 18·21	107·7 ± 0·1	18·1$_9$ ± 0·03
107·7	Mg 25·01	107·7 ± 0·1	25·0$_2$ ± 0·02
107·7	Ti(IV) 36.46	107·7 ± 0·1	36·4$_9$ ± 0·05

* Results are means of triplicate determinations with calculated standard deviations.
† In was eluted with 350 ml of 0·35*M* HCl containing 45% of acetone.

Table 3. Analytical methods used

Species	Method
In, Ga, Fe(III)	Complexometrically with EDTA; back-titration with $ZnSO_4$ at pH 5·5 with Xylenol Orange as indicator. Small amounts of indium by atomic-absorption spectroscopy.
Zn, Pb(II)	Complexometrically with EDTA at pH 5·5 with Xylenol Orange as indicator. Small amounts of zinc by atomic-absorption spectroscopy.
Al	Complexometrically with DCTA; back-titration with $ZnSO_4$ at pH 5·5 with Xylenol Orange as indicator.
Ca, Mn(II)	Complexometrically in excess of ammonia with EDTA; Methylthymol Blue as indicator; hydroxylamine hydrochloride present for Mn(II).
Cu(II), Co(II)	Complexometrically with EDTA, Naphthyl Azoxine S as indicator at pH 6 (pyridine buffer).
Ni(II)	Complexometrically in slight excess of ammonia with EDTA; murexide as indicator.
Mg	Complexometrically with EDTA at pH 10; Eriochrome Blue-Black B as indicator.
Li, Na	Gravimetrically as the sulphates.
U(VI)	Gravimetrically as U_3O_8 after precipitation with CO_2-free ammonia.
Be	Gravimetrically as ammonium nitrosophenylhydroxylamine (cupferron) precipitate.
Ti(IV)	By differential spectrophotometry as H_2O_2 complex at high absorbance.

DISCUSSION

The method described provides an excellent means for the selective separation of indium from other elements. Indium can be eluted with 300 of 0·50*M* hydrochloric acid containing 30% of acetone from a column of 60 ml of AG50W-X8 cation-exchange resin as described. Species such as Zn, Pb(II), Ga, Ca, Mg, Be, Ti(IV), Mn(II), Fe(III), U(VI), Na, Co(II), Cu(II) and Ni(II) are retained by the column quantitatively. When 0·35*M* hydrochloric acid containing 45% of acetone is used for the elution of indium, lithium is also retained, but the elution of indium is not quite as fast. With 0·50*M* hydrochloric acid containing 30% of acetone more than 99% of the indium is in fact eluted with first 200 ml of eluting agent. Since occasionally a slight tailing of indium was observed an eluent volume of 300 ml was used to ensure quantitative (>99·9%) recovery. Separations are sharp and quantitative under these conditions and as little as 64·7 μg of zinc can be separated from more than 1 g of indium, and 170·1 μg of indium from about 340 mg of zinc. Since the separations of zinc and lead from indium are the most critical (except for those from lithium and sodium) it can be assumed that other bi- and multivalent elements can be separated from indium at the same ratios with at least equal ease and accuracy. There also seems to be no reason why even larger amounts of indium could not be separated from submicrogram amounts of other elements, though this was not investigated experimentally. For the separation of trace amounts of indium from large amounts of other elements, 0·35*M* hydrochloric acid containing 45% of acetone is the more favourable eluting agent for indium because with the sole exception of zinc, all other elements are considerably more strongly retained (Table 1).

Elements such as Ba, Sr, Zr, Hf, Th, Sc, Y, La and the lanthanides, and also Rb and Cs have not been investigated in detail, but their known distribution coefficients[19] indicate that they should be retained together with zinc *etc.* quantitatively. Cd, Bi(III), Au(III), Pt(IV), Pd, Rh(III), Mo(VI) and W(VI) can be eluted with 0·20*M* hydrobromic acid containing 50% of acetone before the elution of indium, as has been shown previously.[21] Ir(III), Ir(IV), As(III), As(V), Se(IV), Tl(III), Hg(II), Ge(IV), Sb(III) and Sb(V) should show the same behaviour, though they have not been investigated quantitatively. Besides elements such as Ta(V) and Ag, which tend to interfere because of hydrolysis or precipitate formation when present in large amounts, tin seems to be the only element which accompanies indium when the procedure described is used. Separation of indium from tin is possible by anion-exchange in 0·5*M* hydrochloric acid.[14]

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Zusammenfassung—Indium kann von Zn, Pb(II), Ga, Ca, Be, Mg, Ti(IV), Mn(II), Fe(III), Al, U(VI), Na, Cu(II), Ni(II) und Co(II) durch selektive Elution mit 0·50*M* Salzäure in 30% wäßrigem Aceton von einer Säule mit dem Anionenaustauschharz AG50W-X8 getrennt werden, da alle genannten Elemente von der Säule festgehalten werden. Verwendet man zur Elution von Indium 0·35*M* Salzsäure in 45% wäßrigem Aceton, dann wird auch Lithium von der Säule festgehalten, aber die Elution von Indium wird etwas verzögert. Ihren Verteilungskoeffizienten zufolge sollten auch Ba, Sr, Zr, Hf, Th, Sc, Y, La und die Lanthaniden, Rb und Cs festgehalten werden; Cd, Bi(III), Au(III), Pt(IV), Pd(II), Rh(III), Mo(VI) und W(VI) können vor der Elution von Indium mit 0·20 *M* Bromwasserstoffsäure eluiert werden; Ir(III), Ir(IV), As(III), As(V), Se(IV), Tl(III), Hg(II), Ge(IV), Sb(III) und Sb(V) sollten diese Elemente begleiten, obwohl das im einzelnen nicht untersucht wurde. Wesentliche Verteilungskoeffizienten, Elutionskurven und Analysenergebnisse synthetischer Gemische von Indium mit anderen Elementen werden mitgeteilt.

Résumé—On peut séparer l'indium de Zn, Pb(II), Ga, Ca, Be, Mg, Ti(IV), Mn(II), Fe(III), Al, U(VI), Na, Cu(II), Ni(II) et Co(II) par élution sélective avec l'acide chlorhydrique 0·50*M* en acétone aqueuse à 30% d'une colonne de résine échangeuse de cations AG50W-X8, tous les autres éléments étant retenus par la colonne. Le lithium est inclus dans les éléments retenus par la colonne quand on utilise l'acide chlorhydrique 0,35*M* en acétone aqueuse à 45% pour éluer l'indium, mais l'élution de l'indium est légèrement retardée. Ba, Sr, Zr, Hf, Th, Sc, Y, La et les lanthanides, Rb et Cs devraient aussi être retenus d'après leurs coefficients de partage. Cd, Bi(III), Au(III), Pt(IV), Pd(II), Rh(III), Mo(VI) et W(VI) peuvent être élués avec l'acide bromhydrique 0,20*M* en acétone aqueuse à 50% avant l'élution de l' indium, et Ir(III), ir(IV), As(III), As(V), Se(IV), Ti(III), Hg(II), Ge(IV), Sb(III) et Sb(V), quoique non étudiés en détail, devraient accompagner ces éléments. On présente les coefficient de partage et les courbes d'elution et les résultats correspondants pour des analyses de mélanges synthétiques d'indium avec d'autres éléments.

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METHYL CALCEIN BLUE AND OTHER ANALOGUES OF CALCEIN BLUE

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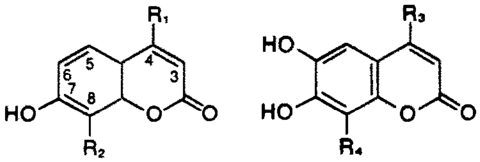
Summary—4-Methylumbelliferone-8-methylenesarcosine (Methyl Calcein Blue) and four related metallofluorochromic indicators derived from umbelliferone, 4-methylumbelliferone, and 4-methylesculetin by condensation with formaldehyde and iminodiacetic acid or glycine have been synthesized, the structures established, the absorbance and fluorescence measured as functions of pH, and the reactions with copper(II) and calcium studied with attention to the effects on fluorescence. All of the compounds display a maximum fluorescence at pH about 9. The fluorescence of each is quenched by copper(II). The calcium derivatives of the compounds derived from the umbelliferones and iminodiacetic acid fluoresce at high pH but those from the umbelliferones and glycine or sarcosine do not. At high pH, 4-methylesculetin and the amino-acids derived from it do not fluoresce either alone or in the prescence of calcium.

In an earlier paper[1] we described the properties of 4-methylumbelliferone-8-methyleneiminodiacetic acid, a compound earlier given the common name Calcein Blue by Wilkins.[2] Wilkins[3] was also the first to prepare Methyl Calcein Blue, a metallofluorochromic indicator synthesized by the condensation of 4-methylumbelliferone, formaldehyde and sarcosine (*N*-methylglycine). As with Calcein Blue, the work reported by Wilkins on Methyl Calcein Blue was limited to explaining some advantages of the compound as an indicator, and to reporting its use as an indicator in the determination of aluminium, nickel and manganese by titration with hydroxyethylethylenediaminetriacetic acid (HEDTA). We have now examined Methyl Calcein Blue in some detail; it proves to be 4-methylumbelliferone-8-methylenesarcosine · $1{\cdot}5H_2O$ (structure **IX** below). We have also examined four closely related compounds: umbelliferone-8-methyleneiminodiacetic acid (**V**), umbelliferone-8-methyleneglycine · $0{\cdot}5H_2O$ (**VII**), 4-methylumbelliferone-8-methyleneglycine (**VIII**), and 4-methylesculetin-8-methyleneiminodiacetic acid · $0{\cdot}5H_2O$ (**X**).



I $R_1 = H, R_2 = H$ (Umbelliferone)
II $R_1 = CH_3, R_2 = H$ (4-Methylumbelliferone)
III $R_3 = H, R_4 = H$ (Esculetin)
IV $R_3 = CH_3, R_4 = H$ (4-Methylesculetin)
V $R_1 = H, R_2 = -CH_2N(CH_2CO_2H)_2$
VI $R_1 = CH_3, R_2 = -CH_2N(CH_2CO_2H)_2$ (Calcein Blue)
VII $R_1 = H, R_2 = -CH_2NHCH_2CO_2H$
VIII $R_1 = CH_3, R_2 = -CH_2NHCH_2CO_2H$
IX $R_1 = CH_3, R_2 = -CH_2N(CH_3)CH_2CO_2H$ (Methyl Calcein Blue)
X $R_3 = CH_3, R_4 = -CH_2N(CH_2CO_2H)_2$

The investigation of these compounds followed essentially the same course as that of Calcein Blue and the calculations and reasoning follow the pattern presented in the earlier paper.[1] Results are given in the following section, and the summary and discussion are confined to the differences found between these compounds and Calcein Blue. These differences are significant inasmuch as the nature of the chelating group in some of the compounds has been considerably altered. A more detailed treatment of this work and a compilation of the graphs presenting the potentiometric, absorbance, and fluorescence data will be found in the thesis of G. M. Huitink.[4]

EXPERIMENTAL

Synthesis and intermediate compounds

The Mannich condensation was used in the synthesis of compounds V–X, the molar proportions of reactants found best being hydroxycoumarin 1·0, amino-acid 1·5, and formaldehyde 1·5. The solvents and procedures given below for the individual compounds are the optimum found in the course of numerous preparations.

The chemicals used were commercial materials without further purification: disodium iminodiacetate monohydrate, Geigy Chemical Company; glycine, Eastman Organic Chemicals; sarcosine, Mann Research Laboratories, Inc. The formaldehyde used was a 37% aqueous solution. All water used was distilled and then demineralized by passage through Amberlite MB-1.

Apparatus and procedures

Electrophoresis studies were done with a Model R, Series D, Beckman Paper Electrophoresis Cell (Durrum Type).

NMR spectra were obtained with a Varian Associates A-60 Nuclear Magnetic Resonance Spectrometer. The spectra of **III**, **V**, **VII**, **VIII**, and **IX** were obtained in a deuterium oxide–potassium carbonate solvent, those of **IV** and **X** in D_6-dimethylsulphoxide. Tetramethylsilane and Tier's salt were used as standards, in D_6-dimethylsulphoxide and D_2O respectively.

Measurements of pH were made with a Corning Model 10 pH-meter equipped with a Beckman No. 40495 high alkalinity glass electrode and a Beckman asbestos fibre S.C.E. Potentiometric titrations were carried out in 0·1M potassium chloride medium with 0·1M sodium hydroxide made up in 0·1M potassium chloride.

Solubility measurements (of compounds **V** and **X**) as a function of pH were made by shaking buffers with excess of compound for 12 hr. An appropriate volume of the filtrate was then adjusted to a specific pH (10·0 for **V**. 4·0 for **X**) diluted to specific volume with 0·1M potassium chloride. and the absorbance measured (at 367 nm for **V**, 342 nm for **X**), and the concentration calculated from calibration curves. The intrinsic solubility, S_i, was obtained by linear extrapolation to $1/[H^+] = 0$ of plots of S *vs.* $1/[H^+]$ and the acid dissociation constant was obtained[5] from a plot of $pK_a = pH - \log[(S/S_i) - 1]$. For both **V** and **X** the plots were linear and both parallel and close to that for Calcein Blue.[1]

Absorption spectra

The absorption spectra of **I**, **II**, **V**, **VII**, **VIII** and **IX** were obtained at intervals of 0·5 pH over the pH range 1·5–13·0. Solutions were prepared by mixing 375 μl of a $3{\cdot}11 \times 10^{-3}M$ stock solution of the compounds, 0·25 ml of 0·01M EDTA and 10 ml of buffer. The solutions were then diluted to 25 ml with 0·1M potassium chloride. Absorption spectra were obtained with a Cary Model 15 Recording Spectrophotometer. The pH was checked after the absorbance measurement.

Additional absorbance measurements were made on solutions containing the acidic form and the basic form of the compounds and on solutions of pH numerically equal to the estimated $pK_a \pm$ 0·0, 0·2, 0·4 and 0·6, the measurements being made on a Beckman DU spectrophotometer. Values for the acid dissociation constants were obtained from the results by using the equation $pK_a = pH - \log(A - A_{HA})/(A_{A^-} - A)$, which is simply derived from the mathematical equation defining K_a, the terms A, A_{HA}, and A_{A^-} being the absorbances of the solutions of $pH = pK_a \pm x$, and of solutions in which the substances were entirely in the acid or salt forms.

The absorption spectra of **IV** and **X** at pH 4 and 9 were obtained for buffered solutions. Solutions containing 1 ml of $3{\cdot}11 \times 10^{-3}M$ stock solution of the compounds and 0·75 ml of 0·1M EDTA in 75 ml of 0·1M potassium chloride were titrated spectrophotometrically with 0·2M potassium hydroxide. Values for the acid dissociation constants were obtained from graphs of absorbance *vs.* pH; absorbances obtained from buffered solutions of **IV** and **X** could not be used because of serious chemical reaction of the compounds with the buffer components.

Fluorescence spectra

Fluorescence excitation and emission spectra of **I**, **II**, **V**, **VII**, **VIII** and **IX** were obtained with an Aminco-Bowman Spectrofluorometer and Mosely XY Recorder. A fluorometer, G. K. Turner Associates, Model 10, equipped with a flow-through cell, was used to monitor fluorometric titrations.

Stock solutions, $3{\cdot}11 \times 10^{-3}M$, of the various compounds were prepared, a little potassium hydroxide being added to facilitate dissolution. Volumes of 15 μl of **I**, **II**, **V**, **VII**, **VIII** and **IX** were mixed with 0·25 ml of 0·01*M* EDTA and 10 ml of buffer solution and diluted to 25 ml with 0·1*M* potassium chloride. The fluorescence excitation and emission spectra were then obtained and the pH again measured. The pH range 1·5–13·0 was covered at intervals of 0·5 pH. Plots of relative fluorescence *vs.* pH were made and acid dissociation constants taken as the pH at the point of inflection of these curves.

The effect of copper on the fluorescence of **V**, **VII**, **VIII** and **IX** over the pH range 3·5–10·5 was studied by essentially the same procedure but with omission of the EDTA and addition of 15 μl of $3{\cdot}11 \times 10^{-3}M$ copper(II). Similarly the effect of calcium was determined over the pH range 7·0–13·0.

The relative fluorescence of **IV** and **X** was obtained at pH 2·5–11·0 by fluorometric titration of solutions containing 7 μl of stock solution and 0·75 ml of 0·01*M* EDTA in 75 ml of 0·1*M* potassium chloride with 0·2*M* potassium hydroxide. Acid dissociation constants were obtained from the titration results. The effects of copper(II) were investigated in the same way, omitting the EDTA and adding 7 μl of $3{\cdot}11 \times 10^{-3}M$ copper(II).

Preparation of reagents

Umbelliferone (**I**) was prepared by the procedure of *Organic Reactions*:[6] m.p. 234–235°, literature value 227–228°. The preparation of 4-*methylumbelliferone* (**II**) was reported earlier.[1] *Esculetin* (**III**) was prepared by the method of Amiard and Allias:[7] m.p. 261–271°, literature value 270°. 4-*Methylsculetin* (**IV**) was prepared by the method of *Organic Syntheses*:[8] m.p. 279–281°, literature value 272–274°. *Umbelliferone-8-methyleneiminodiacetic acid* (**V**) was prepared with the same procedure and ratios of reactants as for **VI** (*Calcein Blue*).[1] Yellow crystals were obtained, which were unchanged on heating to 300°. The neutralization equivalent found was 308·3, and analysis gave C 54·6%, H 4·4%, N 4·4%: $C_{14}H_{13}NO_7$ (m.w. 307·2) requires C 54·73%, H 4·27%, N 4·56%.

Umbelliferone-8-methyleneglycine (**VII**) was prepared with the same procedure and ratios of reactants as for **IX**, but no spongy material formed and the product precipitated immediately. Yellow crystals were obtained, which were unchanged on heating to 300°. The equivalent weight found by neutralization was 256·5. The water content found by the Karl Fischer method was 0·41 mole per mole of **VII**. Analysis gave C 55·5%, H 4·6%, N 5·7%: $C_{12}H_{11}NO_5 \cdot \frac{1}{2}H_2O$ (m.w. 258·2) requires C 55·57%, H 4·69%, N 5·43%. 4-*Methylumbelliferone-8-methyleneglycine* (**VIII**) was prepared in the same way as **VII**. Yellow crystals, unchanged on heating to 300° were obtained. The equivalent weight found was 264·9. Analysis gave C 59·1%, H 5·0%, N 5·4%: $C_{13}H_{13}NO_5$ (m.w. 263·2) requires C 59·30%, H 4·98%, N 5·32%.

Methyl Calcein Blue (4-methylumbelliferone-8-methylenesarcosine, **IX**) was prepared as follows. A mixture of 0·12 mole (21·44 g) of 4-methylumbelliferone, 0·18 mole (16·03 g) of sarcosine and 0·18 mole (17·76 ml) of 37% formaldehyde in 200 ml of water was maintained at 90–95° until the solution became clear and a spongy material formed, and then for another 30 min. The spongy material was removed. The clear yellow filtrate on standing for 12 hr yielded a light yellow precipitate which was filtered off. The solid was dissolved in water by the addition of sufficient potassium hydroxide, some insoluble matter was removed by filtration, and the pH was adjusted to 4·5 by the dropwise addition of dilute hydrochloric acid (1 + 5). A precipitate formed which was filtered off and washed with demineralized water and acetone. The product was slurried three times with acetone and then air-dried. Yellow crystals, unchanged at temperatures up to 300° were obtained. The neutralization equivalent found was 303·6. Analysis gave C 55·5%, H 6·0%, N 4·4%: $C_{14}H_{15}NO_5 \cdot 1\frac{1}{2}H_2O$ (m.w. 304·3) requires C 55·26%, H 5·96%, N 4·60%.

4-*Methylesculetinmethyleneiminodiacetic acid* (**X**) was prepared in the same way as for **VI**. Fine grey crystals were obtained, unchanged on heating to 300°. The neutralization equivalent found was 348·8. Analysis gave C 51·7%, H 4·7%, N 4·0%: $C_{15}H_{15}NO_8 \cdot \frac{1}{2}H_2O$ (m.w. 346·3) requires C 52·02%, H 4·66%, N 4·06%.

RESULTS

Spectroscopic data

The results for the investigation of the absorption and fluorescence spectra are summarized in Table 1, and the NMR data and their interpretation are given in Table 2. The absorption spectra of **IV** at various pH values resembled those of **I** and **II** but a second maximum was present (Fig. 1). The fluorescence spectra of **IX** are shown in Fig. 2. Unlike that of **II**, but resembling that of Calcein Blue (Ref. 1, Fig. 5), the fluorescence decreased at high pH, the maximum occurring at pH 8·85 (see Fig. 3).

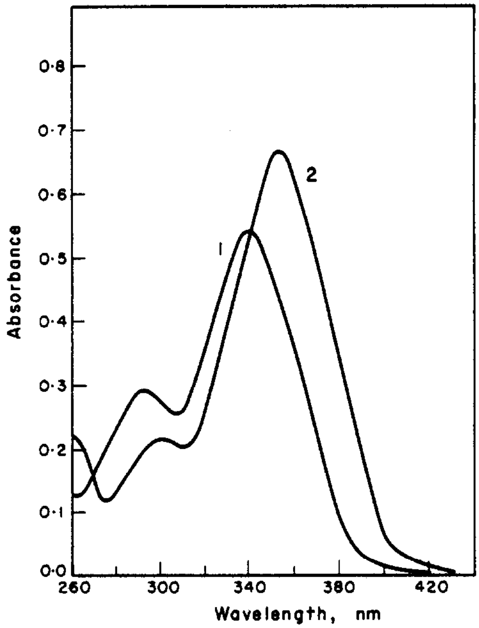


Fig. 1. Absorption spectra of 4-methylesculetin (compound IV) at (1) pH 4; (2) pH 9.

Table 1. Spectrophotometric data

	Absorption*			Fluorescence		
Compound	pH	λ_{max}, nm	ϵ, $\epsilon l.mole^{-1}.cm^{-1}$	pH	Excitation λ_{max}, nm	Emission λ_{max}, nm
Umbelliferone*†	4	325	$1{\cdot}49 \times 10^4$	4	330	460
	10	365	$1{\cdot}93 \times 10^4$	10	370	460
4-Methylesculetin	4	340	$1{\cdot}16 \times 10^4$	9	370 shoulder at 300 nm)	460
	9	360	$1{\cdot}46 \times 10^4$			
Umbelliferone-8-methyleneimino-diacetic acid*†	4	325	$1{\cdot}49 \times 10^4$	4	328	455
	10	367	$1{\cdot}61 \times 10^4$	9	370	455
					(fluorescence maximal at pH 9·1)	
Umbelliferone-8-methyleneglycine	4	322	$1{\cdot}53 \times 10^4$	4	330	455
	10	369	$1{\cdot}90 \times 10^4$	9	370	455
					(fluorescence maximal at pH 8·5)	
4-Methylumbelliferone-8-methyleneglycine*†	4	322	$1{\cdot}52 \times 10^4$	4	328	450
	10	365	$1{\cdot}85 \times 10^4$	9	366	450
					(fluorescence maximal at pH 8·5)	
Methyl Calcein*† Blue	4	321	$1{\cdot}58 \times 10^4$	4	328	448
	10	360	$1{\cdot}85 \times 10^4$	9	365	448
					(fluorescence maximal at pH 8·85)	
4-Methylesculetin-methyleneimino-diacetic acid	4	342	$1{\cdot}26 \times 10^4$	9	369	459
	9	360	$1{\cdot}50 \times 10^4$			

* Absorption spectra and variation of absorbance with pH similar to those 4-methylumbelliferone and Calcein Blue (Ref. 1, Figs. 2 and 3).

† Fluorescence spectra and variation of fluorescence with pH similar to those of Calcein Blue and 4-methylumbelliferone (Ref. 1. Figs 4 and 5).

Table 2. NMR data

Compound	δ, *ppm*	Pattern	Peaks	Proton integration	*J*	Coupling	Position	Notes
III	5·92	AB	Doublet	1	9	*ortho*	3	
	7·54		Doublet	1			4	
	6·74		Singlet	1			5	absent in **IV** by analogy with **II**
	6·52		Singlet	1			8	
IV	6·08		Singlet	1			3	
	6·74		Singlet	1			8	
	7·02		Singlet	1			5	
V	3·79		Singlet	4			(—N—CH$_2$—CO$_2^-$)$_2$	
	4·42		Singlet	2			(—N—CH$_2$—Ar)	
	5·94	AB	Doublet	1	9	*ortho*	3	
	7·68		Doublet	1			4	
	6·63	AB	Doublet	1	9	*ortho*	6	confirms location of methyleneiminodiacetic acid at 8
	7·29		Doublet	1			5	
VII	3·54		Singlet	2			(—N—CH$_2$—CO$_2^-$)	
	4·05		Singlet	2			(—N—CH$_2$—Ar)	
	5·82	AB	Doublet	1	9	*ortho*	3	
	7·53		Doublet	1			4	
	6·52	AB	Doublet	1	9	*ortho*	6	confirms location of methyleneglycine at 8
	7·11		Doublet	1			5	
VIII	2·14		Singlet	3			CH$_3$ at 4	
	3·52		Singlet	2			(—N—CH$_2$—CO$_2^-$)	
	4·07		Singlet	2			(—N—CH$_2$—Ar)	
	5·72		Singlet	1			3	
	6·61	AB	Doublet	1	9	*ortho*	6	absence of peak at 6·16 ppm in **II** and *ortho* protons confirm location of methyleneglycine at 8
	7·20		Doublet	1			5	
IX	2·07		Singlet	3			CH$_3$at 4	
	2·72		Singlet	3			(—N—CH$_3$)	
	3·67		Singlet	2			(—N—CH$_2$—CO$_2^-$)	
	4·15		Singlet	2			(—N—CH$_2$—Ar)	
	5·67		Singlet	1			3	
	6·63	AB	Doublet	1	9	*ortho*	6	absence of peak at 6·16 ppm in **II** and *ortho* protons confirm location of methylenesarcosine at 8
	7·15		Doublet	1			5	
X	2·53		Singlet	3			CH$_3$ at 4	
	3·05		Singlet	4			(—N—CH$_2$—CO$_2^-$)$_2$	
	4·56		Singlet	2			(—N—CH$_2$—Ar)	
	6·10		Singlet	1			3	olefinic proton*
	7·00		Singlet	1			5	aromatic proton*

* Only one aromatic proton is present and there is no direct evidence enabling a particular assignment to the 5— or to the 8— position. The position of the two peaks coincided with those of **IV** (6·08 ppm for position 3—, 7·02 ppm for position 5—) and lie close to those of **II**, **III** and **VI**, so that the probable assignment is 6·01 to position 3— and 7·00 to position 5—. The methyleneiminodiacetic acid group thus occupies position 8.

Table 3. Acid dissociation constants of Methyl Calcein Blue and related compounds

Compound	Constant	Value found	Method	Group involved
Umbelliferone (I)	pK_1	7·83	Absorbance	Phenol
		7·68	Fluorescence	
4-Methylumbelliferone (II)	pK_1	7·82	Absorbance	Phenol
		7·78	Fluorescence	
4-Methylesculetin (IV)	pK_1	7·69	Potentiometric	First Phenol
		7·40	Absorbance	
		7·35	Fluorescence	
	pK_2	11·72	Fluorescence	Second Phenol
Umbelliferone-8-methylene-iminodiacetic acid (V)	pK_1	2·94	Solubility	Carboxyl
	pK_2	6·90	Potentiometric	Phenol
		6·95	Absorbance	
		6·90	Fluorescence	
	pK_3	11·18	Fluorescence	Ammonium
Umbelliferone-8-methylene-glycine (VII)	pK_1	6·65	Potentiometric	Phenol
		6·79	Absorbance	
		6·70	Fluorescence	
	pK_2	11·70	Fluorescence	Ammonium
4-Methylumbelliferone-8-methyleneglycine (VIII)	pK_1	6·85	Potentiometric	Phenol
		6·88	Absorbance	
		6·85	Fluorescence	
	pK_2	12·12	Fluorescence	Ammonium
4-Methylumbelliferone-8-methylene sarcosine (IX) (Methyl Calcein Blue)	pK_1	6·78	Potentiometric	Phenol
		6·71	Absorbance	
		6·60	Fluorescence	
		12·98	Fluorescence	Ammonium
4-Methylesculetin-8-methyleneiminodiacetic acid (X)	pK_1	3·03	Solubility	Carboxyl
	pK_2	6·22	Potentiometric	Phenol
		6·35	Absorbance	
		6·68	Fluorescence	
	pK_3	11·38	Fluorescence	Ammonium

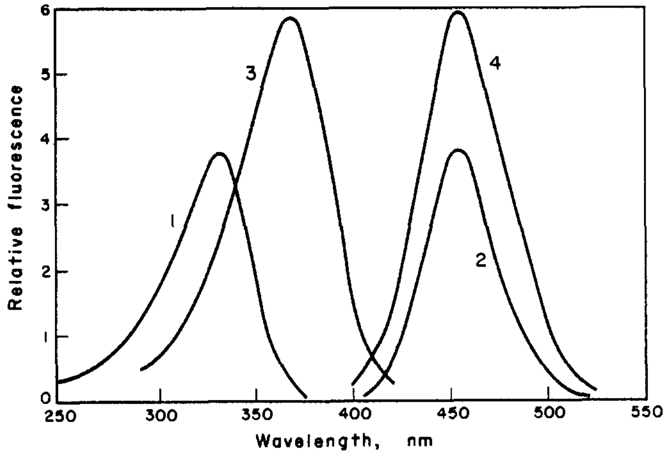


Fig. 2. Fluorescence excitation and emission spectra of Methyl Calcein Blue (compound IX). (1) Excitation, pH 4, emission monochromator set at 448 nm. (2) Emission, pH 4, excitation monochromator set at 328 nm. (3) Excitation, pH 9, emission monochromator set at 448 nm. (4) Emission, pH 9, excitation monochromator set at 365 nm.

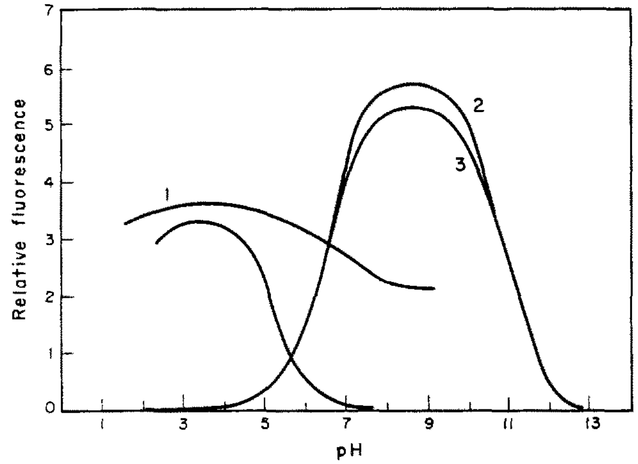


Fig. 3. Variation of fluorescence of Methyl Calcein Blue (compound **IX**) with pH. Emission monochromator set at 448 nm for all curves. (1) Excitation monochromator set at 328 nm. (2) Excitation monochromator set at 365 nm. (3) In the presence of excess of calcium, excitation monochromator set at 365 nm. (4) In the presence of copper(II), excitation monochromator set at 328 nm for pH < 6 and at 365 nm for pH > 6.

Dissociation constants

Spectrophotometric titration (Fig. 4), fluorescence data (Fig. 5), potentiometric titration and solubility data were used as appropriate for obtaining the acid dissociation constants, which are summarized in Table 3. The solubility data are given in Table 4.

In the potentiometric titrations, **V** gave two breaks in the curve, one at $a = 1{\cdot}0$ and pH 5·12, the second at $a = 2{\cdot}0$ and pH 9·34 (a = number of equivalents of base added per equivalent of acid). The pH at $a = 0{\cdot}5$ was 4·30, but this was not a good value for pK_1, the solubility of **V** being so low that the sample dissolved completely only as the first break was being approached. The pH at $a = 1{\cdot}5$ gave a good value (6·90) for pK_2. **VII** gave a single break at $a = 1{\cdot}0$, pH = 8·45. The pH at $a = 0{\cdot}5$ (6·65) indicated that the proton of the phenol group was neutralized and that the acetic acid group formed a zwitter-ion that was not titrated. **VIII** and **IX** behaved similarly to **VII** and **X** behaved similarly to **V**.

Effect of calcium and copper on the fluorescence

Copper(II) quenched the fluorescence of **VII**, **VIII** and **IX** over the pH range 7–10·5, and that of **IV** (Fig. 5), **V** (pH 4–10·5), **VI** (Ref. 1, Fig. 1) and **X** (similar to **IV**) over a wider range of pH. Two breaks occurred in the curve for the fluorimetric titration of **X** with copper(II) at pH 9·1, indicating the addition of first one and then a second ion of copper.

Table 4. Solubility data.

Compound **V**					
pH		3·26	3·84	3·96	4·06
S, *mg* 100 *ml*		22·66	65·66	84·80	94·33
S_i*, *mg*/100 *ml*	7·20				
Compound **X**					
pH		3·34	3·76	4·06	4·41
S, *mg* 100 *ml*		1·58	3·55	5·63	12·94
S_i*, *mg* 100 *ml*	0·52				

* S_i = intrinsic solubility.

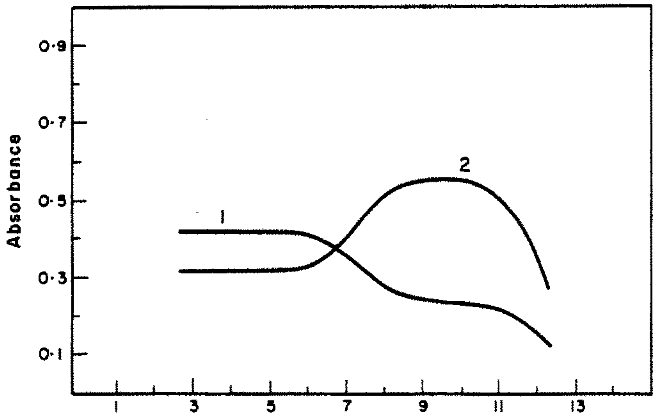


Fig. 4. Absorbance of 4-methylesculetin as a function of pH at (1) 340 nm; (2) 360 nm.

In the prescence of calcium at high pH, V fluoresces intensely, in this respect resembling VI (Ref. 1, Fig. 5). Titration of V with alkali in the presence of a tenfold amount of calcium yielded a curve closely resembling that for the same titration of VI (Ref. 1, Fig. 1). The formation constant calculated[1] from the curves was $K_{\mathrm{Ca(V)^-}} = 1{\cdot}5 \times 10^7$. In the presence of calcium at high pH, VII and VIII do not fluoresce, behaving similarly to IX (Fig. 3). Unlike V and VI, X does not fluoresce in the presence of calcium at high pH. The parent material IV (4-methylesculetin) differs from the umbelliferones I and II in not fluorescing at high pH, and this behaviour is carried over to the methyleneiminodiacetic acid derivative (X).

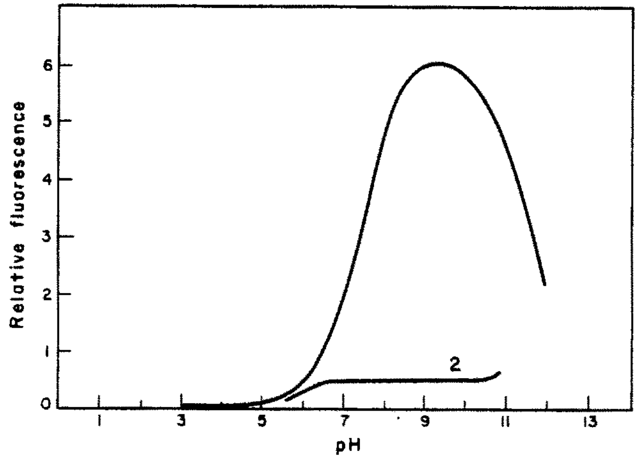


Fig. 5. Fluorescence of 4-methylesculetin as a function of pH, (1) alone; (2) in the presence of copper(II). Excitation monochromator set at 370 nm, emission monochromator set at 460 nm.

DISCUSSION

The acid dissociation constants of the various compounds studied are summarized in Table 3. Among the methyleneimino acid compounds, only the three derived from iminodiacetic acid, **V**, **VI** and **X**, have a titratable carboxyl group, and each of these only one. All six compounds **V**–**X** are therefore zwitter-ions, a carboxyl group proton having been transferred to a nitrogen atom. The remaining free carboxyl group in each of the compounds **V**, **VI** and **X** is unusually strong for a carboxyl group, $pK_1 = 2{\cdot}94$, 2·97 and 3·03, respectively, owing to the presence of the positive charge on the neighbouring ammonium ion. This effect is exerted also on the neighbouring phenolic groups, the phenolic groups of **V**–**X** each being an order of magnitude more acidic than those of the parent phenols **I**, **II** and **IV**.

As is almost always the case, the ultraviolet absorption and the fluorescence excitation spectra of each of these compounds practically superimpose. Although umbelliferone and 4-methylumbelliferone fluoresce at high pH, the methyleneimino acid derivatives of them do not. For this the explanation offered earlier[1] is offered again, that neutralization of the ammonium ion reduces the rigid, hydrogen-bonded structure attached to the aromatic nucleus and by allowing unrestricted rotation about the bonds in the methyleneimino acid group provides a non-radiative mechanism for the dispersion of the energy of the excited state.

The fluorescence of the two compounds derived from iminodiacetic acid and the umbelliferones, that is **V** and **VI**, is restored at high pH by calcium and this is attributed, as before,[1] to the formation of the tight, non-rotating, multidentate chelate structure about the calcium atom, involving the phenol and both acetic acid groups. The fluorescence of those compounds lacking a second acetic acid group (**VII**, **VIII** and **IX**) is not restored at high pH by calcium.

Unlike the umbelliferones, 4-methylesculetin does not fluoresce at high pH; this is attributed to opening of the pyrone ring, the one phenolic group having been neutralized below pH 9, the pH at which maximum fluorescence occurs. The fluorescence of the iminodiacetic acid derivative, **X**, is not restored by calcium at high pH as happens with **V** and **VI**; presumably again this is because of ring opening.

The properties of the iminodiacetic acid derivatives of umbelliferone and of 4-methylumbelliferone are so alike that only the latter, Calcein Blue, need be considered for practical use as a metallofluorochromic indicator because not only is umbelliferone difficult to prepare (4-methylumbelliferone being relatively easy) but umbelliferone and its derivatives decompose in alkaline solutions far more rapidly than do 4-methylumbelliferone and Calcein Blue.

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Zusammenfassung—4-Methylumbelliferon-8-methylensarcosin (Methylcalceinblau) und vier damit verwandte, von Umbelliferon, 4-Methylumbelliferon und 4-Methylaesculetin durch Kondensation mit Formaldehyd und Iminodiessigsaüre oder Glycin abgeleitete Metallfluoreszenzfarbindikatoren wurden dargestellt und ihre Struktur festgelegt. Ihre Absorption und Fluoreszenz wurde in Abhängigkeit vom pH gemessen und die Reakton mit Kupfer(II) und Calcium im Hinblick auf Fluoreszenzeffekte studiert. Alle Verbindungen zeigen die starkste Fluoreszenz ungefähr bei pH 9. Bei allen wird die Fluoreszenz durch Kupfer(II) gelöscht. Die Calciumderivate der von den Umbelliferonen und Iminodiessigsäure abgeleiteten Verbindungen fluoreszieren bei hohem pH, die aus den Umbelliferonen und Glycin oder Sarcosin nicht. 4-Methylaesculetin und die davon abgeleiteten Aminosäuren fluoreszieren bei hohem pH weder allein noch in Gegenwart von Calcium.

Résumé—On a synthétisé la 4-méthylombelliférone-8-méthylènesarcosine (Bleu de Méthylcalcéine) et quatre indicateurs métallofluorochromes dérivées de l'ombelliférone, de la 4-méthylombelliférone et de la 4-méthylesculétine par condensation avec le formaldéhyde et l'acide iminodiacétique ou la glycine, les structures ont été établies, l'absorption et la fluorescence mesurées en fonction du pH, et les réactions avec le cuivre(II) et le calcium ont été étudiées en portant l'attention sur les influences sur la fluorescence. Tous les composés présentent une fluorescence maximale à un pH d'environ 9. La fluorescence de chacun d'eux est éteinte par le cuivre(II). Les dérivés du calcium des composés dérivés des ombelliférones et de l'acide iminodiacétique sont fluorescents à pH élevé, mais ceux provenant des ombelliférones et de la glycine ou de la sarcosine ne le sont pas. A pH élevé, la 4-méthylesculétine et les amino-acides qui en sont dérivés ne sont pas fluorescents, ni seuls ni en présence de calcium.

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SHORT COMMUNICATIONS

DETERMINATION OF SMALL AMOUNTS OF LEAD IN URANIUM

(*Received* 11 *February* 1974. *Accepted* 30 *April* 1974)

The extraction and determination of small amounts of uranium in the presence of large amounts of interfering elements has been discussed in a number of recent publications[1,2]. Here the analytical problem has been approached from a different aspect, considering uranium as an interfering element during the determination of very small amounts of lead. The determination is based on the complexation of lead by nitrilotriacetic acid in alkaline hexamine solution, under which conditions uranium is not significantly complexed (owing to formation of hydroxides); the latter is then extracted as a ternary diphenylacetic acid–hexamine–uranium complex into a chloroform solution of diphenylacetic acid. Several extractions are needed, the number increasing with the amount of uranium to be removed. The aqueous phase is then acidified to release the lead from the nitrilotriacetate complex, and the polarogram is recorded over the region from 0 to −1·0 V *vs.* the SCE.

EXPERIMENTAL

Reagents

Uranyl sulphate solution (0·05*M*) was prepared as described in a previous paper.[1] Diphenylacetic acid solutions (0·25*M*) were prepared by dissolving 53·1 g of the reagent in one litre of chloroform. The nitrilotriacetic acid (0·5*M* in 1*M* sodium hydroxide) and hexamine (saturated) solutions employed were as described previously.[1] The hydrochloric acid was *p.a.* grade.

Apparatus

Polarographic measurements were made with a Radelkis OH–102 polarograph and a two-electrode system in which the potential values were referred to a saturated calomel electrode immersed directly in the test solution.

Polarographic determination of lead

The lead–nitrilotriacetate complex exhibits a poorly developed wave at about −1·4 V *vs.* the SCE, which at more negative potentials converges with the current increase due to hydrogen evolution (Fig. 1*b*). However, when a solution of this complex is acidified, the wave shifts to around −0·45 V, is well defined and easily measured.

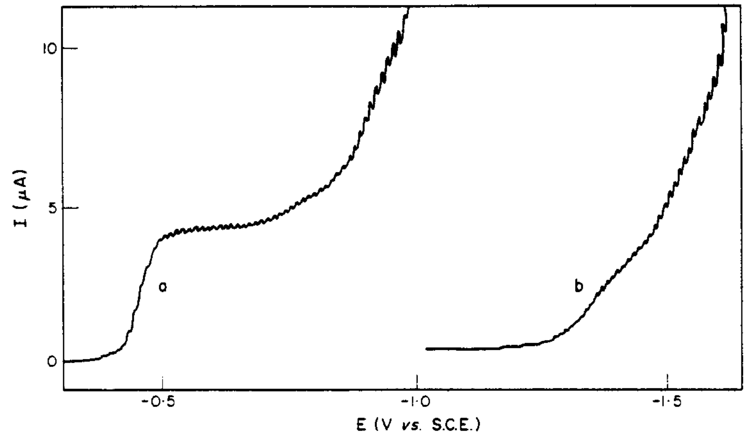

Fig. 1. The polarographic waves of lead in nitrilotriacetic acid solution. (*a*) pH 1–2, (*b*) pH 6–9; $5 \times 10^{-4}M$ lead(II), scan-rate 0·25 V/min.

This is the usual reduction wave for the lead aquo-ion, as the NTA complex is dissociated in acid solution. In the presence of large amounts of uranium, which exhibits a wave at −0·2 V in acid medium,[2] the polarographic determination of lead is not possible, and the extraction procedure described here must be used to remove the uranium.

Extraction and determination of lead

The determination was carried out by adding 5 ml of nitrilotriacetic acid (NTA) solution to an appropriate volume of the test solution (5–40 ml), followed by sufficient hexamine solution (2–5 ml) to bring the pH to between 5 and 6·5. Extraction was then carried out with 10-ml portions of the diphenylacetic acid–chloroform solution until both phases were colourless, followed by one more extraction to ensure completeness. The phenylacetate–hexamine–uranium complex is extracted, lead-NTA is not. To the aqueous phase was added 1 ml of concentrated hydrochloric acid and the resulting solution was filtered into a 50-ml volumetric flask and diluted to the mark with distilled water. The resulting solution was deaerated with purified nitrogen and polarographed in the region from 0 to −1·0 V (*vs.* SCE) at a scan-rate of 0·25 V/min. The lead wave appeared at −0·45 V and was preceded by a very small wave at −0·2 V, which was attributed to the reduction of residual uranium remaining after the extraction.[2,3] The height of this latter wave did not increase with increasing amounts of uranium in the original solution, nor could it be eliminated by performing additional extractions. However, owing to its small size, it in no way interfered with the lead wave and its measurement.

It was found that the calibration curve was linear over the range 10^{-5}–$5 \times 10^{-3}M$ lead(II) in the final solution and that the accuracy and precision of measurement were practically unaffected by changing the lead and uranium concentrations. For example, various large amounts of uranium were separated by extraction from amounts of lead chosen so as to give a final concentration for the polarographic determinations of $5 \times 10^{-5}M$. It was found that a 500-fold amount of uranium was without effect on the lead determination and that the increased number of extractions (seven in this case) did not have a particularly marked effect on the accuracy of measurement (±5%). The limiting amount of uranium tolerable was too high to be determined and is given by the number of extractions which the experimenter is willing to carry out and the required accuracy (which will necessarily decrease, if only slightly, with an increasing number of extractions).

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Summary—Small amounts of lead in the presence of large amounts of uranium can be determined by complexing the lead with nitrilotriacetic acid in aqueous solution at about pH 6 (adjusted with hexamine) and extracting the uranium into a chloroform solution of diphenylacetic acid. The aqueous phase is then acidified and the lead determined polarographically.

Zusammenfassung—Kleine Mengen Blei in Gegenwart großer Mengen Uran können bestimmt werden, indem das Blei in wäßriger Lösung bei etwa pH 6 (mit Hexamethylentetramin eingestellt) mit Nitrilotriessigsäure komplex gebunden und das Uran in eine Lösung von Diphenylessigsäure in Chloroform extrahiert wird. Die wäßrige Phase wird dann angesäuert und das Blei polarographisch bestimmt.

Résumé—On peut doser de petites quantités de plomb en la présence de grandes quantités d'uranium en complexant le plomb par l'acide nitrilotriacétique en solution aqueuse à pH 6 environ (ajusté par l'hexamine) et en extrayant l'uranium dans une solution chloroformique d'acide diphénylacétique. La phase aqueuse est alors acidifiée et le plomb déterminé polarographiquement.

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EXTRACTION WITH LONG-CHAIN AMINES—VIII

EXTRACTION OF THE CHROMIUM–DCTA COMPLEX AND ITS COLORIMETRIC DETERMINATION

(*Received* 8 *January* 1974. *Accepted* 3 *March* 1974)

It is well-known that on prolonged boiling with EDTA the strongly hydrated chromium (III) ion forms an intensely purple $CrY(H_2O)^-$ complex in weakly acid solution, which has been recommended for the colorimetric determination of chromium.[1] The composition and colour of this 1:1 complex are strongly dependent on the acidity of the solution. The existence of altogether four complexes has been demonstrated.[2] In addition to the complex already mentioned the neutral $CrHY(H_2O)$ is formed, then with increasing pH of the solution the blue hydroxo-complex, $CrY(OH)^{2-}$, gradually appears, and in strongly alkaline media (pH 13) the green $CrY(OH)_2^{3-}$ complex is formed. The complexing agents NTA, DTPA, DCTA and HEDTA behave similarly.[3] Their suitability for colorimetry has recently been evaluated by den Boef and Poeder.[4]

The colorimetric determination of chromium as Cr-EDTA or Cr-DCTA is, however, disturbed by higher concentrations of those metals which form coloured complexes under the same conditions, such as iron, cobalt, nickel and copper. During the determination of chromium the prior separation of these elements is necessary, *e.g.*, for analysis of bronzes prior separation of copper is carried out by electrolysis,[5] for the analysis of steels iron is separated as the hydroxide.[6]

Since the EDTA and DCTA complexes of chromium are very stable, a method for eliminating basic interferences in this determination was sought. In connection with a systematic study of extractions with high molecular-weight amines, attention was also paid to extraction of various EDTA and DCTA complexes. It was, for example, found that the Cr–DCTA complex is easily extracted from weakly acidic solutions by a chloroform solution of trioctylmethylammonium chloride (Aliquat 336-S). If coloured bivalent cations form complexes under the given conditions, they are extracted either not at all or to a negligible extent. Because they are not completely extracted, the EDTA complexes are not suitable. The extraction of the Cr–EDTA complex with n-hexylammonium chloride was recently studied by Irving and Al-Jarrah[7] from a purely physical chemical point of view. The behaviour of various DCTA complexes with tervalent metals is interesting. The Fe complex is extracted and the Co(III)–DCTA complex is only partially extracted. The red Mn(III)–DCTA complex which is formed by the rapid oxidation of the manganese(II) in the presence of DCTA[8] is quantitatively extracted by Aliquat 336-S and is quite stable.

The easy extraction of the Cr–DCTA complex provides the possibility of a quite selective determination of chromium and was studied in detail in this work.

EXPERIMENTAL

Reagents and solutions

A $5 \times 10^{-2}M$ solution of Cr^{3+} was prepared by dissolving 24·97 g of $KCr(SO_4)_2 . 12H_2O$ in 100 ml of water. A $10^{-3}M$ solution of Cr^{3+} was prepared by appropriate dilution of this solution.

Solutions of cobalt, nickel, copper and tervalent iron sulphates ($5 \times 10^{-2}M$) were prepared in the usual manner, and determined chelatometrically, as was a 0·05 *M* solution of 1,2-diaminocyclohexanetetra-acetic acid.

A 5% chloroform solution of trioctylmethylammonium choride (TOMA—General Mills Aliquat S 336) was employed.

Phenylacetic acid and hexamine were used in the solid form.

Experimental conditions

Effect of the duration of heating. According to the literature,[3] the Cr–DCTA complex is formed quantitatively at pH 3 after boiling a solution of chromium(III) and DCTA for 10 min. This agrees with our own observations, which indicate that a period of 10–15 min is quite satisfactory. This period was used in all further experiments.

Effect of pH. A series of experiments was carried out in which 2 ml of 0·05*M* chromium(III) sulphate and 4 ml of 0·05*M* DCTA were diluted to 30 ml and the pH was adjusted to 1·02–5·83 with sulphuric acid or sodium hydroxide. After boiling for 15 min and cooling, the solution was diluted to 50 ml in a volumetric flask, then 10 ml of the resulting solution were pipetted into a separating funnel and extracted for 3 min with 5 ml of a 5%

solution of TOMA in chloroform. After separation, the organic phase solution was filtered through a dry filter into a 1-cm cuvette and its spectrum from 360 to 700 nm recorded. The absorption spectrum has two maxima at 385 and 540 nm. The height of the first maximum is 55% that of the second. It was found that the maximum absorbance is obtained by boiling the solutions at pH 3·70–4·50.

Effect of DCTA concentration. In the same manner a series of solutions with varying amounts of 0·05*M* DCTA was prepared. From the results it is clear that increasing the amount of DCTA up to a 4:1 DCTA:Cr ratio is without effect on the formation and extraction of the complex.

Effect of neutral salts. The effect of neutral salts was studied similarly. A solution containing 2 ml of 0·05*M* Cr(III) and 5 ml of 0·05*M* DCTA was prepared and various amounts of KNO_3, NaCl, K_2SO_4, $NH_4H_2PO_4$ were added. After adjustment of the pH and boiling for 15 min, the solution was diluted in a volumetric flask to 50 ml and a 10-ml aliquot tested for extraction of chromium. From Table 1 it can be seen that chlorides, nitrates and phosphates have a very unfavourable effect on the extraction of the Cr–DCTA complex. Sulphates are without effect even at higher concentrations. The effect of organic anions was not studied in detail. In practical determinations of chromium only solutions containing sulphates are important. Such solutions are obtained by dissolving alloys in sulphuric acid or by final fuming with sulphuric acid. At higher metal concentrations it is, of course, necessary to expect high sulphate concentrations. Thus the effect of dilution on the extraction of the Cr-DCTA complex was also studied. It was, for example, found that the molar absorbance of the complex is not affected by 2–4 g of sodium sulphate contained in 100 ml of solution.

Table 1. The influence of neutral salts on the Cr–DCTA extraction with TOMA. (*A* = mg of salt in 50 ml; *B* = the per cent decrease in absorbance)

NaCl		KNO_3		NH_4HPO_4		Na_2SO_4	
A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
36	11	10	3·8	11	0	0	0
90	24	25	7·6	25	5	612	2·1
180	39	50	19	58	19	1225	3·1
360	58	100	49	115	36	2450	5·6
900	77						
1800	87						

Extractability of the Cr–DCTA complex. In the previous experiments, the Cr–DCTA complex was extracted with a single 5-ml aliquot of 5% TOMA solution. The quantitativeness of the extraction was determined as follows: 2 and 4 ml of 0·005*M* chromium were mixed with 3 ml of 0·05*M* DCTA in a small beaker and diluted to 30 ml; the pH was adjusted to about 3·7 and the solution was boiled for 15 min. After cooling the solution was transferred to a 100-ml separatory funnel and extracted for 1 min with 5 ml of 5% TOMA solution. After separation of the phases, the organic phase was filtered into a 1-cm cuvette and measured. The aqueous phase was washed with chloroform and the extraction repeated with 5 ml of TOMA and the absorbance measured. A third extraction was carried out in the same manner, again after washing the aqueous phase with chloroform, and the aqueous phase left was shown to be free of chromium. From the measured values it was determined that the extraction of chromium is 84–86% efficient under the given conditions. Since three extractions are necessary, the chloroform extracts are combined and stripped with 5 ml of 1*M* potassium nitrate, which is measured after filtration. The sensitivity of the determination is thus considerably increased. Beer's law is obeyed up to 650 μg of Cr in the 5 ml of potassium nitrate solution.

Determination of chromium in the presence of high concentrations of iron and copper

In a study of various complexing agents, den Boef and Poeder[4] found that a tenfold amount of copper and iron relative to chromium does not interfere. Thus we decided to study the determination of chromium in the presence of much higher concentrations of these cations. For the separation of iron and copper from chromium, their extraction as phenylacetates was chosen.

The weakly acidic solution of iron(III) and chromium(III) is diluted with water to about 50 ml in a 100-ml separating funnel, and 500 mg of phenylacetic acid, 250 mg of hexamine and 20 ml of chloroform are added. The organic phase is separated after a 1-min extraction. The extraction is repeated twice in the same manner. The aqueous phase is then washed with 10 ml of pure chloroform, and transferred to a beaker, and the pH is adjusted to 3·5–3·8 with 1*M* sulphuric acid or potassium hydroxide. Then 2 ml of 0·05*M* DCTA are added and the solution is boiled for 15 min. After cooling, the pH is again adjusted to 3·5–3·8, and the solution is transferred into a separating-funnel and extracted three times with 5-ml portions of 5% chloroform solution of TOMA. The combined extracts are stripped with 5 ml of 1*M* potassium nitrate. The aqueous phase is filtered through a dry filter into a 1-cm cuvette and the absorbance measured at 540 nm against water.

For the determination of 104 μg of chromium in the presence of 120 mg of iron (0·08% Cr) or in the presence of 240 mg of copper (0·04% Cr) the error was about ± 5%.

Determination of chromium in the presence of nickel and cobalt

In agreement with the work of den Boef and Poeder,[4] it was found that considerably higher concentrations of nickel and cobalt (as the DCTA complexes) do not interfere in the determination and the chromium can be determined in the aqueous phase after the appropriate boiling with DCTA. It is, of course, necessary that all the elements be bound as DCTA complexes.

The determination of chromium in the presence of high concentrations of nickel or cobalt (100–200 mg of the metal) was unsuccessful, since it was necessary to employ high concentrations of DCTA, resulting in a high ionic strength which considerably decreased the extractability of the Cr–DCTA complex. Even four extractions were not sufficient to give reliable results for chromium.

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Summary—Chromium(III) is extracted as the DCTA complex by ion-association with trioctylmethylammonium chloride (Aliquat 336-S), into chloroform, and stripped into 1*M* potassium nitrate for spectrophotometric measurement at 540 nm. Iron(III) and copper(II) are removed beforehand by extraction whith phenylacetic acid. High concentrations of nickel or cobalt prevent complete extraction.

Zusammenfassung—Chrom(III) wird als DCTA-Komplex durch Ionenassoziation mit Trioctylmethylammoniumchlorid (Aliquat 336-S) in Chloroform extrahiert und zur spektrophotometrischen Messung bei 540 nm in 1*M* Kaliumnitrat zurückextrahiert. Eisen(III) und Kupfer(II) werden vorher durch Extraktion mit Phenylessigsäure entfernt. Hohe Konzentrationen von Nickel oder Kobalt verhindern die vollständige Extraktion.

Résumé—Le chrome(III) est extrait en chloroforme à l'état de complexe avec le DCTA par association d'ions avec le chlorure de trioctylméthylammonium (Aliquat 336-S), et réextrait en nitrate de potassium 1*M* pour mesure spectrophotométrique à 540 nm. Le fer(III) et le cuivre(II) sont éliminés auparavant par extraction avec l'acide phénylacétique. Des concentrations élevées de nickel ou de cobalt empêchent l'extraction complète.

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EXTRACTION OF CHROMIUM–DCTA COMPLEX WITH TRIOCTYLMONOMETHYLAMMONIUM CHLORIDE (ALIQUAT-336)*

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Chromium(III) forms a stable, water-soluble, violet complex with DCTA when the two solutions at pH 4·5 are boiled for 10 min. The 1:1 complex formed has absorption maxima at 395 and 540 nm.[1–3] Přibil and Veselý[4] have given a method for the determination of chromium(III) and aluminium in the presence of chromate based on use of DCTA. The violet Cr–DCTA complex can be extracted quantitatively by trioctylmethylammonium chloride (Aliquat-336) in chloroform. This method can thus be employed for the determination of chromium in the presence of other coloured cations. The results are reported in this paper.

EXPERIMENTAL

Reagents

Aliquat-336. Trioctylmethylammonium chloride (Aliquat-336), 2·5% solution in chloroform. The solution was purified by shaking successively with 20% sodium hydroxide, 6*M* hydrochloric acid and 20% sodium chloride solution (10 min shaking, 5:1 phase-volume ratio, chloroform:water).[5]

DCTA, 0·05 *M*. All other reagents used were of analytical grade. The diluents used were purified by conventional methods.

Procedure

Adjust the solutions of chromium(III) and DCTA separately to pH 4·5. Then mix them together in suitable proportion and boil for 10 min. Make the volume up to 25 ml in a standard flask with redistilled water, and extract 5 ml of this solution successively with two 2·5-ml portions of the Aliquat-336 solution. Adjust the volume of the combined organic phase to 5 ml, filter it into a 5-mm cell and measure the absorbance at 545 nm.

RESULTS AND DISCUSSION

Optimum conditions for extraction

The calibration curve based on the absorbance of the organic extract is linear over the range 40–1000 ppm. The comparable curve for the aqueous layer is linear in the range 40–600 ppm. The organic:aqueous phase-volume ratio can be varied from 1:1 to 1:5 without affecting the absorbance of the extract. Maximum extraction takes place between pH 4 and 5. Below pH 3 the ligand is precipitated and above pH 6 some of the metal is. The best extractions are obtained with Cr:ligand ratio between 1:1 and 1:2, and a concentration of Aliquat-336 of at least 2·5%.

A number of common organic solvents were examined. The order of effectiveness is: chloroform ~ nitrobenzene > cyclohexane > hexane > kerosene ~ benzene ~ petroleum ether (60–80°) ~ trichloroethylene ≫ carbon tetrachloride.

Interferences

The effect of anions on the extraction was established with 5 ml of the complex solution containing 1·28 mg of chromium(III). The results are tabulated in Table 1. It is seen that sulphate ions give the best results and do not interfere even if present in large excess. Citrate, tartrate and oxalate in up to 5 times the concentration of chromium used can be tolerated. Nearly equal quantity of chloride does not interfere, while nitrate interferes seriously even when its concentration is only a fifth of that of the chromium.

The effect of cations was similarly studied and the results are shown in Table 2. Aluminium causes serious interference.

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* Paper presented at the Diamond Jubilee Session of the Indian Science Congress held at Chandigarh, January, 1973.

Table 1. Influence of anions on the extraction of Cr–CDTA complex

Anion	Amount added, *mg*	Absorbance	Anion	Amount added, *mg*	Absorbance
Sulphate	25·00	0·480	Citrate	10·00	0·450
	15·00	0·480		8·00	0·475
	10·00	0·480		6·50	0·480
	5·00	0·480		4·00	0·480
Chloride	2·90	0·390	Acetate	6·00	0·460
	1·463	0·450		4·20	0·470
	1·00	0·478		2·10	0·480
	0·75	0·480		1·00	0·480
Nitrate	0·600	0·445	Tartrate	12·00	0·458
	0·425	0·460		10·50	0·468
	0·215	0·476		7·50	0·480
	0·200	0·480		5·00	0·480
Oxalate	8·50	0·465			
	6·50	0·478			
	5·00	0·480			
	4·00	0·480			

Absorbance in the absence of added salts = 0·480.
All the anions were used in the form of their sodium salts.

Table 2. Influence of cations on the extraction

Metal ion	Amount added, *mg*	Absorbance	Metal ion	Amount added, *mg*	Absorbance
Cobalt	5·00	0·468	Iron	1·75	0·472
	3·69	0·475		0·875	0·470
	1·471	0·480		0·438	0·480
	1·103	0·480		0·219	0·480
Nickel	3·50	0·435	Manganese	5·50	0·471
	1·84	0·448		3·44	0·478
	1·01	0·479		3·20	0·480
	0·918	0·480		3·00	0·480
Copper	3·00	0·466	Zinc	1·00	0·475
	2·00	0·475		0·75	0·478
	1·50	0·480		0·50	0·480
	1·00	0·480		0·40	0·480
Aluminium	0·400	0·450			
	0·21	0·460			
	0·105	0·479			
	0·091	0·480			

Absorbance in the absence of added salts = 0·480.
Only sulphates of the metals were used.

Nature of the extracted species

The nature of the extracted species as determined by the slope of plots of the log of the distribution ratio *vs.* log of the concentration of Aliquat and also by Job's method is Cr:DCTA:Aliquat-336 = 1:1:1.

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Summary—The violet complex formed between chromium(III) and DCTA can be quantitatively extracted by Aliquat-336 in chloroform as [Cr(DCTA)] [Aliquat-336]. The conditions for quantitative extraction have been established. The method facilitates the determination of chromium in the presence of other coloured cations.

Zusammenfassung—Der violette Komplex aus Chrom(III) und DCTA kann durch Aliquat-336 in Chloroform quantitativ als [Cr(DCTA] [Aliquat-336] extrahiert werden. Die Bedingungen für die quantitative Extraktion wurden ermittelt. Das Verfahren erleichtert die Bestimmung von Chrom in Gegenwart anderer gefärbter Kationen.

Résumé—Le complexe violet formé entre le chrome(III) et le DCTA peut être extrait quantitativement par l'Aliquat-336 en chloroforme à l'état [Cr(DCTA)] [Aliquat-336]. On a établi les conditions d'extraction quantitative. La méthode facilite le dosage du chrome en la présence d'autres cations colorés.

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TWO POSSIBLE COLORIMETRIC INDICATORS FOR USE IN STUDYING MAGNESIUM COMPLEXATION KINETICS

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It is not normally possible to determine binding or kinetic constants between magnesium and biologically important materials such as nucleic acids or nucleotides by using ultraviolet–visible spectrophotometry, since the absorbance changes accompanying complex formation are much too small.[1] Colorimetric indicators such as Eriochrome Black T or Calmagite (which show significant colour changes in the visible spectral range) have been used[2] for the determination of equilibrium constants for magnesium binding to various polynucleotides.[3,4] Unfortunately these indicators cannot be used to monitor changes in magnesium concentration in kinetic studies on binding to such materials, since the presence of a phenolic group in the indicator (with a pK_a of *ca.* 12) causes the complexation rate with magnesium to be much too slow for the rapid changes in magnesium concentration to be monitored. The normal range[5] of relaxation times for magnesium complexation reactions is $\sim$200–1000 μsec while the reaction of Eriochrome Black T with magnesium at pH 8·8 and $[Mg^{2+}] = 1 \times 10^{-3}M$ has a relaxation time of 450 msec.[6]

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In order to surmount this problem, an effort has been made to find colorimetric indicators which do not suffer from this kinetic disadvantage but which still bind sufficiently strongly to magnesium ions. Kinetic and equilibrium data for magnesium binding to two such species, kojic acid (5-hydroxy-2-hydroxymethyl-4-pyrone) and 3,5-dinitrosalicylic acid anions, are presented here.

EXPERIMENTAL

Kinetic studies were performed with a temperature-jump apparatus which has been described elsewhere.[7] Equilibrium constants for proton binding (K_{HL}) and magnesium-ion binding (K_{MgL}) were determined by using a Beckman DK2a spectrophotometer; pH measurements were carried out on a Polymetron 42D pH meter. All data refer to 25·0° and 0·5M potassium chloride medium.

3,5-Dinitrosalicylic acid was recrystallized twice from water, and all other reagents were of the highest purity commercially available.

RESULTS

Equilibrium constants were determined by the Benesi–Hildebrand method[8] and are shown in Table 1, along with kinetic data for the reactions. Changes in the spectrum for both ligands were observed in the visible–near ultraviolet range (300–500 nm).

Table 1. Equilibrium and kinetic data for the binding of magnesium ions to 3,5-dinitrosalicylic acid and kojic acid at 25° in 0·5M KCl medium

	pK_a*	K_{MgL},† *l./mole*	$10^6 \times k_f$,§ *l. mole^{-1} sec^{-1}*	k_b,‡ *sec^{-1}*
3,5-dinitrosalicyclic acid	6·66	145	0·31	2200
Kojic acid	7·63	390	0·28	720

* K_a = acid dissociation constant (pK_a = log K_{HL})
† K_{MgL} = metal binding constant (pK_a = log K_{HL})
§ k_f = complexation rate constant with magnesium
‡ k_b = complex dissociation rate constant

DISCUSSION

The equilibrium constants for both systems are fairly high for magnesium and the formation rate constants are consistent with the Eigen mechanism,[9] the somewhat lower rate for 3,5-dinitrosalicylic acid being due to the electron-withdrawing nature of the nitro groups.[10] The relaxation times are in the usual range for magnesium complexation reactions and should be useful for monitoring magnesium complexation kinetics especially where a conformational change gives rise to a slow relaxation time.

The amplitudes of the temperature-jump effects with kojic acid were small and this probably reflects a low enthalpy change. Such an effect is not disadvantageous in a kinetic sense.

The observed changes are in a suitable spectral region since they do not overlap with the ultraviolet absorption bands associated with π–π^* transition in biological molecules.

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Summary—Complexation-rate and equilibrium data for 25·0° and 0·5*M* KCl medium are presented for two colorimetric indicators for magnesium: 3.5-dinitrosalicylic acid and kojic acid. The forward rate constants are both consistent with an S_N1 mechanism and the complex formation constants are 145 and 390 l./mole respectively.

Zusammenfassung—Für zwei Magnesium-Farbindikatoren, 3,5-Dinitrosalicylsäure und Kojisäure, werden Geschwindigkeiten und Gleichgewichtsdaten der Komplexbildung bei 25,0° in 0,5*M* KCl mitgeteilt. Die Geschwindigkeitskonstanten der Hinreaktion sind beide mit einem S_N1-Mechanismus verträglich; die Komplexbildungskonstanten betragen 145 bzw. 390 l/Mol.

Résumé—On présente les données de vitesse de complexation et d'équilibre à 7,0° et en milieu KCl 0,5*M* pour deux indicateurs colorimétriques du magnésium: l'acide 3,5-dinitrosalicylique et l'acide kojique. Les constantes de vitesse directes sont toutes deux en accord avec un mécanisme S^N1 et les constantes de formation de complexe sont 145 et 390 l/mole respectivement.

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SELECTIVE EXTRACTION AND SEPARATION OF IRON(III) WITH 4-METHYLPENTAN-2-OL

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4-Methylpentan-2-ol has been used in this laboratory for the solvent extraction of molybdenum,[1] tungsten,[2] rhenium[3] and gold.[4] In this communication, we propose a simple and rapid method for the selective extraction and separation of iron(III) with this reagent from 5·5–6*M* hydrochloric acid. The iron (III) is then stripped with water and determined titrimetrically.

EXPERIMENTAL

Reagents

Stock solution of iron(III). Analytical-grade ferric chloride (12·10 g) dissolved in 500 ml of distilled water and standardized titrimetrically.[5]

Procedure

Mix an aliquot of solution containing 5 mg of iron(III) with enough hydrochloric acid to give a final acid concentration of 6*M* in a total volume of 10 ml. Shake the solution for 1 min with 10 ml of pure 4-methylpentan-2-ol. Let the layers settle and separate them. Strip the iron from the organic phase with two 10-ml portions of water and determine it in the aqueous phase titrimetrically.[5]

RESULTS AND DISCUSSION

Effect of varying the conditions

The concentration of 4-methylpentan-2-ol was varied from 10 to 100% with benzene as diluent and the hydrochloric acid concentration was varied from 1 to 6·5*M*. The results (Fig. 1) show that iron(III) is quantitatively

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Résumé—On présente les données de vitesse de complexation et d'équilibre à 7,0° et en milieu KCl 0,5*M* pour deux indicateurs colorimétriques du magnésium: l'acide 3,5-dinitrosalicylique et l'acide kojique. Les constantes de vitesse directes sont toutes deux en accord avec un mécanisme S^N1 et les constantes de formation de complexe sont 145 et 390 l/mole respectivement.

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SELECTIVE EXTRACTION AND SEPARATION OF IRON(III) WITH 4-METHYLPENTAN-2-OL

(*Received* 25 *February* 1974. *Accepted* 10 *March* 1974)

4-Methylpentan-2-ol has been used in this laboratory for the solvent extraction of molybdenum,[1] tungsten,[2] rhenium[3] and gold.[4] In this communication, we propose a simple and rapid method for the selective extraction and separation of iron(III) with this reagent from 5·5–6*M* hydrochloric acid. The iron (III) is then stripped with water and determined titrimetrically.

EXPERIMENTAL

Reagents

Stock solution of iron(III). Analytical-grade ferric chloride (12·10 g) dissolved in 500 ml of distilled water and standardized titrimetrically.[5]

Procedure

Mix an aliquot of solution containing 5 mg of iron(III) with enough hydrochloric acid to give a final acid concentration of 6*M* in a total volume of 10 ml. Shake the solution for 1 min with 10 ml of pure 4-methylpentan-2-ol. Let the layers settle and separate them. Strip the iron from the organic phase with two 10-ml portions of water and determine it in the aqueous phase titrimetrically.[5]

RESULTS AND DISCUSSION

Effect of varying the conditions

The concentration of 4-methylpentan-2-ol was varied from 10 to 100% with benzene as diluent and the hydrochloric acid concentration was varied from 1 to 6·5*M*. The results (Fig. 1) show that iron(III) is quantitatively extracted from 5·5–6 M hydrochloric solution with undiluted 4-methylpentan-2-ol. At higher acid concentrations ($>6M$), the extraction coefficient decreases, which may be attributed to competition by the acid itself for the solvent.

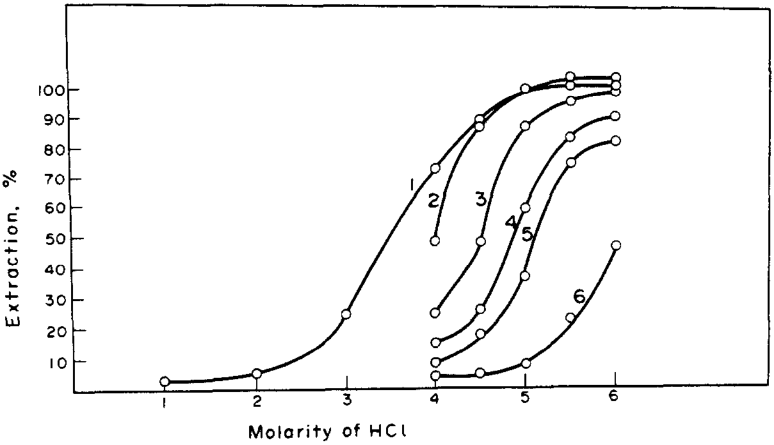

Fig. 1. Degree of extraction of iron(III) as a function of HCl concentration. 4-Methylpentan-2-ol concentration in solvent (benzene as diluent): *1*—100%; *2*—75%; *3*—50%; *4*—40%; *5*—25%; *6*—10%.

Variation of the metal ion concentration showed that the extraction of iron(III) is possible even at tracer levels. However, milligram amounts of iron are preferable for accurate determination of the iron in steel samples.

Various salting-out agents such as lithium, magnesium and aluminium chloride were tested (Fig. 2). Lithium chloride exerts a pronounced salting-out effect, giving complete extraction of iron at lower acidity. Magnesium and aluminium chlorides enhance the extraction of iron(III) but do not make it quantitative at lower acidities. In terms of cost, use of lithium chloride offers no advantage.

The period of equilibration was varied from 15 to 180 sec. To ensure complete extraction of the metal, solutions should be shaken for at least 1–2 min.

Interferences

Varying amounts of foreign ions were taken with a fixed amount of iron (5 mg) and the recommended procedure was applied. There was no interference (*i.e.*, < 1% deviation) from Ti (2 mg), Zr (15 mg), V(V) (5 mg), Cr(III) (5 mg), Cr(VI) (3·5 mg), Mo(VI) (5 mg), W(VI) (5·25 mg), Mn(II) (15 mg), Co(II) (3·5 mg), Ni (3·5 mg), Ru(III) (7 mg), Rh(III) (10 mg), Pd(II) (20 mg), Os(VIII) (8 mg), Ir(III) (10 mg), Pt(IV) (10 mg), Cu(II) (3·5 mg),

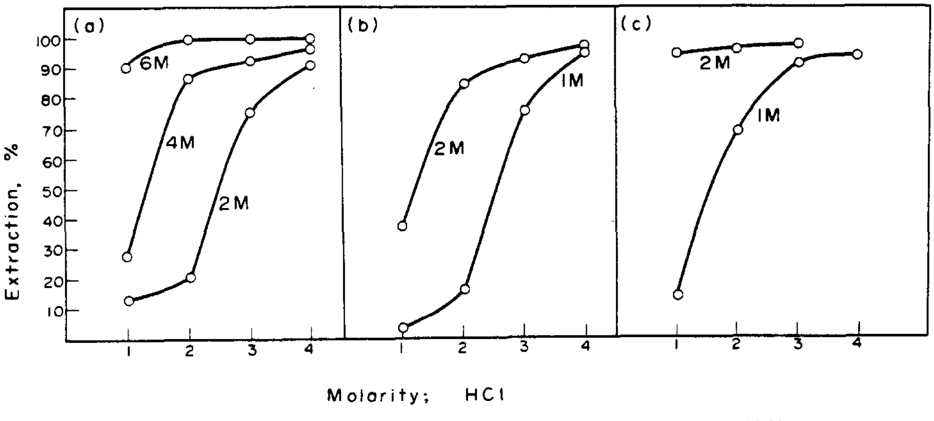

Fig. 2. Effect of salting-out agents: *A*—LiCl; *B*—$MgCl_2$; *C*—$AlCl_3$.

Au(III) (8·7 mg), Zn (17·5 mg), Cd (17·5 mg), Ga (10 mg), In (5 mg), Tl(III) (10 mg), Pb (17·5 mg), Sb(III) (15 mg), Bi (17·5 mg), Th (5 mg), U(VI) (5 mg), Ce(IV) (5 mg), phosphate (10 mg), EDTA (20 mg), citrate and tartrate (25 mg). Molybdenum(VI), tungsten (VI) and gold(III) are also extracted but do not interfere in the determination of iron. Tungsten(VI) can be masked with oxalic acid. However, ions such as selenium(IV), tellurium(IV), ascorbate, fluoride and thiocyanate interfere and must be absent.

Separation of iron(III) from synthetic mixtures

Under the optimum conditions for extraction of iron(III), none of the metals commonly associated with iron in Al-, Co-, Ni-, Ti- and Zn-based samples, is extracted. The recovery of iron is better than 99·8%. Analysis of binary mixtures has shown that the recovery of the metal ions left in the aqueous phase is also almost quantitative (98·5–99·5%). The results of analysis of various synthetic mixtures by the proposed method are shown in Table 1.

Four samples of alloy steel were analysed separately by the proposed method and the results from duplicate analyses are reported in Table 2. The method permits extraction and determination of iron in about 15 min.

Table 1. Analysis of synthetic mixtures

Composition of the synthetic mixture	Recovery of Fe (duplicate analysis), %
Fe, 5 mg; Mn, 5 mg; W, 0·5 mg	99·8
Fe, 5 mg; Mn, 1 mg; Ni, 1 mg; Cr, 3 mg; Mo, 0·5 mg	99·9
Fe, 5 mg; Mn, 0·5 mg; Ni, 1 mg; Cr, 1 mg; Cu, 2 mg; Mo, 1 mg	99·8
Fe, 5 mg; Al, 4·8 mg; V, 0·5 mg	99·9
Fe, 5 mg; Al, 1 mg; Cu, 1 mg; Mn, 0·5 mg	99·9
Fe, 5 mg; Cu, 1 mg; Mn, 0·5 mg; Ti, 1 mg; Zn, 3 mg; Ni, 1 mg; Cr, 1 mg	99·9
Fe, 5 mg; Ni, 1 mg; Cu, 1 mg; Mn, 0·5 mg; Co, 2 mg; Cr, 1 mg; V, 0·5 mg;	99·8
Fe, 5 mg; U, 10 mg	99·8

Table 2. Analysis of standard samples

Alloy	Composition of alloy, %	Fe present, %	Fe found, %
21b	C 6·84, Si 0·12, S 0·04, P 0·03, Mn 0·43, W 0·46	92·1	91·9, 91·9
33b	C 2·24, Si 2·00, P 0·11, S 0·03, Mn 0·64, Ni 2·24, Cr 0·61, Mo 0·40	91·7	91·7, 91·6
33c	C 3·31, Si 1·88, S 0·06, P 0·11, Mn 0·86, Ni 1·98	91·0	90·8, 90·9
33d	C 2·30, Si 1·63, S 0·02, P 0·02, Mn 0·63, Ni 2·38, Cr 0·52, Cu 1·54, Mo 0·48	90·3	90·2, 90·2

Acknowledgement—The authors wish to thank the University authorities for providing laboratory facilities. Thanks are also due to the Council of Scientific and Industrial Research (India) for awarding a fellowship to one of them (S. B. G.).

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5. A. I. Vogel. *Textbook of Quantitative Inorganic Analysis.* 3rd Ed., p. 309. Longmans, London, 1957.

Summary—4-Methylpentan-2-ol is used for quantitative extraction of iron(III) from 5·5–6*M* hydrochloric acid. The iron(III) is then stripped with water and determined titrimetrically. Te(IV), Se(IV), ascorbate, fluoride and thiocyanate interfere and must be absent. Mo(VI), W(VI) and Au(III) are co-extracted but do not interfere in the determination.

Zusammenfassung—4-Methylpentan-2-ol wird zur quantitativen Extraktion von Eisen(III) aus 5,5–6*M* Salzsäure verwendet. Eisen(III) wird dann mit Wasser rückextrahiert und titrimetrisch bestimmt. Te(IV), Se(IV), Ascorbat, Fluorid und Thiocyanat stören und müssen abwesend sein. Mo(VI). W(VI) und Au(III) werden mitextrahiert, stören jedoch bei der Bestimmung nicht.

Résumé—Le 4-méthylpentane-2-ol est utilisé pour l'extraction quantitative du fer(III) de l'acide chlorhydrique 5,5–6*M*. Le fer(II) est alors réextrait à l'eau et dosé titrimétriquement. Les Te(IV), Se(IV), ascorbate, fluorure et thiocyanate gênent et doivent être absents. Les Mo(VI), W(VI) et Au(III) sont coextraits mais negênent pas dans le dosage.

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FORMATION CONSTANTS OF Cd(II) COMPLEXES WITH DITHIZONE AND RELATED COMPOUNDS

(*Received* 26 *March* 1974. *Accepted* 30 *March* 1974)

In an earlier report comparing the equilibrium formation constants of zinc(II) and nickel(II) chelates of dithizone (diphenylthiocarbazone) and related reagents, the then surprisingly larger sensitivity of zinc to the steric hindrance exerted by *ortho* substituents was noted.[1] It was speculated that this could be explained by the coplanarity of the vicinal phenyl ring and the chelate ring in the zinc dithizonate, which would be strained upon the presence of an *ortho* substituent. By contrast, the absence of any similar adverse effect in the nickel dithizonate was taken to result from a significant deviation from coplanarity of the phenyl and chelate rings since in such a spatial relationship the *ortho* substituent could not exert any steric hindrance. Subsequent X-ray crystallographic determinations[2–4] confirmed these speculations (with the usual caveat about possible differences between crystal and solution structures) with the phenyl and chelate rings being coplanar in the case of zinc and perpendicular in the case of nickel.

With the thought that the presence or absence of steric influence on formation constants upon *ortho* substitution might provide indirect information on the relationship of the vicinal phenyl and chelate rings in other metal dithizonates, we decided to study a series of cadmium(II) dithizonates. Inasmuch as cadmium has a larger radius than zinc(II) one might expect that steric influences on cadmium would play a decreasing role in determining structural relationships and solution equilibrium properties in its dithizonate complexes.

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Summary—4-Methylpentan-2-ol is used for quantitative extraction of iron(III) from 5·5–6*M* hydrochloric acid. The iron(III) is then stripped with water and determined titrimetrically. Te(IV), Se(IV), ascorbate, fluoride and thiocyanate interfere and must be absent. Mo(VI), W(VI) and Au(III) are co-extracted but do not interfere in the determination.

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EXPERIMENTAL

Reagents

Ligands. Diphenylthiocarbazone, di(*o*-tolyl)thiocarbazone, di(*p*-tolyl)thiocarbazone, di(2,4-dimethylphenyl)-thiocarbazone, and di(1-naphthyl)thiocarbazone were prepared and purified as described previously.[1]

Dioxan. Purified[1] and freshly distilled before use.

Cd solution. An approximately 0·1*M* $Cd(ClO_4)_2$ solution was standardized by EDTA titration.

Buffer solutions were freed from trace metal contamination by extraction with a carbon tetrachloride solution of dithizone.

Apparatus

Spectrophotometer. A Cary Model 14 was used for absorbance measurements.

pH Meter. A Beckman Model G equipped with glass and saturated calomel electrodes and calibrated with Beckman buffers at pH 4 and 7 was used for pH measurements.

Spectrophotometric determination of formation constants of 1:1 *cadmium chelates*

The procedure, similar to that previously employed,[1] involves a measurement of the absorbances (at various pH values) of a series of solutions containing both cadmium and chelating agent in a ratio of at least 100:1 to avoid formation of the 1:2 metal complex. The following expression, valid when the total metal concentration is much greater than the ligand concentration and the pH range of the experiment is one in which the neutral ligand is the predominant species, was used for the calculation of the 1:1 complex formation constants, β_1

$$\beta_1 = \frac{[H^+](A - \epsilon_{HL} T_L)}{T_M K_a (T_L \epsilon_{ML} - A)}$$

where T_M is the concentration of cadmium(II), T_L the ligand concentrations, ϵ_{HL} and ϵ_{ML} the molar absorptivities of the reagent and complex, respectively, at the wavelength employed for the measurement.

RESULTS AND DISCUSSION

As can be seen from Table 1, the cadmium complexes of the dithizones are significantly more stable than those of zinc. This is in keeping with the order observed with anionic monodentate ligands such as the halides, hydroxide, acetate, *etc.* as well as for sulphur-containing chelating agents.[5] With ligands containing either two nitrogen atoms or one nitrogen and one oxygen as bonding atoms, however, cadmium complexes are invariably less stable than those of zinc. This may represent a "like favours like" situation in which the large, more polarizable ("softer") cadmium ion forms more stable complexes with highly polarizable ("soft") sulphur-containing ligands.

Table 1. Formation constants of Cd, Zn, and Ni complexes at 25°C in 50% v/v aqueous dioxan medium at ionic strength 0·30*M*.

Reagent	p*K*	Cd	Zn*	Ni*
Diphenylthiocarbazone	5·80	7·11	6·18	5·83
Di(*o*)tolylthiocarbazone	6·23	5·95	4·50	5·90
Di(*o*)tolylthiocarbazone	6·40	7·40	6·45	6·60
Di(2,4-dimethylphenyl)thiocarbazone	6·87	6·19	4·80	6·40
Dinaphthylthiocarbazone	5·23	5·76	4·24	5·38

* Taken from reference 1.

A further comparison of the data in Table 1 reveals that cadmium is also significantly subject to the adverse sterically hindering influences but to a somewhat lesser extent than zinc, in keeping with expectations arising from its greater ionic radius. These results signify that the vicinal phenyl and chelate rings are coplanar in cadmium dithizonate but are forced out of plane in the presence of an *ortho* substituent on the phenyl rings. An X-ray crystallographic study would be useful in unequivocally solving this question.

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Summary—The stability constants of cadmium complexes of compounds related to dithizone are reported. Substitution in the *ortho* position lowers the stability constant. It is probable that this is a consequence of deviation from coplanarity of the phenyl and chelate rings.

Zusammenfassung—Die Stabilitätskonstanten von Cadmiumkomplexen mit Dithizon-ähnlichen Verbindungen werden behandelt. Bei *o*-substitution werden die Konstanten kleiner, vermutlich als Folge einer Abweichung in der Coplanarität von den Phenyl- und Chelatringen.

Résumé—On rapporte les constantes de stabilité de complexes du cadmium de composés se rattachant à la dithiozone. La substitution en position *ortho* abraisse la constante de stabilité. Il est probable que ceci est une conséquence de la déviation de la coplanéité des cycles phényle et chélate.

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GAS-CHROMATOGRAPHIC DETERMINATION OF SELENIUM AS AN ORGANO-SELENIUM COMPOUND WITH ACETOPHENONE

(*Received* 20 *February* 1974. *Accepted* 30 *March* 1974)

Recent developments in gas–liquid chromatography (GLC) have made it possible to work out methods of high sensitivity for the determination of selenium in natural and industrial products. They are based on the reaction between selenium(IV) and substituted diamines and detection of the product by electron-capture GLC.[1–5]

This paper describes a relatively rapid and universally applicable method based on a preliminary selective separation of the element in the form of an organo-selenium compound, followed by GLC determination. The extraction separation is performed according to our earlier work on the interaction between selenium(IV) and saturated aliphatic and aromatic ketones.[6–9] Acetophenone is used in the present work. In a strongly acidic solution selenium(IV) reacts with acetophenone stepwise by forming various compounds differing in their composition and properties. The optimum conditions for this reaction were found, under which a compound of suitable volatility and thermal stability for GLC determination was obtained.

EXPERIMENTAL

Reagents

Standard selenium solution (1000 μg/ml) was prepared by dissolving 1 g of pure selenium in minimum volume of nitric acid, evaporating the solution to dryness on a water-bath, taking up the residue with hydrochloric acid and diluting to 1 litre. Other solutions were prepared by appropriate dilution.

Concentrated hydrochloric, nitric, phosphoric, sulphuric and perchloric acids were all analytical grade (Merck).

Benzene and hexane were purified by rectification. Acetophenone was redistilled in vacuum.

Aluminium oxide (neutral) was heated for 4 hr at 450° and deactivated by addition of 3% of water.

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Aluminium oxide (neutral) was heated for 4 hr at 450° and deactivated by addition of 3% of water.

Sample preparation

The samples of metals, alloys, minerals, ore concentrates, soils and biological materials are dissolved by heating up to 1 g of sample (depending on the Se content) in 7 ml of perchloric acid and 3 ml of sulphuric, phosphoric or nitric acid, depending on the nature of the sample. Perchloric acid converts selenium into selenium(VI), thus preventing possible losses due to volatilization. Smith's work on perchloric acid should be consulted before organic samples are treated (see, *e.g.*, reference 10).

Apparatus

A Varian Aerograph Model 2100-40 gas chromatograph connected to a Model 20-2 recorder with a disc integrator was used. The chromatograph was equipped with a ^{63}Ni electron-capture detector. The column (U-type, 1·8 m length and 3 mm bore, was packed with 3% SE on Varaport 30,100–120 mesh. Temperatures used were: detector 290°, injection port 240° and column 215°. The carrier-gas (nitrogen) flow-rate was 100 ml/min. The sensitivity setting (attenuation) was 4.

Extractive separation of selenium

The formation of the organo-selenium compound takes place in strongly acidic medium. In our previous work[11] we have found that perchloric, phosphoric and sulphuric acids facilitate the reaction, probably by their dehydrating action. Nitric acid interferes even when present in traces. After complete dissolution of the sample, 10 ml of 8–9*M* hydrochloric acid are added to reduce selenium(VI) to selenium(IV) and then 0·025 ml of acetophenone are added. The mixture is heated for 40–60 min on a water-bath at 70–80°. It is then cooled, and then shaken with two 3-ml portions of benzene. The combined benzene extracts are then evaporated to 0·5–1·0 ml.

For selenium concentrations close to the detection limit of the method, separation of the organo-selenium compound from acetophenone and its by-products is recommended. For this purpose the benzene extract is evaporated to 1 ml and run through a column of 1 g of alumina in a glass tube (5–7 mm bore). Acetophenone and its by-products are eluted with 20 ml of hexane, and the organo-selenium compound is eluted with 20 ml of benzene. The benzene eluate is evaporated to dryness by heating at 40° under reduced pressure. The residue is dissolved in 0·5–1·0 of benzene and 3–7 μl of the solution are injected into the gas chromatograph.

Gas chromatograph determination

Figure 1 shows gas-chromatograms of a 3-μg/ml selenium solution with and without purification. In each case 5 μl were injected. As the sensitivity of the electron-capture detector may change with time, a comparison method was chosen, a 0·2-μg/ml benzene solution of *p,p'*-dichlorodiphenylchloroethylene (*pp'*DDE) being used as a reference substance.

The calibration curve plotted in terms of the ratio of the area of the Se peak (*S*) to the height of the *pp'*DDE peak (*h*) *vs.* selenium concentration is almost linear for the range 0·5–10 μg of Se. The relative standard deviation for the average value (5 μg) is ±6% (8 variates, 95% probability).

Applications

The influence of many interfering elements which might be present together with selenium in different samples has been studied. The concentration levels of these elements were selected in accordance with the expected values

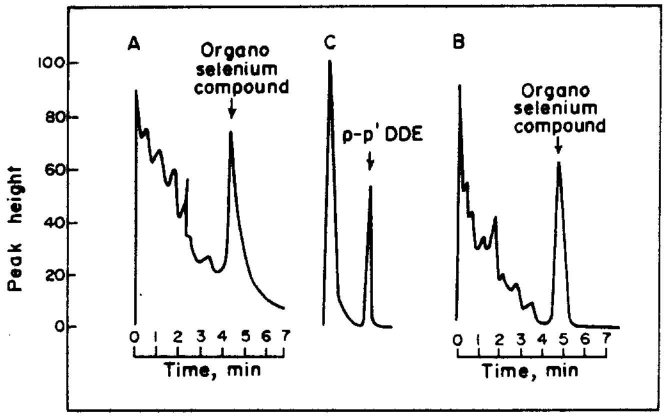

Fig. 1. Chromatograms of ·5 μl of organo-selenium compound (Se concentration in benzene, 3 μg/ml). (*A*)—Without purification; (*B*)—after purification on alumina column; (*C*)—reference substance *pp'*DDE, 5 μl, 0·02 μg/ml.

in the corresponding samples. No interference was found from 1 g of Fe, Cu, Pb; 0·5 g of Te; 5 mg of Ag, Au, As, Al, Bi, Cd, Co, In, Mn, Ni, Sn, Sb, Tl, W, Zr.

The method has been applied to the determination of selenium in metals, ore concentrates and biological samples.

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Summary—A gas-chromatographic method with electron-capture detection is presented for the determination of selenium after reaction with acetophenone to obtain an organo-selenium compound. This compound is extracted into benzene and chromatographed on an alumina column. The relative standard deviation for the average value (5 μg) is ±6% ($n = 8$, $P = 95\%$). The method has been applied to the determination of selenium in metals, alloys, ores and biological samples.

Zusammenfassung—Ein gaschromatographisches Verfahren mit Elektroneneinfang-Nachweis zur Bestimmung von Selen nach Reaktion mit Acetophenon zu einer Organoselenverbindung wird angegeben. Die Organoselenverbindung wird in Benzol extrahiert und auf einer Aluminiumoxidsäule chromatographiert. Die relative Standardabweichung des Mittelwerts (5 μg) beträgt ±6% ($n = 8$, $p = 95\%$). Das Verfahren wurde auf die Bestimmung von Selen in Metallen, Legierungen, Erzen und biologischen Proben angewandt.

Résumé—On présente une méthode chromatographique en phase vapeur avec détection par capture d'électrons pour le dosage du sélénium après réaction avec l'acétophénone pour obtenir un composé organo-sélénié. Ce composé est extrait en benzène et chromatographié sur une colonne d'alumine. L'écart type relatif pour la valeur moyenne (5 μg) est ±6% ($n = 8$, $P = 95\%$). On a appliqué la méthode au dosage du sélénium dans des métaux, alliages, minerais et échantillons biologiques.

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ON THE PROPERTIES OF CALCEIN BLUE

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Summary—A satisfactory method for the preparation of Calcein Blue has been devised. Elemental analysis, equivalent weight by neutralization, and the NMR spectrum show the compound to be 4-methylumbelliferone-8-methyleneiminodiacetic acid·0·25H_2O. The ultraviolet absorbance and fluorescence have been studied as a function of pH and, combined with potentiometric titration and solubility date, have yielded for the acid dissociation constants the values $pK_1 = 3{\cdot}0$, $pK_2 = 6{\cdot}9$, and $pK_3 = 11{\cdot}3$. These acid functions are identified respectively as carboxyl, phenol, and ammonium ion, the free Calcein Blue being a zwitter-ion. Calcein Blue fluoresces in both acidic and basic solution when excited at a suitable wavelength. The fluorescence of the doubly-charged anion formed on the neutralization of the phenol group, when excited at 360 nm, reaches a maximum at pH 9, and decreases to zero with the neutralization of the ammonium ion; the wavelength of maximum emission is 455 nm. In the presence of calcium, the fluorescence increases with alkalinity up to pH 9 and then remains constant. The calcium derivative is a 1:1 compound, formation constant 10^{-1}. The fluorescence of Calcein Blue at all pH values is quenched by copper(II). The calcium derivative is changed on standing in highly alkaline solution, presumably by ring opening, to another fluorescent material; thus Calcein Blue, although satisfactory as an indicator, is not useful for the direct fluorometric determination of calcium.

A metallofluorescent indicator produced by the condensation of 4-methylumbelliferone, formaldehyde and iminodiacetic acid was prepared independently and concurrently by Wilkins[1] and Eggers,[2] who assigned to it, respectively, the names Calcein Blue and Umbellikomplexon ("UK"). Wilkins[1] reported that the material was useful as an indicator in the EDTA titration of calcium and certain transition elements, and Eggers examined the absorption and fluorescence spectra in the presence of some fifteen metal ions. Papers appeared later describing uses of the compound in the determination of various metals.[3–5] To supplement these papers we now supply certain basic information: purity, composition, structure, properties as an acid, fluorescence as a function of pH, nature of the reaction with calcium, possible use for the direct fluorometric determination of calcium.

EXPERIMENTAL

Synthesis

Attempts to introduce methyleneiminodiacetic acid groups into 4-methylumbelliferone by the Mannich condensation in alkaline aqueous solution as used in the synthesis of Calcein[6] met with varying success; acetic acid, adopted in later work on Calcein,[7] proved a more satisfactory medium. The optimum ratio of 4-methylumbelliferone to disodium iminodiacetate to formaldehyde was found to be 2:3:3.

4-Methylumbelliferone. 4-Methylumbelliferone was synthesized[8] and recrystallized twice by dissolving it in warm 95% ethanol and precipitating by the addition of demineralized water. The product was dried under a heat lamp. M.p. 189–192°, literature value 186–188°.

Calcein Blue. To 140 ml of glacial acetic acid at 70° was added with constant stirring 0·12 mole (21·25 g) of disodium iminodiacetate. To this mixture was added 0·3 mole (5·29 g) of 4-methylumbelliferone. This was followed by the dropwise addition of 0·13 mole (11·8 ml) of 37% formaldehyde. The reaction was allowed to proceed at 65–75° for 8 hr with constant stirring. The white crystalline product was filtered off, washed with demineralized water, and recrystallized by dissolving it in demineralized water and enough 30% potassium hydroxide solution to raise the pH to 6·7, filtering, adding to 175 ml of hydrochloric acid (1 + 5) and adjusting the pH to 4 by dropwise addition of potassium hydroxide solution. The precipitate was filtered off, washed with demineralized water, and recrystallized again in the same manner. The material did not melt below 300°. Equivalent weight by neutralization: 323·3 (to the first equivalence-point); 324·8 (from the first to the second equivalence-point). Found: C 55·4%, H 5·1%, N 4·5%; calculated for $C_{15}H_{15}NO_7$ (m.w. 321·3): C 56·07%, H 4·71%, N 4·36%; calculated for $C_{15}H_{15}NO_7 \cdot 1/4H_2O$ (m.w. 325·8): C 55·29%, H 4·79%, N 4·29%.

4-Methylumbelliferone. Singlet at 2·00 ppm (3), $—CH_3$ at position 4; singlet at 5·46 ppm (1), position 3; doublet centred at 6·16 ppm (1) with proton spin coupling constant (J) of 2 c.p.s. (*meta* coupling), position 8; AMX pattern of two doublets centred at 6·41 and 6·97 ppm, respectively, (one proton for each doublet), J = 9 c.p.s. (*ortho* coupling), both peaks of the doublet centred at 6·41 ppm being further split into doublets centred at 6·34 and 6·47 ppm, respectively, J = 2·5 c.p.s. (*meta* coupling with proton at position 8), assignments: 6·41 ppm to position 6, 6·97 ppm to position 5.

Calcein Blue. Singlet at 2·27 ppm (3), $—CH_3$ at position 4; singlet at 3·79 ppm (4), $—N(CH_2CO_2^-)_2$; singlet at 4·41 ppm (2), $—N—CH_2—$aryl; singlet at 5·92 ppm (1), position 3; AB pattern of two doublets centred at 6·75 and 7·41 ppm, respectively, (each doublet 1 proton), J = 9 c.p.s. (*ortho* coupling); assignment: peak at 6·75 ppm to position 6, peak at 7·41 ppm to position 5 (based on similarity to NMR spectra of 4-methylumbelliferone, esculetin and 4-methylescutin). The peak at 6·16 ppm in the NMR spectrum of 4-methylumbelliferone is missing in Calcein Blue; the two protons attached to the aromatic ring are *ortho* to each other; the methyleneiminodiacetic acid group in Calcein Blue thus occupies position 8.

Behaviour on neutralization

As shown in Fig. 1, two breaks were found in the neutralization curve of Calcein Blue. The Calcein Blue did not dissolve completely until close to the first end-point, so the mid-point of the first step, pH = 4·64, cannot be taken as the value of the first acid dissociation constant. The pH at the mid-point of the second step is probably a good value for the second dissociation constant $pK_2 = pH_{a=1 \cdot 50} = 7 \cdot 00$ (a being the number of moles of alkali added per mole of Calcein Blue).

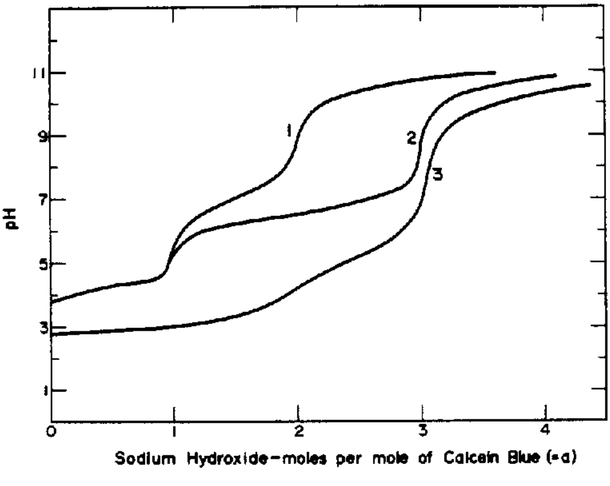


Fig. 1. Titration of Calcein Blue alone and in the presence of calcium and of copper.
1. Calcein Blue; 2. Calcein Blue plus 10 moles of calcium per mole of Calcein Blue; 3. Calcein Blue plus an equimolar amount of copper(II); solvent: 200 ml of 0·1M potassium chloride; initial concentration of Calcein Blue: $1 \cdot 07 \times 10^{-3}M$.

First acid dissociation constant from solubility data. Buffers of appropriate pH and excess of Calcein Blue were shaken for 12 hr. The mixtures were then filtered and appropriate volumes of the filtrates were adjusted to pH 10 and diluted to 25·0 ml in volumetric flasks with 0·1M potassium chloride. Absorbances were measured at 360 nm (Beckman DU spectrophotometer). The results, Table 1, were treated by the method of Krebs and Speakman.[9] The value found for the intrinsic solubility, S_i, from the linear plot of S *vs.* $1/[H^+]$ by extrapolation to $1/[H^+] = 0$, was 1·00 mg/100 ml. The value for the first acid dissociation constant, found from the linear plot of $\log [(S/S_i) - 1]$ *vs.* pH, was $pK_1 = 2 \cdot 97$.

Table 1. Solubility of Calcein Blue as a function of pH

pH	2·36	2·80	3·39	4·45	4·65	4·74
Solubility, *S*, *mg*/100 *ml*	1·20	1·71	3·77	32·37	48·19	59·44

Second acid dissociation constant, from absorbance data. The absorption spectra of 4-methylumbelliferone and of Calcein Blue, Fig. 2, each show a single band in the ultraviolet, the maxima being at almost the same wavelength, shifting to longer wavelength with rising pH: λ_{max} 320 and 322 nm at pH 4 and 360 and 370 nm at pH 10 for 4-methylumbelliferone and Calcein Blue respectively. Only one inflection point was found in the plot of absorbance as a function of pH, Fig. 3. The inflection points lie at pH 7·8 and 7·1, respectively, fair approximations to pK for 4-methylumbelliferone and pK_2 for Calcein Blue respectively.

More precise absorbance measurements were made on solutions at pH values equal to the estimated pK ± 0·2, 0·4 and 0·6 pH units. The results were used to plot $pK = pH - \log(A - A_{HA})/(A_A - A)$, where A, A_{HA} and A_A are the absorbances of a mixture, and of the pure acid form and salt form respectively. The values obtained were 7·82 for 4-methylumbelliferone and 6·92 for Calcein Blue.

Third acid dissociation constant, from fluorescence data. The excitation and emission spectra of 4-methylumbelliferone and of Calcein Blue were obtained at intervals of 0·5 pH over the range 1·5–13·0 by using an Aminco-Bowman Spectrophotofluorimeter. The solutions were prepared by mixing 15 μl of $3{\cdot}11 \times 10^{-3}M$ Calcein Blue, 0·25 ml of 0·01M EDTA, 10 ml of buffer solution (prepared according to Bates[10] and of constant ionic strength), and diluting to 25·0 ml with 0·1M potassium chloride. The pH of each solution was checked after the spectra had been obtained. The spectra at pH 4 and 10 are shown in Fig. 4 and relative fluorescence as a function of pH is shown in Fig. 5.

The maxima in the excitation spectra of 4-methylumbelliferone and of Calcein Blue, Fig. 4, coincide with those in the absorption spectra and like them shift to longer wavelengths with increasing pH. The wavelength of maximum emission is independent of the wavelength of the exciting light, although the change in relative intensity with change in pH parallels the change in absorbance at any excitation wavelengths.

	Wavelength of maximum excitation, *nm*		Wavelength of maximum emission, *nm*
	pH 4·0	pH 10·0	
4-Methylumbelliferone	328	365	455
Calcein Blue	330	360	455

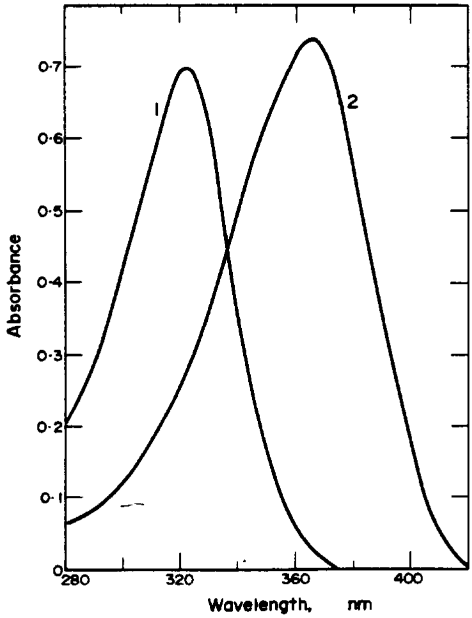


Fig. 2. Absorption spectra of Calcein Blue.
1. At pH 4; 2. at pH 9; the absorption spectra of 4-methylumbelliferone are very similar.

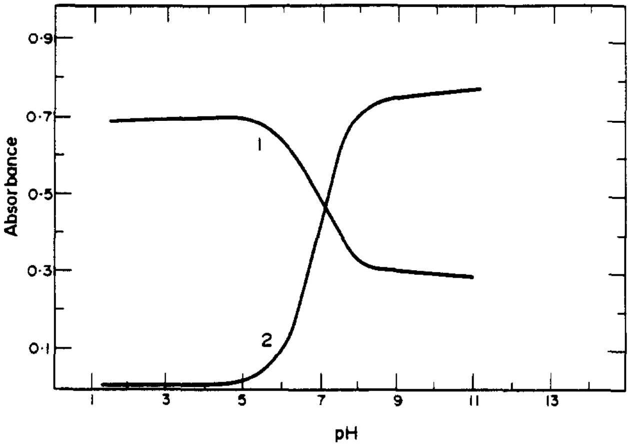


Fig. 3. Absorbance of Calcein Blue as a function of pH.
1. At 325 nm; 2. at 367 nm; the absorbance of 4-methylumbelliferone as a function of pH is very similar; Calcein Blue (4·67 × $10^{-5}M$) in $10^{-4}M$ EDTA/0·06M potassium chloride.

The main difference between the two compounds is the maximum at pH 9·1 for the effect of pH on the fluorescence of Calcein Blue.

The points of inflection of the curves (shown in Fig. 5 for Calcein Blue only) were taken as values for the acid dissociation constants: for 4-methylumbelliferone $pK = 7·78$; for Calcein Blue $pK_2 = 6·95$, $pK_3 = 11·26$. The values of pK and pK_2 are close to those obtained by measurements of absorbance as a function of pH. but the latter are probably better.

Calcein Blue is undoubtedly a zwitter-ion and the first step in titrating it with alkali is the neutralization of the free carboxyl group. No change in absorbance in the ultraviolet occurs during this step. up to pH 5·5, as expected of aliphatic carboxyl groups.

Changes in the absorption in the ultraviolet, in the region of absorption by benzenoid compounds, occurs over the second step, pH 5·5–8·5 and this results from neutralization of the phenol group. The ultraviolet absorption and the changes in absorption with pH of 4-methylumbelliferone and of Calcein Blue are almost identical, the phenol group of Calcein Blue being slightly stronger as an acid.

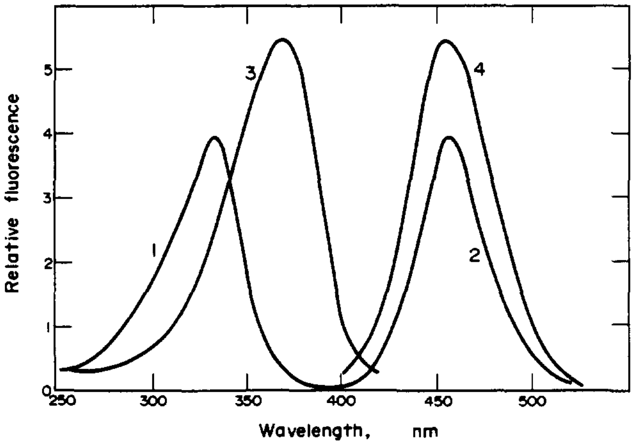


Fig. 4. Fluorescence spectra of Calcein Blue.
1. Excitation, pH 4, emission monochromator set at 455 nm. 2. Emission, pH 4, excitation monochromator set at 330 nm. 3. Excitation, pH 10, emission monochromator set at 455 nm. 4. Emission, pH 10, excitation monochromator set at 360 nm. The fluorescence spectra of 4-methylumbelliferone are very similar.

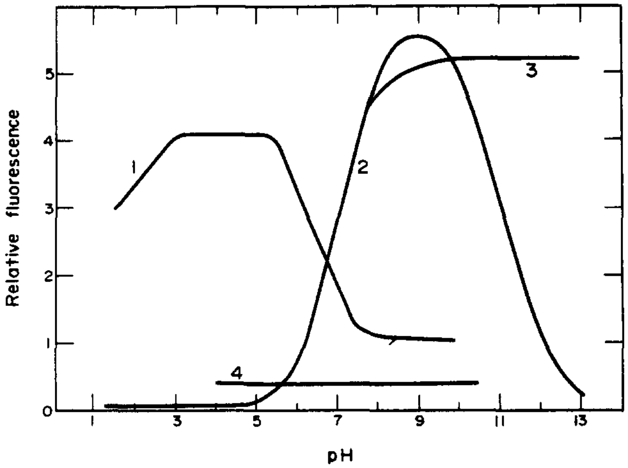


Fig. 5. Variation in fluorescence of Calcein Blue and of the calcium and copper derivatives of Calcein Blue with pH.

1. Calcein Blue, excitation monochromator set at 330 nm. 2. Calcein Blue, excitation monochromator set at 360 nm. 3. Calcium derivative, excitation monochromator set at 360 nm. 4. Copper derivative, excitation monochromator set at 330 nm below pH 6·5, at 360 nm above pH 6·5. Variation in fluorescence of 4-methylumbelliferone with pH is similar to curves 1 and 3.

Both 4-methylumbelliferone and Calcein Blue fluoresce in acidic and basic media if excited with light of the proper wavelength. For the unneutralized acid form of 4-methylumbelliferone and for the dicarboxylate anion of Calcein Blue ($a = 1{\cdot}00$), the maximum excitation occurs at 328 and 330 nm, respectively, close to the absorption maxima, 320 and 325 nm. For the basic forms, following neutralization of the phenol group, maximum excitation occurs at 365 and 360 nm respectively, close to the absorption maxima, 360 and 367 nm of the anions.

The fluorescence of 4-methylumbelliferone remains constant at pH > 9 but that of Calcein Blue decreases, becoming essentially zero at pH 13 (Fig. 5), the change in Calcein Blue corresponding to the neutralization of the betaine. As expected, no change in absorbance in the ultraviolet occurs over this region, because the ammonium group absorbs only at wavelengths shorter than 200 nm and in Calcein Blue the ammonium nitrogen atom is not connected directly to the aromatic ring. The fluorescence results thus gave a value for the third dissociation constant.

Reaction with calcium

Whereas the fluorescence of Calcein Blue decreases from the maximum at pH 9 to almost zero at pH 13, in the presence of an excess of calcium the fluorescence is maintained from pH 9 to 13 (Fig. 5, curve 3). At pH 12·8, the fluorescence intensity increases linearly with calcium concentration, the break in this function indicating a combining ratio of 1:1. In the potentiometric titration of Calcein Blue with alkali in the presence of calcium (Fig. 1, curve 2), the curve coincides with that of Calcein Blue to the first end-point ($a = 1$; pH 5·3). At pH > 5·3 the reaction with calcium makes the acid appear to be much stronger and a new end-point appears after two additional equivalents of base have been added. It is evident that a proton is displaced from the phenol group and another from the ammonium group by calcium and the molecule retains the structure that gives rise to the fluorescence.

The formation constant of the calcium derivative was calculated in two ways, by an approximation method and by an exact method. The symbol H_3Cb is adopted for Calcein Blue, the acid dissociation constants, K_1, K_2, K_3, are defined in the usual way, and two formation constants are defined by

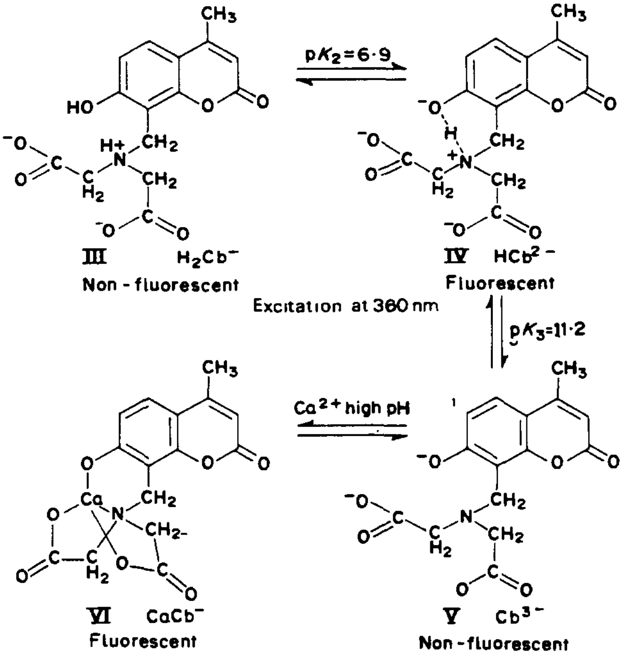
$$\mathrm{HCb^{2-} + Ca^{2+} = CaHCb} \qquad K_{\mathrm{CaHCb}} = [\mathrm{CaHCb}]/[\mathrm{HCb^{2-}}][\mathrm{Ca^{2+}}]. \tag{1}$$

$$\mathrm{Cb^{3-} + Ca^{2+} = CaCb^-} \qquad K_{\mathrm{CaCb^-}} = [\mathrm{CaCb^-}]/[\mathrm{Cb^{3-}}][\mathrm{Ca^{2+}}]. \tag{2}$$

Approximation method. Combination of the equations defining the acid dissociation constants and equation (2) gives

$$K_{\mathrm{CaCb^-}} = [\mathrm{CaCb^-}][\mathrm{H^+}]^2/K_2K_3[\mathrm{Ca^{2+}}][\mathrm{H_2Cb^-}]. \tag{3}$$

Calcein Blue. 4-Methylumbelliferone-8-methyleneiminodiacetic acid. H_3B



DISCUSSION

Structure of the calcium derivative

As with ethylenediaminetetra-acetic acid and related compounds, the positive charge on the ammonium group in Calcein Blue explains the strongly acid character ($pK_1 = 2{\cdot}97$) of the remaining free carboxyl group. Similarly, the unusual strength of the phenol group ($pK_2 = 6{\cdot}9$) is also attributed to the proximity of this group to the positive charge, which is absent in 4-methylumbelliferone ($pK = 7{\cdot}8$).

For both 4-methylumbelliferone and Calcein Blue, neutralization of the phenol group is accompanied by the appearance of fluorescence on excitation by light of the wavelength of the absorption maximum of the phenolate form (structures II and IV), 365 and 360 nm, respectively. Although the absorbance and fluorescence and the variations of these with pH up to pH 8·5 are very close, some difference may exist in the structure of the fluorescent forms, in particular the existence in Calcein Blue of a hydrogen bond between the phenolate oxygen atom and the ammonium nitrogen atom. Formation of this bond would restrict the free rotation about the methylene group and reduce the chance for non-radiative transfer of energy from the excited state; conversely, above pH 9, as the hydrogen bond is broken by the neutralization of the ammonium group, the fluorescence decreases because of the increased rotation and frequency of inter- and intramolecular collision (structure V).

The two protons displaced in the formation of the calcium compound must come from the phenolic and ammonium groups. Because the calcium compound is highly fluorescent and the fluorescence is of about the same intensity as that of Calcein Blue at pH 9, the calcium in effect gives the Calcein Blue the structure corresponding to the conditions of

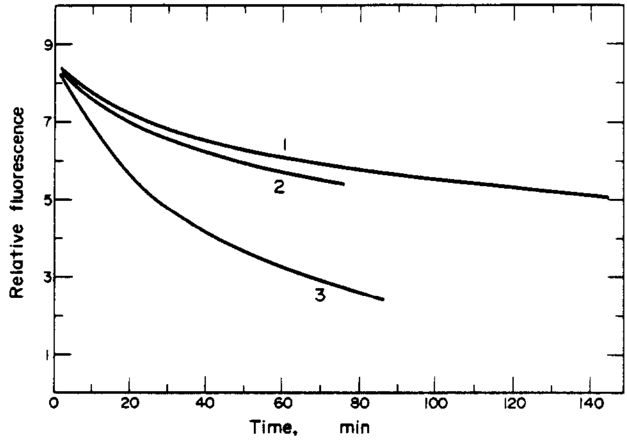


Fig. 6. Stability of the calcium derivative of Calcein Blue.
1. At pH 12·8; 2. at pH 12·9; 3. at pH 13·0.

maximum fluorescence at pH 9. The phenolate oxygen atom, ammonium nitrogen atom, and probably both carboxylate oxygen atoms are bound to the calcium ion (structure VI). Everything is tight-packed, rotation is restricted and the possibility of collisional deactivation reduced.

Because of the low solubility of Calcein Blue some of it remains undissolved almost to the first end-point in the titration with alkali. On the addition of an equimolar amount of copper(II), Calcein Blue is completely dissolved and the pH at the mid-point of the neutralization of the first proton, $pH_{a=0\cdot 50} = 2\cdot 82$, is slightly lower than pK_1 (2·97).

The relation of the fluorescence to the structure of Calcein Blue and its metal derivatives was the subject of a debate between Wilkins[16] and Körbl and Svoboda.[17] Our interpretation of the fluorescence of Calcein Blue is at odds with the concepts both of Wilkins and of Körbl and Svoboda.

Stability and use in the EDTA titration of calcium

The fluorescence of 4-methylumbelliferone decreases when a highly alkaline solution of the compound stands for some time, presumably because the pyrone ring opens. The resulting hydroxycoumarinic acid is fluorescent. A similar phenomenon occurs with Calcein Blue, Fig. 6. Neutral solutions of Calcein Blue are stable and satisfactory for the storage of reagent. In highly alkaline solution the calcium derivative is stable for only 1 hr but this is sufficient for use as indicator in the EDTA titration of calcium.

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Résumé—On a élaboré une méthode satisfaisante pour la préparation du Bleu Calcéine. L'analyse élémentaire, le poids équivalent par neutralisation et le spectre RMN montrent que le composé est l'acide 4-méthylombelliférone 8-méthylèneiminodiacétique, 1/4 H_2O. On a étudié l'absorption ultraviolette et la fluorescence en fonction du pH et, combinées avec le titrage potentiométrique et les données de solubilité, elles ont donné pour les constantes de dissociation acide les valeur $pK_1 = 3{,}0$; $pK_2 = 6{,}9$ et $pK_3 = 11{,}3$. Ces fonctions acides sont identifiées respectivement comme étant un carboxyle, un phénol, et un ion ammonium, le Bleu Calcéine libre étant un zwitterion. Le Bleu Calcéine est fluorescent en solution tant acide que basique. La fluorescence de l'anion doublement chargé formé par neutralisation du groupe phénolique, lorsqu'elle est excitée à 360 nm, atteint un maximum à pH 9, et décroît à zéro avec la neutralisation de l'ion ammonium; la longueur d'onde du maximum d'émission est 455 nm. En la présence de calcium, la fluorescence croît avec l'alcalinité jusqu'à pH 9 puis reste constante. Le dérivé du calcium est un composé 1 : 1, constante de formation $10^{7,1}$. La fluorescence du Bleu Calcéine à toutes les valeurs du pH est éteinte par le cuirvre (II). Le dérivé du calcium est converti par repos en solution fortement alcaline, probablement par ouverture de cycle, en une autre substance fluorescente; ainsi le Bleu Calcéine, quoique satisfaisant comme indicateur, n'est pas utile pour le dosage fluorimétrique direct du calcium.

Zusammenfassung—Ein zufriedenstellendes Verfahren zur Herstellung von Calceinblau wurde entworfen. Elementaranalyse, durch Neutralisation bestimmtes Äquivalentgewicht und NMR-Spektrum weisen die Verbindung als 4-Methylumbelliferon-8-methyleniminodiessigsaure · 1/4 H_2O aus. Ultraviolettabsorption und Fluoreszenz wurden in Abhängigkeit vom pH untersucht und ergaben zusammen mit potentiometrischen Titrationen und Löslichkeitsdaten die Säuredissoziationskonstanten $pK_1 = 3{,}0$, $pK_2 = 6{,}9$ und $pK_3 = 11.3$. Die sauren Funktionen sind eine Carboxylgruppe, eine phenolische Hydroxylgruppe und ein Ammoniumion; freies Calceinblau ist ein Zwitterion. Calceinblau fluoresziert sowohl in saurer als auch in alkalischer Lösung. Die Fluoreszenz des durch Neutralisation der Phenolgruppe gebildeten zweifach geladenen Anions erreicht unter Anregung bei 360 nm ihr Maximum bei pH 9 und fällt bei Neutralisation des Ammoniumions auf Null ab; die Wellenlänge des Emissionsmaximums ist 455 nm. In Gegenwart von Calcium steigt die Fluoreszenz bis pH 9 mit steigendem Alkalinitätsgrad an und bleibt dann konstant. Das Calciumderivat ist eine 1:1-Verbindung mit der Bildungskonstante $10^{7.1}$. Die Fluoreszenz von Calceinblau wird bei allen pH-Werten durch Kupfer(II) gelöscht. Das Calciumderivat wandeltesichbeim stehen in stark alkalischer Lösung, vermutlich durch Ringoffnung, in einen anderen fluoreszierenden Stoff um; demnach ist Calceinblau, obgleich es als Indikator zufriedenstellt, zur direkten fluorometrischen Calciumbestimmung nicht brauchbar.

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PLUTONIUM AND URANIUM DETERMINATION IN ENVIRONMENTAL SAMPLES: COMBINED SOLVENT EXTRACTION–LIQUID SCINTILLATION METHOD

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Summary—A method for the determination of uranium and plutonium by a combined high-resolution liquid scintillation–solvent extraction method is presented. Assuming a sample count equal to background count to be the detection limit, the lower detection limit for these and other alpha-emitting nuclides is 1·0 dpm with a Pyrex sample tube, 0·3 dpm with a quartz sample tube using present detector shielding or 0·02 d.p.m. with pulse-shape discrimination. Alpha-counting efficiency is 100%. With the counting data presented as an alpha-energy spectrum, an energy resolution of 0·2–0·3 MeV peak half-width and an energy identification to ±0·1 MeV are possible. Thus, within these limits, identification and quantitative determination of a specific alpha-emitter, independent of chemical separation, are possible. The separation procedure allows greater than 98% recovery of uranium and plutonium from solution samples containing large amounts of iron and other interfering substances. In most cases uranium, even when present in 10^8-fold molar ratio, may be quantitatively separated from plutonium without loss of the plutonium. Potential applications of this general analytical concept to other alpha-counting problems are noted. Special problems associated with the determination of plutonium in soil and water samples are discussed. Results of tests to determine the pulse-height and energy-resolution characteristics of several scintillators are presented. Construction of the high-resolution liquid scintillation detector is described.

The problem of analysing for plutonium or other alpha-emitting nuclides at low levels in samples containing many interfering substances is severe. The methods most commonly used usually involve a sample dissolution step followed by ion-exchange separation of the plutonium, electroplating of the plutonium on a metal planchette and counting. The time required for ion-exchange and plating usually amounts to about 10 hr and sometimes approaches 16 hr. Counting may be accomplished by the use of a zinc sulphide scintillation foil,[1] a surface barrier detector or a Frisch grid detector.[2] Frisch grid detectors and the zinc sulphide foil may have a counting efficiency as high as 45% while surface barrier detectors are usually limited to a 30% efficiency. Zinc sulphide screens have no energy-resolution ability, necessitating complete reliance on the chemical separation for assurance of the identity of the nuclide being counted. The energy resolution of surface barrier and Frisch grid detectors varies from about 15 to about 200 keV FWHM†, depending on how they are constructed and used. In the case of surface barrier detectors, energy resolution must be sacrificed to obtain counting efficiency so that, with the highest efficiency (~30%), the resolution is typically 100–200 keV FWHM. With proper construction a Frisch grid detector will give both a high resolution (20–50 keV) and a counting efficiency of 30–40%; however, construction, operation, and maintenance are difficult.

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† FWHM = full peak width at half maximum peak height.

In the determination of low-level alpha-emitting nuclides, particularly plutonium, energy discrimination is desirable since the multitude of oxidation states and complex forms in which plutonium and uranium can exist makes effective chemical separation of these elements from each other and from other alpha-emitting nuclides less than 100% reliable from sample to sample. For example, it is known that the behaviour of plutonium is affected by previous sample history.[3,4]

The ideal low-level plutonium-determination method would be simple, rapid, and more reliable than existing methods and would allow for some alpha-energy discrimination. Our present work indicates that a method that combines solvent extraction and high-resolution liquid scintillation would meet these requirements. Beginning with a sample in solution, only two extractions, one stripping step, and one volume reduction are required to obtain the sample in a form ready to count. The time required for this is about 40–60 min as compared to 10–16 hr for ion-exchange and electroplating. Counting requires simple equipment, is 100% efficient for alpha particles, has low background and can give an energy resolution of 200–300 keV FWHM.

Liquid scintillation has previously been used for alpha-counting[5–14] and also for counting plutonium in environmental samples.[10–14] However, no methods reported to date (except one[11]) have combined a high-resolution liquid scintillation method that allows identification of alpha-energies, with a solvent extraction procedure that separates interfering and quenching ions and places the nuclides of interest in a scintillator.

EXPERIMENTAL

Apparatus

A diagram of the phototube and reflector arrangement may be seen in Fig. 1. The reflector surface was of diffuse white, highly reflective material. Of the reflective coatings tried, Eastman white reflectance paint and magnesium oxide bonded with dilute sodium silicate appeared best. In order to reduce light loss by internal reflection at interfaces between materials with different refractive indices, the cavity between the face of the phototube and the reflective surface was filled with Dow-Corning "200" silicone oil. A 10 mm O.D. Pyrex or quartz tube containing 0·5–1·5 ml of sample-containing scintillator was immersed in this oil between reflector and phototube for counting. Tests made with various reflectors, sample containers, and sample volumes are discussed later.

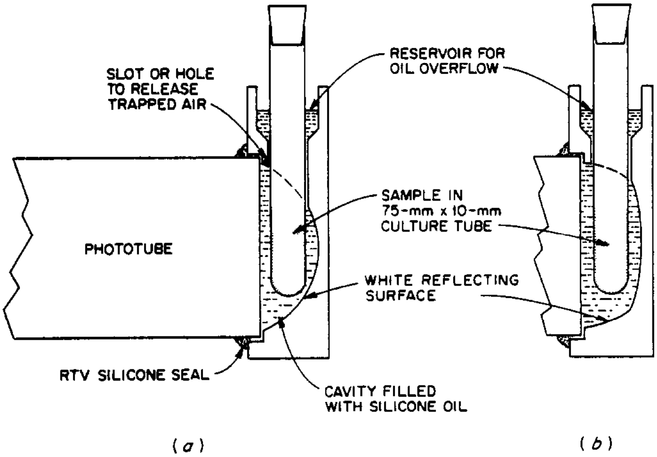

Fig. 1. Sample in holder-reflector on phototube.

The detector assembly was enclosed within a light-tight enclosure with interlock switches that turned off the phototube high-voltage supply before the enclosure could be opened. A 3 in. lead shield helped reduce background from external radiation.

A low-noise preamplifier (ORTEC Model 113) and a linear amplifier (Tennelec TC-202) were used to feed the signal to a 400 channel analyser (Packard Model 116).

The pulse-shape discrimination equipment consisted of an ORTEC Model 437A time-to-pulse-height converter, an ORTEC Model 260 time pick-off with a Model 403A control, an ORTEC Model 455 timing SCA, an ORTEC Model 416A logic shaper and delay and a Tennelec TC 215 delay amplifier. The use of this equipment is described elsewhere.[15]

Reagents

Two organic extractants were used: a tertiary amine nitrate ($TANO_3$), and di(2-ethylhexyl)phosphoric acid (HDEHP) Any of several aliphatic tertiary amines in which the smallest radical is octyl is probably suitable. Several tertiary amines have been shown to be good extractants for Pu(IV).[16]

Purified tri-n-octyl amine (Eastman) and a similar proprietary product Adogen 364 were used with equal success for extraction of Pu(IV) from the nitrate solution. A 0·3*M* solution of the amine in toluene was converted into the nitrate by contacting it with an equivalent amount of aqueous nitric acid. However, tertiary amines containing more than about 0·1% of primary or secondary amines should not be used. Both primary and secondary amines are known to react with the nitrous acid used in the procedure. Secondary amines react to produce dark, oily nitrosamines. A sample of tri-n-octylamine (Eastman practical) was found not suitable as received because of loss of up to 90% of the plutonium in a given sample and failure to separate uranium. The production of dark oily material was observed. Analysis showed the amine to contain 5% of secondary and 1% of primary amine. It is believed that the presence of these primary and secondary amine impurities is responsible for the poor results obtained with this material.

The HDEHP was obtained from Union Carbide Chemicals Division. As received, it contained about 1% of impurities of an unknown nature, probably 2-ethylhexanol and other alcohols. For use in the extractive scintillator, the material was purified by converting a 0·5*M* solution in toluene into the sodium salt by contacting it with sodium hydroxide in saturated sodium sulphate solution. The NaDEHP solution was then washed with saturated sodium sulphate solution, followed by reconversion into the acid form (HDEHP) with dilute sulphuric acid. This reconverted HDEHP solution was subsequently washed several times with water and stored over granular, anhydrous sodium sulphate. It is important that no nitrates be contacted with the HDEHP solution in this procedure since traces of nitrate are extracted and cause discolouration of the scintillation solution and serious quenching.

The scintillator chosen for this work was 2-(4′-biphenylyl-6-phenylbenzoxazole) (PBBO). Some others, notably 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (butyl PBD), and 2-(1-naphthyl)-5-phenyloxazole (αNPO) gave results that were nearly as satisfactory. Data from comparative tests on a number of scintillators are presented later. The extractive scintillator solution was composed of PBBO 4 g/l., naphthalene 200 g/l. and HDEHP 64 g/l., in toluene.

The naphthalene used in this study was either Eastman "scintillator grade" or reagent-grade material that had been resublimed in our laboratory. Sublimation improved the effectiveness (in increasing pulse-height and resolution) of all the naphthalene we tried, even scintillation grade.

It is important that all the reagents used to make the scintillator solution be as free as possible from colour and impurities in order to obtain the maximum pulse-height and resolution.

The organic diluent, toluene, and the other chemicals used in this work were of reagent grade quality.

Procedure

Preparation of sample solution. The sample is brought into solution, by a suitable method, in 1–4*M* nitric acid or in 1*M* nitric acid that is 3–4*M* in nitrate salts. It is necessary that the plutonium be in solution in a nitrate medium of this concentration in order to obtain maximum extraction of Pu(IV) by the tertiary amine nitrate extractant.[17] Any procedure that will bring the sample into solution in this medium is acceptable. However, plutonium forms many complexes and in most natural environments also tends to form Pu(IV) polymers. These complexed and polymerized forms are difficult to dissolve. Satisfactory dissolution of the sample can be the most difficult part of this or any other scheme of analysis for plutonium. Recovery of uranium from similar samples will usually be less difficult.

Fluoride ion is often used to dissolve silicate and to catalyse the dissolution of plutonium oxides or hydroxides. Although low concentrations of fluoride (up to 0·005*M*) in the solutions from which plutonium is to be extracted by $TANO_3$ (see Table 2) do not appear to interfere with the extraction, larger ones do, and samples in which hydrofluoric acid was used to remove silicates typically gave plutonium recoveries of only 50–80%. Aluminium or zirconium nitrate added to such solutions complexes the fluoride and aids in plutonium recovery. Neither aluminium nor zirconium interferes or is extracted. Boric acid, which is sometimes added to complex fluoride in such systems,[1] did not seem to be as effective in our tests..

Small amounts of sulphate and phosphate did not interfere with plutonium recovery. The synthetic soil samples used were 0·003*M* in PO_4^{3-} and 0·0007*M* in SO_4^{2-}. However, phosphate above 0·02*M* does interfere in the amine nitrate extraction (Table 2), and mixtures of fluoride with phosphate interfere even at the phosphate levels expected from a 10 g soil sample. The presence of fluoride and phosphate, possibly as fluorophosphate, would be expected in soil samples leached with hydrofluoric acid or fused with potassium fluoride.

Large amounts of dissolved silicates sometimes lead to the formation of emulsions and the accumulation of solids at the organic–aqueous interface.[18] The severity of these problems appears to be related to some unknown factors in sample dissolution. For example, some real soil samples gave emulsion problems while others did not, but synthetic soil samples which contained as much dissolved silica or more never gave any emulsion problems.

Extraction with $TANO_3$. A 20–30 ml volume of sample in a nitrate solution to which 0·05–0·1 g of ferrous sulphate has been added, is warmed. A period of 5 min is allowed for reduction of Pu(V and VI) to Pu(III and IV). Then 1 g of sodium nitrite is added and the solution is stirred for 2–3 min to oxidize Pu(III) to Pu(IV). Finally the solution is cooled to room temperature or below.

The cooled sample solution is contacted with an equal volume of 0·3*M* $TANO_3$ in toluene for 1 min (but 1/5 of this volume is adequate). Moderate shaking by hand in a small separatory funnel for 1 min is sufficient to ensure complete equilibration. A longer period is not desirable since it increases the possibility of undesirable reactions between nitrous acid and amines. The volume ratio is not critical within the limits stated.

If uranium recovery is also desired, the aqueous phase should be contacted with three additional portions of $TANO_3$ (each equal in volume to the aqueous phase) and the organic extracts combined.

Separation of uranium and iron. The organic phase is contacted with three small volumes (1/4–1/3 of the organic phase volume) of 0·7*M* nitric acid. If uranium rejection is desired, the washes should be discarded. If uranium separation and recovery are desired, the washes should be combined and saved. Any insoluble material that accumulates at the interface, as with soil samples, should be retained with the organic phase; it may contain some plutonium.

It is possible to count both plutonium and uranium simultaneously and sum the counts separately for the separate peaks. If combined uranium and plutonium counting is desired, the combined organic extracts obtained as described above should be stripped with perchloric acid without being washed with 0·7*M* nitric acid.

In all these equilibrations, phase separation will be facilitated by the use of small pear-shaped separatory funnels with the standard stop-cock replaced with a 1·5–2·0-mm capillary stop-cock. Shaking by hand is to be preferred to mechanical shaking, for rapid phase disengagement.

Stripping the organic phase. The organic phase containing the plutonium and uranium is contacted with three small volumes (1/3–1/2 of the organic phase volume) of 2*M* perchloric acid.

In this step the amine nitrate is converted into the amine perchlorate, which is not an extractant for plutonium or uranium. The phases should be separated carefully to exclude any organic phase. If insoluble interfacial material is present, as in the case with some soil samples, the use of hot 2*M* perchloric acid will aid phase separation and improve plutonium recovery.

Fuming with perchloric acid. The perchloric acid solution is collected in a small beaker. 0·1–0·2 g of lithium chloride or lithium nitrate is added, and the solution is heated until all perchloric acid is removed and fused lithium perchlorate (m.p. 236°) remains.

The presence of lithium perchlorate allows all the perchloric acid to be removed without danger of baking the plutonium onto the beaker irreversibly. A small air-jet aids in removing the last perchloric acid fumes. It is desirable to add nitric acid before fuming, to aid in the smooth decomposition of traces of organic material. If the lithium perchlorate melt is not clean and colourless, the decomposition of organic material has not been completed, and additional nitric acid and perchloric acid should be added and the fuming step repeated.

Extraction with HDEHP in scintillator. After cooling, the fused lithium perchlorate is dissolved in 10 ml of a solution containing sodium peroxydisulphate ($Na_2S_2O_8$, 50 g/l.) and silver nitrate (10 mg/l.). The solution is warmed, then cooled to room temperature and extracted with a known volume of extractive scintillator, and an aliquot is taken for counting.

If the perchloric acid has been effectively removed by fuming, the pH of the aqueous solution will be about 2. If the pH is < 1, extraction may not be quantitative in a single contact. Adjustment of the pH with base is not recommended. Local precipitation of plutonium, without redissolution, is almost certain to occur. The extraction should be made in a small capillary-tipped separatory funnel. A 25 ml Friedman and LaMere weight-burette makes an excellent separatory funnel for this purpose. Moderate shaking by hand for no more than 1 min is recommended. Scintillator solutions shaken longer by hand or more vigorously by machine show some loss of ability to resolve alpha-energy. This may be due to oxidation of the scintillator.

If nearly complete recovery is important, three extractions are made, using 0·5 ml of extractive scintillator each time, and the extracts are combined. The total volume of scintillator recovered will be less than 1·5 ml (~1·4 ml) because of entrainment on the glassware, but the plutonium (or uranium) recovery will be >99%.

A second approach, which is somewhat simpler, faster, and more quantitative in instances where sufficient activity is present, is to add an accurately known volume of extractive scintillator (1·2–1·5 ml) and then pipette 1 ml for counting after equilibration. The total activity in the sample is then found by multiplying the volume of scintillator added (in ml) by the recorded count.

Counting. The scintillator solution containing the sample in a 10 mm O.D. Pyrex or quartz tube, is placed in the detector and counted for a period of time sufficient to obtain the desired statistical accuracy.

The use of high-resolution detector and multichannel analyser is recommended. The capability of this detector to distinguish energies often allows more than one nuclide to be counted simultaneously; and even if this is not the intent of the procedure, it renders it possible to determine whether the nuclide of interest, and only the nuclide of interest, is being counted.

Energy resolution may be improved by freezing, evacuation and refilling with argon or helium as described by Horrocks[7] or by the addition of an organic reducing agent, sodium bis(2-methoxyethoxy) aluminium hydride.

Background count in the region under the plutonium peak is normally about 1 c.p.m. when 3 in. of lead shielding is used with no special attention to the radioactive content of the detector components or sample tube. The use of a quartz rather than borosilicate glass sample tube reduces the background to 0·3 c.p.m., and the use of pulse-shape discrimination equipment gives backgrounds of 0·05–0·01 c.p.m.[15] If pulse-shape discrimination is to be used, the sample must be deoxygenated by 2 or 3 cycles of freezing, evacuation and refilling with helium or argon.

Analysis of spectrum. The counts under the desired peak are summed, and the background is subtracted to obtain the total count. Typical spectra from high and low count-rate samples may be seen in Figs. 2 and 3. If the sample contains a single nuclide with a disintegration rate of 100 d.p.m. or more, the background will be less than 1% of the total under the peak. With these conditions, a counting error of 1% or less may be obtained without subtraction of background if at least 10,000 counts are accumulated under the peak. With higher disintegration rates, the counting error will depend on the total number of counts accumulated.

A complex spectrum with overlapping peaks, or a spectrum from a sample of low count-rate where background becomes an appreciable fraction of the count under the peak, requires some method of curve resolution or background subtraction.

In some cases it is desirable to add to the sample a known quantity of another plutonium isotope such as ^{236}Pu to monitor the recovery of ^{238} ^{239}Pu. This liquid scintillation method allows the isotopes ^{239}Pu and ^{236}Pu to be counted simultaneously. However, added ^{236}Pu may not accurately reflect the recovery of other plutonium already in a natural (environmental) sample.

Materials and equipment

Choice of scintillator. In developing the high-resolution scintillator solution, a number of commercially available fluors were tested (see Table 1). These fluors were compared from the standpoint of their pulse-height response to alpha-excitation and their ability to resolve alpha-energies, by using $^{238-234}$U and ^{232}Th plus daughters. Typical spectra are shown in Figs. 4(*a*) and 4(*b*). There are large differences between the best and worst situations, as may be seen in Figs. 4(*b*) and 4(*c*). All the fluors were compared for both sets of nuclides, two media being used: one was a 0·04% w/v solution of the fluor in toluene, and the other the same solution with the addition of 20·0% w/v of resublimed naphthalene. In each case 1 ml of the scintillator solution to be tested was mixed with the radioactive tracer in 0·1 ml of a 0·2*M* solution of HDEHP in toluene. The spectrum was collected on

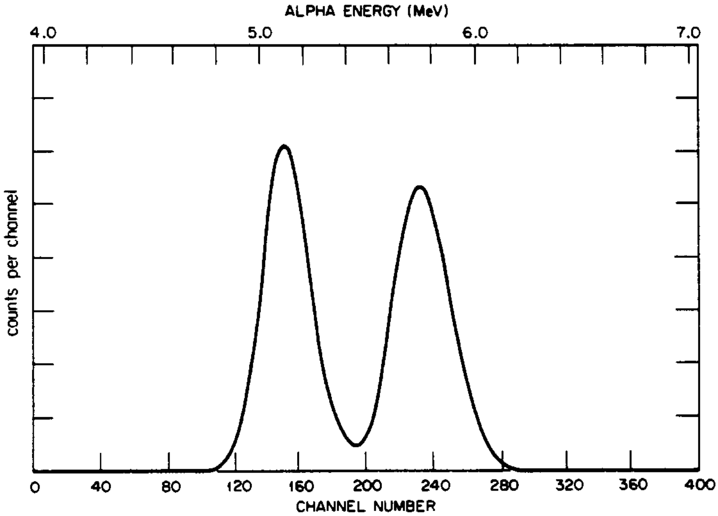

Fig. 2. Spectrum of ^{239}Pu (5·15 MeV) and ^{244}Cm (5·80 MeV) in deoxygenated PBBO scintillator. Each nuclide was present at about 2000 d.p.m. level. Spectrum was collected for 20 min.

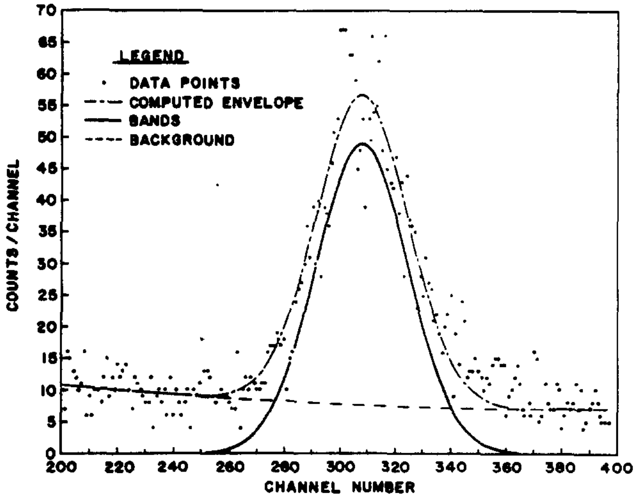

Fig. 3. Typical spectrum of a low count-rate sample of ^{239}Pu. 15 hr count. manual background subtraction gave 2·39 d.p.m. Computer gave 2·27 d.p.m.

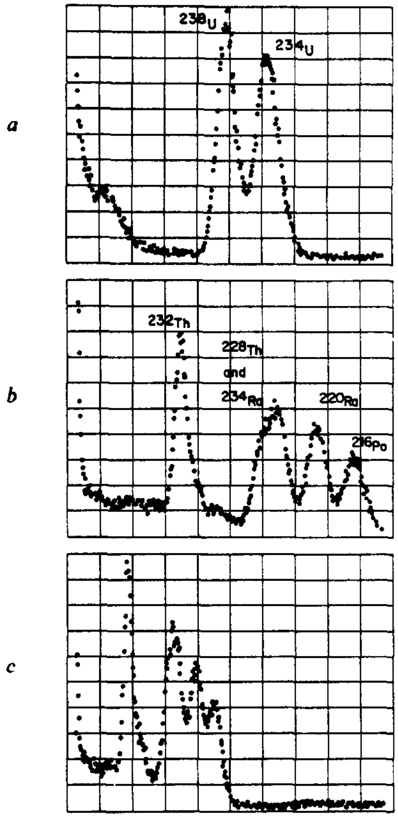

Fig. 4. Examples of pulse-height response and energy-resolution of commercially available fluors: *a*. Natural uranium, ~100 d.p.m.: PBBO scintillator, 4 g/l. + 200 g/l. naphthalene in toluene; *b*. Thorium + daughters. ~200 d.p.m.; PBBO scintillator, 4 g/l. + 200 g/l. naphthalene in toluene; *c*. Thorium + daughters, ~200 d.p.m.: DPA (9,10-diphenylanthracene) scintillator, 4 g/l. in toluene.

Table 1. Pulse-height and energy-resolution measurements on commercially available fluors

Fluor	Relative distance to last peak	Order	Peak/valley height ratio	Order	Combined order
Fluor (4 g/l.) in toluene, $^{238-234}$U					
PBBO	48	1	2·70	1	1
Butyl PBD	47	2	2·61	2	2
PBD	47	2	2·60	3	3
PPO	48	1	2·11	5	4
αNPO	34	3	2·27	4	5
BBOT	29	4	1·72	6	6
POPOP	17	7	1·30	9	9
BisMSB	27	5	1·62	7	7
DPA	21	6	1·35	8	8
Fluor (4 g/l.) + naphthalene (200 g/l.) in toluene, $^{238-234}$U					
PBBO	54	1	3·78	1	1
Butyl PBD	43	2	2·83	2	2
PBD	36	6	1·91	7	5
PPO	42	4	2·50	6	5
αNPO	41	4	2·51	5	4
BBOT	39	5	2·61	4	4
POPOP	41	4	2·76	3	3
BisMSB	29	7	1·73	8	6
DPA	29	7	1·73	8	6
Fluor (4 g/l.) in toluene, ^{232}Th + daughters					
PBBO	63	2	10·8	2	2
Butyl PBD	63	2	8·33	5	3
PBD	64	1	13·5	1	1
PPO	56	3	8·57	4	3
αNPO	48	4	9·86	3	3
BBOT	39	5	7·62	6	4
POPOP	20	7	6·30	8	6
BisMSB	39	5	6·78	7	5
DPA	30	6	6·27	9	6
Fluor (4 g/l.) + naphthalene (200 g/l.) in toluene, ^{232}Th + daughters					
BBO	78	1	10·8	2	1
Butyl PBD	63	4	11·5	1	2
PBD	66	2	9·83	6	4
PPO	65	3	10·67	3	3
αNPO	60	5	9·85	5	6
BBOT	66	2	9·43	7	5
POPOP	59	6	10·67	3	5
BisMSB	45	7	9·86	4	7
DPA	39	8	7·67	8	8

the multichannel analyser and photographed. Measurements of the peak positions and peak-height/valley-height ratios were taken from the photographs. The results are presented in Table 1.

Extensive tests of mixed fluors were not made, but resolution with mixed PPO and Me$_2$POPOP [2,2′-*p*-phenylene-bis(4-methyl-5-phenyl)oxazole] was poorer than with either alone.

The fluors tested, listed in order of their apparent ability to resolve alpha-peaks, were PBBO, butyl PBD, PBD, PPO, αNPO, BBOT, POPOP, BisMSB and DPA. *Trans*-stilbene was also tested but gave pulse-height response and resolution so poor as not to be comparable with the other fluors. Each of the fluors was also tested at a concentration of 4 g/l. in 2-ethylnaphthalene; however, for the most part the results were very similar to those in toluene with naphthalene (200 g/l.) added. For this reason, and for reasons of cost and availability, the 2-ethylnaphthalene is probably not a practical solvent, and the results are not presented here.

Purity of the reagents has been found to be important in all the tests made. The fluors were used as obtained from the supplier, but the naphthalene was resublimed.

Quenching in the extractive scintillator. The effect of quenching in alpha liquid-scintillation counting is usually different from that in beta liquid-scintillation counting. Whereas counting efficiency is always reduced in the latter, it is rarely affected in the former. Only pulse-height response and energy resolution are reduced by quenching in alpha-counting.

Quenching effects in the extractive scintillator are quite small as compared with those observed in the usual scintillation solution containing dioxan and alcohol. Also, since the nuclide is introduced in the same way each time, quenching effects are constant, so that a given alpha-energy produces a pulse of a given height. The small variations that are observed arise from various coloured impurities that may be extracted into the scintillator in varying amounts, from metal impurities, and from varying amounts of extractant. Most of these variables are easily controlled. The extractant, HDEHP, used here in the scintillator gives a reduction in pulse height of only 10% when at the $0{\cdot}2M$ level (64 g/l.), and the reduction decreases nearly linearly to zero (extrapolated) at zero HDEHP concentration. The quenching effect of HDEHP and several other scintillators has been reported elsewhere.[19]

Large amounts of uranium and plutonium, *i.e.*, approaching $0{\cdot}01M$, reduce the pulse height, but these quantities are much greater than any that would normally be encountered in environmental work.

Pulse height and resolution can be improved by treating the nuclide-containing scintillator with two or three cycles of freezing in liquid nitrogen, evacuation, back-filling with argon or helium, and thawing as described by Horrocks.[7] This procedure is time-consuming, however, and we find that nearly as much improvement can be obtained by the addition of 15 mg of sodium bis(2-methoxyethoxy) aluminium hydride "Vitride" (Eastman Organic Chemicals), to each 1 ml of extractive scintillator just before the counting. When pulse-shape discrimination[15] is to be used, however, it is necessary to remove oxygen by freezing and evacuation in order to obtain sufficient time-of-decay differences between the alpha-produced and the beta- or gamma-produced pulses.

Light collection and reflector construction

We have not made a definitive investigation of the problem of obtaining the most efficient light-collection system and at the same time obtaining the maximum alpha-energy resolution from the detector system. We have, however, made a large number of experiments, and the observations from these experiments should be a valuable guide to the construction of a detector or to further work toward defining the parameters that are important in obtaining the desired characteristics in the detector system.

In general, the best results have been obtained with a small concave reflector such as those shown in Figs. 1(*a*) and 1(*b*). The results from these two designs were indistinguishable. These and other tests on variously shaped reflectors suggest that the exact inside shape of the reflector is not very important, although small volumes between the reflecting surface and the phototube face have given better results.

The nature of the reflecting surface does, however, appear to be very important. In all our tests a diffuse white material of high reflectivity was found to be superior to a specular reflector. Of the large number of white surfaces tested, two appear superior in pulse-height response and energy resolution. These were (1) magnesium oxide bonded with dilute sodium silicate and (2) Eastman "white reflectance paint". Nearly as good was fine-grained white "Styrofoam", such as that used in packing material (but not the expanded bead type). Reflectors made from "Styrofoam", however, lacked the physical sturdiness and leak-tightness (to the immersion oil) of coated metal fixtures.

The magnesium oxide reflector surface is prepared as follows: 1 volume of 40° Be sodium silicate is mixed with 2·5–3·0 volumes of water, and 1 g of powdered reagent-grade, or reflectance-standard magnesium oxide is mixed into this solution to form a smooth thin paint. This can be brushed or sprayed on the surface to be coated. Several coats (6–8) are required to build up a dense white surface about 1 mm thick. At least 2 hr at room temperature or very gentle heat is required for drying between coats. Attempts at more rapid drying result in cracking the surface. While the last coat is still damp, dry magnesium oxide may be pressed into the surface and the excess brushed off later. The final surface should be bright white with no trace of the underlying metal surface showing through.

A considerable amount of time was spent in testing various sample–phototube–reflector arrangements that seemed to promise improved resolution and pulse height but instead gave very poor results. In order to prevent other experimenters from experiencing the same disappointments and wasted time, it seems pertinent to list some of these seemingly attractive ideas that did not work. All arrangements in which a specular reflective surface was used were very poor; pulse height and, particularly, resolution were inferior in every case. It should be noted that because of the size and shape of the practical sample chosen (1 ml in a 1 cm culture tube), it was not possible to obtain an optical image of the entire tube on the photocathode; thus this arrangement was not tested. Several smaller volumes of sample were tested in the standard flat-white reflector, however, and these gave no improvement in resolution. Also, thin samples placed flat against the phototube face with a white reflecting surface behind them gave poor resolution. Samples of various sizes with no reflector, positioned at various distances in a black non-reflective box, gave very poor resolution and pulse height. A small opening or a slit between sample and phototube diminished pulse height and resolution.

We do not feel that the optimum arrangement has been obtained. Additional work should be done to improve the reflector–phototube combination.

Spectrum analysis, resolution and alpha-energy identification

Samples with a single known nuclide present and a count-rate at least 100 times that of the background require no spectrum analysis since the background is less than 1% of the total count. However, even with a count-rate this high, there are advantages to collecting a spectrum. If the identity of the nuclide is not certain, the alpha-energy can usually be established to within ±0·1 MeV by the liquid scintillation spectrum since alpha-energy is linear with peak position or channel number. If the extractive scintillator system is maintained at a standard composition, the position of the peak will be sufficiently reliable for energies to be read from a previous calibration of the system. Such a system calibration has already been described.[7,8,11] Internal calibration of the system is easily done by the addition of suitable extracted nuclides to the scintillator-sample. If the alpha-energy producing a given peak is in question, tiny amounts of one or more known nuclides extracted into a suitable organic extractant may be added to give peaks of known energy from which the scale may be calibrated and the unknown energy obtained.[11]

The subtraction of background is usually the primary problem in the analysis of samples with very low count-rates. Figure 3 shows a typical spectrum of a low count-rate plutonium sample contained in a Pyrex tube. The total counting time was 15 hr; pulse-shape discrimination was not used. For most samples of this type, the background has been estimated by taking the sum of the counts in 20 channels on each side of the peak, at a position far enough away from the peak so that none of the peak is included, and calculating the average number of counts per channel of background. The product of this number and the number of channels in the peak gives the background under the peak. This value, subtracted from the total counts in the peak, gives the net counts due to plutonium in the peak. The same result can be obtained by a computer curve-fitting routine. When spectra contain several overlapping peaks, the use of computer curve-fitting procedures becomes a necessity. An example of curve resolution by this method may be seen in Fig. 5, in which both uranium and plutonium are counted. The area under each peak, corresponding to the net alpha-counts of that energy, was calculated by a modification of a program originally designed to resolve optical spectra.[20] Comparisons of peak areas calculated by computer fitting and by manual estimation agreed to within ±5% when subtracting background from a low count-rate sample.

It is possible to make reasonably good manual estimates of areas under such overlapping peaks simply by plotting and sketching in the individual peaks with some point-by-point summation in the overlap region. We have used this procedure in combination with cutting out and weighing the desired peak, and have obtained areas within about ±10% of the known value.

In cases where impurities in the scintillator have caused the ^{234}U and ^{239}Pu peaks to merge so that resolution is difficult, a reasonable estimate of the ^{239}Pu activity may be made by subtracting the product of the number of counts found in the ^{238}U peak (which is usually better resolved in such cases) and the ^{234}U/^{238}U activity ratio in the sample (the value of this ratio will be 1 if the decay chain is at equilibrium) from the count for the combined ^{234}U–^{239}Pu peak.

RESULTS AND DISCUSSION

Table 2 illustrates the ability of the extraction procedure to recover plutonium quantitatively, as well as the effect of fluoride, phosphate, and uranium on the extraction. The

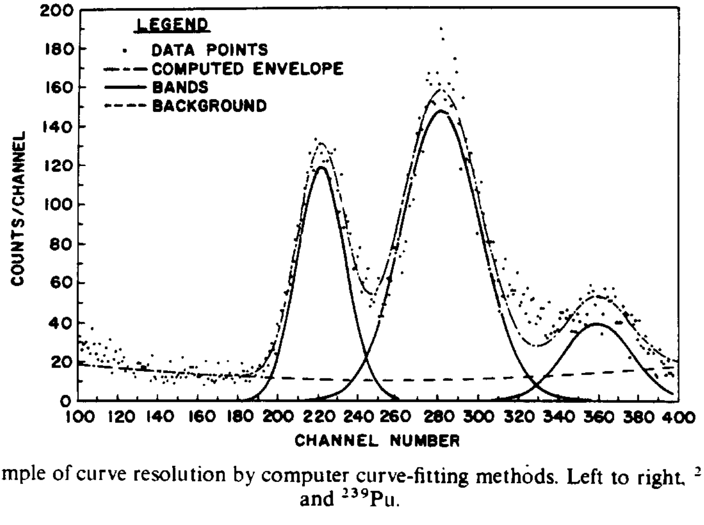

Fig. 5 Example of curve resolution by computer curve-fitting methods. Left to right, ^{238}U, ^{234}U, and ^{239}Pu.

Table 2. Plutonium extraction from 5*M* $\mathrm{NaNO_3}$–1*M* $\mathrm{HNO_3}$

Pu added, *d.p.m.*	Contaminant added	Pu recovered		Total count	Relative std. devn. of counting, %
		d.p.m.	%		
6·07	None	5·93	97·6	3555	1·7
6·07	None	5·98	98·5	3582	1·7
6·07	None	5·99	98·6	3591	1·7
6·07	5800 dpm U	6·12	101·0	3432	1·7
6·07	11,600 dpm U	5·82	95·8	1864	2·3
607	None	602·2	99·2	4015	1·6
607	None	605·8	99·8	4039	1·6
607	None	618·0	101·8	4120	1·6
607	5820 dpm U	614·0	101·1	4090	1·6
607	60,000 dpm U	485·0	80·0*	3240	1·7
607	0·0005*M* $\mathrm{F^-}$	604·0	99·5	4027	1·6
607	0·005*M* $\mathrm{F^-}$	609·1	100·3	4060	1·6
6066	0·025*M* $\mathrm{F^-}$	5459	90·0	36,396	0·5
6066	0·050*M* $\mathrm{F^-}$	4380	72·2	29,198	0·6
6066	0·050*M* $\mathrm{F^-}$†	4744	78·2	31,624	0·6
6066	0·10*M* $\mathrm{F^-}$§	4416	72·8	29,440	0·6
1214	0·002*M* $\mathrm{PO_4^{3-}}$	1185	97·6	11,846	0·9
1214	0·008	1197	98·6	11,970	0·9
1214	0·008	1193	98·3	11,934	0·9
1214	0·015	1110	91·4	11,096	0·9
1214	0·016	1100	90·6	10,999	0·9
1214	0·021	1044	86·0	10,440	0·9
1214	0·027	982	80·9	9821	1·0
1214	0·032	472	38·9	4722	1·5
1214	0·008*M* $\mathrm{PO_4^{3-}}$ + 0·005*M* $\mathrm{F^-}$	923	76·0	9226	1·0
1214	0·004*M* $\mathrm{PO_4^{3-}}$ + 0·002*M* $\mathrm{F^-}$	1032	85·0	10,319	0·9
1214	0·004*M* $\mathrm{PO_4^{3-}}$ + 0·001*M* $\mathrm{F^-}$	1050	86·5	10,501	0·9

* Oxidation state of plutonium not adjusted properly because of excess of uranium.
† Aged 24 hr in glass after $\mathrm{F^-}$ was added.
§ Aged three days in glass after $\mathrm{F^-}$ was added.

aqueous medium for the first extraction with $\mathrm{TANO_3}$ was 1*M* nitric acid–5*M* sodium nitrate in each case. Uranium appears to interfere at a level of about 60,000 d.p.m. per 50 ml sample (0·03*M* in the final sample), probably by interference with control of the plutonium oxidation state. Fluoride appears to interfere at about the 0·025*M* level in this system and when phosphate and fluoride are present together at about 0·004*M* $\mathrm{PO_4^{3-}}$ and 0·001*M* $\mathrm{F^-}$. If samples are omitted in which interferences are known to occur, the average recovery was 100·5% for samples containing plutonium at the 607 d.p.m. level and 98·3% at the 6·07 d.p.m. level.

The ability to recover and count plutonium and obtain a reproducible answer from a typical environmental-type sample was examined by using a waste-water sample of low but unknown plutonium content. The water also contained unknown amounts of other ions and a visible amount of suspended mud. (A sample of such material should be very representative of that which would be encountered in analysing environmental water samples for plutonium contamination.) The water samples were made 0·1*M* in nitric acid, boiled down to a volume of about 20 ml, filtered, adjusted in acidity, and extracted. The

Table 3. Analysis of typical waste-water sample

Volume taken, *litres*	Spike added, *d.p.m.*	Total count*, *d.p.m.*	Background, *d.p.m.*	Count, *d.p.m. p/litre*†	Std. devn., *d.p.m. p/litre*
1	1824	3760	1003	1·56	0·09
1	1800	3540	1065	1·13	0·09
1	1824	3527	1083	1·03	0·09
1	0	829§	470	1·12	0·07
1	0	1515	835	1·14	0·05
2	0	2866	1193	1·39	0·04
3	0	4364	1311	1·50	0·03

* Counting period was 15 hr except where noted.

† One ml of extractive scintillator was counted from 1·5 ml added. Thus

$$\frac{\Sigma\,\text{count} - (\text{spike} + \text{background})}{\text{min counted}} \times 1{\cdot}5 = \text{d.p.m. per litre.}$$

The background for the barren scintillator in the area of the plutonium peak was $\sim$ 1·0 c.p.m.

§ Counting period was 480 min.

results of these tests are shown in Table 3. As shown, the average of these values is 1·27 d.p.m. per litre, with an average deviation of 0·18, or 14% of the average value. The standard deviation of counting, considering both total sample count and background count, varied from ±0·03 to ±0·09 d.p.m. per litre. It should be noted (Table 3) that 1-, 2-, and 3 litre volumes were used in the analysis and, in addition, three samples were spiked with a known amount of plutonium.

Analysis of this sample by another group in this laboratory by an ion-exchange separation followed by electroplating and counting with a ZnS foil scintillator gave 0·3 and 0·7 d.p.m. per litre in separate determinations. Our results suggest that these values are too low.

The determination of plutonium (and uranium) in soil samples is probably the most difficult of the environmental plutonium analyses presently done on a routine basis. The most difficult and the most controversial aspect of this analysis is leaching (or dissolving) the soil sample. The question of whether a particular leaching, dissolution, or fusion procedure places all of the plutonium in a sample into solution has been discussed repeatedly.[21] It is beyond the scope of this work to investigate in detail the problem of dissolving soil samples. This work is directed primarily toward an improved method of separation and counting after the plutonium (or other nuclide of interest) has been brought into solution by some satisfactory procedure. Further, it should be noted that the availability of plutonium in the environment to milder leaching agents such as carbonic or acetic acids is a pertinent question relevant to the hazard that environmental plutonium presents to man and biota, and that the techniques presented here are easily adapted to the assay of plutonium (or other alpha-emitters) in such solutions.

In procedures involving soil leaching or fusion, a technique often used to monitor the recovery is to spike the original soil sample with a known amount of ^{236}Pu and to assume that the ^{236}Pu recovery obtained can be applied also to the $^{238-239}$Pu. The authors feel that such a procedure is unreliable and can monitor only losses subsequent to the dissolution step. Consideration should be given to the following: some time may be required for plutonium to come into equilibrium with the soil, and the behaviour of plutonium is known to be affected by its previous history.[3,4] Specifically, it would seem reasonable to

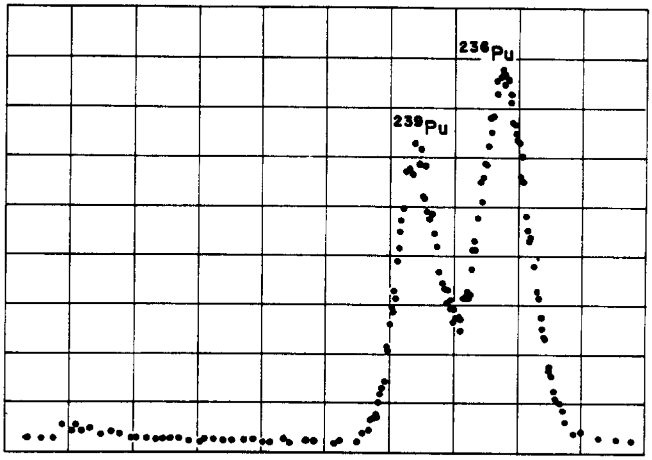

Fig. 6. Plutonium sample with ^{236}Pu spike for recovery monitoring.

be able to leach 100% of the recently added ^{236}Pu spike from a soil sample while only a much smaller fraction of the $^{238-239}$Pu is released. However, aside from any question about the validity of ^{236}Pu spiking, the procedure may be used with high-resolution liquid scintillation spectrometry. Figure 6 shows an example of ^{239}Pu and ^{236}Pu counted simultaneously with no special effort made to improve the energy resolution. Even here, peak separation is sufficient to allow reasonably quantitative counting of each isotope simply by summation of the counts under the curve. Computer curve-fitting could improve the counting results, as could improved resolution by further treatment of the sample as outlined above under "*Quenching in the extractive scintillator*".

We have not attempted any investigation of the problem of recovering plutonium from soil samples; however, we have done some preliminary work and the results of this, along with results from other work on the present method, lead to some worthwhile observations. A solution made to approximate the composition of a leached soil[22] (Table 4) was spiked with plutonium. Table 5 shows typical results of analysing such a solution. The average recovery was 98·6%..However, when such a solution was boiled with hydrochloric–nitric–hydrofluoric acid mixture, precipitated and redissolved in nitric acid as an actual soil sample would be, with boric acid used as a fluoride complexer, the recovery of plutonium varied between 40 and 80%. This is the usual range of recovery to be expected from soil samples when an ion-exchange resin procedure is used. About half of the unrecovered plutonium was usually found in the 0·7*M* nitric acid wash, while the remainder was

Table 4. Composition of synthetic soil sample*

Compound added†	Quantity, *g/l.*	Compound added†	Quantity, *g/l.*
$Na_2SiO_3 . 9H_2O$	20	$Ca(NO_3)_2 . 4H_2O$	0·8
$Al(NO_3)_3 . 9H_2O$	60	KCl	0·6
$Fe(NO_3)_3 . 9H_2O$	30	$NaH_2PO_4 . H_2O$	0·4
$Mn(NO_3)_2 . 4H_2O$	0·5	Na_2SO_4	0·1
$Mg(NO_3)_2 . 6H_2O$	4		

* Concentrated NHO_3, 64 ml, was added to make the solution 1·0*M* in HNO_3.
† Hydration assumed to be that indicated on label of reagent bottle.

Table 5. Plutonium recovery from leach solution from synthetic soil

Pu added. *d.p.m.*	Contaminant added	Pu recovered		Std. devn., %
		d.p.m.	%	
12.136	None	12.243	100·9	0·4
12.136	None	11,932	98·3	0·4
12.136	None	11.843	97·6	0·5
6.220	5 g $FeNO_3$	6058	97·4	0·5

distributed between the stripped organic phase and the original aqueous solution. The addition of saturated aluminium nitrate solution to saturate the aqueous phase in the $TANO_3$ extraction improved recovery to the 91–93% range. Three samples that were boiled as described above but to which no hydrofluoric acid was added gave greater than 98% recovery. If we note from Table 2 that fluoride interferes with plutonium extraction, these facts strongly suggest that many of the problems associated with the recovery of plutonium from soils result from the addition of fluoride or the failure to remove it completely. If solids are separated while excess of fluoride is present, insoluble PuF_4 may be lost with the solids.[23] If fluoride is carried through to the final solution (as CaF_2 for example), difficulties in extraction or in ion-exchange recovery may be experienced. Our work indicates that aluminium nitrate is a more effective complexing agent than boric acid for preventing fluoride interference in the $TANO_3$ extraction. This is consistent with published complex-formation constants.[24,25] However, even aluminium forms weaker fluoride complexes than does plutonium. Zirconium is a stronger fluoride complexer than plutonium, but may not be practical for this use because of cost considerations and possible non-equilibrium between Zr^{4+} and hydrous zirconium polymer. Neither aluminium nor zirconium is extracted in the $TANO_3$ system.

The recovery of plutonium added to an actual leached soil appeared to depend on the preparation of the leach. If solutions were free from precipitate and either fluoride was not added or care was taken to remove and complex fluoride, recovery of plutonium added to the leach was high, usually greater than 95%. With leaches known to contain uncomplexed fluoride or containing visible solids, recovery was usually low, typically 40–80%.

The recovery of plutonium added to actual soil samples was likewise variable. Three procedures were tried: leaching with concentrated nitric and hydrofluoric acid; fusion with potassium fluoride followed by pyrosulphate fusion and dissolution in dilute acid; fusion with sodium carbonate containing 10% sodium peroxide. In all cases the plutonium was added as a solution in 1·0*M* hydrochloric acid, and the soil was dried before leaching or fusion. The soil was from the top 4 in. of an alluvial bottom land along the Clinch River near Oak Ridge, Tennessee. The soil had been dried and then screened to remove sticks and stones. Between 15 and 20 samples were run by each of the procedures above.

In the leaching tests, a 10 g soil sample was boiled in a mixture of concentrated nitric and hydrofluoric acids for 3–4 hr and then hydrochloric acid was added and the boiling continued for another hour. The acid leach was treated with hydroxide in the presence of borate ion, and the precipitate was dissolved in 1*M* nitric acid–2*M* aluminium nitrate for extraction. Recovery varied between 40 and 70%. This is the range of recovery usually reported for this type of treatment.

The fluoride fusion followed by pyrosulphate was carried out according to a procedure developed by Sill and associates.[26] Whereas considerable silicate material remained undissolved when the leaching procedure was used.

this fusion method completely dissolved the entire 10 g sample. The fluoride and silica are volatilized when the product from the potassium fluoride fusion is converted into pyrosulphate by the addition of sulphuric acid and sodium sulphate. The pyrosulphate product is dissolved in dilute hydrochloric or nitric acid and treated with sodium hydroxide. The precipitate is redissolved in nitric acid or nitric acid plus aluminium nitrate and then extracted. Recovery varied between 30 and 98% with most results around 50–80%. Carrying the plutonium on a precipitate of barium sulphate as suggested by Sill might have given better results, but this procedure was not tried. Considerable variation in the appearance of the pyrosulphate fusion product and in the manner in which it dissolved was noted and is believed to be related to the variability of the results. Differences in the results could not be related to any known variation in the experimental technique. .

Carbonate fusion was the simplest and most rapid of the three procedures tried and gave as good, or better, average results. The 10 g sample was fused with 50 g of sodium carbonate containing 5 g of sodium peroxide. The cooled fusion was crushed, then dissolved in dilute nitric acid, and the solution treated with sodium hydroxide. Dissolved sodium silicate was removed by decantation and by washing the precipitate with 0·1M sodium hydroxide. The hydroxide precipitate was dissolved in nitric acid or nitric acid plus aluminium nitrate, for extraction. Plutonium recovery by this method varied from 83 to 90%.

It is clear that additional work needs to be done on a simple, reliable and reproducible method for bringing soil samples into solution in such a way that the plutonium in them can be completely recovered.

In summary, the results indicate clearly that use of the counting method and extraction procedure will result in quantitative recovery of plutonium from a solution 1–3M in nitric acid and 1 5M in total nitrate. The separation of plutonium from large quantities of interfering ions of the type usually found in soil or other environmental samples is complete. The method can be easily modified to recover uranium also, and it is possible to count both uranium and plutonium in the same sample and resolve the ^{238}U, ^{234}U, and ^{239} ^{238}Pu peaks. It is possible to introduce ^{236}Pu as a plutonium recovery monitor, resolve the ^{236}Pu and ^{239}Pu peaks and, on this basis, correct for ^{239}Pu losses in the chemical steps following the initial leaching. However, as stated earlier, it is doubtful if such a procedure could accurately reflect initial leaching losses.

The general concept of combining high-resolution alpha liquid scintillation spectrometry with solvent extraction has potential application to a wide variety of counting problems. Although the resolution of 0·2–0·3 MeV is sufficient for many applications, the authors feel that it could be improved by appropriate improvements in the detector assembly. Lower detection limits depend on background, and limits of 0·01 d.p.m. or lower by use of using pulse-shape discrimination and effective shielding appear feasible.

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Résumé—On présente une méthode pour le dosage de l'uranium et du plutonium par une méthode combinée de scintillation liquide à haute résolution—extraction par solvant. En admettant qu'un compte d'échantillon égal au compte de bruit de fond est la limite de détection, la limite de détection inférieure pour ces éléments et d'autres nucléides émetteurs alpha est 1,0 dis/min avec un tube échantillon en pyrex, 0,3 dis/min avec un tube échantillon en quartz utilisant une protection de détecteur présente ou 0,02 dis/min avec une discrimination de forme d'impulsion. L'efficacité du comptage α est 100%. Avec les données de comptage présentées comme un spectre d'énergie α, une résolution d'énergie de demi-largeur de pic de 0,2–0,3 MeV et une identification d'énergie à ±0,1 MeV sont possibles. Ainsi, dans ces limites, l'identification et la détermination quantitative d'un émetteur alpha spécifique, indépendants d'une séparation chimique, sont possibles. La méthode de séparation permet une récupération plus grande que 98% d'uranium et de plutonium de solutions échantillons contenant de grandes quantités de fer et d'autres substances interférentes. Dans la plupart des cas l'uranium, même quand il est présent dans un rapport molaire de 10^8 fois, peut être séparé quantitativement du plutonium sans perte du plutonium. On mentionne des applications potentielles de ce concept analytique général à d'autres problèmes de comptage alpha. On discute de problèmes spéciaux associés au dosage du plutonium dans le sol et des échantillons d'eau. On présente les résultats d'essais pour déterminer les caractéristiques de hauteur d'impulsion et de résolution d'énergie de plusieurs scintillateurs. On décrit la construction du détecteur de scintillation liquide à haute résolution.

Zusammenfassung—Ein Verfahren zur Bestimmung von Uran und Plutonium mit einer kombinierten Methode aus hochauflösender Flüssigkeits-Szintillationszählung und flüssig-flüssig-Extraktion wird mitgeteilt. Nimmt man als Nachweisgrenze gleiche Proben- und Untergrund-Zählraten an, so beträgt die untere Nachweisgrenze für diese und andere alpha-emittierende Nuklide 1,0 dis/min mit Pyrex-Probenrohr, 0,3 dis/min Quarzprobenrohr und herkömmlicher Detektorabschirmung oder 0,02 dis/min mit Impulsform-Diskriminierung. Die Alpha-Zählausbeute beträgt 100%. Gibt man die Zähldaten als Alpha-Energiespektrum wieder, dann sind eine Energieauflösung von 0,2–0,3 MeV PeakHalbwertsbreite und eine Energie-Identifizierung auf ±0,1 MeV möglich. Daher sind innerhalb dieser Grenzen die Identifizierung und die quantitative Bestimmung eines bestimmten AlphaEmitters unabhängig von einer chemischen Abtrennung möglich. Das Abtrennverfahren liefert eine Uran- und Plutoniumausbeute über 98% aus gelösten Proben, die große Mengen Eisen und andere störende Stoffe enthalten. In den meisten Fällen kann Uran, selbst wenn es im 10^8-fachen Molverhältnis vorliegt, quantitativ von Plutonium getrennt werden, ohne daß Plutonium verlorengeht. Mögliche Anwendungen dieses allgemeinen anlytischen Konzepts auf andere Alpha-Zählprobleme werden angegeben. Die mit der Bestimmung von Plutonium in Boden- und Wasserproben verknüpften besonderen Probleme werden diskutiert. Die Ergebnisse von Versuchen, die Impulshöhe- und Energieauflösungseigenschaften mehrerer Szintillatoren zu ermitteln, werden mitgeteilt. Die Konstruktion des hochauflösenden Flüssigkeits-Szintillationsdetektors wird beschrieben.

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IODOMETRIC SUBMICRO DETERMINATION OF α-AMINO-ALCOHOLS BY AN AMPLIFICATION REACTION

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Summary—New methods are described for the iodometric submicro determination of α-amino-alcohols possessing primary, secondary or tertiary amino-groups which involve 6-, 12-, and 18-fold amplification reactions, respectively. The methods are based on reaction of the α-amino-alcohols with an excess of potassium periodate in a slightly alkaline medium, masking of the unreacted periodate with molybdate at pH 3·2 and, after addition of iodide, iodometric determination of the equivalent amounts of iodate released. In addition to being simple and rapid, the methods are sufficiently selective and specific and also highly accurate, being particularly suitable for the analysis of submicro amounts (50–150 μg); the average recovery is 99·9%.

Amplification reactions are receiving much attention, being of special attraction in organic microanalysis, which always calls for higher sensitivity. Oxidation of α-dihydroxy compounds with periodic acid by the well-known Malaprade[1] reaction offers the only possible amplification methods for this important class[2] of organic substances. The powerful oxidizing properties of periodates in addition to their selectivity under controlled pH conditions led to pursuit of their utilization in the development of new amplification methods[3,4] especially after the problem of determining iodate in presence of excessive amounts of periodate had been solved.[5]

Periodate oxidation of α-amino-alcohols was first observed by Nicolet and Shinn[6] and investigated later more carefully by Fleury *et al.*,[7] who gave a full account of the optimum conditions, *e.g.*, pH, reaction period, and temperature necessary for quantitative reaction. Procedures for the determination of mono-, di-, and triethanolamines[8,9] have been reported on the basis of estimating the resulting formaldehyde and ammonia. Serine and threonine were oxidized with a known excess of standard periodate solution and the method was completed either by the iodometric titration of the unreacted periodate or by determining the aldehyde and ammonia[10] produced. In one case, the aldehyde formed after periodate oxidation was determined by reaction with 3-methyl-2-benzothiazolinone hydrazone.[11]

In the present investigation, new amplification methods are described for the submicro determination of α-amino-alcohols containing primary, secondary or tertiary amino-groups. The methods depend upon reaction with excess of periodate at pH 8–8·5, masking of the unreacted periodate with molybdate at pH 3·2, and iodometric determination of the equivalent amount of iodate liberated. As far as we know, no such methods have so far been mentioned in the literature.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and doubly distilled water was always used.

α-Amino-alcohols. Aqueous solutions of concentration *ca.* 100 mg/l. were used.

Ammonium molybdate. A 25% solution of the tetrahydrate.

Buffer solution pH 2·2. Made from 40 ml of 0·2*M* sodium acetate and *ca.* 100 ml of glacial acetic acid.

Potassium bicarbonate, 0·02*N solution.*

Potassium periodate. A solution of 1 g of potassium periodate (recrystallized from hot water) in 300 ml of water, heated if necessary.

Sodium thiosulphate, 0·002*M*. Standardized against 3 × $10^{-4}M$ potassium iodate.

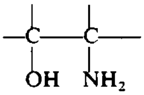
Procedures

For serine, threonine, and monoethanolamine. Place 0·5–1·5 ml of the 0·01% amino-alcohol solution or 50–150 μg of sample in a 50-ml conical flask, add 5 ml of bicarbonate solution, 1 ml of periodate solution, and leave for 1 min. Add 3·5 ml of acetate buffer, 3·5 ml of molybdate solution, *ca.* 25 mg of potassium iodide, stopper the flask and shake it for 1 min. Titrate the reaction mixture with thiosulphate, using starch as indicator near the end-point. Carry out a blank determination.

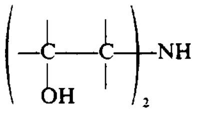
For diethanolamine. Place the sample (50–150 μg or a 0·5–1·5 ml portion of the 0·01% solution), into a 50-ml conical flask containing 7 ml of bicarbonate solution, add 2 ml of periodate solution, and immerse the flask in a water-bath for 6 min at 50–60°C. Cool under tap water, add 5 ml of acetate buffer, 7 ml of molybdate solution, *ca.* 25 mg of potassium iodide and titrate as above. Run a blank determination.

For triethanolamine. Add the same size of sample as before to 10 ml of bicarbonate solution in a 50-ml conical flask, add 3 ml of periodate solution, and immerse the flask in a water-bath for 35 min at 70–80°C. Cool, add 7 ml of acetate buffer, 10 ml of molybdate solution, *ca.* 25 mg of potassium iodide, and perform the usual thiosulphate titration. Run a blank.

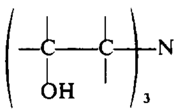
Since the overall reactions may be represented as



$$-\underset{OH}{\overset{|}{C}}-\underset{NH_2}{\overset{|}{C}}- \equiv IO_3^- \equiv 6\,I^- \equiv 6\,S_2O_3^{2-}$$



$$\left(-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\right)_2 NH \equiv 2\,IO_3^- \equiv 12\,I^- \equiv 12\,S_2O_3^{2-}$$



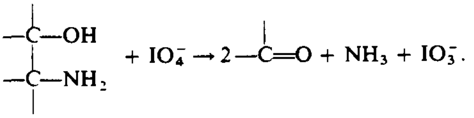
$$\left(-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\right)_3 N \equiv 3\,IO_3^- \equiv 18\,I^- \equiv 18\,S_2O_3^{2-}$$

then 1 ml of 0·002*M* thiosulphate ≡ 35·03 μg of serine, 39·70 μg of threonine, 20·36 μg of monoethanolamine, 35·04 μg of diethanolamine or 49·73 μg of triethanolamine.

RESULTS AND DISCUSSION

Several physicochemical methods have been described in the literature for the determination of α-amino-alcohols and related compounds. These are mainly spectrophotometric[12,13] or gas-chromatographic[14] methods, which require special equipment. The periodate oxidation of α-amino-alcohols may be considered as the simplest and most common approach to achieve a sensitive and selective analytical procedure for this estimation. All the periodate oxidation methods previously reported for the determination of α-amino-alcohols depend upon the estimation of the unreacted periodate,[10] spectrophotometric measurement of the formaldehyde[10,11] or the titration of the ammonia[7,10] produced. In order to develop a suitable and accurate submicro method for this class of organic compounds, consideration was given to determining the equivalent amount of iodate released, the unreacted periodate being masked with molybdate.[2]

Preliminary studies on α-amino-alcohols containing a primary amino group, showed that under the experimental conditions used, the reaction proceeds according to the equation:



$$\begin{array}{l} -\overset{|}{C}-OH \\ -\underset{|}{C}-NH_2 \end{array} + IO_4^- \rightarrow 2-\overset{|}{C}{=}O + NH_3 + IO_3^-.$$

This reaction is remarkably fast at room temperature, as it proceeds quantitatively in 1 min, giving rise to one mole of iodate per mole of compound, in agreement with previous work.[15,16] The negligible blank values found show that the periodate is decomposed only in the determination reaction. Analyses covering the range 50–150 μg of serine, threonine, and monoethanolamine gave average recoveries of 100·3, 100·3, and 99·7% (Table 1), respectively. Fleury *et al.*,[7] also reported that these compounds react completely in 1 min but they used a reaction temperature of 4°C. In the present work, however, quantitative recoveries could only be achieved on allowing the reaction to proceed at room temperature. Schulek and Maros[10] found that if serine or threonine are reacted with excess of periodate in bicarbonate medium for 10 min, then in an acetic acid medium for a further

Table 1. The iodometric submicro determination of α-amino-alcohols by amplification reactions

Compound	Weight, μg Taken	Weight, μg Found	Recovery, %	Average recovery, %
	50·00	50·1	100·2	
		50·2	100·4	
Serine	100·00	100·5	100·5	100·3
		100·3	100·3	
	150·00	150·2	100·1	
		150·4	100·3	
	50·00	49·9	99·8	
		50·3	100·6	
Threonine	100·00	100·5	100·5	100·3
		100·4	100·4	
	150·00	150·5	100·3	
		150·6	100·4	
	47·26	46·9	99·3	
		47·0	99·5	
Monoethanolamine	94·52	94·1	99·5	99·7
		94·1	99·6	
	141·78	141·8	100·0	
		141·9	100·1	
	51·38	51·0	99·2	
		51·0	99·3	
Diethanolamine	102·76	102·2	99·4	99·6
		102·7	99·9	
	154·14	154·6	100·3	
		153·8	99·8	
	46·30	45·9	99·2	
		45·9	99·1	
Triethanolamine	92·60	92·4	99·8	99·5
		92·3	99·7	
	138·90	138·5	99·7	
		138·4	99·6	

period of 60 min, the reactions proceed as follows:

$$CH_2OH\text{-}CHNH_2\text{-}COOH + 2\,IO_4^- \rightarrow HCHO + HCOOH + NH_3 + CO_2 + 2\,IO_3^-$$

$$CH_3\text{-}CHOH\text{-}CHNH_2\text{-}COOH + 2\,IO_4^- \rightarrow CH_3CHO + HCOOH + NH_3 + CO_2 + 2\,IO_3^-$$

On investigating the two reactions under the experimental conditions reported by Schulek and Maros,[10] it was found that only 1·9 moles of iodate are obtained instead of the expected 2 moles per mole of compound, indicating incomplete stoichiometry under such conditions. The low recovery obtained may be attributed to the incomplete oxidation of the formaldehyde, originally produced, to formic acid. However, this did not prevail in the present work owing to the 1-min reaction period and the slightly alkaline medium used. In this way, the reaction proceeded to give only one mole of iodate, two moles of the aldehyde, and one mole of ammonia without any chance for possible side-reactions, *e.g.*, further oxidation of the formaldehyde and/or the ammonia formed. Furthermore, in addition to achieving quantitative results based on the 6-fold amplification the whole analysis is completed within 3–4 min as compared with the 70 min in the procedure of Schulek and Maros.[10]

According to Fleury *et al.*,[7] diethanolamine (containing a secondary amino-group) reacted completely with periodate at pH 8 in 1 min at 4°C. However, in this work a reaction time of 6 min at a temperature of 50–60°C was found essential to obtain quantitative results based on liberation of 2 moles of iodate per mole of compound. Since these conditions gave rise to an average recovery of 99·6% (Table 1), the reaction may then be represented as

$$(CH_2OH\text{-}CH_2)_2NH + 2\,IO_4^- \rightarrow 4\,HCHO + NH_3 + 2\,IO_3^-$$

As clear from the equation, an amplification is obtained on addition of iodide. Under these conditions, the blank value amounted to 0·1–0·15 ml of 0·002M thiosulphate. The amplification factor is difficult to define, and is best described as being 6-fold per alcohol group.

Periodate oxidation of triethanolamine, which has a tertiary amino-group, has been reported to be of special interest.[7,10] This reaction was stated to be quantitative only at pH 7·6 and a temperature of 37°C, when allowed to proceed for at least 1 hr.[7] Unfortunately, recoveries consistently 50% low were obtained under such conditions. The reaction of triethanolamine with periodate is proposed as proceeding in accordance with the equation

$$(CH_2OH\text{-}CH_2)_3N + 3\,IO_4^- \rightarrow 6HCHO + NH_3 + 3\,IO_3^-$$

The low results necessitated a study of the various factors influencing the reaction, namely the effect of pH, reaction period, temperature, and the molar ratio of iodate to triethanolamine (TEA). Briefly, Fig. 1 illustrates the combined relationship between all these variables. Neither the increase in the pH alone from 8 to 9·8 nor the individual increase in the molar ratio of IO_4^-:TEA from 100 to 200 caused any substantial variation in the recovery of TEA. However, a significant change in the rate of reaction was observed on increasing the temperature to 80°C. Only at this temperature did the reaction start to go relatively rapidly, being complete within 30–35 min. Under these conditions an average recovery of 99·5% (Table 1) was achieved for TEA and the blank value did not exceed 0·2–0·25 ml of 0·002M thiosulphate.

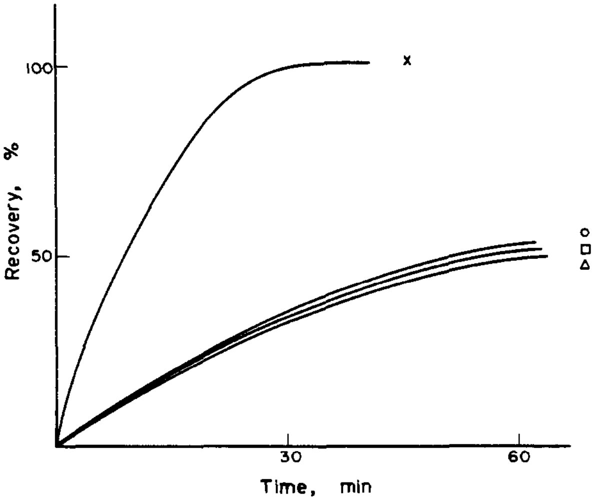


Fig. 1. Effect of reaction time, pH, temperature, and IO_4^-/TEA ratio on the recovery of TEA. △ pH = 8, T = 37°C, IO_4^-/TEA = 100; □ pH = 9·7, T = 37°C, IO_4^-/TEA = 100; ○ pH = 8, T = 37°C, IO_4^-/TEA = 200; × pH = 8, T = 80°C, IO_4^-/TEA = 100.

In conclusion, the amplification methods presented in this work for α-amino-alcohols are very valuable both analytically and structurally. As to the former aspect, the methods are simple, rapid and accurate owing to the highly sensitive iodometric finish which enables submicro amounts to be determined. Concerning the latter aspect, though α-amino-alcohols resemble α-diol compounds in that both are selectively attacked by periodate oxidation, yet the production of ammonia is characteristic only for α-amino alcohols.[15,16] Moreover, the amplification factor relative to iodate produced is constant, and hence relative to the type of compound analysed is 6 fold (1 mole of IO_3^-), 12 fold (2 moles of IO_3^-), or 18 fold (3 moles of IO_3^-) for α-amino-alcohols containing primary, secondary or tertiary amino groups, respectively.

Interferences

α-Amino-acids and α-diamines were found not to interfere in the determination of α-amino-alcohols possessing a primary amino-group, *e.g.*, serine, threonine, and monoethanolamine, even if they are present in 30 fold amounts. This is explainable since α-amino-acids and α-diamines react with periodate only after heating at elevated temperatures for prolonged periods[7] of at least 1 hr. Hence, the procedure developed is considered to be highly selective, especially for the determination of serine and threonine in presence of α-amino-acids. Compounds with an α-diol structure were found to interfere seriously, as expected, in the determination of α-amino-alcohols of any kind.

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Résumé—On décrit de nouvelles méthodes pour le submicro-dosage iodométrique d'α-aminoalcools possédant des groupes aminés primaires, secondaires ou tertiaires, qui mettent en jeu des réactions d'amplification de facteurs 6, 12 et 18 (par rapport au composé à doser), respectivement. Ces méthodes sont basées sur la réaction des α-aminoalcools avec un excès de periodate de potassium dans un milieu légèrement alcalin, la dissimulation du periodate qui n'a pas réagi avec le molybdate à pH 3,2 et, après addition d'iodure, le dosage iodométrique des quantités équivalentes d'iodate libéré. Outre qu'elles sont simples et rapides, les méthodes sont suffisamment selectives et spécifiques et aussi hautement précises, convenant particulièrement à l'analyse de submicroquantités (50–150 μg); la récupération moyenne est 99,9%.

Zusammenfassung—Neue Methoden zur jodometrischen Submikrobestimmung von α-Aminoalkoholen mit primären, sekundären oder tertiären Aminogruppen werden beschrieben. Sie umfassen, im Verhältnis zur Stammverbindung, 6-, 12- und 18-fache Verstärkungsreaktionen. Die Analysen beruhen auf der Reaktion der α-Aminoalkohole mit einem Überschuß von Kaliumperjodat in schwach alkalischem Medium, Maskieren des nicht verbrauchten Perjodats mit Molybdat bei pH 3,2 und, nach Zugabe von Jodid, jodometrischer Bestimmung der freigesetzten äquivalenten Jodatmengen. Die Analysen sind nicht nur einfach und rasch auszuführen, sondern auch ausreichend selektiv und spezifisch sowie sehr genau; besonders sind sie zur Bestimmung von Submikromengen (50–150 μg) geeignet. Die mittlere Ausbeute beträgt 99,9%.

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DETERMINATION OF GOLD IN COPPER-BEARING SULPHIDE ORES AND METALLURGICAL FLOTATION PRODUCTS BY ATOMIC-ABSORPTION SPECTROMETRY

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Summary—A method is described which is specific for the determination of gold in sulphide copper ores and concentrates. Direct decomposition with *aqua regia* was found to be incomplete. A carefully controlled roasting stage followed by treatment with hydrochloric acid and then *aqua regia* was effective for dissolving all the gold. The gold is extracted into 4-methylpentan-2-one (methylisobutylketone) then aspirated into a very lean air–acetylene flame and the gold determined by atomic-absorption spectrometry. No interferences were observed from large concentrations of copper, iron or nickel.

Since the introduction of atomic-absorption spectrometry as an established analytical method, many papers have been published on the determination of gold in ores and geological materials. For many years the classical fire-assay method has been used for gold analysis but, owing to the rather lengthy procedure involved, many laboratories now prefer to use atomic-absorption techniques. As the gold is usually present in very small concentrations in a complex matrix a concentration and separation step is often used before the atomic-absorption analysis. Various methods of concentration have been reported; these have included co-precipitation with tellurium,[1] selenium[2] or extraction into organic solvents such as methyl isobutyl ketone (MIBK).[3,4] Metallurgical testwork in this laboratory on copper-bearing sulphide ores necessitated the development of a rapid, accurate method for the determination of gold in this type of ore, as well as in the various flotation products obtained from pilot plant testwork. A literature search showed several conflicting reports on sample treatment, sample weights, and interference phenomena. The great majority of papers published rely on an *aqua regia* attack to dissolve the gold, but for sulphide ores direct *aqua regia* attack was found to be unsatisfactory. Because gold occurs as discrete particles in the matrix minerals the statistical chance of obtaining representative analytical samples decreases with decreasing sample size,[5] and thus the precision of the analysis improves with increase in the sample weight taken. Law and Green[4] used sample weights of 500 g but other workers report accurate results from only 2·5 g per analysis.[6] During development work in this laboratory satisfactory results were obtained with 20-g samples for ores containing up to 5 ppm of gold. For concentrates and other samples containing 5–30 ppm of gold a sample weight of 5–10 g was used. Very low gold assays were obtained on sulphide samples unless a roasting step was included before the acid attack. Unless the roasting conditions were carefully controlled gold could be lost from the sample by partial volatilisation of gold compounds.

This paper describes the method used to extract gold from the sulphide samples, together with the subsequent atomic-absorption procedure. Samples analysed have ranged in gold concentration from 0·1 to 40 ppm.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical-reagent grade unless otherwise stated. All water used was mixed-bed demineralized water.

Equilibrated 0·1M *hydrochloric acid.* The acid was shaken with MIBK in a separating funnel for 2 min and allowed to settle, and the acid fraction was collected.

Equilibrated MIBK. Hydrochloric acid (1 + 4) was shaken with MIBK for 2 min and allowed to settle and the solvent layer was collected.

Standard gold solution (1 *ml* $\equiv$ 1000 *μg of gold*). Concentrated hydrochloric acid (16 ml) and concentrated nitric acid (4 ml) were added to 0·2500 g of gold wire (Johnson–Matthey "Specpure"), then the mixture was warmed gently. When the gold had dissolved, the solution was cooled and transferred to a 250 ml volumetric flask and diluted to volume with hydrochloric acid (1 + 4) and mixed well.

Preparation of calibration solutions. A 5 ml portion of the 1000 μg/ml gold solution was pipetted into a 100 ml volumetric flask and diluted to the mark with hydrochloric acid (1 + 4) to give a 50 μg/ml gold solution. Gold standards covering the range 0–20 μg/ml were prepared by addition of 0–4·0 ml portions of the 50 μg/ml standard to 80 ml of hydrochloric acid (1 + 4) in 250 ml separating funnels, addition of 10·0 ml of equilibrated MIBK from a pipette and shaking the mixture vigorously for 1 min. On settling, the aqueous phase was removed and the MIBK layer shaken for 15 sec with 15 ml of equilibrated 0·1*M* hydrochloric acid. The MIBK standard was retained in a stoppered glass tube. Calibration standards were prepared for each series of samples analysed. Higher calibration standards were prepared from samples containing more than 20 ppm of gold.

Apparatus and operating conditions

A Techtron A.A.5 atomic-absorption spectrophotometer was used, fitted with an AB.51 burner, digital read-out and a Perkin–Elmer Kel-F non-corrodible adjustable nebulizer.

For gold determinations the optimum operating conditions were as follows. Wavelength 242·8 nm; lamp current 4 mA; spectral band-pass 0·3 nm; Burner height 8 mm below light path; acetylene flow 1·6 rotameter units; air flow 6·5 rotameter units; solvent uptake rate 4·3 ml/min. There must be no trace of yellow luminosity in the flame while aspirating MIBK.

Under these conditions the sensitivity found for gold was 0·07 μg/ml. The detection limit was 0·05 μg/ml, which for a 20 g sample corresponds to 0·025 ppm of gold. With the fixed Techtron nebulizer the sensitivity obtained was only 0·15 μg/ml. The sensitivity is defined as the concentration of an element in μg/ml which gives 1% absorption (0·0044 absorbance). The limit of detection is that quantity of the analyte element which gives a reading equal to twice the standard deviation of a series of at least ten determinations, at or near the blank level.

Procedure

For gold levels of 0–5 ppm use 20·0 g samples, and for 5–20 ppm use 10·0 g samples. Weigh the finely ground sample (100-mesh) into a silica dish. If arsenopyrite is present, roast for 2 hr at 480°, then raise the temperature to 600°C and roast for a further 2 hr. In the absence of arsenopyrite, roast for 2 hr at 600° only. Cool the sample, transfer it to a 600 ml beaker, add 80 ml of 50% v/v hydrochloric acid and heat on a water-bath at 90°C for 2 hr. The beaker should be covered with a "Speedivap" or similar cover-glass. Add 20 ml of concentrated nitric acid and evaporate the solution to incipient dryness on a hot-plate. Cool the beaker, then add 80 ml of 20% v/v hydrochloric acid and boil. Cool, transfer the contents of the beaker to a 250-ml separating funnel and add 10·0 ml of equilibrated MIBK. Stopper, and shake vigorously for 1 min. Allow the phases to separate then discard the aqueous phase. Add 15 ml of equilibrated 0·1*M* hydrochloric acid and shake for 15 sec. Allow to settle, then discard the aqueous phase and filter the MIBK layer through a phase-separating paper directly into a glass sample-tube.

Aspirate the samples and standards, using equilibrated MIBK to wash out the nebulizer between samples. For some of the samples high in gold the burner head is angled slightly to reduce sensitivity.

RESULTS AND DISCUSSION

Initial development work was carried out on a sulphide ore and a copper concentrate prepared from the ore. Both samples were analysed for gold by the fire-assay method. Gold contents of 2·77 and 16·4 ppm were reported for the ore and concentrate respectively. The concentrations of other elements present in the two samples are given in Table 1.

Roasting of samples

Low gold assays have been reported for sulphide minerals when the analysis has been carried out without a preliminary sample roasting.[7] An explanation given is that *aqua regia*

Table 1. Analyses of sulphide ore and concentrate

	Sulphide ore	Sulphide concentrate
Cu%	2·2	20·0
Fe%	38·3	33·5
As%	0·2	0·03
S%	4·2	20·0

Table 2. Gold analyses for ore and concentrate after roasting trials

Roasting temperature, *C*	Gold assay on ore, *ppm*	Gold assay on concentrate, *ppm*
500	1·14	9·0
550	2·12	14·6
600	2·54	16·0
650	2·50	17·0
700	1·82	17·0
750	1·68	17·1
800	1·62	17·1

will not oxidize sulphides to sulphate, and free sulphur then separates out, collects the gold and limits acid attack on the metal. Roasting the samples before the acid treatment destroys the sulphides present and prevents the formation of sulphur.

The optimum temperature stated[7] for roasting sulphide minerals was 600°C, as above this temperature low gold assays were reported, possibly owing to partial volatilization of gold or its compounds. To verify this report, two series of roasting trials were carried out, one series using the ore and the second using the concentrate. Identical roasting procedure was adopted for both samples and consisted of roasting four portions of each material for 2 hr at temperatures ranging from 500° to 800°C in 50°C increments. Each batch of 28 samples was then analysed for gold by the method described in the experimental procedure. Results are shown in Table 2.

The low results for the two lower temperatures are due to incomplete breakdown of the sulphides present in the samples before acid treatment. As no gold losses occurred on roasting the concentrate samples, even at high temperature, it was thought that the arsenic present in the ore might have aided the volatilization of gold. Arsenic is present in the ore as arsenopyrite, FeAsS. As the arsenic imparts undesirable properties to copper metal the arsenopyrite is eliminated in the copper concentration process. Thus, the arsenic:gold ratio in the concentrate is approximately 15:1, whereas in the ore it is approximately 800:1. If a low boiling point Au/As alloy were formed, this would possibly explain the loss of gold from the ore at roasting temperatures above 600°C. As early as 1936 Spence[8] reported that, if during the roasting of arsenopyrite, the temperature was allowed to rise too quickly, then appreciable gold losses occurred. In an attempt to remove the arsenic, four sulphide ore samples were slowly heated to 480°C then maintained at this temperature for 2 hr. The arsenopyrite breaks down at this temperature and the arsenic volatilizes. The temperature was then raised to 700°C and the samples maintained at this temperature for a further 2 hr. Analysis of the four samples gave an average figure of 2·47 ppm gold, demonstrating that no gold had been lost.

Table 3. Recovery of gold in presence of 2% copper and 38% iron

Sample	Absorbance
1. Blank solution with 50 μg of Au	0·491
2. Sample with no Au added	0·004
3. Sample with 50 μg of Au	0·484
4. Sample with 50 μg of Au	0·486
5. Sample with 50 μg of Au	0·487
6. Sample with 50 μg of Au	0·485
7. Sample with 50 μg of Au	0·500

Decomposition with Aqua regia

It was not found possible to extract all of the gold present in the ore by treatment of the roasted sample with *aqua regia*. Gold assays after *aqua regia* decomposition gave values of only 0·3–0·5 ppm on the ore sample. Mineralogists, studying gold ores which were resistant to either cyanide or mercury attack, have reported that gold particles were sometimes coated with a layer consisting mainly of hydrated oxides of iron.[9] These coatings are found chiefly on gold particles present in iron/sulphide ores. When the coating is removed with dilute hydrochloric acid, both mercury and cyanide readily attack the gold. On application of this technique to the sulphide ore, *i.e.*, heating the ore sample, after roasting, with 50% v/v hydrochloric acid and then adding *aqua regia*, gold values of 2·66 ppm were achieved.

Interferences in the determination of gold

Gold is extracted into MIBK from 20% v/v hydrochloric acid as gold(III) chloride. The distribution coefficient for the extraction[10] is greater than 1000. Several other elements, including iron, are also extracted[11] into MIBK from 20% v/v hydrochloric acid. Large concentrations of iron in the MIBK were shown to cause interferences in the gold determinations, by molecular absorption. A hydrogen lamp was used to overcome this type of interference, but it was considered preferable to remove the iron from the solvent by a single 15 sec scrubbing with equilibrated 0·1*M* hydrochloric acid. The equilibrated acid is used to prevent the dissolution of MIBK in the acid during the scrubbing.

Hildon and Sully[1] have reported that both copper and iron cause low extraction of gold into MIBK when present in the sample solution. Six 20 g sulphide ore samples were processed as described in the analytical method. The gold was extracted from all six by shaking with MIBK, then the six gold-free aqueous phases were transferred to clean 250 ml separating funnels; 50 μg of gold were then added to each of five of the solutions and also to a blank solution of 100 ml of 20% v/v hydrochloric acid. The gold was then extracted into 10·0 ml of MIBK as described in the experimental procedure and the gold measured by atomic absorption. Results are given in Table 3.

These results show that the 2% copper and 38% iron have a negligible effect on the gold extraction.

A synthetic solution containing 4% w/v copper and 8% w/v iron in 20% v/v hydrochloric acid was prepared. This represents a solution resulting from the decomposition of a 20 g sample containing 20% copper and 40% iron, by the analytical procedure described. Five 100 ml aliquots were measured into 250 ml separating funnels, then 50 μg of gold were

Table 4. Recovery of gold in presence of 20% copper and 40% iron

Sample	Absorbance
1. Blank solution with 50 μg of Au	0·491
2. Sample with no Au	0·001
3. Sample with 50 μg of Au	0·500
4. Sample with 50 μg of Au	0·491
5. Sample with 50 μg of Au	0·492
6. Sample with 50 μg of Au	0·494

added to each of four of the solutions and also to a blank solution of 100 ml of 20% v/v hydrochloric acid. The gold was extracted into 10·0 ml of MIBK and the gold measured by atomic absorption. Results are given in Table 4.

It was concluded that the presence of up to 20% copper and 40% iron in the samples does not effect the solvent extraction of gold into MIBK under the experimental conditions specified.

Accuracy and precision

As well as the sulphide ore and concentrate samples, two standard reference materials were analysed for gold. These materials were both obtained from the Canadian Department of Energy, Mines and Resources, Ottawa. The first sample (PTM.1) was a nickel/copper matte and contained 44·8% nickel, 30·2% copper, 1·58% iron and 21·6% sulphur. The second Canadian sample (PTC.1) was a copper sulphide concentrate and contained 5·0% copper, 0·6% nickel, 0·3% cobalt, 24·2% iron and 24·1% sulphur. Accuracy and precision data are presented in Table 5.

Table 5. Accuracy and precision data on sample types analysed

Sample	Au by fire-assay, *ppm*	Certified Au, *ppm*	Number of determinations	Average Au, *ppm*	Relative standard deviation, %
Sulphide ore	2·77	—	30	2·66	7·3
Sulphide concentration	16·4	—	21	17·1	3·8
PTM.1	—	1·82	20	1·72	3·0
PTC.1	—	0·65	22	0·52	16·0

The precision of the gold analysis is largely governed by the distribution of gold particles in the sample.

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Résumé—On décrit une méthode qui est spécifique pour le dosage de l'or dans les minerais de sulfure de cuivre et les concentrats. On a trouvé que la décomposition directe avec l'eau régale est incomplète. Un stade de grillage soigneusement contrôlé suivi d'un traitement à l'acide chlorhydrique puis à l'eau régale a été efficace pour dissoudre tout l'or. L'or est extrait en 4-méthylpentan 2-one (méthylisobutylcétone), puis aspiré dans une flame air-acétylène très appauvrie et l'or est dosé par spectrométrie d'absorption atomique. On n'a pas observé d'interférences de grandes concentrations de cuivre, fer ou nickel.

Zusammenfassung—Ein Verfahren wird beschrieben, das besonders für die Bestimmung von Gold in sulfidischen Kupfererzen und -konzentraten gedacht ist. Es zeigte sich, daß der direkte Aufschluß mit Königswasser unvollständig verläuft. Alles Gold konnte gelöst werden durch sorgfältiges Rösten und anschließende Behandlung mit Salzsäure und dann Königswasser. Das Gold wird in 4-Methylpentan-2-on (Methylisobutylketon) extrahiert, dann in eine sehr magere Luft–Acetylen-Flamme gesaugt und das Gold durch Atomabsorptions–Spektrometrie bestimmt. Bei hohen Konzentrationen von Kupfer, Eisen oder Nickel wurde keine Störung beobachtet.

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ON THE REDUCTION OF OXYGEN IN AQUEOUS SOLUTION BY ELECTROLYTICALLY PRECIPITATED CADMIUM

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Summary—The reduction of oxygen in aqueous solution by electrolytically precipitated cadmium, used in a reductor column, has been studied in two ways. First, by analysis of the effluent for the hydrogen peroxide formed as a reaction intermediate, the conditions for quantitative reduction have been found. Attention is called to the fact that an effluent free from hydrogen peroxide also implies quantitative reduction of all dissolved oxygen. The practical consequences are pointed out. A comparison is also made with some other reductors. Secondly, the oxidation of electrolytically precipitated cadmium by hydrogen ion is strongly inhibited, so at pH 7 it is possible to determine oxygen as the equivalent amount of cadmium ion produced in the reductor column. The conditions of quantitative reduction of oxygen are determined and found to be in agreement with those obtained by the first method. From the results the solubility of oxygen in water in equilibrium with air is estimated and found to agree with a published result considered as reliable. An outline is given of a method for determination of oxygen in aqueous solution by measurement of the amount of cadmium ions produced.

Earlier observations[1–3] on the use of a reductor containing cadmium precipitated electrolytically according to Treadwell[4] showed its superiority to the Jones reductor with regard to requisite bed volume. The hydrogen evolution was also much smaller; the overvoltage of hydrogen on this form of cadmium is, in fact, so large that no evolution of hydrogen from 0·5*M* sulphuric acid is visually observed within a reasonable time. It follows that its efficiency as a reducing agent must be close to 100% and it should therefore be possible to determine, instead of the reduced substance, the equivalent amount of cadmium. This procedure should be of value when it is difficult or impossible to determine the reduced substance, *e.g.*, the reduction of certain organic substances, or the reduction of oxygen in aqueous solution to water. The last-mentioned example has been studied here partly with a view to determining the conditions for quantitative reduction of intermediately formed hydrogen peroxide, partly to ascertain the possibility of developing an entirely new method for the determination of oxygen in aqueous solution.

EXPERIMENTAL

Preparation of electrolytically precipitated cadmium

Smaller amounts (10–20 g) of cadmium may be prepared according to Treadwell,[4] by electrolysis of a nearly saturated solution of cadmium sulphate between platinum electrodes at a current density of about 30 A/dm^2. Larger amounts are conveniently prepared in the following manner. Starting materials are cadmium rods and cadmium sulphate of reagent quality. The cathode is a 10 mm diameter cadmium rod reaching to the bottom of a 2 litre squat-form beaker and introduced into closely fitting PVC tubing so that only a 5 mm length of its lower end is in contact with the electrolyte. The anode, placed just below the surface of the electrolyte, is made by melting cadmium in a 100 ml porcelain crucible and introducing a cadmium rod into the melt before it solidifies. This arrangement of the electrodes allows natural convection. On the bottom of the beaker and under the anode is placed a 5 × 7 cm crystallizing dish to collect the slime which is transported down from the anode.

The electrolyte, about 1·5 l., is a 40% (w/w) $CdSO_4$ solution acidified to pH ~ 3 with sulphuric acid. A voltage of 10–20 V will give a current of 3–6 A. The cadmium precipitates as fine dendritic needles; the higher the current density, the finer the precipitate. A well-defined current density cannot, however, be maintained, as the surface of the cathode continually grows as cadmium is precipitated. Electrolysis with high current density for longer times requires cooling of the electrolyte with an outer bath. The precipitated crystals are removed every quarter of an hour with a glass hook, and collected under water, which is later added to the electrolyte to compensate for evaporation. The cadmium crystals are matted together; to break the structure they are shaken with ~0·1M nitric acid, washed free from reaction products and kept under water. They may also be kept dry in a desiccator over silica gel if washed with methanol and immediately dried *in vacuo*. A fraction more free from matted lumps and suitable for filling of narrow tubes is obtained by sieving under water.

The reductors

The reductor tubes were straight glass tubes narrowed at both ends to 4 mm o.d. To facilitate filling they were constructed in two parts, a longer and a shorter, which could be joined glass to glass with a PVC ligature. The cadmium crystals were introduced under water to avoid entrapped air, and enclosed between Pyrex-wool plugs; for bed dimensions, see the table headings. The solution to be reduced was pumped or sucked through the reductor at different constant flow-rates by a peristaltic pump with Tygon tubing (Gilson "Minipuls II"). The cadmium hydroxide layer formed on the crystals by dissolved oxygen was removed before each series of experiments by washing with a few bed volumes of 0·25M sulphuric acid followed by the same volume of the solution to be reduced or, when convenient, by 0·01M imidazole–0·0025M sulphuric acid buffer solution. After prolonged use the cadmium bed was discoloured at the entrance end by traces of copper from the reagents and the distilled water. So far this has not caused any trouble.

Removal of oxygen from solutions

A solution free from oxygen for experiments on the reaction of cadmium with hydrogen ion was prepared by purging with nitrogen while vigorously stirring with a magnetic stirrer, the nitrogen being washed with 0·2M chromium(II) chloride-0·2M hydrochloric acid and with water. The requisite time was experimentally determined. The Tygon tubing used in the peristaltic pump was found to allow diffusion of small quantities of oxygen into the solution, which must therefore not be passed from the pump to the reductor but must be sucked through the reductor connected glass to glass to a tube dipping in the oxygen-free solution.

Equilibration of solutions with air

The solution, 0·5–1 l., was introduced into a 2·5 l. bottle of ~150 cm^2 cross-section which was placed in a thermostat. The stopper of the bottle was provided with holes for stirrer, tube to the reductor, and tube for introduction of a stream of air. Stirring was performed at 100 r.p.m. with an L-shaped glass rod dimensioned to give a steady rotation of the solution without vortices or bubbles. The air, introduced 5 cm above the surface and passing out through the play in the stirrer hole, was washed with 1M sodium hydroxide, and then saturated with water in a gas-washing bottle placed in the thermostat; the flow-rate was ~1 l./min. Samples were taken at various times by suction through the reductor with the peristaltic pump and 50 ml portions pipetted and titrated with EDTA (see below). The barometer was read a few times during the experiment; if the pressure varied by more than 1 mmHg the experiment was rejected. The results were corrected to correspond to air saturated with water vapour at the temperature of the experiment and a barometric pressure of 760 mmHg, by multiplication by the factor $(760 - p)/(B - p)$ where B is the observed barometric pressure, corrected for scale temperature, and p the saturation vapour pressure of water at the temperature of the experiment.

Determination of hydrogen peroxide

Hydrogen peroxide was determined by titration with 0·01M ceric sulphate with ferroin as indicator. A sample of 25 ml was pipetted into a 4 cm optical cell arranged in parallel with an identical cell containing water for comparison. The sample was made 0·5M in sulphuric acid, 50 μl of 0·001M ferroin were added and the titrant was added from a micro piston burette permitting additions of $1 \pm 0{\cdot}1$ μl. The method was tested on hydrogen peroxide solutions of known concentrations, and gave results which were satisfactory for the purpose. The end-point could be observed with an uncertainty of ± 1 μl.

Determination of cadmium

At μM concentrations cadmium was determined by atomic absorption, at higher concentrations by potentiometric titration according to Reilly *et al.*[5,6] with 0·01M EDTA, standardized in the same way against cadmium ("Specpure" cadmium rod, Johnson–Matthey & Co.). Amalgamated silver was used as indicating electrode, a mercurous sulphate electrode as reference. The buffer system used was imidazole–sulphuric acid at pH ~ 7, the imidazole in concentrations of 0·01–0·04M. The potential was measured to 0·1 mV with a digital voltmeter. The titrant was added from a calibrated piston burette permitting additions of 10 ± 1 μl. In 0·01M imidazole buffer the rate of change of the potential with titrant at the equivalence point was ~35 mV/10 μl. The equivalence point was calculated from the second derivative.

THE HYDROGEN PEROXIDE INTERFERENCE

Metals such as Ag, Cd, Pb, Zn or their amalgams have for a long time been used for reductions before redox titrations. The usual procedure is to pass the solution through a tube containing a bed of the finely divided metal or, for a liquid amalgam, to shake it with the solution. It has been found that dissolved oxygen is also at least partly reduced and this reduction seems to take place in two steps

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad E^0 = 0{\cdot}68\ \mathrm{V}$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad E^0 = 1{\cdot}77\ \mathrm{V}.$$

The second step, the reduction of hydrogen peroxide, proceeds considerably more slowly than the first, in spite of its much higher standard potential, a fact for which a simple mechanistic reason was suggested by Chalmers *et al.*[7] Therefore, if the metal or the amalgam is shaken with an aqueous solution in presence of air, a steady state is obtained, studied by Liebhafsky,[8] and a certain concentration of hydrogen peroxide is found in the solution. If the solution contains a substance which is reduced by the metal, but the reduced form of which is oxidized by hydrogen peroxide, the reduction will not be quantitative; an atmosphere free from oxygen is required. In careful work, reductions with liquid amalgams are performed under carbon dioxide.

When the reduction is performed in a reductor column the conditions will be different. Dilute aqueous solutions in equilibrium with air contain about 1 m-equiv of oxygen per litre. If such a solution, containing a substance such as the above-mentioned, is passed through the reductor, the reduction will be quantitative as long as this substance is present in the reductor in adequate concentration; the reduced substance reacts with any hydrogen peroxide formed and is again reduced. On subsequent washing of the reductor, however, a limit is soon reached when this destruction of the peroxide no longer occurs; it can now only be reduced by the metal. The rate of reduction of oxygen as well as of hydrogen peroxide by the metal must, however, be a function of the reducing power of the metal, its surface area, and the flow-rate of the solution. The effluent will be free from peroxide only if all dissolved oxygen is reduced and the remaining peroxide is given sufficient time for its reduction to water. For a given reductor the flow-rate must be the determining variable. Probably, failure to realise these facts is the explanation of the contradictory statements on the peroxide interference found in the literature. This conclusion was confirmed by the following experiments.

Solutions of different acidities and in equilibrium with air at room temperature (~20°C) and ambient pressure were passed through a cadmium reductor at different flow-rates and the hydrogen peroxide in the effluent was immediately determined. The results are given in Table 1. The flow-rate has been expressed in bed-volumes/min to facilitate comparison of different bed-volumes.

A couple of experiments were also performed with reductors filled with commercial granular cadmium (Merck's "Cadmium pulv. gross., Zur Füllung von Reduktoren") and with zinc (Baker's A.R., 30 mesh), amalgamated to contain 1% Hg. These results are given in Table 2.

From the results in Table 1 it appears that at sufficiently low flow-rate the peroxide concentration of the effluent in all the cases decreases below the detection limit. This must imply that all the dissolved oxygen has been used up, a conclusion confirmed later on in

Table 1. Hydrogen peroxide in effluents from reductors containing electrolytically precipitated cadmium. The experiments at a flow-rate of 40 bed-volumes/min were performed with bed dimensions 0·11 cm^2 × 2·7 cm = 0·30 cm^3, remaining experiments with bed dimensions 0·36 cm^2 × 2·7 cm = 1·0 cm^3

Solution	H_2O_2, *µmole/l.*, found at a flow-rate, *bed-volumes/min*, of 40	12	5	2	1
0·5*M* H_2SO_4	5·2	0·2	<0·2	<0·2	—
0·1*M* H_2SO_4	4·6	0·2	<0·2	<0·2	—
0·01*M* H_2SO_4	5·8	0·6	<0·2	<0·2	—
0·001*M* H_2SO_4	2·8	0·2	<0·2	<0·2	—
0·01*M* CH_3COOH– 0·01*M* CH_3COONa	4·6	0·2	<0·2	<0·2	—
0·01*M* CH_3COONH_4	1·8	0·2	<0·2	—	—
H_2O	11·8	12·8	4·2	0·2	<0·2

this paper, and the hydrogen peroxide interference has thus been eliminated. This fact directly contradicts the statement made by Salam Khan and Stephen[9] that for satisfactory results to be obtained with any metallic reductor, it is necessary to exclude oxygen completely from the solution.

No definite tendency to pH-dependence of the reduction rate can be inferred from these results. On the contrary, the low reduction rate in pure water is remarkable. By reduction of the oxygen dissolved in 1 litre of water at equilibrium with air about 500 µmoles of $Cd(OH)_2$ are formed, the solubility of which is about 10 µmole/l. The cadmium hydroxide not dissolved will probably form a layer on the cadmium crystals, thereby considerably reducing their efficiency; in the sulphuric acid and acetate solutions used here, the solubility of the hydroxide is adequate.

As to the practical use of the reductor before a redox titration the following conclusions can be drawn. At a flow-rate of 5–10 bed-volumes/min the hydrogen peroxide error will be <0·4 µ-equiv/l. and will probably rapidly approach zero if the flow-rate is further reduced. However, this requires that the sample solution as well as the washing solution is able to dissolve cadmium hydroxide in adequate amounts. The reductor should not be washed with only water except before a period of non-use. As the effluent is completely free from oxygen it should show good keeping qualities against oxidation as long as air is excluded.

The results in Table 2 also show a decrease in peroxide concentration with decreasing flow-rate. The reduction was, however, considerably slower than that with electrolytically

Table 2. Hydrogen peroxide in 0·1*M* H_2SO_4 passed through reductors containing commercial granular cadmium or amalgamated zinc. Bed dimensions: 0·36 cm^2 × 2·7 cm = 1·0 cm^3

Flow-rate, *bed-volumes/min*	H_2O_2, *µmole/l.*, found in effluent from reductor containing cadmium	amalg. zinc
10	3·2	23·5
5	1·7	10·7
2	0·6	2·1
1	0·2	1·7
0·5	—	0·4

Table 3. The rate of reaction between cadmium and hydrogen ion in some solutions. Bed dimensions: 0·11 cm^2 × 7·3 cm = 0·80 cm^3

Solution	Cd, *μmole/l.*, found at a flow-rate, *bed-volumes/min*, of 1·2	2·6	5·2	10·4	15·2
0·01*M* imidazole–0·0025*M* H_2SO_4	0·54	0·36	0·29	0·21	—
0·01*M* H_2SO_4	8·0	4·6	2·8	1·7	1·2
0·1*M* H_2SO_4	—	19·8	12·2	7·4	5·5
	Excess of Cd found, *μmole/l.*				
0·01*M* H_2SO_4–500*μM* $CdSO_4$	2·6	2·6	1·2	1·0	—
0·1*M* H_2SO_4–500*μM* $CdSO_4$	—	5·6	4·4	—	1·6

precipitated cadmium, clearly demonstrating the great advantage of this form of cadmium. The lower efficiency of the granular cadmium must be ascribed to its smaller specific surface, that of the amalgamated zinc to the same cause but also to the amalgamation which to some extent has decreased its reducing power. In both cases evolution of hydrogen was observed at the lower flow-rates and this may well have contributed to the lowered efficiency. The considerably greater risk of hydrogen peroxide interference when using a Jones reductor, is demonstrated.

In this connection it is of interest to consider the observation made by Miller and Chalmers[10] when using a silver reductor. Though the silver, precipitated by copper from a silver nitrate solution, had a large specific surface, and a flow-rate, calculated from their data, of only 1–2 bed-volumes/min was used, they nevertheless detected hydrogen peroxide in the effluent if air was not excluded from the solution. This may be considered as an example of low reducing power of the metal.

THE REACTION BETWEEN CADMIUM AND HYDROGEN ION

The reduction of oxygen in aqueous solution by cadmium produces an equivalent amount of cadmium hydroxide. If this is dissolved, a determination of the cadmium concentration in the solution will give the original concentration of oxygen. This requires

Table 4. The time required for equilibration between air and 0·01*M* imidazole–0·0025*M* H_2SO_4 solution under the experimental conditions used. Bed dimensions: 0·36 cm^2 × 5·5 cm = 2·0 cm^3. Flow-rate: 5 bed-volumes/min. (*i*) Starting solution over-saturated, B = 754·1 mmHg. (*ii*) Starting solution under-saturated, B = 754·4 mmHg. The results given are corrected to correspond to air saturated with water at 20·0°C and 760 mmHg

Time sample was taken, *min*	Concentration of Cd (or O) found (*i*), *μM*	(*ii*), *μM*
0	610·8	532·4
15	588·0	554·4
30	580·4	560·8
60	570·9	564·8
90	568·5	566·7
120	566·7	567·1
150	566·7	566·9

among other things that the reaction between cadmium and hydrogen ion is strongly inhibited. The rate of this reaction in some solutions of interest was investigated. Oxygen was removed from the solutions by purging with nitrogen. They were then sucked through the reductor at different flow-rates and the resulting cadmium concentrations determined by atomic absorption or by titration of 50 ml samples. The results are given in Table 3.

From the first three experiments it appears that, for a certain solution, the amount of cadmium dissolved per unit of time decreases somewhat when the cadmium concentration increases. On this account the last two experiments were performed in which cadmium sulphate had been added to the solutions in an amount approximately corresponding to the dissolved oxygen under normal conditions. As expected, the amount of cadmium dissolved was considerably reduced. No such experiment using the imidazole buffer solution was performed, as the response was expected to be smaller than the experimental error.

The imidazole buffer solution, pH ~ 7·0, was used at its maximum buffer capacity. It was selected because it forms a complex with cadmium ion of sufficient stability to keep cadmium in solution but yet permits titration with EDTA. At flow-rates >2 bed-volumes/min the cadmium concentration found is $<0{\cdot}1\%$ of that which would be produced by a normal oxygen concentration in the solution. This error should, however, be further decreased in an actual analysis on account of the previously mentioned influence of the cadmium concentration.

It may be questioned whether the nitrogen used for the experiments had been completely freed from oxygen. Extrapolation of the results obtained at pH 7 to the reciprocal rate of 0 min/bed-volume gives a value of $0{\cdot}18\mu M$ Cd which should be the maximum cadmium concentration caused by a possible oxygen content in the nitrogen. If this correction is accepted, the cadmium dissolved at a flow-rate of 5 bed-volumes/min should be ~0·1 μmole/l.

DETERMINATION OF OXYGEN AS CADMIUM

A $0{\cdot}01M$ imidazole–$0{\cdot}0025M$ sulphuric acid solution was equilibrated at 20·0°C with air saturated with water and at the ambient barometric pressure. The conditions for quantitative reduction of the dissolved oxygen were then determined with the resulting cadmium concentration as a measure.

The time required for equilibration at 20·0°C was determined starting both from over- and under-saturated solutions. They were produced by vigorous shaking with air at 15 or 25°C for a minute followed by rapid warming or cooling to the experimental temperature. The results are given in Table 4. It appears that equilibrium has been attained after 120 min, and to at least 99·7% even after 90 min. In the following experiments the equilibrium was assumed to be attained after 90 min when the solution had been shaken with air at 20°C immediately before starting.

The reduction as a function of the flow-rate was then determined. The results are given in Table 5. The experiments on the reduction of hydrogen peroxide, Table 1, indicated quantitative reduction of oxygen at flow-rates somewhat lower than 12 bed-volumes/min. This is confirmed by the results of Table 5. Quantitative reduction has been obtained at flow-rates of 10 bed-volumes/min and lower. The reduction is rapid; even at a flow-rate of 33 bed-volumes/min 98·5% is reduced.

From the 16 results of Tables 4 and 5 obtained at equilibrium or for quantitative reduction, a mean oxygen concentration of $566{\cdot}9\ \mu M$, or 9·070 mg/l. in the imidazole buffer solution, is calculated. The standard deviation of a single result is $0{\cdot}42\ \mu M$ or 0·007 mg/l. re-

Table 5. Reduction of dissolved oxygen as a function of flow-rate. Temperature 20·0°C. The results are corrected to correspond to air saturated with water at 20·0°C and 760 mmHg

Flow-rate, *bed-volumes/min*	Concentration of Cd (or O) found, *μM*	
	Bed dimensions: 0·11 cm^2 × 2·7 cm = 0·30 cm^3	
	B = 758·8 mmHg	*B* = 751·1 mmHg
33	559·7	558·5
20	564·1	563·8
10	567·1	566·4
5	567·1	567·2
	Bed dimensions: 0·36 cm^2 × 5·5 cm = 2·0 cm^3	
	B = 740·5 mmHg	*B* = 756·7 mmHg
5	567·1	567·5
5	566·3	566·5
2	566·1	567·1
2	566·5	567·5

spectively. The solubility of oxygen in pure water under the actual conditions can be estimated if the decrease in solubility caused by the buffer substances is, as a rough correction, set equal to that obtained in 0·01*M* sodium chloride. The latter is calculated from the tables given by Truesdale *et al.*[11] to be 0·028 mg/l. Applying this correction, the solubility of oxygen in water in equilibrium with air saturated with water vapour at 20·0°C and 760 mmHg is estimated to be 9·098 mg/l. The uncertainty of the correction is estimated to be within 0·01 mg/l.

The most reliable values for the solubility of oxygen in water at a pressure of 760 mmHg are probably those given by Klots and Benson,[12] *cf* Grasshoff.[13] From these, and accepting Carpenter's[14] value for the oxygen content of air, 20·94% by volume, the actual solubility is calculated to be 9·094 mg/l. This agrees with the estimated value within the uncertainty of the latter.

DISCUSSION

From the results obtained here it should be possible to develop a method for the determination of oxygen in water or dilute water solutions. For every kind of sample, however, the preliminary treatment and the conceivable presence of interfering substances must be considered.

The preliminary treatment of a sample implies that its pH must be adjusted to near 7 with a buffer which is able to keep cadmium in solution, and this must be done without altering the oxygen content of the sample in an unknown way. In some cases neutralization by acid or base must precede or be combined with the final adjustment, but in many cases it should be adequate to make the sample 0·01*M* with respect to the imidazole buffer used here. A 5*M* stock solution of this buffer can be made, and the volume needed of this is only 0·2% of the sample volume; in this way the correction for the oxygen content of the buffer solution will be small and may in many cases be omitted. The addition may be done as for the addition of reagents in the well-known Winkler method or, in flow-systems like that of the Technicon Auto-Analyzer, before the reductor step so that the sample/buffer volume ratio is kept constant.

Apart from metal ions such as Cd^{2+} or Zn^{2+} which will pass through the reductor unchanged and then be titrated, interfering substances are those which are reduced, producing cadmium ions, and those which interfere with the cadmium determination proper; a combination of both may occur. An interfering substance of the former type is for instance nitrate, which at pH 7 is reduced to nitrite. Its occurrence in natural waters limits the use of the method for this kind of sample. In principle, however, if its concentration is low compared with that of the oxygen, a correction may be applied by determination of nitrite before and after reduction. A possible alternative is to remove nitrate ion by the acetate or sulphate form of an anion-exchanger, in a flow-system introduced before the addition of the buffer.

The nature of the substances interfering with the cadmium determination depends, of course, on the method used. In the titration method used in this paper, larger amounts of chloride, as in sea-water, destroy the potential jump by complexation with the mercuric ions participating in the electrode reaction. Removal of chloride by evaporation with some appropriate acid before titration is possible but will considerably lengthen the procedure. The difficulty may also be avoided by using a visual indicator but probably with a lower precision. The presence of calcium and magnesium in reasonable concentrations should not interfere, especially if the titration pH is kept as low as possible.

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Résumé—On a étudié par deux voies la réduction de l'oxygène en solution aqueuse par le cadmium précipité électrolytiquement, utilisé dans une colonne à réduction. Premièrement, on a trouvé les conditions pour la réduction quantitative par analyse de l'effluent pour le peroxyde d'hydrogène formé en tant qu'intermédiaire de réaction. On attire l'attention sur le fait qu'un effluent exempt de peroxyde d'hydrogène implique aussi la réduction quantitative de tout l'oxygène dissous. Les conséquences pratiques sont dégagées. On effectue aussi une comparaison avec quelques autres appareils à réduction. Deuxièmement, l'oxydation du cadmium précipité électrolytiquement par l'ion hydrogène est fortement inhibée, de sorte qu'à pH 7 il est possible de déterminer l'oxygène comme la quantité équivalente d'ion cadmium produite dans la colonne à réduction. On a déterminé les conditions de réduction quantitative de l'oxygène et l'on a trouvé qu'elles sont en accord avec celles obtenues par la première méthode. Des résultats, on estime la solubilité de l'oxygène dans l'eau en équilibre avec l'air, et la trouve en accord avec un résultat publié considéré comme sûr. On donne un schéma d'une méthode pour le dosage de l'oxygène en solution aqueuse par mesure de la quantité d'ions cadmium produite.

Zusammenfassung—Die Reduktion von Sauerstoff in wäßriger Lösung durch elektrolytisch gefälltes Cadmium in einer Reduktorsäule wurde auf zwei Arten untersucht. Zuerst wurden durch Analyse der abfließenden Lösung auf das als Zwischenprodukt gebildete Wasserstoffperoxid die Bedingungen für eine quantitative Reduktion gefunden. Es wird darauf aufmerksam gemacht, daß eine von Wasserstoffperoxid freie abfließende Lösung ebenfalls die quantitative Reduktion alles gelosten Sauerstoffs bedeutet. Die praktischen Konsequenzen werden dargelegt. Es wird auch ein Vergleich mit einigen anderen Reduktoren angestellt. Zweitens ist die Oxidation von elektrolytisch abgeschiedenem Cadmium durch Wasserstoffionen stark gehemmt; deswegen kann man bei pH 7 Sauerstoff bestimmen als die äquivalente Menge zu den in der Reduktorsäule erzeugten Cadmiumionen. Die Bedingungen für die quantitative Reduktion von Sauerstoff wurden ermittelt; es waren dieselben wie die auf die erste Methode gefundenen. Aus den Ergebnissen wurde auf die Löslichkeit von Sauerstoff in Wasser geschlossen, das mit Luft im Gleichgewicht steht; der erhaltene Wert stimmte einem in der Literatur angegebenen, als zuverlässig betrachteten Wert überein. Für die Bestimmung von Sauerstoff in wäßriger Lösung durch Messung der erzeugten Cadmiumionenmenge wird eine Arbeitsvorschrift skizziert.

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TITRATIONS USING AN APPARATUS FOR RECORDING THE ANTILOGARITHM OF pH OR pM

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Summary—A titration apparatus plotting either the concentration of sample ion or the concentration of titrant ion has been tested. An antilog apparatus, converting measured e.m.f. values into concentrations is connected to ordinary titration equipment. The instrument has been tested by means of acid–base titrations (titrations of mixtures of weak acids and of a weak and a strong acid), precipitation titrations (determination of the chloride concentration in tap-water, titration of mixtures of halides), titrations with ion-selective electrodes (determination of the fluoride content of toothpaste) and complexometric titrations (determination of copper with EDTA, using mercuric ion as indicator ion and amalgamated silver rod as indicator electrode, or using a copper-selective indicator electrode). The method considerably simplifies the evaluation of the results as compared to conventional potentiometric titrations.

Evaluation of titrations by using Gran functions has gained popularity during recent years, even outside Scandinavia. The method was first presented at the first IUPAC Congress in Analytical Chemistry, held in Oxford in 1952. At that meeting the present author[1] pointed out that the use of antilogarithmic–linear paper would simplify the calculation of the Gran function. The idea was taken up in 1970 by Orion Research Incorporated.[2]

Evaluating a titration curve according to the Gran method is also a simple task if one has access to an electronic computer, and computer programs have been published by, among others, Dyrssen, Jagner and Wengelin.[3] However, as far as the present author has been able to find out, nobody has until now designed a titration apparatus for recording concentrations from measured pM, pH or e.m.f. values, *i.e.*, for the direct recording of a Gran plot.

This paper describes some attempts to utilize for this purpose the possibilities offered by modern electronics. The instrument that was used for analogue calculation of antilogarithms was made by Optilab AB Stockholm. It works in the following manner.

To transform a logarithm pM to the corresponding number $10^{-\text{pM}}$ the instrument utilizes an "exponential ramp" that results when a capacitor is discharged through a resistor having a constant resistance value. The principal advantages of the method, which has been successfully tested in other instruments, are that it is very accurate and nearly independent of temperature variations. This is a necessity for obtaining results of the high quality required. A linear ramp is run simultaneously with the exponential ramp. When the voltage of the linear ramp attains the value pM, the exponential ramp is interrupted and its voltage is transferred to a memory. The ramping is repeated about ten times a second and the output signal of the memory is consequently roughly continuous.

The antilog apparatus is inserted between the pH-meter and the recorder in a recording titration apparatus and the recorder then plots the concentration of the indicator ion as a function of the volume of added titrant. The titration apparatus was a Metrohm Potentiograph Model E336 A, equipped with a piston burette, the piston being driven synchronously with the recording paper. For measuring pH-values an Orion digital pH-motor Model 701 was used.

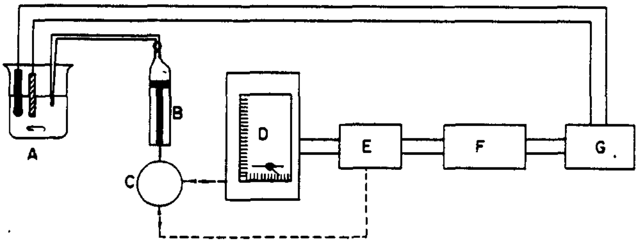

Fig. 1. Schematic diagram of the apparatus. *A*—titration vessel with electrodes and stirrer, *C*—motor, driving the piston of burette *B*, the paper of the recorder *D* and a helipot R_3 in the volume-correcting unit *E* (refer to Fig. 2). *F* is the antilog apparatus and *G* a pH-meter.

Naturally, it is not practical in an acid–base titration to convert the entire pH range 0–14 into a single linear scale. If the recorder is adjusted to full deflection at pH 0, the reading will be 1/100 of full deflection at pH 2, and at pH 3 only 1/1000 of the full scale value; at still higher pH values the reading will rapidly approach zero. Therefore, one feature of the instrument is the possibility of selecting the most suitable measuring range. After the equivalence point in the titration it is more interesting to record 1/[H] or K_w/[H], *i.e.*, [OH] instead of [H]. The instrument performs the necessary switching automatically. A flow-scheme is given in Fig. 1.

The pH-meter is used as a millivoltmeter and no readings are taken during the course of the titration. The measured e.m.f. for a certain ionic species M is given by

$$E_c = E_c^0 + (RT/nF)\ \ln[\mathrm{M}], \tag{1}$$

where $E_c^0 = E_M^0 + E_{ref} + (RT/nF)\ \ln\gamma_M$ + junction potentials. E_M^0 denotes the normal potential, E_{ref} the potential of the reference electrode, γ_M the activity coefficient and [M] the concentration of the ion M^{n+}. The notation E_c indicates that the equation is valid for concentrations instead of activities. According to equation (1),

$$[\mathrm{M}] = 10^{(E_c - E_c^0)n/Q} = 10^{E_c n/Q} \times 10^{-E_c^0 n/Q}, \tag{2}$$

where $Q = (RT\ln 10)/F$. The last factor in equation (2) is a constant if E_M^0, E_{ref}, γ_M and the junction potentials remain constant. The e.m.f. value E_c is divided by Q in the pH-meter, whereas the multiplication by n is made in the antilog apparatus. The E_c^0 value may be adjusted with the calibration control and the value of Q with the temperature control of the pH-meter. Thus we finally have

$$[\mathrm{M}] = \text{constant} \times \text{antilog}(E_c n/Q). \tag{3}$$

This quantity [M] is recorded by the instrument. Usually, it is not necessary to know the value of the constant. It is, however, possible to determine its value by calibration with known concentrations of M. In order to ensure linear Gran plots, it is necessary that the Q-value is not only constant, but also correct.

The use of the apparatus is best made clear by some examples. In this paper some acid–base, precipitation and complexation titrations will be presented.

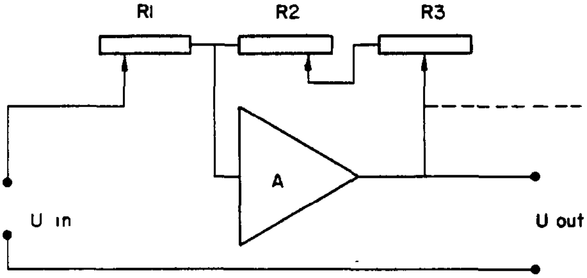

Fig. 2. Schematic diagram of the volume corrector. A is an operational amplifier, R_1 and R_2 helipots having maximum resistance 50 kΩ and R_3 a helipot having 10 kΩ maximum resistance.

Example 1. *Titration of a strong acid*

In the titration of a strong acid with a strong base, the concentration of hydrogen ions decreases linearly with the volume of base added before the equivalence point. After the equivalence point, the hydroxide ion concentration increases linearly with the volume of added base. In both cases the recorded values should be corrected for dilution.

Consequently, if

(a) before the equivalence point $(V_0 + V) \times [\mathrm{H}] \times$ constant and

(b) after the equivalence point $(V_0 + V) \times 1/[H] \times$ *constant*

are plotted as functions of V (V_0 being the volume of the sample solution at the start of the titration and V the volume of added titrant), two linear branches intersecting each other at the equivalence point will result. The correction for dilution can be made with the aid of an operational amplifier as outlined in Fig. 2.

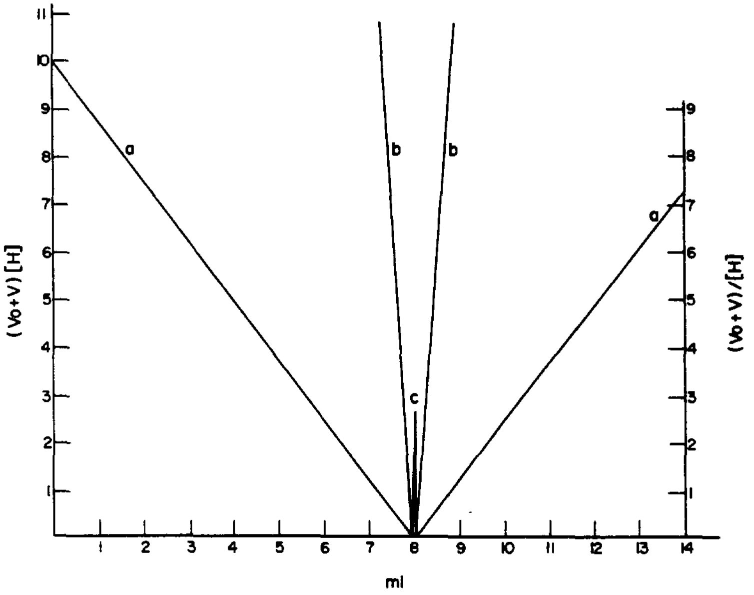

Fig. 3. Titrations of hydrochloric acid with 0·1M sodium hydroxide. Before the equivalence point, $(V_0 + V)[\mathrm{H}]$ and after the equivalence point $(V_0 + V)/[\mathrm{H}]$ were recorded in arbitrary units as functions of the volume of added titrant. Different sensitivities were used for the different titrations (a) and (b). The peak at (c) is due to the automatic switching from [H] to 1/[H] causing electric interference.

A is an operational amplifier and R_1, R_2 and R_3 are variable resistors. The output of the antilog apparatus is connected to the points marked U_{in} and the recorder to the points marked U_{out}. The maximum resistance of R_3 is 10 kΩ and it is connected to the piston burette so as to have zero resistance at $V = 0$ with an increase of 500 Ω for every ml of titrant. The resistance values of R_1 and R_2 are $V_0 \times 500\,\Omega$. According to the rules for operational amplifiers,

$$U_{out} = \frac{R_2 + R_3}{R_1} \times U_{in} = \frac{V_0 + V}{V_0} \times U_{in}.$$

(After the paper was completed, a somewhat simpler solution of the problem of correcting for dilution has been published,[4] but the circuit cannot be used for multiplication by V as required by example 2.)

Figure 3 shows the curves obtained for a titration of 80 ml of 0·01M hydrochloric acid with 0·1M sodium hydroxide. Sodium chloride was added to both solutions in order to achieve a constant ionic strength of approximately 0·5. For Fig. 3a, the sensitivity of the instrument was adjusted so as to give full deflection on the recorder at the start of the titration and at the point where sodium hydroxide had been added in 10-ml excess. As a result, two straight lines that intersect each other at the equivalence point were obtained. The antilog apparatus changes the sign of the signal at the equivalence point. The equivalence volume found was in agreement with the calculated value, 8·05 ml.

Greater accuracy is achieved by choosing higher sensitivity and recording only the region close to the equivalence point, as shown in Fig. 3b.

Example 2. Titration of a weak acid

In a titration of a weak acid, for example acetic acid, HAc, the concentration of HAc decreases linearly with the volume of sodium hydroxide added before the equivalence

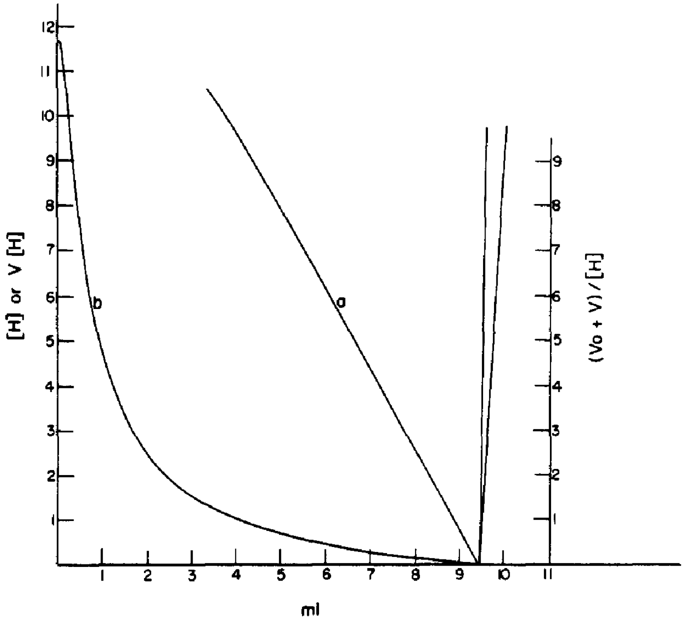

Fig. 4. Titration of acetic acid with 0·1M sodium hydroxide. Branch (a) represents V[H] and branch (b) (V_0 + V)[H], both in arbitrary units. After the equivalence point, (V_0 + V)/[H] was recorded.

point. Before the equivalence point, $V[\mathrm{H}]$, and after it, $(V_0 + V)/[\mathrm{H}]$ should be plotted as functions of V in order to obtain straight lines intersecting each other at the equivalence point (refer, *e.g.*, to Johansson[5]). The first branch can be recorded by setting R_1 (Fig. 2) at 500 Ω and R_2 at zero and letting R_3 increase linearly with the volume of added titrant as in the previous example. The titration curve will then start at the origin and pass through a maximum value subsequently intersecting the V-axis at the equivalence volume. The titration curve is shown in Fig. 4*a*. The first part of the curve was irregular and is therefore not reproduced here. Figure 4*b* shows the result of plotting $(V_0 + V)[H]$ and $(V_0 + V)/[\mathrm{H}]$ as functions of V. This plot also permits a simple evaluation of the equivalence volume.

Example 3. *Titration of mixtures of weak acids*

Naturally, titration of hydrochloric acid or acetic acid presents no problem even when conventional recording titrators are used, and the suggested antilog apparatus does not have any advantages. However, the picture will be somewhat different when mixtures of acids are to be titrated.

Figure 5 shows the results of titration of different mixtures of formic acid and acetic acid. The differences between the curves are large enough to permit evaluation of the concentration of both acids in an unknown mixture by titration. The following procedure is recommended.

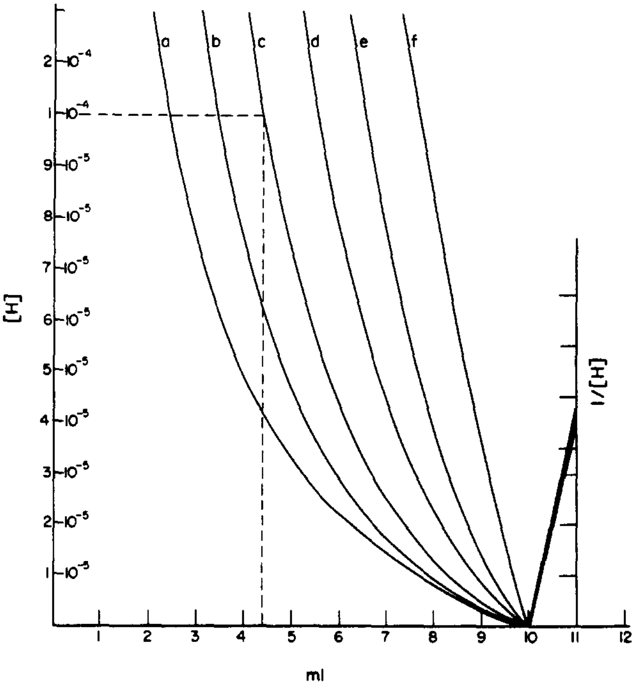

Fig. 5. Titrations of mixtures of 0·1M acetic acid and 0·1M formic acid in the proportions 10 + 0, 8 + 2, 6 + 4, 4 + 6, 2 + 8, 0 + 10 ml (*a*–*f*). Before the equivalence point, [H] was recorded. The full-scale deflection corresponded to $[\mathrm{H}^+] = 10^{-4}M$ and the scale was calibrated by using 1M acetic acid + 1M sodium acetate buffer, which corresponds to $[\mathrm{H}^+] = 3{\cdot}16 \times 10^{-5}M$. After the equivalence point, 1/[H] was recorded in arbitrary units.

A solution having a known concentration of hydrogen ions is used to adjust the antilog apparatus. As an example, [H] may be $0{\cdot}316 \times 10^{-4}M$, *i.e.*, $-\log[\mathrm{H}] = 4{\cdot}50$, the result of mixing equal amounts of $1M$ acetic acid and $1M$ sodium acetate solutions. (The notation $-\log[\mathrm{H}]$ is used in place of pH to stress that concentrations are used instead of activities.) The titrations shown in Fig. 5 were made in this way, the ionic strength being kept constant at 0·5 by addition of sodium chloride to the solutions.

The concentrations of formic acid and acetic acid can be calculated in the following way. Assume that V_0 ml of a solution having concentration C_{01} of formic acid (HFo) and C_{02} of acetic acid are titrated with V ml of strong base having concentration C_B. The formic acid consumes V_{e1} ml and the acetic acid V_{e2} ml of the titrant at equivalence. The electroneutrality condition

$$[\mathrm{Fo}^-] + [\mathrm{Ac}^-] + [\mathrm{OH}^-] = [\mathrm{Na}^+] + [\mathrm{H}^+],$$

and the equilibrium conditions

$$K_{\mathrm{HAc}} = \frac{[\mathrm{HAc}]}{[\mathrm{H}]\,[\mathrm{Ac}]}; \quad K_{\mathrm{HFo}} = \frac{[\mathrm{HFo}]}{[\mathrm{H}]\,[\mathrm{Fo}]},$$

yield

$$\frac{V_0 C_{01}}{1 + [\mathrm{H}]K_{\mathrm{HFo}}} + \frac{V_0 C_{02}}{1 + [\mathrm{H}]K_{\mathrm{HAc}}} = VC_B + (V_0 + V)([\mathrm{H}] - K_w/[\mathrm{H}]),$$

or

$$\frac{V_{e1}}{1 + [\mathrm{H}]K_{\mathrm{HFo}}} + \frac{V_{e2}}{1 + [\mathrm{H}]K_{\mathrm{HAc}}} = V + (V_0 + V)[\mathrm{H}]/C_B, \tag{4}$$

if $[\mathrm{OH}^-]$ may be neglected when the solution is acidic.

We may rewrite equation (4) as follows:

$$\frac{V_{e1}}{r} + \frac{V_{e2}}{s} = t,$$

where $r = 1 + [\mathrm{H}]K_{\mathrm{HFo}}$
$s = 1 + [\mathrm{H}]K_{\mathrm{HAc}}$
$t = V + (V_0 + V)[\mathrm{H}]/C_B$

If we write $V_e = V_{e1} + V_{e2}$ we finally get

$$V_{e1} = \frac{r(V_e - st)}{r - s}; \quad V_{e2} = \frac{s(V_e - rt)}{s - r}.$$

A number of points on the titration curve may be used for the calculation of V_{e1} and V_{e2}. Since the calculation is made without a computer it is most convenient to choose some suitable [H] value, *e.g.*, $10^{-4}M$. Further, V_e is easily read from the titration curve.

Example. Curve *c* in Fig. 5. A mixture containing 6·00 ml of $0{\cdot}1M$ acetic acid, 4·00 ml of $0{\cdot}1M$ formic acid and 70 ml of $0{\cdot}5M$ sodium chloride solution was titrated with a solution $0{\cdot}1M$ in sodium hydroxide and $0{\cdot}4M$ in sodium chloride. $V_e = 10{\cdot}00$ ml and $V = 4{\cdot}40$ ml at $[\mathrm{H}] = 10^{-4}M$ are read off the curve. With $K_{\mathrm{HFo}} = 0{\cdot}31 \times 10^4$ and $K_{\mathrm{HAc}} = 3{\cdot}16 \times 10^4$ (valid at the ionic strength in question) we get $r = 1 + 0{\cdot}31$, $s = 1 + 3{\cdot}16$ and $t = 4{\cdot}40 +$

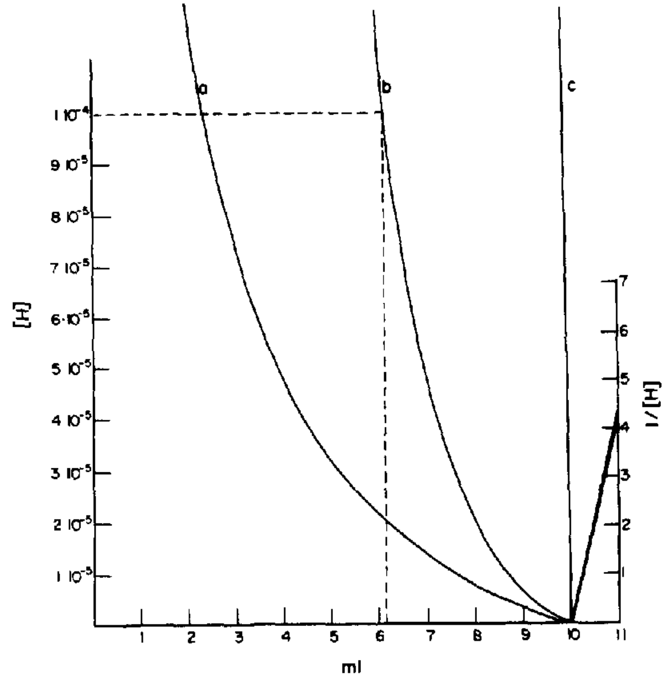

Fig. 6. Titrations of acetic acid and hydrochloric acid with 0·1*M* sodium hydroxide. Curve (*a*) pure acetic acid, curve (*c*) pure hydrochloric acid and curve (*b*) 5 + 5 ml mixture of acetic acid and hydrochloric acid. Refer to the caption of Fig. 5.

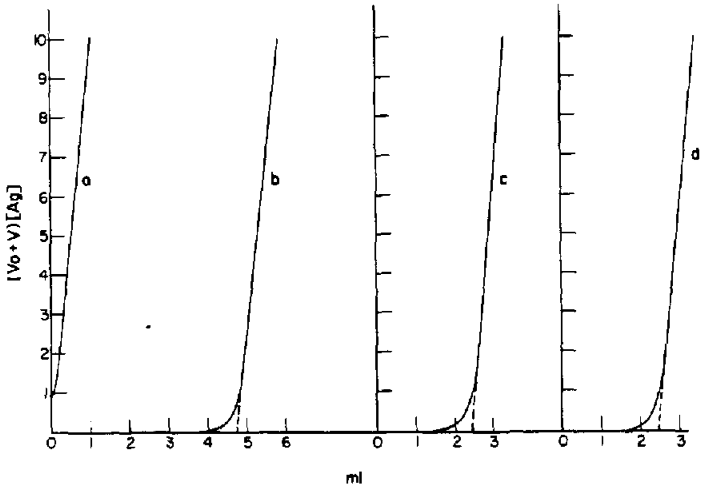

Fig. 7. Titrations of dilute solutions of chloride ion. (*a*) Titration of distilled water. (*b*) titration of 80 ml of 6·25 × 10^{-4}*M* sodium chloride, and (*c*) and (*d*) titrations of tap-water. Only (V_0 + V)[Ag], *i.e.*, the branch resulting after the equivalence point, was recorded, in arbitrary units.

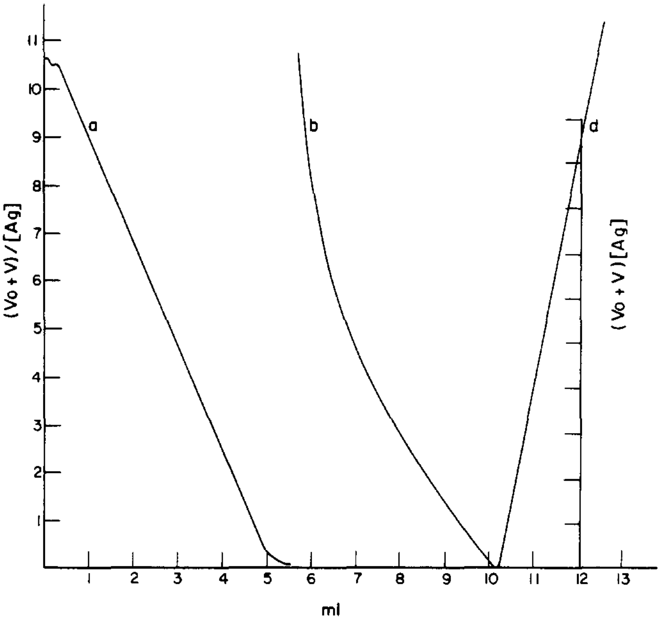
(Vo + V) / [Ag]
(Vo + V) [Ag]
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Fig. 8(*a*).

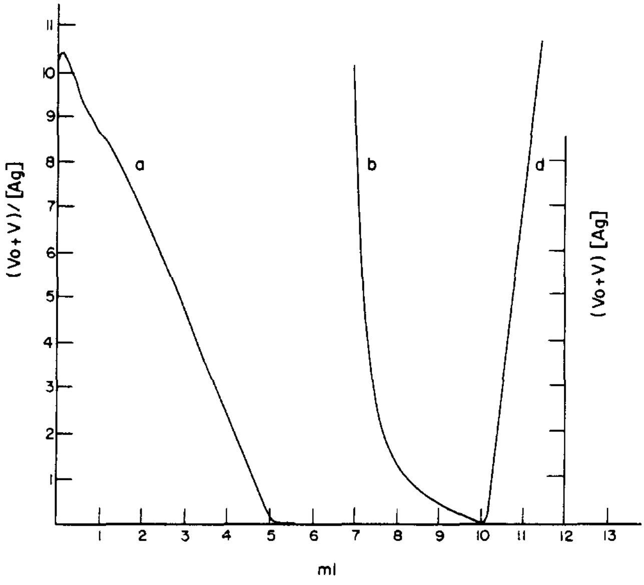
(Vo + V) / [Ag]
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Fig. 8(*b*).

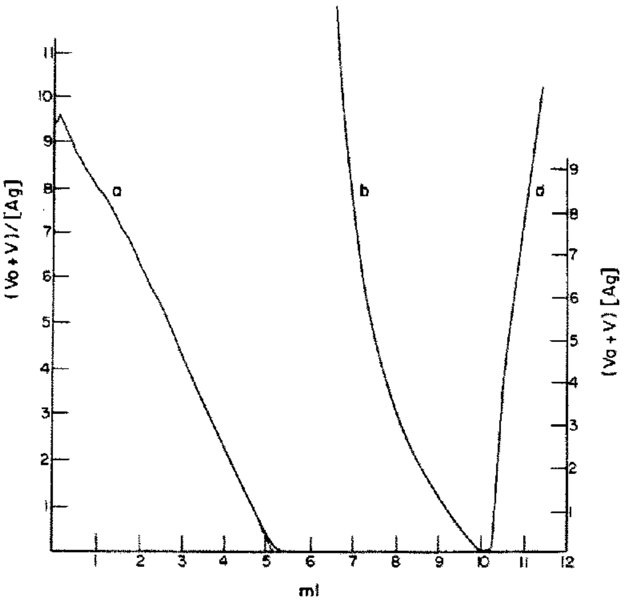

Fig. 8(*c*).

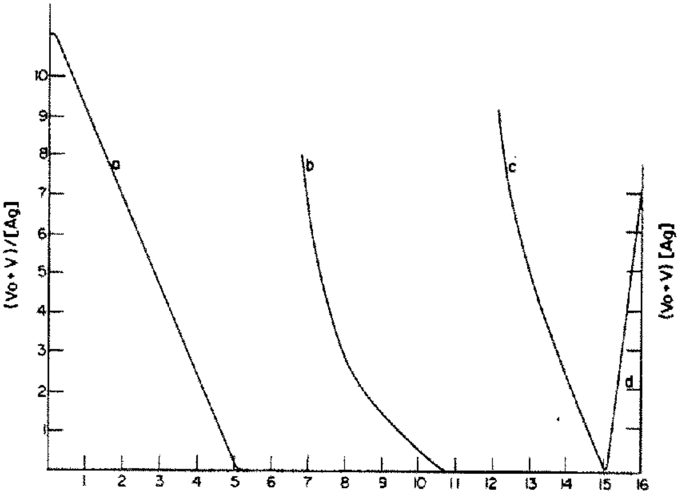

Fig. 8(*d*).

Fig. 8. Titrations of halide mixtures. Branch **a** represents precipitation of the least soluble silver halide. **d** represents excess of silver ion. (*a*) Bromide + chloride: (*b*) iodide + chloride: (*c*) iodide + bromide: (*d*) iodide + bromide + chloride. When the titration of one of the components was complete, the deflection of the recorder pen was zero. The sensitivity was then increased by manual adjustment and the titration continued.

85×10^{-3}. Consequently, we find $V_{e1} = 3{\cdot}99$ ml, $V_{e2} = 6{\cdot}01$ ml, as compared with the true values 4·00 and 6·00 ml.

Example 4. Titration of a mixture of a strong and a weak acid

A solution containing 5·00 ml of 0·1*M* hydrochloric acid and 5·00 ml of 0·1*M* acetic acid was titrated in the same way as described in example 3. The calculations are analogous, the only difference being that K_{HCl} is put equal to zero. Figure 6 shows the titration curves obtained by titrating the mixture and 10 ml of each of the acid solutions composing the mixture. $V = 6{\cdot}12$ ml at $[H] = 10^{-4}M$, and $V_e = 10{\cdot}03$ ml, are read off the diagram, yielding $V_{e1} = 5{\cdot}01$ ml (for the hydrochloric acid) and $V_{e2} = 5{\cdot}02$ ml (for the acetic acid) as compared to the true values 5·03 and 5·00 ml, respectively.

When titrating according to examples 3 and 4, no correction should be made for the dilution.

Example 5. Titration of halide ions with silver ion

The titration of a single halide in, *e.g.*, 0·01*M* concentration in aqueous solution is simple and no titration curves will be given here. As may be predicted, the curves consist of two straight branches; the halide ion concentration decreasing before and the silver ion concentration increasing after the equivalence point linearly with the volume of added titrant. When the concentration of halide ions is low, it is often advantageous to consider only the branch recorded after the equivalence point. Figure 7 shows the curve obtained by titration of 80 ml of $6{\cdot}25 \times 10^{-4}M$ sodium chloride (approx. 0·1*M* with respect to nitric acid) with 0·01*M* silver nitrate. The consumption is 5·06 ml, the true value 5·05 ml. In the same figure, the results of two titrations of 75 ml of tap-water + 5 ml of 2*M* nitric acid are shown. According to both titrations, the tap-water contains 12·3 mg of sodium chloride, per litre, the accepted value being 12 mg/l.

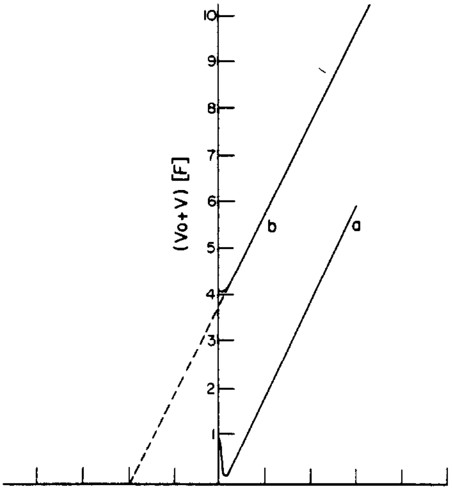

Fig. 9. Determination of fluoride in toothpaste. (*a*) Titration of a blank with 0·05*M* sodium fluoride solution. (*b*) Titration of 2 g of toothpaste in the same way as in (*a*).

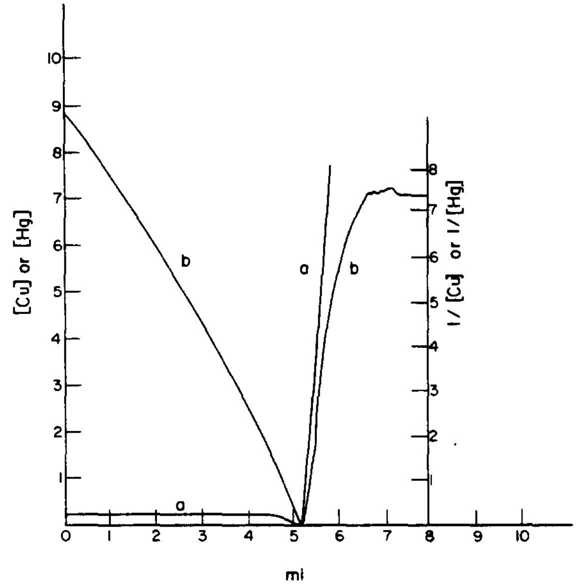

Fig. 10. Titration of 5 ml of 0·05*M* copper sulphate with 0·05*M* EDTA. (*a*) Mercuric ion as indicator ion and an amalgamated silver rod as indicator electrode. (*b*) Cu(II)-selective electrode as indicator electrode.

Figure 8 shows results for some titrations of mixtures of halides. With only two components present, the results are correct. With chloride, bromide and iodide all present, the concentration of iodide and the sum of the halide concentrations are correct, but the bromide concentration is about 8% high.

All these titrations were performed with a Beckman silver/silver chloride electrode and an Orion double-junction reference electrode Model 90–02–00 having 0·5*M* potassium nitrate in the outer sleeve.

Example 6. Determination of fluoride in toothpaste

A convenient way of determining fluoride (not monofluorophosphate) in toothpaste is by making standard additions of fluoride and measuring the e.m.f. of a fluoride-selective electrode after each addition. The results may be evaluated by using a Gran function and extrapolating. The results of one such titration are presented in Fig. 9, obtained by titrating 2·0 g of toothpaste with 0·05*M* sodium fluoride. The sodium fluoride solution was added very slowly, the time consumed by the entire titration being 15 min. The result, 2·05 mg of sodium fluoride per gram of toothpaste should be compared with the published value, about 2 mg/g.

The indicator electrode was an Orion fluoride-selective electrode Model 94–09–00 and the reference electrode was Orion Model 90–02–00 with double junction.

Example 7. Complexation titration

In complexation titrations, it is sometimes advantageous to follow the titration with the aid of an indicator ion. Silver ions and mercuric ions are often used for this purpose, primarily because good electrodes can be made that respond to these ions. Gran curves have proved useful in the evaluation of the titrations. The problem has been treated by Johansson[6] among others. The titration presented in that paper has been repeated, using the antilog apparatus. The titration curve is shown in Fig. 10.

A solution prepared by mixing 5 ml of 0·05M copper sulphate, 25 ml of 0·1M sodium acetate, 25 ml of 0·1M acetic acid and 45 ml of water was titrated with 0·05M EDTA. Mercuric ion, added in the form of its complex with EDTA, was used as indicator ion (0·25 ml of 0·01M HgEDTA was added). As indicator electrode an amalgamated silver rod was used and the reference electrode was an Orion Model 90–02–00 double-junction reference electrode. The equivalence volume of the titration was 5·10 ml (calculated value 5·10 ml). Figure 10 also shows the results of a titration made without addition of indicator ion, but with use of a copper(II)-selective electrode (Hansen, Lamm and Ruzicka type[7]) as indicator electrode. The resulting equivalence volume was the same but the titration was slower.

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Résumé—On a essayé un appareil de titrage traçant, soit la concentration de l'ion de la prise d'essai, soit la concentration de l'ion agent de titrage. Un appareil antilog, convertissant les valeurs mesurées de la f.é.m. en concentrations, est connecté à un équipement de titrage ordinaire. On a essayé l'instrument au moyen de titrages acide-base (titrages de mélanges d'acides faibles ou d'un acide faible et d'un acide fort), de titrages par précipitation (dosage de la concentration en chlorure dans l'eau du robinet, dosage de mélanges d'halogénures), de titrages avec des électrodes spécifiques (détermination de la teneur en fluorure de pâte dentifrice) et de titrages complexométriques (dosage du cuivre par l'EDTA, utilisant l'ion mercurique comme ion indicateur et une tige d'argent amalgamé comme électrode indicatrice, ou utilisant une électrode indicatrice spécifique du cuivre). La méthode simplifie considérablement l'évaluation des résultats par comparaison aux titrages potentiométriques classiques.

Zusammenfassung—Ein Titrationsgerät wurde ausprobiert, das entweder die Konzentration des Probenions oder die des Titrantenions aufzeichnet. An das gewöhnliche Titrationsgerät wird ein Antilog-Umsetzer angeschlossen, der die gemessenen EMK-Werte in Konzentrationen umwandelt. Das Instrument wurde mit Säure-Basen-Titrationen (Titrationen von Gemischen schwacher Säuren und einer schwachen und einer starken Säure), Fällungstitrationen (Bestimmung der Chloridkonzentration in Leitungswasser, Titration von Halogenidgemischen), Titrationen mit ionenselektiven Elektroden (Bestimmung des Fluoridgehalts von Zahnpasta) und komplexometrische Titrationen (Bestimmung von Kupfer mit EDTA mit Quecksilber als Indikatorion und einem amalgamierten Silberstab als Indikatorelektrode oder mit einer kupferselektiven Indikatorelektrode) getestet. Die Methode vereinfacht die Berechnung der Ergebnisse beträchtlich, verglichen mit üblichen potentiometrischen Titrationen.

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PRECONCENTRATION AND DETERMINATION OF CADMIUM IN WATER BY REVERSED-PHASE COLUMN CHROMATOGRAPHY AND ATOMIC ABSORPTION

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Summary—Studies were made of the solvent extraction of cadmium(II) from hydrochloric acid into a tri-n-octylamine–cyclohexene mixture. Distribution ratios, as a function of amine and acid concentration, were determined and this information was used to establish optimum extraction conditions and the probable nature of the extracted species. This system was used as the basis for the development of a reversed-phase column chromatographic technique for preconcentrating Cd(II). The amine–cyclohexene phase was coated on an inert macroreticular resin (XAD-2) to provide a stable column. With this system, Cd(II) in acidified water samples as large as 3 l. may be concentrated to 10 ml and determined by conventional atomic absorption. Interferences were studied, and the method was applied to the analysis of fresh-water streams for Cd(II).

The majority of analytical methods for trace cadmium in natural-water systems involve direct flame atomic-absorption or solvent extraction followed by flame atomic-absorption or ultraviolet-visible spectrophotometry.[1–6] The direct technique suffers from lack of sensitivity, the limit for most commercial instrumentation being 0·01 μg/ml, well above the actual cadmium concentration in most aqueous systems. Solvent extraction methods, although increasing sensitivity, generally require a large volume of organic phase. Recently flameless atomic-absorption has shown promise although the instrumentation is specialized and, in most cases, quite expensive.[7]

The purpose of this present work was to develop a reliable, sensitive and inexpensive column chromatographic method for preconcentrating cadmium(II) from natural-water samples. The aqueous solution to be analyzed is made $1M$ in hydrochloric acid and is the mobile phase. The liquid ion-exchanger is tri-n-octylamine (TOA) dissolved in cyclohexene and is the stationary phase.

The system Cd(II)/H_2O/HCl/TOA/cyclohexene was investigated from the standpoint of liquid–liquid solvent extraction and reversed-phase column chromatography. The solvent extraction studies were used to find optimum retention conditions for preconcentration on the column. Reference was made to reversed-phase paper chromatography data in order to ascertain the behaviour of potentially interfering ions.[8]

EXPERIMENTAL

Apparatus

Atomic-absorption spectrophotometer. A model AA5 Varian Techtron atomic-absorption spectrophotometer fitted with a 100 × 0·5 mm Techtron burner, a Varian cadmium hollow-cathode lamp, and a Leeds & Northrup Model 680 potentiometric recorder.

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The optimum working conditions were:

Wavelength	228·8 nm
Lamp current	3 mA
Bandpass	0·200 nm
Scale expansion	variable to ×10
Flame	air–acetylene

Pressure and flow-rate of fuel and oxidant were adjusted to give maximum signal for cadmium in the desired matrix.

Potentiometric measurements. A Leeds & Northrup expanded-scale pH-meter (Model 7410) was used. Cadmium and copper concentrations were determined with Orion model 94-48A and 94-29A ion-selective electrodes and pH was determined with a Leeds & Northrup Model 117169 glass electrode. The reference electrode for both systems was an Orion 90-91 Ag–AgCl cell.

Reagents

Cadmium standard solution. ACS reagent-grade $CdCl_2 \cdot 2\frac{1}{2} H_2O$ was dissolved in demineralized water and standardized against EDTA by potentiometric titration, the cadmium ion-selective electrode being used. The EDTA was previously standardized against reagent-grade copper by means of the copper ion-selective electrode.

All other chemicals were reagent grade, with the exception of tri-n-octylamine and cyclohexene, which were practical grade.

Resins. XAD-2 and XAD-7 (Rohm & Haas) were ground in a Waring blender, sieved, washed with solvents of various polarities and air-dried at 90°C.

Procedures

Liquid–liquid solvent extraction. Organic phases studied were 5·0, 10·0, 15·0 and 20·0% v/v TOA in cyclohexene Equal volumes (30 ml) of the organic and aqueous phases [the aqueous phase containing varying concentrations of hydrochloric acid and Cd(II)] were shaken for 5 min (sufficient time for equilibration) in a 125 ml separating funnel. The phases were allowed to separate and a 25 ml aliquot of the aqueous phase was taken for determination of cadmium by a standard-addition procedure.

The aliquot was neutralized with aqueous ammonia, a standard amount of Cd(II) stock solution was then added, the solution was diluted to volume and the Cd(II) concentration determined by atomic-absorption spectrophotometry (AAS). The concentration of Cd(II) in the organic phase was determined by material balance, and distribution ratios (D) were calculated as a function of amine and acid concentration.

Reversed-phase column chromatography. The inert macroreticular resin XAD-2 (or XAD-7, which was also investigated) was slurried with ethanol. It was then packed to a height of 8 cm in a 1·2 × 14 cm glass tube fitted with a Teflon stop-cock and a 1 mm diameter tip. A 25 ml aliquot of 5% v/v TOA solution in cyclohexene was used to displace the ethanol and was sorbed by the resin. Then the interstitial cyclohexene solution was displaced with demineralized water under slight air pressure. The interstitial volume (4·8 ml) and the volume of the stationary liquid phase (4·3 ml) were determined.[9]

Before use, each column was washed with 100 ml of 0·25M hydrochloric acid which had been pre-equilibrated with the organic phase. Then 2·00 ml of $1{\cdot}314 \times 10^{-2}M$ Cd(II) in 0·25M hydrochloric acid were added to the column and the cadmium was eluted with 0·25M hydrochloric acid at a flow-rate of 3–5 ml/min. Fractions were collected, neutralized, and analysed for Cd(II) by AAS. An elution curve was constructed and the "breakthrough" point and $\bar{v}$ (retention volume) were determined. These values were used to estimate similar quantities on columns with higher concentrations of TOA/cyclohexene through the expression relating $\bar{v}$ to the experimentally obtained solvent extraction distribution ratio. This allowed the choice of resin, column conditions and acid molarity so that the "breakthrough" volume was sufficiently large for retention of all Cd(II) from acidified natural-water samples as large as 3 l. in volume.

Elution of the sorbed cadmium. It was necessary to find an efficient eluent which would remove most (or all) of the cadmium from the column in the smallest possible volume. Several systems were tested, among them being water, various organic solvents (to remove the cadmium through removal of the stationary organic phase) aqueous ammonia or ammonia–ammonium acetate buffer, sulphuric acid, EDTA and ethylenediamine. The effect of concentration and pH was studied for each system. The most efficient was found to be 1·0M ammonium sulphate/0·1M EDTA/water adjusted to a pH of 5·5.

An elution curve for each eluent was prepared by sorbing a known amount of Cd(II) in 1M hydrochloric acid onto the column, eluting with the desired solution and then determining the concentration of cadmium in 1·0-ml fractions of the eluent.

Preconcentration and analysis of natural-water samples. Coarse XAD-2 resin was ground in an electric blender, sieved to 60–80 mesh, and washed with acetone; the fines were decanted, and the resin was dried at 90°C for 2 hr. The prepared resin was slurried with 25·0 ml of 20% v/v solution of TOA in cyclohexene, then packed into a column 8 cm in height and equilibrated with 1M hydrochloric acid. The excess of organic phase was removed by using moderate air pressure during the equilibration, to minimize subsequent column bleed. Synthetic standards were prepared from a stock Cd(II) solution and made 1M in hydrochloric acid. Natural-water samples

Table 1. Preconcentration as a function of initial sample volume

Aqueous std., *ml*	Conc. HCl added, *ml*	Total vol., *ml*	Eluate collected, *ml*	Cd(II) recovered, %	Preconc. factor*
917	83	1000	10·0	92 ± 2	84
1834	166	2000	10·0	89 ± 2	163
2751	249	3000	10·0	90 ± 3	248

* Preconc. factor = Sample volume/eluate volume × fraction of Cd(II) recovered.

were collected in 1 gallon polyethylene containers, acidified immediately (to 1*M*) with hydrochloric acid and refrigerated (2–3°C) for 24 hr before analysis. The reference solution was demineralized water made 1*M* in hydrochloric acid.

A siphon arrangement was used to feed continuously 1, 2, or 3 l. of samples or reference solution through the column at a flow-rate of 5 ± 1 ml/min. A loop was inserted in the siphon so that the system would shut off automatically, thus allowing unattended overnight operation.

Excess of acid was removed by washing the column with 25·0 ml of demineralized water at a rate of 3 ml/min and discarding the wash. The eluent (previously described) was added, the first 2·5 ml of eluate discarded, and a 10·0 ml fraction, which contained the cadmium, was collected in a volumetric flask at a flow-rate of 1 ml/min. (It may be necessary to add 3 drops of conc. ammonia solution to the flask to prevent precipitation of the EDTA. This also raises the pH to protect the nebulizer from corrosion.)

The cadmium in the eluate was determined by AAS. The calibration curve was prepared by means of a series of standard solutions of Cd(II) in eluent, and a correction was applied for a blank test on reference solutions treated in the same way as the samples. From the recovery data (Table 1) and the original sample volume before acidification, the initial cadmium ion concentration was calculated.

RESULTS AND DISCUSSION

Distribution ratios

Distribution ratios for Cd(II) were measured for various concentrations of hydrochloric acid in the aqueous phase and of TOA in the organic phase. A plot of log *D vs.* log [TOA]

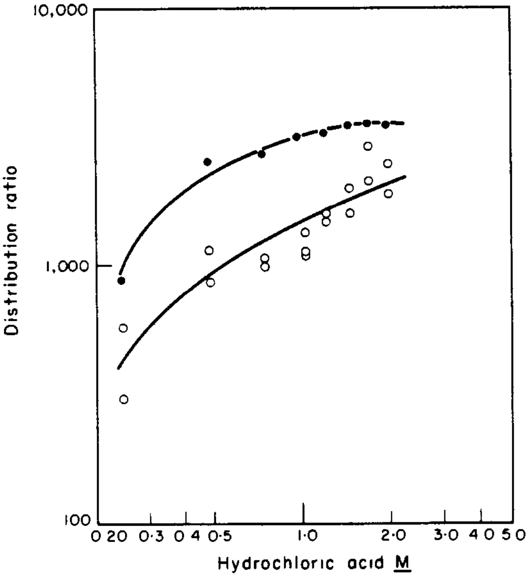

Fig. 1. Distribution ratio as a function of HCl concentration. ● Kraus and Nelson's data[11] for Dowex-1 anion-exchange resin. ○ Our data for 5·0% (v/v) TOA in cyclohexene.

yields a slope of 2·0. This implies a combining ratio of two protonated amine molecules for each tetrachlorocadmium anion. This is consistent with previous observations.[10]

The effect of hydrochloric acid concentration on the distribution ratio for Cd(II) at constant TOA concentration is plotted in Fig. 1. For purposes of comparison, data for Cd(II) and an ion-exchange resin (hydrochloric acid system)[11] are also shown. As expected, the behaviour of the two systems is similar. However, the liquid anion-exchanger, TOA, was chosen for this application because the efficiency may be enhanced by increasing the amount of TOA on the column.

Column conditions

The resin. XAD-2 and XAD-7 were investigated as possible inert solid supports for the organic phase. Elution curves for Cd(II), using 0·25*M* hydrochloric acid and 5% TOA, were obtained for each resin. XAD-2 produced a $\bar{v}$ of 1340 ml whereas that for XAD-7 was only 360 ml. The expected value of $\bar{v}$ (assuming no synergistic resin effect) was calculated from the equation

$$\bar{v} = DV_s + V_m,$$

where $\bar{v}$ is the theoretical retention volume (column chromatography), D is the distribution ratio (solvent extraction), V_s is the volume of the stationary liquid phase on the column (4·3 ml) and V_m is the interstitial volume of the column (4·8 ml). The expected $\bar{v}$ was found to be 1380 ml, which was in excellent agreement with the experimental value obtained for the XAD-2 column. As a result XAD-2 was chosen as the solid support.

The organic phase. TOA was chosen because of its ability to extract metal ions which can form anionic chloro-complexes. Cyclohexene was chosen because of its inertness and low solubility in water ($\ll$ 0·1%).

Acidity. Hydrochloric acid (1*M*) was used for all preconcentration studies. This ensures a satisfactory concentration with the minimum dilution of sample.

Elution of Cd(II). To achieve the greatest preconcentration factor it is necessary to remove reproducibly a large (but not necessarily quantitative) fraction of the Cd(II) in a small volume of eluent. Of the several combinations investigated, the most efficient combined a prewash with water followed by elution with a solution 1·0*M* in ammonium sulphate and 0·1*M* in EDTA, adjusted to pH 5·5.

The water wash removes excess of acid from the column, thus shifting the Cd(II) equilibrium towards elution. The sulphate is a competitive anion for the amine sites, and the EDTA aids in complexation of the Cd(II); the resulting complex ion has a low affinity for the organic phase.

The recovery and reproducibility for different sample sizes are given in Table 1.

Sensitivity

The AAS calibration curve for Cd(II) in the eluent is linear up to a cadmium concentration of at least 1 mg/l. The sensitivity, defined as the concentration corresponding to 99% transmittance (or 0·004 absorbance), was found to be 0·03 mg/l. Use of a 3-litre sample, incorporating a preconcentration factor of 248, allows the determination of as little as 0·12 μg/l. This is below the present Federal government (U.S.A.) standard for cadmium in potable water, which is 0·01 mg/l.[12]

Interferences

The use of a selective quantitative technique minimizes the possibility of serious interference in the final analysis step, as long as all standard solutions are prepared in a matrix similar to the eluent. Previous studies[8,10,11] of amine/hydrochloric acid systems show that the metal ions most likely to be present in large amounts in natural-water systems are not strongly extracted by TOA. Therefore competition between cadmium and other metal ions should not be a serious difficulty. Loss of cadmium to the walls of the polyethylene container has been shown to be negligible,[13] if the solutions are acidic. Trace amounts of cadmium, within reagent-grade tolerances, may be introduced by the acid used. We found the actual amount small but variable and dependent upon the "lot"-number of the acid. The use of the same "lot" of acid and a blank determination minimized this difficulty.

Analysis of natural-water samples

Samples were obtained from the Herring Run in Maryland and east branch of the Brandywine river in Pennsylvania. No previous report of cadmium in the former has been found; in the latter, Cd(II) concentrations between 0·7 and 3·0 μg/l. were found by using flameless AAS.[14] The results obtained by using the present method are shown in Table 2.

Table 2. Summary of analyses of natural water samples for cadmium

	I	II	III
Sample location	Herring Run (Maryland, U.S.A.)	E. Brandywine R. (Pennsylvania, U.S.A.)	E. Brandywine R. (Pennsylvania, U.S.A.)
Depth	surface	surface	bottom
Water temp., °C	0	18	18
Air temp., °C	−5	28	28
Stream height	normal	normal	normal
Season	winter	summer	summer
Number of replicates	4	4	4
Cadmium found, μg/l.	<0·12	0·4	0·4

In order to show that the water did not contain cadmium in non-ionic form, other samples were spiked with known quantities of Cd(II). After a period of time (3 days–1 week) the samples were analysed according to the procedure above. Recovery of added Cd(II) was quantitative in each case, within the expected experimental error of the method (±5%).

Future studies

Preliminary studies indicate that zinc(II) and mercury(II) are also efficiently extracted by TOA from hydrochloric acid solution. It should be possible to preconcentrate and determine Cd, Zn and Hg simultaneously with this system.

With a modification of the procedure outlined, a direct solvent extraction of Cd(II) is also possible and the organic phase may be directly aspirated into the flame, should this be more desirable.

It should be emphasized that the final analysis step is not restricted to flame AAS alone. Use of the preconcentration technique with inherently more sensitive quantitative techniques such as voltammetry or flameless AAS should increase the sensitivity to an even greater extent. Also elution of the Cd(II) with an organic solvent may increase the preconcentration factor and improve the AAS sensitivity through solvent enhancement in the flame.

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Résumé—On a effectué des études sur l'extraction par solvant du cadmium(II) à partir d'acide chlorhydrique dans un mélange tri-*n*-octylamine-cyclohexène. On a déterminé les rapports de partage, en fonction de la concentration en amine et acide, et cette information a été utilisée pour établir les conditions optimales d'extraction et la nature probable de l'espèce extraite. On a utilisé ce système comme base pour le développement d'une technique de chromatographie sur colonne à phases inversées pour la préconcentration du cadmium(II). On a recouvert une résine macroréticulaire inert (XAD-2) par la phase amine-cyclohexène pour obtenir une colonne stable. Avec ce système, on peut concentrer le Cd(II) dans des échantillons aqueux acidifiés aussi grands que 3 l. à 10 ml, et le doser par absorption atomique classique. On a étudié les interférences, et la méthode a été appliquée à l'analyse de courants d'eau douce pour le Cd(II).

Zusammenfassung—Die Extraktion von Cadmium(II) aus Salzsäure in ein Gemisch aus Tri-n-octylamin und Cyclohexen wurde untersucht. Die Verteilungsverhältnisse wurden in Abhängigkeit von Amin- und Säurekonzentration bestimmt; diese Ergebnisse wurden dazu verwendet, die Extraktionsbedingungen optimal einzustellen und die wahrscheinliche Natur der extrahierten Spezies zu ermitteln. Dieses System wurde als Grundlage zur Entwicklung eines säulenchromatographischen Verfahrens mit umgekehrten Phasen zur Voranreicherung von Cadmium(II) verwendet. Die Amin-Cyclohexen-Phase wurde auf ein inertes grob vernetztes Harz (XAD-2) aufgebracht; so wurde eine stabile Säule hergestellt. Mit diesem System kann Cd(II) in angesäuerten Wasserproben von bis zu 3 l. auf 10 ml aufkonzentriert und mit üblichen Atomabsorptionsverfahren bestimmt werden. Störungen wurden untersucht; das Verfahren wurde auf die Bestimmung von Cd(II) in Süßwasserströmen angewendet.

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SHORT COMMUNICATIONS

DISPOSITIF DE PRELEVEMENT MICROANALYTIQUE DE PRODUITS ALTERABLES

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L'analyse de composés s'altérant rapidement à l'air ambiant, qu'ils soient hygroscopiques, oxydables, carbonatables, etc., impose d'effectuer les prélèvements et les pesages en atmosphère de gaz inerte, azote ou argon par exemple. L'analyse des mêmes composés à l'échelle microanalytique exige que soient remplies des conditions supplémentaires inhérentes à la petitesse des prélèvements.

Dans ce domaine, l'emploi de pistolets desséchants,[1-4] est limité aux prélèvements des substances hygroscopiques dont la tension de vapeur n'est pas trop élevée et qui, plus généralement, peuvent supporter une élévation de température: il implique, en outre, l'utilisation, non dépourvue d'inconvénients, de microcochonnets en verre ou en silice comme véhicules de transport et de pesage des prélèvements analytiques (au sein de nacelles), du pistolet à la balance, puis de cette dernière à l'appareil d'analyse; en effet, le pesage en microcochonnet donne lieu à réduction de la précision des pesées; en outre, si brève que soit la durée des manipulations du cochonnet dans l'atmosphère ambiante, elle est parfois suffisante pour permettre la pénétration de l'air par diffusion et, en conséquence, l'altération du produit prélevé.

Par ailleurs, en règle générale, le microanalyste devrait proscrire, avant analyse, tout traitement des produits qui lui sont confiés (traitement thermique sous pression éventuellement réduite, voire sous vide, dans le cas de l'emploi de pistolets desséchants). Il ne devrait soumettre ces produits à l'analyse que dans les conditions où le chimiste demandeur les a préparés et conditionnés.

D'autres techniques de prélèvements de produits altérables ou instables, décrites dans la littérature, sont dépourvues de tout caractère d'universalité, qu'elles ne soient applicables qu'à des prélèvements de liquides hygroscopiques,[5,6] ou pyrophoriques,[7,8] ou qu'elles soient spécifiquement adaptées à des méthodes ou appareils d'analyse particuliers.[9,10]

L'emploi de la boîte à gants, pour prélèvements en atmosphère contrôlée, est plus universel mais comporte des inconvénients, surtout à l'échelle microanalytique. En effet, malgré une consommation plus importante d'azote et l'emploi de réactifs desséchants, et en raison du volume relativement grand de la boîte à gants, il est quasiment impossible d'obtenir une atmosphère parfaitement sèche et dépourvue d'oxygène *dans un temps suffisamment court* pour qu'il soit compatible avec des dosages *rapides*, en série. En outre, la nécessité d'employer des microcochonnets en verre, pour le transport et le pesage des prélèvements analytiques, présente les inconvénients déjà remarqués ci-dessus (*cf.* "Pistolets desséchants").

Les difficultés d'emploi de la boîte à gants (auxquelles s'ajoute l'incommodité de son usage en travail continu) et, par ailleurs, notre souci de pouvoir effectuer avec un appareil unique *tous* types de prélèvements de substances solides ou liquides, en vue du dosage de *tous* éléments par application de *toutes* méthodes ou de l'utilisation de *tous* appareils de microanalyse nous ont conduits à concevoir et mettre au point un dispositif aussi universel que possible, adapté au travail microanalytique. Sa description est l'objet du présent exposé.

PARTIE EXPERIMENTALE

Appareillage

Notre dispositif permet d'effectuer les prélèvements sous atmosphère d'argon, dans une enceinte de faibles dimensions.

L'enceinte à prélèvements, en verre Pyrex (Fig. 1), est constituée par un corps cylindrique de 40 mm de diamètre extérieur, de 35 mm de diamètre intérieur et de 60 mm de longueur. Il est pourvu à son extémité supérieure d'un raccord conique mâle WITEG n° 7 (45/39), non rodé, porteur d'un joint torique en perbunan dans sa partie basse et d'une bague en polytétrafluoroéthylène (Teflon), dans sa partie haute* (5, Fig. 1), permetant d'éviter tout graissage. Un raccord WITEG, non rodé comportant un ajutage à robinet, s'adapte sur le précédent raccord mâle en assurant la fermeture étanche de l'enceinte (6, Fig. 1). Celle-ci comporte, en outre, à sa partie inférieure, un

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* Distributeur, en France.: SVT, Paris.

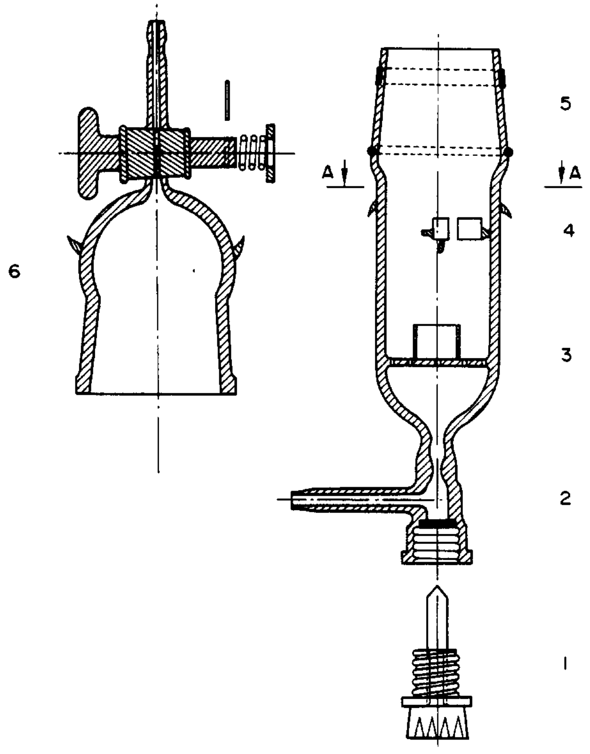

Fig. 1. Enceinte à prélèvements.

tube d'arrivée du gaz inerte (2, Fig. 1), muni d'un robinet "TORION" à pointeau en polytetrafluoroéthylène* (1, Fig. 1), et d'un ajutage adducteur latéral. Des ergots en verre soudés de part et d'autre des deux parties du couvercle peuvent recevoir des ressorts maintenant la fermeture étanche sous légère pression du gaz inerte.

Le corps cylindrique de l'enceinte comporte à sa base une platine en verre Pyrex soudée à la paroi, perforée sur sa périphérie de 6 trous de 2 mm de diamètre et d'un 7 ème trou, de même diamètre, en son centre. Un tronçon de tube coaxial formant un logement cylindrique de 15 mm de diamètre et de 10 à 12 mm de hauteur est soudé à la platine (3, Fig. 1 et Fig. 2).

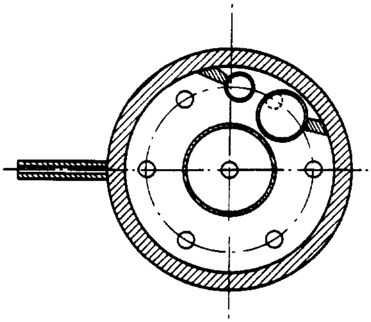

Fig. 2. Coupe AA (Fig. 1).

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* Fournisseur: SOVIREL, Paris.

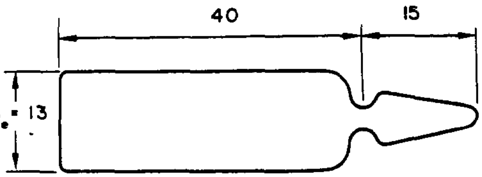

Fig. 3. Tube à échantillon (cotes en mm).

A 40 mm au-dessus de la platine, sont soudés, côte à côte, à la paroi de l'enceinte, deux autres logements cylindriques, de verre Pyrex, de 7 mm de hauteur, dont l'un a 8 mm de diamètre intérieur et le second 5 mm (4, Fig. 1 et Fig. 2).

L'ajutage adducteur de l'enceinte est raccordé au manodétendeur d'un cylindre d'argon comprimé par un tuyau plastique. L'enceinte de prélèvements est disposée verticalement dans une pince de laboratoire fixée à une tige support.

Afin de faciliter les opérations de prélèvements, il est recommandable de conditionner les produits altérables à analyser, sous atmosphère de gaz inerte, dans un tube à échantillon scellé, en verre de 0,5 mm d'épaisseur, ayant la forme et les dimensions représentées sur la Fig. 3.

Mode operatoire

Remplir l'enceinte d'argon par balayage pendant 2 à 3 minutes. A cette fin, ouvrir successivement le robinet du couvercle rodé, puis celui d'adduction d'argon, à la base de l'appareil. Régler le débit d'argon au moyen du manodétendeur de façon a sentir un léger souffle de ce gaz à la sortie du robinet supérieur.

Tracer un trait de lime sur l'étranglement du tube à échantillon (Fig. 3) et l'introduire dans l'enceinte balayée par le courant d'argon en le disposant dans le logement tubulaire, prévu à cette fin, sur la platine en verre.

Serrer la partie supérieure du tube, au-dessus de son étranglement, dans une pince métallique dont les extrémités sont recouvertes d'une matière plastique (morceau de tuyau de polychlorure de vinyle, par exemple) et exercer un léger effort latéral afin d'ouvrir le tube par cassure en deux parties, au niveau de l'étranglement.

La technique de prélèvement à laquelle il est alors fait appel, dépend de l'état physique du produit à analyser et de la technique de dosage ensuite mise en oeuvre.

Echantillons solides

Les solides sont prélevés dans des petits godets d'aluminium ou d'argent de 3,5 mm de diamètre et de 9 mm de hauteur, manipulés à l'aide de brucelles.

Nous employons les godets d'argent, notamment pour le microdosage de l'oxygène, d'après Fraisse,[11] et pour les microdosages du carbone, de l'hydrogène et de l'azote sur l'analyseur CHN "Technicon".

Tarer le godet de prélèvement et l'introduire dans le plus petit des logements de verre soudés à la paroi intérieure de l'enceinte. Prélever le produit dans le tube à échantillon, à l'aide d'une microspatule (en tige de nickel ou d'acier inoxydable de 2 mm de diamètre et de 150 mm de longueur, dont le méplat a été recourbé à angle droit à 2 mm de son extrémité), et le déposer dans le godet. Sceller le godet en pinçant son ouverture avec des pinces plates* dont les surfaces de contact sont plaquées de platine (en feuille). Peser le godet après l'avoir nettoyé extérieurement par soufflage d'air à l'aide d'une petite poire en caoutchouc, et en déduire la masse du prélèvement.

Il est recommandable d'effectuer en série continue tous les prélèvements (en godets) nécessaires à l'analyse d'un échantillon de produit et d'effectuer aussi rapidement que possible les déterminations correspondantes, soit, pratiquement, dans l'heure qui suit ces prélèvements.

Lors de l'analyse de substances réfractaires dont la minéralisation est difficile, il est possible d'introduire, dans le fond du godet, une pointe de spatule d'un réactif approprié (oxydes tels que V_2O_5, WO_3, Co_3O_4, etc...) dans le cas d'une combustion dans l'oxygène, par exemple), avant le prélèvement.

Echantillons liquides

Les liquides sont prélevés en microampoules de verre Pyrex d'un type classique, manipulées à l'aide de brucelles. Tarer l'ampoule. Prélever le liquide dans le tube à échantillon en mettant en oeuvre la technique connue de chauffage préalable du corps de l'ampoule suivie de son refroidissement naturel après immersion de son capillaire ouvert dans ledit liquide. Extraire l'ampoule de l'enceinte et la sceller rapidement après centrifugation. Peser l'ampoule et en déduire la masse de prélèvement analytique.

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* Pinces FACOM, France, n° 401.

Il est également recommandable d'effectuer en série tous les prelèvements nécessaires sur un même échantillon de produit, mais les ampoules étant scellées, il est possible de les conserver longtemps avant leur utilisation en vue des déterminations microanalytiques proprement dites.

*Prélèvements en sachets de terphane**

La mise en oeuvre des méthodes de dosage de divers éléments (chlore, brome, phosphore, silicium, métaux) peut impliquer l'emploi de petits sachets de terphane, à l'instar de Reverchon[12] pour le prelèvement de composés solides ou liquides. Ces sachets sont manipulés à l'aide de brucelles.

Composés solides. Tarer le sachet de prélèvement et l'introduire dans le plus grand des logements de verre soudés à la paroi intérieure de l'enceinte. Prélever le produit dans le tube à échantillon à l'aide de la microspatule et le verser dans le fond du sachet. Pincer le sachet à sa partie supérieure à environ 1 mm des lèvres de l'ouverture à l'aide d'une pince coupante, extraire le sachet de l'enceinte, le nettoyer extérieurement par soufflage d'air à l'aide d'une petite poire en caoutchouc et sceller les deux lèvres à l'air chaud.[12] Peser le sachet et en déduire la masse du prélèvement analytique.

Composés liquides. Introduire dans le sachet de terphane une languette de papier filtre sans cendres de 20 × 4 mm, pliée en quatre. Tarer le sachet et sa garniture et l'introduire dans le grand logement de verre (*cf.* composés solides). Prélever le liquide dans le tube à échantillon, par capillarité, dans une ultramicropipette d'environ 0,5 mm de diamètre intérieur et de 50 mm de longueur, et introduire sa pointe dans le sachet de terphane où le liquide est absorbé par le papier filtre. Extraire la pipette, puis sceller et peser le sachet comme dans le cas des composés solides.

Mise en oeuvre et resultats

L'argon, gaz inerte de balayage et de remplissage de l'enceinte de prélèvement, est employé, de préférence, à l'azote, du fait de sa densité beaucoup plus élevée, ce qui offre les avantages de rendre négligeables et, en tous cas, non nuisibles, les échanges gazeux avec l'air ambiant et, en permettant de travailler sous faible débit, de limiter la consommation du gaz.

L'enceinte peut servir également à la conservation d'échantillons de produits altérables, en cours d'analyse: à cette fin, il suffit de la clore, à l'aide de son couvercle, et d'y maintenir une légère pression d'argon; la durée de cette conservation peut varier selon l'instabilité des produits.

Lorsqu'il est nécessarire d'effectuer une série de prélèvements sur différents produits, il est recommandable de disposer, à cette fin, d'une batterie d'enceintes qui peuvent être montées sur un support commun.

Grâce à l'emploi du dispositif décrit, il nous a été possible d'effectuer de nombreux dosages microanalytiques sur des produits altérables dans des conditions de rapidité et de sûreté satisfaisantes conduisant à l'obtention de résultats d'analyses aussi précis que dans le cas de produits stables.

Dans un laboratoire de microanalyse important, il est recommandable d'affecter un operateur a un poste de prélèvements de produits altérables; il effectue alors simultanément tous les prélèvements nécessités par l'analyse d'un même produit et les distribue ensuite aux différents postes de dosages intéressés.

Il convient enfin de remarquer que nous avons appliqué notre technique de prélèvements de produits altérables dans les domaines milligrammiques et décimilligrammiques avec le même succès; dans ce dernier cas, il importe de disposer d'une balance à grande rapidité de pesage telle que la balance électromagnétique Mettler Me 22, à tarage automatique.

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* Polyester de l'acide téréphtatalique également dénommé "polytéréphtalate d'éthylène" par le fabricant.

11. D. Fraisse. *Thèse d'Etat*. Paris VI, (n° A. 0 8537), 1973.
12. R. Reverchon. *Bull. Soc. Chim. Franc.*, 1972, 829.

Résumé—Les auteurs décrivent un dispositif comportant une enceinte en verre de faibles dimensions, permettant d'effectuer des prélèvements milligrammiques et décimilligrammiques de produits altérables, solides et liquides, sous atmosphère d'argon, en vue de tous dosages microanalytiques élémentaires.

Summary—A small glass device is described for microanalytical or submicroanalytical sampling of unstable solid or liquid substances, in an argon atmosphere.

Zusammenfassung—Ein kleines Glasgerät wird beschrieben, das die Probenahme für die Mikro- oder Submikroanalyse instabiler fester oder flüssiger Substanzen in Argonatmosphäre erlaubt.

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NEW TYPE OF BLUE TERNARY COMPLEX OF ARSENAZO I WITH PLUTONIUM (IV) IN THE PRESENCE OF HYDROGEN PEROXIDE

PRELIMINARY INVESTIGATIONS

(*Received* 26 *March* 1974. *Accepted* 20 *June* 1974)

Binary compounds formed by plutonium, in different oxidation states, with reagents of the "arsenazo" type [mono- and bis (azophenyl-*o*-arsono)chromotropic acid derivatives] are widely used for the spectrophotometric determination of μg amounts of plutonium owing to their favourable stability and colour characteristics.[1–5]

However, no single peroxy ternary complex compound has been reported previously. The existence of the first compound of this type was postulated by the author in 1967 in connection with the Pu(IV)–arsenazo I–H_2O_2–HNO_3 system.[1]

In the following we will deal briefly with the preparation and the main spectrophotometric features exhibited by this interesting new type of compound.

EXPERIMENTAL

Reagents

Arsenazo I, 0·1% solution.

Plutonium solutions. Different stock (0·1–5 mg/ml) plutonium solutions were prepared in sulphuric, nitric and perchloric acid media as described elsewhere,[1–3] starting from a PuO_2 sample supplied by the French Atomic Energy Commission (C.E.N.–F.A.R.).

Buffer solution, pH 2·8. Equimolar solutions of monochloroacetic acid and sodium monochloroacetate were mixed in appropriate proportions.[1,2]

Apparatus

Spectrophotometers. A Beckman DK-2A double-beam spectrophotometer was used with 20, 10 and 5 mm light-path glass cells. Beckman Model B and DU manual spectrophotometers were used for routine work. A transportable "Plexiglas" cell-container of our own design was used to carry out the spectrophotometric work with the recording spectrophotometer when dealing with plutonium solutions.

Glove box. "Technochimie" glove boxes were used to carry out all the work involving plutonium.

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Glove box. "Technochimie" glove boxes were used to carry out all the work involving plutonium.

Heat-lamp. Infrared "Quartz et Silice" lamps (250 W) set on special stainless-steel supports of our own design were used to carry out all the thermal treatments and oxidation-state conditioning of the plutonium samples.

pH meter. Metrohm Model Kompensator E 388 high-precision pH-meter furnished with a calomel–glass EA 120 U combined electrode system.

Radiochemical apparatus. Scintillation alpha-counting detector–amplifier devices and plutonium standards prepared by electrolytical deposition were of J. E. N. design. Micropipettes and 5 and 10 ml volumetric flasks assembled into special plastic transport units of our own design were used.

RESULTS AND DISCUSSION

While comparing the applicability of arsenazo I and arsenazo III to the spectrophotometric determination of the oxidation states of plutonium in different media of low acidity, we noted the possible existence of quite a new type of complex compound of arsenazo I with Pu(IV).[1,2] The plutonium samples are submitted *in situ* to a "clean" valency-conditioning treatment based on the use of 30% hydrogen peroxide in 4–7*M* nitric acid. The whole conditioning treatment which converts the plutonium quantitatively into the quadrivalent oxidation state requires the additional use of 9*M* sodium nitrite after the conclusion of the peroxide treatment. The whole procedure is carried out under standardized boiling conditions[1,2] in order to guarantee that no trace of any of the chemicals used remains in the conditioned solution since both peroxide and nitrite severely interfere with, or even prevent, the reaction of arsenazo I with Pu(IV) in monochloroacetic acid–monochloroacetate buffer medium.[1–3] When the nitrite step was omitted from the conditioning treatment, two different effects were

Table 1. Effect of the methods used to obtain plutonium IV quantitatively, on the application of the arsenazo I method.

Medium	Initial oxidation state of plutonium	Time elapsed after the preparation of the solution	Pu present (alpha-radiometry), *μg/ml* ± 2·5%	Pu found, *μg/ml* ± 3%, by arsenazo I standard method after the *in situ* chemical pretreatment shown		
				None	H_2O_2	H_2O_2 + $NaNO_2$
1*N* H_2SO_4	Pu(III)	2 hr	101	16	102	94
1*N* HNO_3	Pu(III)	2 hr	106	47	110	100
1*N* $HClO_4$	Pu(III)	2 hr	111	53	105	105
0·5 *N* HNO_3	Pu(IV)	2 hr	56	56	83	53
1*N* HNO_3	Pu(IV)	1 hr	58	57	91	62
7*N* HNO_3	Pu(IV)	50 days	58	54	90	56
0·04*N* HNO_3	Pu(IV)	1 hr	47	41	55	50
0·04*N* HNO_3	Pu(IV)	1 week	47	22	62	50
0·04*N* HNO_3	Pu(IV)	3 weeks	33	4	57	34
0·04*N* HNO_3	Pu(IV)	10 weeks	(71)	0	103§	70§
0·1*N* HNO_3	Pu(IV)	1 hr	110	110	-*	111
0·1*N* HNO_3	Pu(IV)	3 weeks	108	101	165	110
0·1*N* HNO_3	Pu(IV)	54 days	111	86	168	107
0·1*N* HNO_3	Pu(IV)	211 days	–	64	101†‡	—
0·1*N* HNO_3	Pu(VI)	71 days	222	93	325	226
0·3*N* HNO_3	Pu(VI)	330 days	244	181	278	244
0·5*N* HNO_3	Pu(VI)	1 hr	118	0	45*	111
0·5*N* HNO_3	Pu(VI)	3 weeks	117	4	171	116
0·5*N* HNO_3	Pu(VI)	73 days	117	4	154	104†
1*N* $HClO_4$	Pu(VI)	3 days	116	0	161	105†§
1*N* $HClO_4$	Pu(VI)	3 weeks	114	25	-*	105†§
1*N* $HClO_4$	Pu(VI)	79 days	114	71	164	103‡§
1*N* $HClO_4$	Pu(VI)	249 days	—	99	166	113
0·1*N* H_2SO_4	Pu(IV)	undetermined‖	100	103	146	104

* The solution was discoloured to a very great extent because of decomposition of the Pu(IV)–arsenazo I–H_2O_2 complex and the large excess of free ligand by the free hydrogen peroxide.

† Low results were obtained by the direct arsenazo I standard method because of the unnoticed influence of time on old buffer solutions, which have been shown[2] to interfere seriously with the method if the aging process of the monochloroacetic–monochloroacetate buffer solutions is not properly controlled.

‡ Low results might have been obtained owing to the hydrolysis of Pu(IV)—even when bound to the arsenazo I reagent as a complex—through the addition of the neutralizing NaOH solution before the final dilution to volume.

§High results have been obtained owing to peptization of the $Pu(OH)_4$ precipitate retained on blue-band paper which was used to separate the liquid and solid phase present in very dilute Pu(IV) nitric solutions. This phenomenon was only observed when the same filter was used for two succesive filtrations of this kind of solution, implying the more or less extensive drying of the first solid phase retained on the filter.

‖ Pu(IV) solutions in H_2SO_4 media of acidity ⩾0·04*N* have been shown to be quite stable for periods of years.[1]

observed. Either extensive decolorization took place, occasionally leading to more or less clear orange or yellowish solutions, or there was a 50% increase in the expected absorbance at 600 nm. Whilst the normal arsenazo I-Pu(IV) binary complex[3, 4] exhibits very good kinetic stability for many days, the corresponding arsenazo I-Pu(IV) complex originated in solutions submitted previously to the hydrogen peroxide conditioning treatment decomposed, with decreasing absorbance over a 48 hr period.

In Table 1 we have summarized the evidence which suggests the existence of a new type of complex.

The new arsenazo I-Pu(IV) complex has been shown to originate when 25–100 μg of plutonium are boiled *in situ* in 10 ml volumetric flasks in 5–7*M* nitric acid media with 0·1–0·2 ml of 30% hydrogen peroxide for at least 30 sec, the total volume being 0·5–2 ml, and this treatment is followed by addition of 1 ml of $2 \times 10^{-3}M$ aqueous arsenazo I and 1 ml of 5·3*M* monochloroacetic acid–monochloroacetate buffer (no older than one month) and enough water to dilute to about 8 ml. Then 2–8*M* sodium hydroxide sufficient to just neutralize the free nitric acid left after the thermal treatment is added (parallel blank samples are prepared simultaneously under exactly the same experimental conditions in order to assess the necessary average amount of alkali to be added, phenolphthalein being used as visual indicator). Then the flasks are filled to volume, the solutions are thoroughly mixed and after a development period of 1–4 hr the absorbances are measured in 10 ml glass cells at 600 nm against a reagent blank.

We decided to investigate the main spectrophotometric characteristics of this new complex species which we assume to be a ternary complex of the arsenazo I, peroxide and plutonium (IV).

In Fig. 1 we reproduce the main spectral and kinetic characteristics exhibited by the new compound, when the cation is present in great excess. The experimental results, together with the analysis of Figs. 1 and 2, allow the following conclusions to be made:

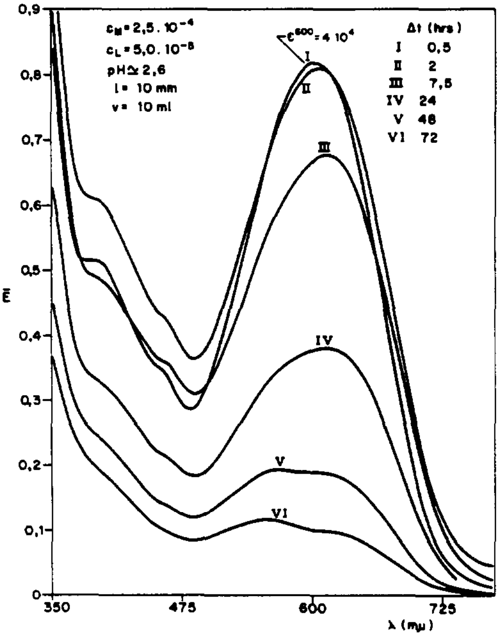

Fig. 1. Spectroscopic features and decomposition kinetics of the arsenazo I-H_2O_2-Pu(IV) blue ternary complex(monochloroacetic acid–sodium monochloroacetate buffer medium).

(*i*) the peroxy arsenazo I-Pu(IV) complex exhibits a light blue colour, in contrast to the characteristic pink colour shown by the normal arsenazo I-Pu(IV) complex.

(*ii*) the new complex exhibits a wide absorption band with λ_{max}at 610 nm, compared with 570 nm for the normal complex (Fig. 2).

(*iii*) The peroxy complex exhibits poor kinetic stability, decolorization occurring in 2 hr after preparation of the complex. This contrasts sharply with the normal complex, which reaches maximum absorbance practically instantaneously after mixing of the arsenazo I and Pu(IV) solutions and remains practically unchanged for many days.

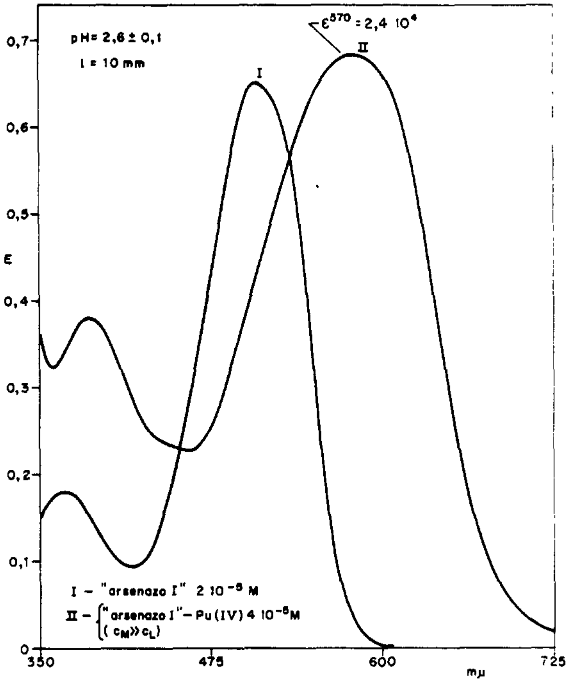

Fig. 2. Spectroscopic features of the pure arsenazo I reagent(I) and its binary pink complex with Pu(IV) in monochloroacetic acid–monochloroacetate buffer medium(II).

(*iv*) The apparent maximum molar absorptivity of this new complex is about $(4 \pm 0{\cdot}1) \times 10^4$ l.mole^{-1}. cm^{-1} that of the normal complex being $(1{\cdot}8 \pm 0{\cdot}1) \times 10^4$ at 610 nm.

Preliminary experiments carried out to investigate the new ternary complex in aqueous alcoholic buffered media with a large excess of plutonium relative to ligand proved unsatisfactory because of the immediate precipitation of a bluish-pink flocculent compound.

CONCLUSIONS

Although we have assumed that only the one type of peroxy arsenazo I–Pu(IV) ternary complex species is formed when either ligand or plutonium is in excess, this is not definitely established. It is reasonable because of the agreement between the ratio of the molar absorptivities at 600–610 nm of the peroxy and the normal complex when either the ligand (Table I) or plutonium (Fig. 1) is in excess.

The investigation of the Pu(IV)–H_2O_2–HNO_3 system has hitherto proved rather difficult because of its intrinsic complexity: the instability characteristics shown by the new intermediate bluish species in the Pu(IV)–H_2O_2 system; the strong tendency of Pu(IV) to undergo extensive hydrolysis and polymerization in nitric acid; the autocatalytic decomposition of H_2O_2 and/or the peroxy complex compounds formed with Pu(IV), the formation and decomposition of the Pu(IV)–nitrate complexes; the possibility of precipitation of PuO_4, etc.

On the other hand, the available information published on the peroxy compounds of Pu(IV) is very meagre; occasional reference is made to two complex species, brown and red,[6,7] the existence of which has been confirmed by us. No reference has been made to the bluish-pink transient labile Pu(IV)–H_2O_2 species. Further details concerning the influence of different experimental conditions on the formation of the new blue ternary complex reported here will be published in due time, and will throw additional light on the complexity and experimental difficulties encountered as regards the reproducibility of the Pu(IV)–H_2O_2–HNO_3–arsenazo I system. However, the blue complex dealt with here is probably of more theoretical than practical interest, since the increase in sensitivity (~ 50%) over the common binary complex is offset by the difficulty of obtaining reproducibility. Nevertheless, studies of this type of complex will surely contribute towards a greater understanding of the chemical reactivity and reaction mechanisms of this valuable type of analytical reagent.

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Summary—The preparation and spectrophotometric properties of a new type of complex compound of arsenazo I with Pu(IV) in the presence of H_2O_2 are described. The new compound has a blue colour, derived from a wide absorption band with a maximum at 610 nm. and a corresponding molar absorptivity of 4×10^4 l. mole^{-1}.cm^{-1}. From 2 hr after its preparation this curious new compound undergoes for several days a steady decomposition accompanied by decolorization. The formation of similar peroxy Pu(IV) complexes has not so far been shown to take place with arsenazo III or with any other "arsenazo-type" reagent.

Résumé—On décrit la préparation et les propriétés physico-chimiques d'un nouveau type de composé complexe de l'arsénazo I avec Pu(IV) en la présence de H_2O_2. Le nouveau composé a une coloration bleue, découlant d'une large bande d'absorption avec un maximum à 610 nm et un coefficient d'absorption molaire correspondant de 4×10^4 l. mole^{-1} cm^{-1}. A partir de deux heures après sa préparation ce curieux composé nouveau subit pendant plusieurs jours une décomposition régulière accompagnée de décoloration. On n'a pas montré jusqu'ici que la formation de complexes peroxy de Pu(IV) similaires se produit avec l'arsénazo III ou avec n'importe quel autre réactif du type arsénazo.

Zusammenfassung—Die Herstellung und die spektrophotometrischen Eigenschaften eines neuen Typs Komplexverbindung von Arsenazo I mit Pu(IV) in Gegenwart von H_2O_2 werden beschrieben. Die neue Verbindung ist blau, was auf eine breite Absorptionsbande mit Maximum bei 610 nm und einem molaren Extinktionskoeffizienten von 4×10^4 l. mol^{-1} cm^{-1} zurückgeht. Zwei Stunden nach ihrer Darstellung beginnt diese merkwürdige neue Verbindung, sich in mehreren Tagen stetig zu zersetzen, wobei sie sich entfärbt. Die Bildung ähnlicher Peroxy-Pu(IV)-Komplexe ist bisher weder mit Arsenazo III noch irgend einem anderen Reagens vom "Arsenazo-Typ" gezeigt worden.

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ORTHO-EFFECTS OF CARBOXYL, SULPHO AND ARSONO GROUPS ON THE PROTONATION AND DISSOCIATION CONSTANTS OF MONO-AZO AND BIS-AZO CHROMOTROPIC ACID DERIVATIVES

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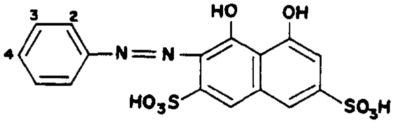
There is a relationship between the protonation and dissociation constants of *ortho*-substituted mono-azo and bis-azo chromotropic acid derivatives[1–3] and the stability constants of their metal complexes[1,4,5] which have been used for spectrophotometric analysis. More detailed studies[illegible] have shown that the relationship is dependent upon the position of the substituent group. This pointed to the desirability of investigating in more detail the *ortho* effect of arsono, sulpho and carboxyl substituents in reagents that are widely used in spectrophotometry.[8]

Values of the equilibrium constants of most of the reagents containing these acid substituents have been determined.[1–3,6,7,9–11] However, there is some dispute over the order of the dissociating groups. We feel the same order of dissociation should be adopted for both the arsenazo III and palladiazo reagents,[9,10] and that the dissociation of the last arsono OH-group ($-AsO_3H^- \rightarrow -AsO_3^{2-}$) takes place after the first dissociation of a proton from an OH-group on the naphthalene nucleus but before dissociation of the second proton from a hydroxyl group on the naphthalene nucleus.[6,7,9,10]

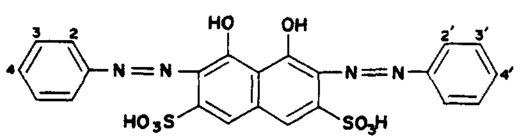
EXPERIMENTAL

Reagents

The following reagents were prepared by standard procedures:[8] two 2-azophenylchromotropic acid derivatives



the substituents at the 4-position being the arsonic acid and carboxylic acid groups, and three 2,7-bisazophenylchromotropic acid derivatives



the substituents being arsonic acid groups at the 2- and 2′-positions (arsenazo III), and carboxylic acid groups at the 2- and 2′- or at the 4- and 4′-positions.

Procedure

Protonation was investigated in sulphuric acid media by standard spectrophotometric procedures.[1–3,6,7] Protonation constants, K_p, and proton dissociation constants of both hydroxyl groups of the naphthalene nucleus, K_1 and K_2, for the five reagents along with the values obtained earlier are given in Tables 1 and 2.

RESULTS AND DISCUSSION

The effect of each substituent is expressed by the magnitude of $\log K/K_0$ where K_0 is the value of the equilibrium constant of the reagent without substituents in the benzene rings ("zero" reagents).

Table 1. Protonation (log K_p) and dissociation (pK_1 and pK_2) constants of the substituted 2-azophenylchromotropic acid derivatives

Substituent	log K_p	pK_1	pK_2
—*	−4·52 (7)†	9·24 (7)	15·03 (7)
2-AsO_3H_2	−6·36 (1)	9·79 (7)	15·55 (7)
2-SO_3H	−5·23 (7)	9·39 (7)	14·62 (7)
2-COOH	−4·87 (1)	10·20 (7)	15·99 (7)
4-AsO_3H_2	−6·18	9·57	14·71
4-SO_3H	−5·55 (7)	9·18 (7)	14·57 (7)
4-COOH	−5·57	9·51	14·81

* "Zero" reagent.

† Reference given in brackets.

Table 2. Protonation (log K_p) and dissociation (pK_1 and pK_2) constants of the substituted 2,7-bis(azophenyl)chromotropic acid derivatives

Substituents	log K_p	pK_1	pK_2
—*	−0·61 (6)†	8·64 (6)	14·40 (6)
2-,2′-di-AsO_3H_2	−5·04 (1)	8·38	15·51
2-,2′-di-SO_3H	−1·25 (6)	10·92 (6)	14·97 (6)
2-,2′-di-COOH	−0·30 (1)	10·60 (3)	15·13 (3)
4-,4′-di-AsO_3H_2	−2·20 (10)	8·15 (9)	14·1 (9)
4-,4′-di-SO_3H	−1·35 (6)	8·34 (6)	14·12 (6)
4-,4′-di-COOH	−1·03 (3)	9·25	14·16

* "Zero" reagent.

† Reference given in brackets.

Table 3. The effect of the substituents in the benzene ring on protonation [$\log(K/K_0)_p$] and dissociation [$\log(K/K_0)_1$ and $\log(K/K_0)_2$] of hydroxyl groups of mono-azo chromotropic acid derivatives, and the *ortho*-effect.

Substituent	$\log(K/K_0)_p$	$\log(K/K_0)_1$	$\log(K/K_0)_2$
2-AsO_3H_2	−1·84	−0·55	−0·52
4-AsO_3H_2	−1·66	−0·33	0·32
Ortho-effect	−0·18	−0·22	−0·84
2-SO_3H	−0·71	−0·12	0·41
4-SO_3H	−1·03	0·06	0·46
Ortho-effect	0·32	−0·18	−0·05
2-COOH	−0·35	−0·96	−0·96
4-COOH	−1·05	−0·27	0·22
Ortho-effect	0·70	−0·69	−1·18

Table 4. The effect of symmetrical substituent pairs on protonation [$\log(K/K_0)_p$] and dissociation [$\log(K/K_0)_1$ and $\log(K/K_0)_2$] of bis-azo chromotropic acid derivatives, and the *ortho*-effect

Substituents	$\log(K/K_0)_p$	$\log(K/K_0)_1$	$\log(K/K_0)_2$
2-,2′-di-AsO_3H_2	−4·43	0·26	−1·11
4-,4′-di-AsO_3H_2	−1·59	0·51	0·30
Ortho-effect	−2·84	−0·25	−1·41
2-,2′-di-SO_3H	−0·64	−2·28	−0·57
4-,4′-di-SO_3H	−0·74	0·30	0·28
Ortho-effect	0·10	−2·58	−0·85
2-,2′-di-COOH	0·31	−1·96	−0·73
4-,4′-di-COOH	−0·42	−0·61	0·26
Ortho-effect	0·73	−1·35	−0·99

Values of substituent effects for mono-azo and bis-azo derivatives are given in Tables 3 and 4, respectively.

The *ortho*-effect is defined as the difference between the effects of substituents in the *ortho* (2-) and *para* (4-) positions:[12,13]

$$ortho\text{-effect} = \log(K/K_0)_{ortho} - \log(K/K_0)_{para},$$
$$= \log(K_{ortho}/K_{para})$$

provided the inductive effects of both *ortho* and *para* substituents are approximately the same.[13] Tables 3 and 4 show the *ortho*-effect values for arsono, sulpho and carboxyl groups for mono-azo and bis-azo derivatives, respectively.

It should be pointed out that in the case of bis-azo derivatives the sum-effect of the pairs of symmetrical substituents (4,4′- and 2,2′-) was expressed, so that the calculated *ortho*-effect (Table 4) represents the sum of the *ortho*-effect value of one substituent (2-position) and the inductive effect of the other substituent (2′-position). This inductive effect value is zero when the effect of both *ortho* and *para* substituents (2′- and 4′-) is approximately the same. The substituent in the 2′-position is located in the benzene ring more distant from the reaction centre (especially in the case of protonation of the azo group) so that its effect is different from that of the first substituent with respect to both its nature and magnitude.

It is evident from Tables 3 and 4 that the magnitudes of the effects of each substituent, especially the value of the *ortho*-effect of substituents ($-COOH$, $-SO_3H$, $-AsO_3H_2$) on the three processes, namely protonation of the azo group and proton dissociations of two hydroxyl groups on the naphthalene nucleus, do not have a simple regularity. This is quite understandable from the different properties of the substituents, particularly steric ones, and also the different substituent positions in relation to the reaction centre, as well as the different nature of the investigation equilibrium processes and the inadequate definition of the *ortho*-effect.[12,13] The differences observed by comparing the same values for mono-azo and bis-azo derivatives can be ascribed to the magnitude and nature of the conjugated π-electron system of these organic molecules.

The effect of substituents on protonation

The strong inductive and, especially, steric effects of the arsono group on bis-azo derivatives,[1] result in a decrease of the basicity of the reagent. The *ortho*-effect also decreases the basicity (−2·84, see Table 4). The arsono group decreases the basicity of the mono-azo derivatives: the effect is considerable with both *ortho* and *para* substituents (−1·84 and −1·66 respectively) but the value of the *ortho*-effect is insignificant. It is difficult to explain the difference between the *ortho*-effects of mono-azo and bis-azo derivatives; presumably they result from many effects exerted either separately or jointly.

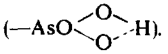
The effect of sulpho groups is manifested as a decrease in basicity by approximately the same order for both mono-azo and bis-azo derivatives as well as with *ortho* and *para* substituents. The *ortho*-effect itself is insignificant (0·35 and 0·10) and reflects a small steric effect of the sulpho group.

The effects of carboxyl groups differ somewhat according to the position of the substituents and the size of the organic molecule; but they are also considerably smaller than those of the arsono and sulpho groups, in agreement with previous observations.[1] A more significant decrease of basicity occurs with *para* di-substituted bis-azo derivatives. The *ortho*-effect increases the basicity of the reagent, thus indicating the absence of the steric effect of the carboxyl group.[1]

The effect of substituents on the pK_1

The effect of the arsono group is relatively small and its *ortho*-effect insignificant. The effect of the carboxyl group on bis-azo derivatives is greater, and that of the sulpho group even more so, while the effect of the same substituents on mono-azo derivatives is very small. The shift of pK_1 of bis-azo derivatives to a more alkaline region by sulpho and carboxyl groups can be explained by the formation of a hydrogen bond between the anions of the acid groups ($-SO_3^-$, $-COO^-$) and the hydroxyl group of the naphthalene nucleus.[3,6] This effect is considerably greater with di-substituted bis-azo derivatives than with mono-azo derivatives, owing to the parallel activity of both substituents in the *para* position (−2·28 and −1·96 for sulpho and carboxyl groups, respectively).

The small effect of the arsono group can be explained if the order of dissociation of the hydroxyl groups in the reagent[9,10] is taken into account. The affect of the arsono group as an $-AsO_3H^-$ ion is very insignificant because of the low probability of formation of a hydrogen bond with the hydroxyl group of the naphthalene nucleus. It is most probable that the hydrogen bond is formed in the arsono group alone



$(-AsO\langle O_2 \rangle H)$.

The *ortho*-effect on mono-azo derivatives is small, being approximately the same for all the substituents investigated. It is hard to explain the relatively small *ortho*-effect on mono-azo derivatives by the absence of hydrogen bonds, which in the case of bis-azo derivatives were taken as predominant in the characterization of the nature of the effect. The causes should be sought in other differences originating from the conjugated π-electron systems of mono-azo and bis-azo derivatives or from the sum effect of pairs of substituents of bis-azo derivatives.

The effect of substituents on pK_2

There is no regularity in the effect of substituents on pK_2. This is because of the dominant effect of the already dissociated hydroxyl group. The *peri* position of these two groups is suitable for the formation of hydrogen bonds.[6,7]

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Summary—The effect of carboxyl, sulpho and arsono groups on the protonation and dissociation constants of mono-azo and bis-azo chromotropic acid derivatives has been investigated. From the value obtained for the effect of the substituents, the equation

$$ortho\text{-effect} = \log K_{ortho} \text{-} \log K_{para}$$

has been derived. The causes of the effect are discussed.

Résumé—On a étudié l'influence des groupes carboxyle, sulfo et arséno sur les constantes de protonation et de dissociation de dérivés monoazo et bisazo de l'acide chromotropique. De la valeur obtenue pour l'influence des substituants, on a déduit l'équation: *ortho*-effet = log K_{ortho} − log K_{para}. On discute des causes de l'influence.

Zusammenfassung—Der Einfluß von Carboxyl-, Sulfo- und Arsonogruppen auf die Protonierungs- und Dissoziationskonstanten von Monoazo- und Bisazochromotropsäurederivaten wurde untersucht. Aus den für den Substituenteneinfluß erhaltenen Werten wurde die Gleichung *ortho*-Effekt = log K_{ortho} − log K_{para} abgeleitet. Die Ursachen des Effekts werden diskutiert.

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PRECIPITATION OF LEAD AS LEAD SULPHATE BY DESTRUCTIVE OXIDATION OF EDTA

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MacNevin and Dunton[1] studied the homogeneous precipitation of ferric hydroxide through release of the cation from its EDTA complex by the slow oxidation of EDTA with hydrogen peroxide at constant pH. A dense and easily filterable ferric hydroxide is obtained by this procedure at pH 3·0. Cartwright[2] studied the oxidation of EDTA with hydrogen peroxide in detail and found that certain oxides caused decomposition of the hydrogen peroxide, thus stopping the oxidation process. However, by taking advantage of the ability of phosphate to stabilize hydrogen peroxide, he was able to produce bismuth, iron, lead, calcium and barium phosphates as dense and readily filterable precipitates from solutions containing the single ions. The method is not selective, as all the metals present in solution are released at the same time from their EDTA complexes. In previous communications we have described procedures for the homogeneous precipitation of lead sulphate through cation replacement by iron, copper and nickel.[3,4] In these methods many metals which generally accompany lead in its alloys or ores did not interfere. Because oxidation of EDTA also releases the metal ion, it was of interest to study this too for homogeneous precipitation of lead sulphate.

EXPERIMENTAL

Reagents

All reagents were of analytical grade. Aqueous lead nitrate solutions 0·005, 0·025 and 0·05M, 5% EDTA solution and 0·2M ammonium sulphate were prepared. Hydrogen peroxide and alkali metal chlorate, bromate and persulphate were used as oxidizing agents for EDTA.

For interference studies, solutions of aluminium(III), copper(II), nickel(II), zinc(II), iron(III) and manganese(II) were prepared from their sulphates to give metal ion concentrations of 10 mg/ml. Solutions of tin and antimony were prepared by dissolving the metal in a minimal amount of 1:1 nitric acid–hydrofluoric acid and diluting to the required volume to give a concentration of 10 mg/ml.

Procedures

For pure lead solutions. To a solution containing 5–100 mg of lead, add 5 ml of 5% EDTA solution and 5 ml of 0·2M ammonium sulphate, dilute to 45 ml, add 1 ml of nitric acid (1 + 3) and 2 ml of 30% hydrogen peroxide or 0·5 g of sodium bromate. Heat the solution on a boiling water-bath for at least 2 hr. Precipitation starts in 10 min and is complete after 2 hr. Continue heating till the final volume of the solution is about 15 ml. Cool for 30 min, and filter off on a sintered-glass crucible (porosity 4) using 1% sulphuric acid and 50% ethanol as the initial and the final wash solutions respectively. Continue washing with ethanol until the washings are free from sulphate. Dry the precipitate at 120°C for 1 hr, cool and weigh as lead sulphate. The conversion factor is $Pb/PbSO_4 = 0{\cdot}6833$.

Analysis of type metal. Dissolve a weighed (10 g) sample of type metal in 15 ml of nitric acid and 15 ml of hydrofluoric acid.[5] Boil for a few min to remove nitrous fumes and dilute to 1 litre in a volumetric flask. Take a 10 ml aliquot in a 100 ml beaker and add 5 ml each of 5% EDTA solution and 0·2M ammonium sulphate, adjust the volume to 50 ml, and continue as described above.

DISCUSSION

The precipitates obtained are dense and easily filterable. They have no tendency to creep and do not absorb moisture on exposure to the atmosphere.

Various oxidizing agents such as chlorate, bromate, persulphate and hydrogen peroxide were studied. It was found that precipitates of superior characteristics were obtained only with bromate or hydrogen peroxide as the oxidant.

Oxidation of EDTA by bromate or hydrogen peroxide was very slow at higher pH, the rate of reaction decreasing with increasing pH. At pH > 3·0, the oxidation was not complete even after boiling for more than 3 hr. However, at pH 1·5–3·0, the oxidation was complete after boiling the solution for at least 2 hr. In this pH range, heating on a water-bath even for more than 3 hr did not result in the complete oxidation of EDTA. At pH < 1·5,

Table 1. Determination of lead in pure solutions

Lead taken, *mg*	Lead found, *mg*	Mean deviation, *mg*	No. of experiments
Hydrogen peroxide method			
5·2	5·2	0·2	3
10·4	10·2	0·3	4
25·9	25·9	0·0	3
51·8	52·1	0·0	4
77·7	77·7	0·0	3
103·6	103·6	0·1	4
Sodium bromate method			
5·2	5·0	0·2	6
10·4	10·4	0·1	4
25·9	25·8	0·2	4
51·8	51·9	0·2	4
77·7	77·8	0·1	4
103·6	103·5	0·1	4

a gradual release of lead from its EDTA complex was achieved by heating even on a water-bath. At pH 1·0 the EDTA complex is unstable to acid and a precipitate of lead sulphate and EDTA is slowly formed on heating, but precipitation is incomplete even on prolonged heating, so cation-release by lowering the pH is not applicable. Judging from the rate of precipitation, the oxidative degradation of EDTA is the predominant factor in the liberation of the lead ions. At pH < 1, rapid precipitation of lead sulphate occurs and hence the oxidation should always be done at pH 1·0–1·5.

Varying concentrations of EDTA and sulphate ion did not affect the quantitative precipitation of lead sulphate. It was found that 1 or 2 ml of 30% hydrogen peroxide or 0·5 g of sodium bromate could oxidize 5 ml of 5% EDTA solution. For other concentrations of EDTA the optimum quantities of oxidant have to be found by trial and error, but an excess of either bromate or hydrogen peroxide has no adverse effect.

Interferences were studied on mixtures of 50 mg of foreign ion with 5 or 50 mg of lead. The results in Tables 1–3 clearly indicate the usefulness of the method for the determination of lead in the presence and absence of interfering metals. Determination of lead in type metal gave an accurate value. It is noteworthy that tin and antimony do not interfere. Chloride does not interfere when present in up to tenfold amount relative to lead.

The method can also be used to determine sulphate.

Table 2. Interference studies for the hydrogen peroxide method

Metal added	Lead taken, *mg*	Lead found, *mg*	Mean deviation, *mg*	No. of experiments
Al(III)	51·8	51·6	0·0	4
Al(III)	5·2	5·2	0·3	4
Cu(II)	51·8	51·7	0·2	4
Cu(II)	5·2	5·1	0·2	4
Ni(II)	51·8	51·6	0·2	3
Ni(II)	5·2	5·0	0·2	3
Zn(II)	51·8	51·9	0·0	3
Zn(II)	5·2	4·9	0·1	3
Fe(III)	51·8	52·0	0·1	4
Fe(III)	5·2	5·0	0·1	4
Mn(II)	51·8	51·9	0·1	3
Mn(II)	5·2	5·1	0·1	3
Sn(II)	51·8	51·8	0·1	4
Sn(II)	5·2	5·2	0·1	4
Sb(III)	51·8	51·9	0·2	4
Sb(III)	5·2	5·1	0·1	4

Table 3. Interference studies for the bromate method

Metal added	Lead taken, *mg*	Lead found, *mg*	Mean deviation, *mg*	No. of experiments
Al(III)	51·8	51·7	0·2	4
Al(III)	5·2	5·1	0·2	4
Cu(II)	51·8	51·9	0·2	4
Cu(II)	5·2	5·0	0·2	4
Ni(II)	51·8	51·7	0·4	4
Ni(II)	5·2	5·1	0·3	4
Zn(II)	51·8	51·7	0·3	4
Zn(II)	5·2	5·1	0·3	4
Fe(III)	51·8	52·0	0·2	4
Fe(III)	5·2	5·1	0·1	4
Mn(II)	51·8	52·0	0·1	4
Mn(II)	5·2	5·3	0·1	4
Sn(II)	51·8	51·7	0·1	3
Sn(II)	5·2	5·0	0·1	3
Sb(III)	51·8	51·6	0·1	3
Sb(III)	5·2	5·1	0·1	3

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Summary—Gravimetric determination of lead (5–100 mg) by homogeneous precipitation of lead sulphate from a solution containing lead(II), EDTA and sulphate by destructive oxidation of EDTA with hydrogen peroxide or sodium bromate is described. Aluminium(III), iron(III), zinc(II), manganese(II), copper(II), nickel(II), tin(II) and antimony(III) do not interfere in the method. The method can successfully be applied to the analysis of type metal.

Résumé—On décrit le dosage gravimétrique du plomb (5–100 mg) par précipitation homogène du sulfate de plomb à partir d'une solution contenant du plomb(II), de l'EDTA et du sulfate, par oxydation destructive de l'EDTA par le peroxyde d'hydrogène ou le bromate de sodium. Les aluminium(III), fer(III), zinc(II), manganèse(II), cuivre(II), nickel(II), étain(II) et antimoine(III) n'interfèrent pas dans cette méthode. La méthode peut être appliquée avec succès à l'analyse d'alliage pour caractères d'imprimerie.

Zusammenfassung—Die gravimetrische Bestimmung von Blei (5–100 mg) durch homogene Fällung von Bleisulfat wird beschrieben. Es wird aus einer Lösung gefällt, die Blei(II), EDTA und Sulfat enthält und in der EDTA mit Wasserstoffperoxid oder Natriumbromat oxidativ zerstört wird. Aluminium(III), Eisen(III), Zink(II), Mangan(II), Kupfer(II), Nickel(II), Zinn(II) und Antimon(III) storen nicht. Das Verfahren kann mit Erfolg für die Analyse von Letternmetall verwendet werden.

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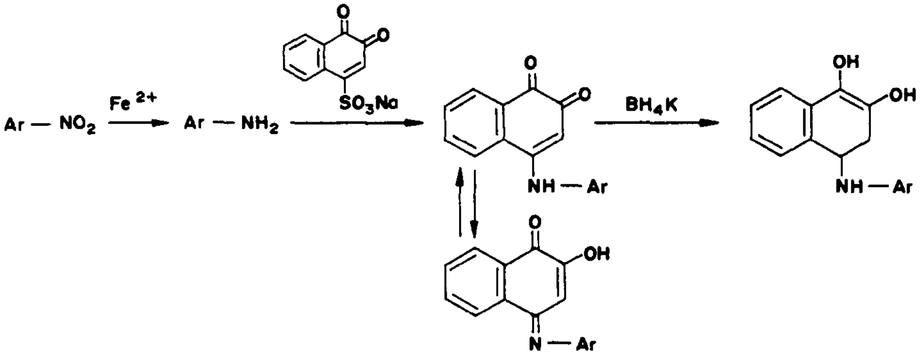
ELEMENTS DE FLUORIMETRIE ORGANIQUE FONCTIONNELLE—IX FLUORIMETRIE DE DERIVES NITRES AROMATIQUES

(*Reçu le* 16 *avril* 1974. *Accepté le* 4 *juin* 1974)

Les dérivés nitrés aromatiques sont aisément réduits par le sulfate ferreux en milieu alcalin, et cette réaction a été récemment mise à profit pour le dosage de ces composés par colorimétrie du fer (III) formé au moyen de thiocyanate de potassium.[1] Le dérivé nitré est parallèlement converti en amine aromatique et l'on sait que, par réaction avec l'acide naphtoquinone-1,2 sulfonique-4, les arylamines primaires fournissent une N-aryl aminonaphtoquinone extractible en chlorure de méthylène. La réduction par l'hydroborure de potassium du condensat ainsi séparé de l'excès de réactif mène à un *o*-diphénol fluorescent.[2]



Selon nos essais, on accède de la sorte à la fluorimétrie des dérivés nitrés aromatiques. La fluorescence bleu-vert, d'intensité proportionnelle à la concentration en produit nitré, autorise les dosages à l'échelle du microgramme.

Dans le tableau suivant les sensibilités sont exprimées selon les normes proposées antérieurement.[2,3]

	Limites du dosage, µg	Lecture 50	
		Essai, µg	Etalon, µg/ml
Nitrobenzène	0,4–2,0	0,8	0,185
o-Nitrotoluène	0,6–3,0	1,2	0,24
p-Nitrotoluène	0,6–3,0	1,2	0,27
o-Nitrophénol	0,7–3,5	1,3	0,23
m-Nitrophénol	0,3–1,5	0,6	0,20
m-Nitrobenzaldéhyde	0,5–2,5	0,95	0,25
m-Dinitrobenzène	0,5–2,5	1,0	0,21

La sensibilité est faible avec l'*o*-nitrobenzaldéhyde (8–40 µg). Les composés suivants ne réagissent pratiquement pas, *p*-nitrophénol, *p*-nitraniline, *p*-nitrophénylhydrazine, *p*-nitrobenzaldéhyde, dinitro-3,5 toluamide et trinitro-1,3,5 benzène.

PARTIE EXPERIMENTALE

Réactifs

(*a*) Solution aqueuse à 1,5% (p/v) de sel de Mohr ($FeSO_4$, $(NH_2)_2SO_4$, $6H_2O$).

(*b*) Solution aqueuse à 0,5% (p/v) de naphtoquinone-1,2 sulfonate-4 de sodium. Cette solution doit être fraîchement préparée et maintenue à l'abri de la lumière.

(*c*) On dissout 0,050 g d'hydroborure de potassium dans 1 ml de soude 0,1 *N* et dilue à 100 ml par l'eau.

Mode opératoire

La prise d'essai du dérivé nitré est dissoute dans 1 ml d'eau ou, si nécessaire, dans un minimum d'éthanol, et l'on dilue à 1 ml par l'eau. A la solution obtenue, on ajoute 0,5 ml de réactif *a*, puis 0,5 ml de soude 0,2 *N*. On mélange, laisse reposer pendant 30 secondes, et ajoute 0,5 ml d'acide sulfurique 0,2 *N*.

La suite des manipulations doit être effectuée à l'abri de la lumière. On prélève 1 ml de la solution obtenue, y ajoute 0,2 ml de réactif *b*, mélange, transvase le contenu du tube à essais dans une ampoule à décanter de 10 ml contenant 2 ml de chlorure de méthylène et ajoute 1 ml d'eau ayant servi à rincer le tube. On agite pendant 5 secondes environ, laisse décanter et recueille la totalité de la phase organique à laquelle on ajoute ensuite 2 ml d'éthanol puis 0,1 ml de réactif *c*. On laisse reposer pendant 1 mn à température ordinaire, ajoute 0,5 ml d'acide chlorhydrique 0,01 *N*, mélange et effectue la lecture à l'excitation 355 nm, émission 460 nm.

L'étalon est une solution d'α-naphtol dans le mélange éthanol–soude 0,2 *N* 4 : 1.

Je remercie Mme. G. Vallée pour sa collaboration à la mise au point technique de la réaction.

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2. J. Bartos et M. Pesez, *Talanta*, 1972, **19**, 93.
3. M. Pesez et J. Bartos, *ibid.*, 1967, **14**, 1097.

Résumé—Le fer (II) en milieu alcalin réduit les dérivés nitrés aromatiques en arylamines. Le colorant obtenu par réaction de l'amine avec l'acide naphtoquinone-1,2 sulfonique-4 est extractible en chlorure de méthylène. La réduction par l'hydroborure de potassium fournit un *o*-diphénol fluorescent, permettant ainsi la fluorimétrie des dérivés nitrés aromatiques à l'échelle du microgramme.

Summary—Aromatic nitro compounds are reduced to aromatic amines by iron(II) in alkaline medium. The dye obtained by reacting the amine with 1,2-naphthoquinone-4-sulphonic acid is extractable into methylene chloride. Reduction by potassium borohydride yields a fluorescent *o*-diphenol, thus allowing the fluorimetric estimation of aromatic nitro compounds on the microgram scale.

Zusammenfassung—Aromatische Nitroverbindungen werden durch Eisen(II) in alkalischem Medium zu aromatischen Aminen reduziert. Setzt man das Amin mit 1,2-Naphthochinon-4-sulfonsäure um, so läßt sich der erhaltene Farbstoff in Methylenchlorid extrahieren. Reduktion mit Kaliumborhydrid liefert ein fluoreszierendes *o*-Diphenol; damit wird die fluorimetrische Bestimmung aromatischer Nitroverbindungen im Mikrogramm-Maßstab möglich.

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SUR UNE COLORIMETRIE D'ALDEHYDES AROMATIQUES PAR L'INTERMEDIAIRE DE LEURS THIOSEMICARBAZONES

(*Reçu le* 16 *avril* 1974. *Accepté le* 4 *juin* 1974)

La réaction colorée que fournissent[1,2] les thiols avec la dichloro-2,3 naphtoquinone-1,4 a été récemment étendue

PARTIE EXPERIMENTALE

Réactifs

(*a*) Solution aqueuse à 1,5% (p/v) de sel de Mohr ($FeSO_4$, $(NH_2)_2SO_4$, $6H_2O$).

(*b*) Solution aqueuse à 0,5% (p/v) de naphtoquinone-1,2 sulfonate-4 de sodium. Cette solution doit être fraîchement préparée et maintenue à l'abri de la lumière.

(*c*) On dissout 0,050 g d'hydroborure de potassium dans 1 ml de soude 0,1 *N* et dilue à 100 ml par l'eau.

Mode opératoire

La prise d'essai du dérivé nitré est dissoute dans 1 ml d'eau ou, si nécessaire, dans un minimum d'éthanol, et l'on dilue à 1 ml par l'eau. A la solution obtenue, on ajoute 0,5 ml de réactif *a*, puis 0,5 ml de soude 0,2 *N*. On mélange, laisse reposer pendant 30 secondes, et ajoute 0,5 ml d'acide sulfurique 0,2 *N*.

La suite des manipulations doit être effectuée à l'abri de la lumière. On prélève 1 ml de la solution obtenue, y ajoute 0,2 ml de réactif *b*, mélange, transvase le contenu du tube à essais dans une ampoule à décanter de 10 ml contenant 2 ml de chlorure de méthylène et ajoute 1 ml d'eau ayant servi à rincer le tube. On agite pendant 5 secondes environ, laisse décanter et recueille la totalité de la phase organique à laquelle on ajoute ensuite 2 ml d'éthanol puis 0,1 ml de réactif *c*. On laisse reposer pendant 1 mn à température ordinaire, ajoute 0,5 ml d'acide chlorhydrique 0,01 *N*, mélange et effectue la lecture à l'excitation 355 nm, émission 460 nm.

L'étalon est une solution d'α-naphtol dans le mélange éthanol–soude 0,2 *N* 4 : 1.

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Summary—Aromatic nitro compounds are reduced to aromatic amines by iron(II) in alkaline medium. The dye obtained by reacting the amine with 1,2-naphthoquinone-4-sulphonic acid is extractable into methylene chloride. Reduction by potassium borohydride yields a fluorescent *o*-diphenol, thus allowing the fluorimetric estimation of aromatic nitro compounds on the microgram scale.

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SUR UNE COLORIMETRIE D'ALDEHYDES AROMATIQUES PAR L'INTERMEDIAIRE DE LEURS THIOSEMICARBAZONES

(*Reçu le* 16 *avril* 1974. *Accepté le* 4 *juin* 1974)

La réaction colorée que fournissent[1,2] les thiols avec la dichloro-2,3 naphtoquinone-1,4 a été récemment étendue à la détection des thiourées, thiosemicarbazides et monothiosemicarbazones.[3] Selon nos essais, on peut accéder ainsi à une colorimétrie sensible des aldéhydes aromatiques.

La réaction est également positive avec les aldéhydes aliphatiques et les cétones, mais les résultats sont très irréguliers et la loi de Beer n'est pas suivie. La méthode n'est pas applicable aux composés insolubles dans l'eau.

PARTIE EXPÉRIMENTALE

Réactifs

(*a*) Solution à 0,1% (p/v) de thiosemicarbazide dans l'acide chlorhydrique 0,1*N*.
(*b*) Solution à 1% de dichloro-2,3 naphtoquinone1,4 dans le chlorure de méthylène.

Mode opératoire

A 1 ml de solution aqueuse d'aldéhyde, on ajoute 0,5 ml de réactif *a* et laisse reposer pendant 10 min à 20°C. On transvase le contenu du tube à essais dans une ampoule à décanter de 10 ml, ajoute 1 ml d'eau de lavage du tube, puis 2 ml de chlorure de méthylène, et agite pendant 20 secondes. On laisse décanter, recueille la totalité de la phase organique et y ajoute 0,5 ml de réactif *b*, 2 ml d'éthanol et 0,5 ml d'ammoniaque 22° Bé ($\sim 12M$). On laisse reposer à l'obscurité à 20°C pendant 1 h avant d'effectuer la lecture (coloration brun-orangé à vert-orangé).

Applications

	λ_{max}, nm	Prise d'essai en μg pour obtenir une densité optique de 0,3 (cuve de 1 cm)
Benzaldéhyde	556	4,9
4-Hydroxy benzaldéhyde	575	48
Pipéronal	570	5,4
Salicylaldéhyde	660	7,2
Vanilline	570	10,4

Nous remercions Mlle. M. Pepin pour sa collaboration à la mise au point technique de la réaction.

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Résumé—La thiosemicarbazone obtenue en faisant réagir un aldéhyde aromatique avec le thiosemicarbazide en milieu acide est extraite en chlorure de méthylène. La coloration développée en ajoutant de la dichloro-2,3 naphtoquinone-1,4 à l'extrait organique autorise la colorimétrie à l'échelle de quelques microgrammes.

Summary—The thiosemicarbazone obtained by reacting an aromatic aldehyde with thiosemicarbazide in acidic medium is extracted into methylene chloride. The colour developed by adding 2,3-dichloro-1,4-naphthoquinone to the organic extract allows the colorimetric determination of a few micrograms.

Zusammenfassung—Das aus einem aromatischen Aldehyd und Thiosemicarbazid in saurem Medium erhaltene Thiosemicarbazon wird in Methylenchlorid extrahiert. Die durch Zugabe von 2,3-Dichlor-1,4-naphthochinon zum organischen Extrakt entwickelte Farbe erlaubt die colorimetrische Bestimmung einiger Mikrogramme.

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SUR UNE COLORIMETRIE DES ACIDES CARBOXYLIQUES PAR HYDROXAMATION DIRECTE

(*Reçu le* 16 *avril* 1974. *Accepté le* 4 *juin* 1974)

La colorimétrie des acides carboxyliques est fréquemment fondée sur une estérification préalable. La révélation des dérivés *p*-nitrophénacyliques obtenus par réaction du sel de sodium de l'acide avec le bromure de *p*-nitrophénacyle,[1] et celle des composés dinitro-2,4 phényliques formés par condensation de l'acide avec le dinitro-2,4 phénol en présence de dicyclohexylcarbodiimide,[2] mettent à profit la présence de groupements nitrés dans la molécule de l'ester. On accède à la colorimétrie des esters du glycol préparés par réaction de l'acide avec l'éthylèneglycol en présence d'acide sulfurique,[3] et à celle des esters méthyliques obtenus par action, sur l'acide carboxylique, du méthanol en présence de dicyclohexylcarbodiimide,[4] par passage à l'acide hydroxamique correspondant et développement de la coloration par l'ion ferrique.

Récemment, Tanimura *et al.*[5] ont décrit une réaction qualitative des acides carboxyliques fondée sur la formation directe de l'acide hydroxamique, évitant le stade intermédiaire d'estérification. Ils opèrent avec le chlorhydrate d'hydroxylamine, tandis que pour les esters on utilise classiquement la base libre. L'agent de déshydratation utilisé est le dicyclohexylcarbodiimide. Les esters ne réagissent pas, et les auteurs attribuent cette sélectivité au fait que les manipulations sont effectuées à température ordinaire et en l'absence de base forte.

Selon nos essais, la méthode peut être rendue quantitative. La loi de Beer étant suivie, on accède ainsi à la colorimétrie des acides carboxyliques. Dans nos conditions expérimentales, les esters ne réagissent pas, et l'on peut doser de la sorte 0,1% (p/v) d'acide acétique dans l'acétate de butyle, par exemple. Notre technique imposant, dans certains cas, un chauffage à 70°C pour la réaction d'hydroxamation, la sélectivité ne peut être attribuée au facteur température. Elle est liée à l'acidité du milieu: avec le chlorhydrate d'hydroxylamine, seuls les acides carboxyliques réagissent; les esters ne fournissent une réaction postitive qu'en milieu alcalin. On utilise généralement à cet effet une solution d'hydroxylamine obtenue par mélange à parties égales de solutions méthanoliques à même concentration de chlorhydrate d'hydroxylamine et de soude.[6] Dans un tel milieu, l'hydroxamation directe de l'acide carboxylique en présence de dicyclohexylcarbodiimide n'a pas lieu et l'estérification préalable devient nécessaire, ainsi que l'ont établi des essais antérieurs.[4]

PARTIE EXPÉRIMENTALE

Réactifs

(*a*) Solution aqueuse à 2% (p/v) de chlorhydrate d'hydroxylamine.
(*b*) Solution à 2% (p/v) de dicyclohexylcarbodiimide dans l'éthanol.
(*c*) Solution à 2% (p/v) de chlorure ferrique (6 H_2O) dans l'éthanol.

Mode opératoire

A 0,5 ml de solution d'acide carboxylique dans l'éthanol, on ajoute 0,1 ml de réactif *a* et 0,5 ml de réactif *b*. On maintient à T^0 pendant le temps *t* (voir *Applications*) à l'obscurité, refroidit si nécessaire, ajoute 3 ml d'éthanol puis 0,1 ml de réactif *c*. Lecture immédiate entre 510 et 550 nm.

Applications

	Température, °C	Temps de repos	λ_{max}, *nm*	Prise d'essai en μg pour obtenir une densité optique de 0,3 (cuve de 1 cm)
Acide formique	20	2 hr	510	60
Acide acétique	70	15 min	520	108
Acide propionique	70	15 min	520	140
Acide butyrique	70	20 min	520	162
Acide palmitique	70	15 min	520	510
Acide lactique	20	1 hr	520	174
Acide succinique	20	45 min	520	135
Acide malique	20	45 min	520	132

	Température, °C	Temps de repos	λ_{max}, nm	Prise d'essai en μg pour obtenir une densité optique de 0,3 (cuve de 1 cm)
Acide tartrique	20	45 min	520	207
Acide mandélique	70	15 min	520	200
Acide benzoïque	20	2 hr	550	127
Glycocolle*	20	4 hr	510	147
Alanine*	20	4 hr	510	265
Leucine*	20	4 hr	510	≈770
Sarcosine*	20	4 hr	510	300

* L'échantillon est dissous dans l'alcool à 80%.

Remarques

(1) La réaction n'est pas applicable à l'acide oxalique, qui est décomposé par le dicyclohexylcarbodiimide.

(2) On peut remplacer l'éthanol par le méthanol comme solvant de l'acide carboxylique.

(3) Pour le dosage d'un acide carboxylique dans son ester, on applique le mode opératoire à une solution à 10% (v/v) de l'ester dans l'éthanol.

Nous remercions Mlle. M. Pepin pour sa collaboration à la mise au point technique de la réaction.

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Résumé—Les acides carboxyliques réagissent avec le chlorhydrate d'hydroxylamine en présence de dicyclohexylcarbodiimide en donnant l'acide hydroxamique correspondant que l'on révèle par le fer (III), permettant ainsi la colorimétrie à l'échelle du dixième de milligramme. Les esters ne réagissent pas, et l'on peut ainsi doser l'acide acétique dans l'acétate de butyle à une concentration d'environ 0,1%.

Summary—Carboxylic acids react with hydroxylamine hydrochloride in the presence of dicyclohexylcarbodi-imide to give the corresponding hydroxamic acid which is developed with iron(III), thus allowing colorimetric determinations on the tenths of a milligram scale. Esters do not react, and acetic acid can be determined in butyl acetate at a concentration of about 0·1%.

Zusammenfassung—Carbonsäuren reagieren mit Hydroxylaminhydrochlorid in Gegenwart von Dicyclohexylcarbodiimid zur entsprechenden Hydroxamsäure, die mit Eisen(III) entwickelt wird. Damit werden colorimetrische Bestimmungen in der Größenordnung von Zehntel Milligrammen möglich. Ester reagieren nicht; etwa 0,1% Essigsäure in Butylacetat können bestimmt werden.

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM BY EXTRACTION OF ITS THIOSULPHATE COMPLEX

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The relative freedom from interference by other elements makes the reaction of molybdate with thiosulphate[1,2] attractive for the determination of molybdenum. The earlier method[3] of photometric determination employed the reaction only for pure molybdenum solutions and did not recognize the influence of temperature, the decomposition of thiosulphate in the solvent phase, and the effect of other ions on the extraction of molybdenum. A mixture of solvents was used for extraction, and required drying before the photometric measurement. Therefore, a reinvestigation of the method was considered of interest in view of the usefulness of the method for analysis of natural and industrial samples.

EXPERIMENTAL

Reagents and test solutions

Solutions of molybdenum, thiosulphate and of interfering elements were prepared as described in a previous paper.[4] The isoamyl alcohol fraction distilling at 128–131°C was used.

Synthetic samples. Prepared by mixing molybdenum in μg amounts with other ions in the desired proportions.

Steels. Steel sample (0·1 g) was dissolved[5] in 10 ml of perchloric acid (1 + 1) and 1 ml of concentrated nitric acid. The solution was made alkaline, 20 ml of glycerol were added to mask any tungsten, and the solution was made 1*M* in hydrochloric acid and 100 ml in volume; 10 ml aliquots were used for analysis.

Procedure

A 10 ml aliquot of just acidic sample solution containing not more than 0·8 mg of molybdenum is taken in a 100 ml separatory-funnel. Enough hydrochloric acid (10*M*) is added to make its final concentration 1*M* in 20 ml of solution. The volume is adjusted with water to about 18 ml (or correspondingly less when more than 2 ml of thiosulphate solution are added, as mentioned below) and the solution is cooled to 10–15°C. Then 10 ml of isoamyl alcohol followed by 2 ml of thiosulphate solution (both at 10–15°C) are added, the mixture is shaken immediately for 2–2·5 min and the solvent phase is separated. The molybdenum left in the aqueous phase is oxidized with bromine (added dropwise) and excess of bromine is removed by shaking for 1 min with 10 ml of carbon tetrachloride. The addition of isoamyl alcohol and thiosulphate solution is repeated and the solution shaken immediately for 2 min. The two isoamyl alcohol extracts are combined and shaken with 10 ml of water for 30 sec to remove free acid and thiosulphate, then passed through a Whatman No. 41 paper into a 25 ml standard flask and made up to the mark with the solvent. The absorbance of the complex is measured at 475 nm against a similarly treated solvent blank, in 1 cm cells.

For each 100 mg of iron(III) or vanadium(V) in the sample add 2 ml more of the thiosulphate solution, and 3 ml for each 100 mg of chromium(VI). For each 10 mg of tungsten(VI) add 1 ml of glycerol, after making the solution alkaline.

RESULTS AND DISCUSSION

The red species formed by molybdenum with thiosulphate in acidic solution is extractable by many organic solvents (Table 1). The complex shows maximum absorbance but little stability in ethyl acetate. Slightly lower but equal absorbance is shown in isoamyl alcohol and an n-butanol–benzene mixture, with equal colour stability. However, the former is preferred, being a single solvent not requiring drying before the spectrophotometry.

Effect of varying experimental conditions

The absorbance of the molybdenum thiosulphate complex increases with the time of shaking (Fig. 1, curve A), reaching a maximum in 2 min, but falls with increasing time of contact with the acid aqueous phase. Increasing the thiosulphate concentration increases the absorbance for up to 36 mg of $Na_2S_2O_3 \cdot 5H_2O$ per ml (Fig. 1, curve B), but higher concentrations decrease it owing to formation of a colloidal brown precipitate. The absor-

Table 1. Dependence of absorbance of the complex on the solvent (Mo in aqueous phase: 2·4 μg/ml)

Solvent	Absorbance*
Ethyl acetate	0·035
Isoamyl alcohol	0·031
n-Butanol–benzene (2:3)	0·031
Isoamyl acetate	0·029
TBP–benzene (1:1)	0·028
TBA–chloroform†	0·021
Methyl isobutyl ketone	§

* Against solvent shaken with reagents.
† Tribenzylamine solution (1% w/v) in chloroform.
§ Colour fades quickly and solvent becomes turbid.

bance increases with acid concentration up to 1*M* hydrochloric acid (Fig. 1, curve C), higher acidities decreasing it slightly. On the basis of these studies, the optimum conditions are 36–40 mg of $Na_2S_2O_3 \cdot 5H_2O$ per ml, 1–1·5*M* hydrochloric acid, and 2–2·5 min equilibration time. These are incorporated into the given procedure.

Effect of diverse ions

More than 1 mg/ml of Sn(II), Cu(II), or Bi(V), or > 10 μg/ml of Pd(II) and Pt(IV) in the aqueous phase will interfere by causing colour in the organic phase; Ru(III) and Os(VIII) cause stable emulsions (Table 2). Cu(II), Bi(V), Sb(III) and Pd(II) form precipitates in the aqueous phase on shaking with the solvent. More than 2 ml of glycerol per 20 ml of aqueous phase decreases the extraction of molybdenum by about 18% but this is recovered in the second extraction. The effect of other ions, complexing agents and other conditions on the absorbance of the molybdenum thiosulphate complex is the same as that on the extraction with methyl isobutyl ketone.[4]

The sulphur from the reaction of thiosulphate and acid extracted into the isoamyl alcohol, makes the solvent turbid in 2–3 min, causing serious errors in the absorbance. The organic phase should therefore be washed with water as proposed. Molybdenum is not lost thereby.

Molybdenum can be quantitatively removed into the solvent by two extractions. However, in the presence of other ions, molybdenum left in the aqueous phase after the first extraction is reduced to Mo(V) which is quantitatively extracted only after bromine oxidation and readjustment of the conditions as already discussed.[4] Glycerol does not interfere. Most of the excess of bromine is removed by a single extraction with 10 ml of carbon

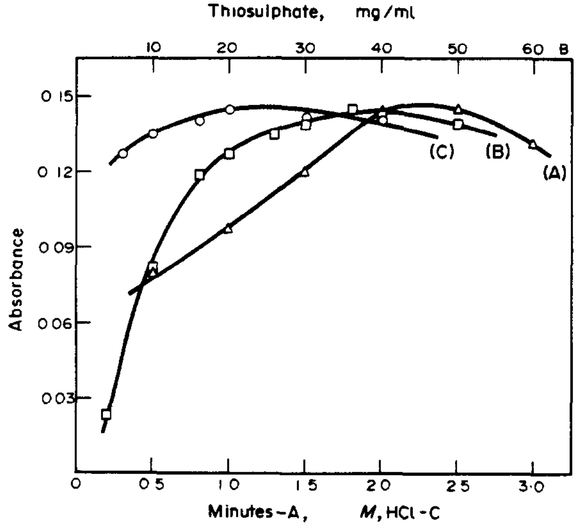

Fig. 1. Dependence of absorbance on conditions of extraction. Conditions: Mo 9·7 μg/ml, $Na_2S_2O_3 \cdot 5H_2O$ 36 mg/ml, 1*M* HCl, 2 min shaking.

Table 2. Absorbance of other ions

Ion* (initial oxidation state)	Appearance of solvent layer	Absorbance
Pd(II)†	orange yellow	0·269
Pt(IV)†	yellow	0·144
Bi(V)	faintly yellow	0·005
Cu(II)	faintly yellow	0·004
Sn(II)	faintly yellow	0·003
Cr(VI)	faintly green	0·000
Ti(IV), V(V), Mn(II), Fe(III), Co(II), Ni(II), U(VI), Ce(IV), Zr(IV), W(VI), Sb(III), Zn(II), Al(III), Cd(II), Pb(II), Nb(V)‡, Re(VII)§	Colourless	0·000
Os(VIII), Ru(III)	dark brown stable emulsions	—

Concentrations in the aqueous phase: * 5 mg/ml; † 2·5 mg/ml; ‡ 1mg/ml; § 5 μg/ml.

Table 3. Analysis of samples by the proposed method

Sample composition Matrix (*mg* of element)	Mo added, *μg*	Mo found, *μg*
V(100) Fe(50) Co(30) Ni(40) Mn(35)	97	97, 96
Ti(12) Cr(20) U(75) Nb(10) Cd(5)	291	290, 291
V(40) W(60) Fe(100)	121	121, 120
V(20) W(80) Mn(20)	48·5	48, 49
V(10) W(20) U(40) Fe(15) Cr(10) Ti(5) Nb(2)	20	20, 20
Cr(15) Zr(10) Fe(10) Co(5) Cd(10)	679	679, 680
High-speed steel (B.C.S. No. 241/1)	0·52%*	0·52%, 0·52%
Stainless steel (B.C.S. No. 246)	2·89%*	2·82%, 2·83%

* Reported value.

tetrachloride. The thiosulphate concentration is readjusted as required, before shaking again with the solvent. The two isoamyl alcohol extractions then remove the molybdenum quantitatively (> 99·7%). The slight loss of molybdenum is compensated by constructing the standard curve under the same conditions.

The red molybdenum thiosulphate complex in isoamyl alcohol has absorption maxima at 345 and 475 nm, the former being 20–25 times as sensitive as the latter. The absorbance at 475 nm is stable for 45 min, fades < 2% in 15 hr, and obeys Beer's law over the range 0–32 μg of molybdenum per ml of solvent.

Applications

The usefulness and applicability of the method are shown (Table 3) by the satisfactory analysis of steels and some synthetic samples containing several interfering elements in concentrations higher than normally met with. The method is simple, taking only about 15 min, and is free from disturbance by several important and frequently interfering species, *viz.* Ti(IV), V(V), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Zr(IV), U(VI), W(VI), Ce(IV), Re(VII), Sb(III), Al(III), Nb(V), Zn(II), Cd(II) and Pb(II) in the amounts usually occurring (the oxidation states shown are those of the ions when added initially in the tests done).

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Summary—A simple and rapid spectrophotometric determination of molybdenum is described. The molybdenum thiosulphate complex is extracted into isoamyl alcohol from 1·0–1·5*M* hydrochloric acid containing 36–40 mg of $Na_2S_2O_3\cdot 5H_2O$ per ml. The absorbance at λ_{max} = 475 nm obeys Beer's law over the range 0–32 μg of Mo per ml of solvent phase. Up to 5 mg/ml of Ti(IV), V(V), Cr(VI), Fe(III), Co(II), Ni(II), U(VI), W(VI), Sb(III), 1 mg/ml of Cu(II), Sn(II), Bi(V) and 10 μg/ml of Pt(IV) and Pd(II) do not interfere. Large amounts of complexing agents interfere. The method has been applied to analysis of synthetic and industrial samples.

Résumé—On décrit un dosage spectrophotométrique simple et rapide du molybdène. On extrait le complexe de thiosulfate de molybdène en alcool isoamylique à partir d'acide chlorhydrique 1–1.5*M* contenant 36–40 mg de $Na_2S_2O_3$. 5 H_2O par ml. L'absorption à λ_{max} = 475 nm suit la loi de Beer dans le domaine 0–32 μg de Mo par ml de phase solvant. Jusqu'à 5 mg/ml de Ti(IV), V(V), Cr(VI), Fe(III), Co(II), Ni(II), U(VI), W(VI), Sb(III), 1 mg/ml de Cu(II), Sn(II), Bi(V) et 10 μg/ml de Pt(IV) et Pd(II) n'interfèrent pas. De grandes quantités d'agents complexants interfèrent. On a appliqué la méthode à l'analyse d'échantillons synthétiques et industriels.

Zusammenfassung—Eine einfache und rasche spektrophotometrische Bestimmungsmethode von Molybdän wird beschrieben. Der Molybdän-Thiosulfat-Komplex wird aus 1,0–1,5*M* Salzsäure, die 36–40 mg $Na_2S_2O_3\cdot 5$ H_2O pro ml enthält, in Isoamylalkohol extrahiert. Die Extinktion bei λ_{max} = 475 nm befolgt im Bereich 0–32 μg Mo pro ml organischer Phase das Beersche Gesetz. Bis 5 mg/ml Ti(IV), V(V), Cr(VI), Fe(III), Co(II), Ni(II), U(VI), W(VI), Sb(III), 1 mg/ml Cu(II), Sn(II), Bi(V) und 10 μg/ml Pt(IV) und Pd(II) stören nicht. Große Mengen von Komplexbildnern stören. Die Methode wurde auf die Analyse synthetischer und industrieller Proben angewandt.

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ANALYTICAL DATA

DISSOCIATION CONSTANTS OF CARBOXYMETHYLOXYSUCCINIC ACID

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The trisodium salt of carboxymethyloxysuccinic acid (CMOS)[1] is at present under consideration for use in synthesis of detergents.[2,3] We are now investigating the chelating properties of the CMOS anion with several metal cations.[4] To be able to determine the formation constants of CMOS complexes by the method of competitive reactions, it is necessary to know the dissociation constants of the acid, defined as follows:

$$H_3A = H^+ + H_2A^- \quad K_1 = [H][H_2A]/[H_3A] \tag{1}$$

$$H_2A^- = H^+ + HA^{2-} \quad K_2 = [H][HA]/[H_2A] \tag{2}$$

$$HA^{2-} = H^+ + A^{3-} \quad K_3 = [H][A]/[HA] \tag{3}$$

These constants have been measured at 25° at an ionic strength of 0·100*M*. The activity coefficients are presumed to have remained constant; thus the dissociation constants measured are concentration constants and not thermodynamic constants.[5] The experimental approach was a modified version of the method of Bates and Pinching.[6]

EXPERIMENTAL

Materials

The CMOS was supplied in the form of the trisodium salt pentahydrate by Lever Brothers Research and Development Division, Edgewater, N.J The absence of other carboxylic acids as impurities was confirmed by NMR and chromatographic techniques. The material was found to be not less than 99·8% pure, by an acidimetric assay.

The trisodium salt was converted into the acid by passing solutions of the salt through a column containing Bio-Rad AG-50W X8 (50–100 mesh) cation-exchange resin in the hydrogen form.

Three stock solutions of CMOS buffers were made up from 0·1000-mole portions of CMOS mixed with enough 1·000*M* sodium hydroxide to neutralize 1/6, 1/2, and 5/6 of the total acidity, respectively, and then diluted to twice the original volume of acid. Thus one solution was nominally 0·0500*M* in both H_3A and NaH_2A, the second 0·0500*M* in both NaH_2A and Na_2HA, and the third 0·0500*M* in both Na_2HA and Na_3A. The concentrations of these stock solutions were checked by titration of the remaining unneutralized acid.

From each CMOS buffer stock solution, 1·0, 3·0, 5·0, 10·0, and 20·0 ml portions (V_b) were transferred to 100·0-ml volumetric flasks. The calculated amount of 1·00*M* sodium perchlorate was then added to each flask such that the ionic strength after dilution would be 0·100*M*.

The pH measurements were made with a Beckman 1019 Research Model pH meter (which had been calibrated with an internal Weston cell) using a Beckman general purpose glass electrode and a Beckman frit-junction silver–silver chloride reference electrode. After internal calibration the meter and glass electrode were standardized to read hydrogen–ion concentration when used with hydrochloric acid solutions of known concentration and an ionic strength of 0·100*M* in sodium perchlorate medium. All solutions were measured in a constant-temperature bath kept at 25·0 ± 0·1°.

CALCULATIONS

Because the three dissociation constants of CMOS are very close, an acidimetric titration curve shows only one inflection point. Such a curve was used to estimate an average dissociation constant (K_i) from the pH measured at half complete neutralization. The three dissociation constants were then computed from pH measurements on three separate sets of CMOS buffer solutions, by using a method of successive approximations.

The first set of buffer solutions contained nominally equimolar amounts of H_3A and NaH_2A. For these solutions it was assumed that the third dissociation could be neglected. The average dissociation constant found from the titration curve was used to estimate K_2, thereby allowing K_1 to be calculated from the hydrogen ion concentration by the following equation:

$$K_1 = \frac{C_{H_2A}[H]^2 + [H]^3}{[H](C_{H_3A} - [H] - K_2) + K_2(C_{H_2A} + 2C_{H_3A})}, \tag{4}$$

where [H] is the hydrogen ion concentration, and C_{H_3A} and C_{H_2A} are the analytical concentrations of H_3A and NaH_2A. This equation was derived from equations (1) and (2) and from the relevant mass balance equations.

The third set of buffer solutions contained nominally equimolar amounts of Na_2HA and Na_3A. For these solutions it was assumed that the first dissociation was complete. The average dissociation constant was again used to estimate K_2, and K_3 was then calculated from the hydrogen ion concentrations by means of the following equation:

$$K_3 = \frac{K_2C_A[H] + [H]^2(K_2 + 2C_A + C_{HA}) + [H]^3}{K_2(C_{HA} - [H])}, \tag{5}$$

where C_{HA} and C_A are the stoichiometric concentrations of Na_2HA and Na_3A respectively.

The second set of buffer solutions contained nominally equimolar amounts of NaH_2A and Na_2HA. In these solutions all three dissociation equilibria must be considered. The first and third equilibria can be described by means of the K_1 and K_3 calculated from the two previous sets of solutions, and a new K_2 was calculated from the hydrogen ion concentration of these solutions by the following equation:

$$K_2 = \frac{(K_1 + [H])[H]^2(C_{HA} + B)}{K_1(K_3 + [H])(C_{H_2A} - B)}, \tag{6}$$

where

$$B = \frac{[H]^2 + (K_1 + K_3)[H] + K_1K_3}{2[H]^2 + K_1[H] + 3K_3[H] + 2K_1K_3}\left(\frac{[H] - C_{HA}K_3}{[H] + K_3} + \frac{[H]C_{H_2A}}{K_1 + [H]}\right). \tag{7}$$

The value of K_2 calculated from equation (6) was used to recalculate K_1 and K_3 from equations (4) and (5). A new value of K_2 was then recalculated from the new K_1 and K_3. The cycle of calculations was repeated until after four iterations, the values of K_1, K_2 and K_3 converged to within 0·001. The computations were performed on a General Electric Time Sharing Service Mark IV computer.

RESULTS AND DISCUSSION

In each cycle of calculations, individual dissociation constants were calculated for each buffer solution in each set. The average results were used to initiate the next cycle of calculations. The averages, ±one standard deviation, obtained after convergence were as follows: $K_1 = (3{\cdot}01 \pm 0{\cdot}05) \times 10^{-3}$, $K_2 = (1{\cdot}70 \pm 0{\cdot}01) \times 10^{-4}$, and $K_3 = (1{\cdot}00 \pm 0{\cdot}05) \times 10^{-5}$. The pH data used in computing the constants, and the pK values obtained after convergence are presented in Table 1. The initial estimate of the average dissociation constant obtained from the neutralization curve was K_i $1{\cdot}3 \times 10^{-4}$.

On the basis of inductive effects, it appears that K_1 refers to the dissociation of hydrogen atom 2, while K_2 and K_3 refer to the dissociations of hydrogen atoms 1 and 3 respectively.

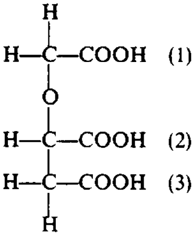

Table 1. pH data used in computing the dissociation constants of carboxymethyloxysuccinic acid, and pK values after convergence, at 25°C and $\mu = 0{\cdot}100M$ in sodium perchlorate.

	Set 1		Set 2		Set 3	
V_b, *ml*	*pH*	pK_1	*pH*	pK_2	*pH*	pK_3
1·0	—	—	3·915	3·770	5·050	4·972
3·0	2·959	2·511	3·826	3·767	$5{\cdot}057_5$	4·990
5·0	2·855	2·530	3·807	3·772	$5{\cdot}064_5$	5·000
7·0	2·784	2·515	3·797	3·772	5·074	5·012
10·0	2·725	2·523	3·788	3·771	5·091	5·032
20·0	2·632	2·526				

Comparison of the pK_1 value of CMOS (2·52) with that reported for the isomeric citric acid (pK_1 = 2·9–3·0)[6,7] and the parent succinic acid (pK_1 = 4·19)[8] shows CMOS to be the strongest of these acids. The greater acid strength of CMOS can be attributed to the inductive effect of the ether oxygen atom.

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Summary—The dissociation constants of carboxymethyloxysuccinic acid (CMOS) have been measured at 25° and an ionic strength of 0·1*M* in sodium perchlorate. The values found were: pK_1 = 2·52, pK_2 = 3·77 and pK_3 = 5·00. CMOS is thus seen to be rather stronger than its isomer citric acid.

Résumé—On a mesuré les constantes de dissociation de l'acide carboxyméthyloxysuccinique (CMOS) à 25° et à une force ionique de 0,1*M* en perchlorate de sodium. Les valeurs trouvées sont: pK_1 = 2,52; pK_2 = 3,77 et pK_3 = 5,00. On voit que le CMOS est plutôt plus fort que son isomère l'acide citrique

Zusammenfassung—Die Dissoziationskonstanten von Carboxymethyloxybernsteinsäure (CMOS) wurden bei 25° und einer Ionenstärke von 0,1*M* in Natriumperchlorat gemessen. Die gefundenen Werte sind: pK_1 = 2,52, pK_2 = 3,77 und pK_3 = 5,00. Man sieht, daß CMOS eine eher stärkere Säure ist als die isomere Citronensäure

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ANNOTATION

COMPARISON OF AN INSTRUMENTAL AND MODIFIED KJELDAHL TECHNIQUE FOR DETERMINATION OF NITROGEN IN NIOBIUM AND TANTALUM ALLOYS

(*Received* 25 *March* 1974. *Accepted* 14 *May* 1974)

The refractory alloys of niobium and tantalum are promising candidates for structural use in space. It is important to be able to monitor changes in nitrogen content in the ppm range for tantalum and niobium alloys. Low concentrations of nitrogen in many metals have been determined by vacuum fusion, inert-gas fusion or by variations of the Kjeldahl procedure. There has been a limited amount of work done showing a comparison of nitrogen results for refractory metals in the same material by the Kjeldahl and instrumental methods.[1,2] This was due in large part to the difficulty in dissolving solid refractory metal samples rapidly. However, since the introduction of the improved chemical dissolution procedure developed by Kallmann *et al.* it is possible to dissolve rapidly solid fragments of refractory metals such as tungsten, molybdenum, niobium and tantalum for Kjeldahl nitrogen determinations.[3]

In an earlier report we compared vacuum-fusion gas analysis and a modified Kjeldahl technique for the determination of nitrogen in tantalum alloys.[2] The present report describes a continuation of this work, namely the determination of nitrogen in niobium alloys.

Attempts in this laboratory to use vacuum fusion and conventional inert-gas fusion analysers for the determination of nitrogen in niobium alloys were unsuccessful. Recovery of the nitrogen was low despite the use of various flux and bath conditions. An instrument based on the principles of pulse heating described by Vasserman and Turovtseva[4] and later used by Goldbeck *et al.*[5] is now commercially available as the Leco Corporation Model TC-30 nitrogen–oxygen determinator.

The purpose of this paper is to demonstrate the applicability of this instrument as compared to a modified Kjeldahl method, for the determination of nitrogen in three tantalum and six niobium alloys.

The modified Kjeldahl results for the tantalum alloys are from a previous report.[2] The instrumental results are new, but are based on samples analysed previously by means of modified Kjeldahl and vacuum fusion techniques.

EXPERIMENTAL

Sample preparation

The sample rods were sliced with a water-cooled abrasive wheel. Wafers were cut into individual samples with a flat shear. One portion of the wafer (0·25 g) was used for the TC-30 analyser and another portion (0·5 g) for the modified Kjeldahl determination. Samples were etched in a solution of 10 ml of hydrofluoric acid (1 + 1) and a few drops of 30% hydrogen peroxide in a Teflon beaker. The solution was warmed for a few minutes to accelerate the etching. Etching was stopped when a matte finish appeared on the samples. After the etching the samples were rinsed with distilled water, acetone, and finally reagent grade diethyl ether. After drying at 110°C, the samples were weighed. The sample intended for the modified Kjeldahl determination was placed in a Teflon dissolution bottle. The sample for instrumental analysis was placed in a platinum wire spiral. This spiral was formed from a 1 g piece of 20-gauge low-oxygen platinum wire with the ends closed to contain the sample.

Instrumental analysis

The instrument used to obtain the nitrogen values reported was a Leco Corporation Model TC-30 simultaneous nitrogen–oxygen determinator. The analyser is equipped with a large sample loading head. The sample is fused with 1 g of platinum in a helium atmosphere at a high temperature in a small, single-use graphite crucible. The graphite crucible is held between water-cooled electrodes and attains a temperature of 2700°C when a 600–800 A current is applied. The graphite crucible is outgassed beforehand at the operating temperature for 45 sec. The sample, contained in a 1-g platinum wire spiral, is dropped into the crucible. Again the crucible and sample are heated for 20 sec. Helium carries the released gases over copper oxide where carbon monoxide is oxidized to carbon dioxide and hydrogen is oxidized to water. Water is absorbed in magnesium perchlorate and the remaining nitrogen and carbon dioxide are separated chromatographically on a silica gel column. Less than 1 min after the end of the fusion, the nitrogen is eluted from the chromatographic column, enters the thermal conductivity cell and is measured. The output of the cell is displayed on an electronic digital voltmeter. The oxygen peak is recorded in the measuring cell about a minute later and is similarly measured and displayed. One sample can be analysed for both nitrogen and oxygen in less than 4 min.

Outgassing and analysis cycles are initiated by push-button operation. Both cycles are automatically controlled by electronic timers and solenoid valves.

Modified Kjeldahl procedure

The apparatus, reagents, and procedure used were essentially the same as those described in an earlier publication.[2] All procedural steps remained the same except for the use of a smaller size sample, owing to the higher nitrogen content of the niobium alloys, and a different etching solution.

DISCUSSION AND RESULTS

The classical vacuum fusion and inert-gas fusion techniques both involve high-temperature fusion of the sample in a graphite crucible so that carbon reduction and thermal decomposition reactions may occur. Quantitative extraction of carbon monoxide for the determination of oxygen in the refractory metals can be achieved if optimal conditions are provided in the fusion crucible. Some molecular nitrogen is also evolved under the same conditions. Although our earlier comparison showed good correlation between vacuum fusion and the modified Kjeldahl procedures for nitrogen in tantalum alloys, we have not been able to extend this to niobium-base alloys. In our laboratory both vacuum and conventional inert-gas fusion have always yielded lower nitrogen values for niobium alloys than the modified Kjeldahl procedure.

Turovtseva and Kunin reported the determination of nitrogen in samples of specially prepared niobium by use of vacuum fusion and an iron bath.[6] Dallman shows a comparison of the Kjeldahl and inert-gas fusion procedures for the determination of nitrogen in niobium metal.[1] We are not aware of any reported comparisons of instrumental and Kjeldahl nitrogen values for niobium alloys. Close agreement was not easily achieved for several reasons. At one time, milled chips, not solid fragments, were used for Kjeldahl samples. Former chemical dissolution procedures were not rapid. The laboratory air is a possible major source of nitrogen contamination. Another reason reported by Somiya was that if the collection time used for oxygen is applied for the extraction of nitrogen, the nitrogen extraction is incomplete.[7] Somiya was able to overcome this problem in the vacuum fusion analysis of steel samples by extending the collection time for nitrogen. Goward has suggested that the problem is due to the difficulty of extracting nitrogen down to its equilibrium value.[8] Dallmann demonstrated the feasibility of simultaneous quantitative oxygen and nitrogen determinations in unalloyed niobium,[1] by inert-gas fusion with a platinum–tin bath and a pyrolytic boron nitride thimble.

Lemm demonstrated that quantitative recovery of nitrogen in steel was possible when a new, small graphite crucible was used for each sample extraction under an inert gas.[9] He also demonstrated that nitrogen recovery progressively decreased when several steel samples were extracted in the same inert-gas fusion crucible.[10]

In the TC-30 instrument, a high current is pulsed through a graphite crucible so that temperatures in excess of 2700°C are rapidly attained. A new graphite crucible is used for each determination. The nitrogen is separated from the oxygen by a chromatographic column. The nitrogen and oxygen are measured by thermal conductivity and the results displayed on separate digital voltmeters. An analysis for both nitrogen and oxygen can be carried out in less than 4 min. Although intended for the determination of gases in steel, the TC-30 can be used for refractory metals by suitable adjustments in procedure and operating conditions. These include wrapping the sample in platinum, to provide a fluid medium for dissolving the refractory metal and complete release of nitrogen, and extending the heating cycle to 20 sec to compensate for the larger mass of metal added to the crucible.

Table 1 shows the nominal chemical analysis of the tantalum and niobium alloys tested. Table 2 indicates that equivalent results for the determination of nitrogen in the niobium alloys are obtained by the TC-30 and the modified Kjeldahl method. The precision of the TC-30 results is not significantly different from that of the modified Kjeldahl method. In the range 30–80 ppm nitrogen, the relative standard deviation was 2–8% by the modified Kjeldahl method and 5–7% by the instrumental method.

Table 1. Nominal composition of alloys tested

Commercial designation	Balance	Composition, % W	Hf	Zr	Ta	V	Mo	Y
T-111	Ta	8	2	—	—	—	—	—
T-222	Ta	10	2·5	—	—	—	—	—
WC-3015	Nb	13	29	1·5	4	—	—	—
Cb-752	Nb	9·8	—	2·7	—	—	—	—
FS-85	Nb	9·5	—	0·8	28	—	—	—
C-129Y	Nb	9	9	—	—	—	—	0·1
B-66	Nb	—	—	1·1	—	5	5	—
Cb-1Zr	Nb	—	—	1	—	—	—	—

Table 2. Comparison of results for determination of nitrogen in several niobium alloys by modified Kjeldahl and TC-30 inert-gas methods

	TC-30 Inert-gas method					Modified Kjeldahl method				
Alloy	Number of values	Mean, *ppm*	Standard deviation, *ppm**	Relative standard deviation, %	Blank† range, *μg*	Number of values	Mean *ppm*	Standard deviation, *ppm**	Relative standard deviation, %	Blank§ range, *μg*
FS-85	12	33	1·6	4·8	0·0–0·5	8	38	1·2	3·1	4·1–5·8
Cb-752	13	39	2·4	6·1	0·5–1·5	10	41	3·2	7·8	5·3–8·8
C-129Y	10	45	2·3	5·1	0·5–1·0	11	46	3·1	6·7	5·3–8·8
WC-3015	14	60	3·1	5·2	0·5–1·0	10	55	1·4	2·5	5·0–7·1
Cb-1Zr	10	80	3·8	4·7	0·5–1·5	12	70	1·3	1·8	5·0–7·1
B-66	10	75	5·2	6·9	0·0–0·5	10	79	2·1	2·6	4·1–5·8

* $S = \sqrt{[(\Sigma d^2)/(n - 1)]}$ where d is the deviation from the mean and n is the number of determinations.

† Range of 3–4 determinations for each of 2 days.

§ Range of 4–6 determinations for each of 2 days.

Table 3. Comparison of results for determination of nitrogen in three tantalum alloys by modified Kjeldahl and TC-30 inert-gas methods

	TC-30 Inert-gas method					Modified Kjeldahl method				
Alloy	Number of values	Mean *ppm*	Standard deviation, *ppm*	Relative standard deviation, %	Blank* range *μg*	Number of values	Mean. *ppm*	Standard deviation, *ppm*	Relative standard deviation, %	Blank† range, *μg*
T-111	9	10	1·1	11	0·5–1·0	13	9	0·3	3	6·3–10·4
T-111	10	22	1·9	9	0·5–1·0	14	24	2·1	9	6·8–8·9
T-222	10	8	0·8	10	0·5–1·0	7	7	0·4	6	7·0–8·1

* Range for 2 days.

† Range for 2–3 days.

The mean values for nitrogen by the two methods agree within 5 ppm for five of the niobium alloys tested. For the alloy Cb-1 Zr, the difference in the mean nitrogen values is 10 ppm. The higher value of 80 ppm was found with the TC-30 analyser. The samples were analysed by both methods during two days. The blank values are the range for that period. The blank for the TC-30 is lower and constant. This should be expected because in the instrumental analysis the sample is not subjected to as many handling operations such as dissolution, distillation, spectrophotometric measurements and longer exposure to the laboratory atmosphere.

Table 3 presents results from the analysis of three tantalum-base alloys. The Kjeldahl results are from the earlier report. The TC-30 and the modified Kjeldahl results were obtained for the same sample rods. The mean values for nitrogen in all three tantalum alloys agree very well by the two methods. The relative standard deviation for the instrumental method was 8–11% and for the modified Kjeldahl method 3–9%.

CONCLUSIONS

The results presented here show that the TC-30 analyser may be used satisfactorily for the determination of nitrogen in the tantalum and niobium alloys tested. The fact that nitrogen values were obtained simultaneously with the determination of oxygen and have an accuracy and precision equivalent to modified Kjeldahl values is of great importance. The instrumental blank is very low and constant. The oxygen and nitrogen values are related to each other and both sample and time are saved.

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Warren F. Davis

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Summary—Results obtained for the determination of nitrogen in two tantalum alloys and six niobium alloys by modified Kjeldahl and Leco TC-30 nitrogen–oxygen determinator are compared. In the 5–25 ppm range, for tantalum alloys, the relative standard deviation was 3–9% by the Kjeldahl procedure and 9–11% by the instrumental technique. In the range 30–80 ppm, for niobium alloys, the relative standard deviation was 2–8% by the Kjeldahl procedure and 5–7% by the instrumental technique.

Résumé—On compare les résultats obtenus pour le dosage de l'azote dans deux alliages de tantale et six aliages de niobium par Kjeldahl modifié et par l'appareil de dosage azote-oxygène Leco TC-30. Dans le domaine 5–25 ppm, pour les alliages de tantale, l'écart type relatif a été de 3–9% par la technique de Kjeldahl et 9–11% par la technique instrumentale. Dans le domaine 30–80 ppm, pour les alliages de niobium, l'écart type relatif a été 2–8% par la technique de Kjeldahl et 5–7% par la technique instrumentale.

Zusammenfassung—Die Ergebnisse der Stickstoffbestimmung in zwei Tantal- und sechs Niob-Legierungen nach einer modifizierten Kjeldahlmethode und mit dem Stickstoff-Sauerstoff-Analysator TG-30 von Leco werden verglichen. Bei den Tantallegierungen betrug für 5–25 ppm die relative Standardabweichung bei der Kjeldahlmethode 3–9% und bei der instrumentellen Methode 9–11%. Bei den Nioblegierungen betrug im Bereich 30–80 ppm die relative Standardabweichung der Kjeldahlmethode 2–8% und der instrumentellen Methode 5–7%.

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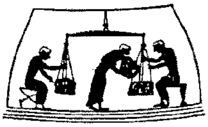

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EDITORIAL

In the Editorial published in the August number of *Talanta*, mention was made of further developments in the services offered to readers. One of the most important of these will be the delineation of areas in which analytical research is much needed, and a series of articles and "guest" Editorials will be used for this purpose. One of the reasons for this innovation is the evident lack of communication between industrial chemists and academic research workers, which results in the latter being ignorant of the needs of the former, and the former being unaware of the untapped potential offered by the latter. For the convenience of our many readers who are not native readers of English, we propose to transfer the French and German summaries of papers from their present position in each article, to the position at present occupied by the English and Russian card-index summaries. They will thus be available for cutting out and pasting onto index cards. The English card-index summaries will be retained, but the Russian summaries will be dropped, mainly because they are expensive to set in type, and it does not seem fair to expect the majority of subscribers to subsidize the interests of a very small minority; in this way we can avoid passing on some of the ever-increasing cost of printing. It is also intended to publish a series of short review articles, which will serve the purpose of updating earlier reviews while giving a critical appraisal of a particular field of analysis.

Talanta. Vol. 21, p. i. Pergamon Press. 1974. Printed in Great Britain

PAPERS RECEIVED

Extractive photometric simultaneous determination of iron(II) and copper(II) with *syn*-phenyl-α-pyridyl ketoxime: analysis of ferrites: Chandrakant K. Bhaskare and Sunalini G. Kawatkar. (29 *May* 1974)

Aquomolybdenum(III) chloride as a reducing titrant: A potentiometric study: S. R. Sagi and P. R. Mohan Rao. (31 *May* 1974)

Formation constants of mercury(II) with some buffer/masking agents and the formation of mixed-ligand complexes: W. E. van der Linden and C. Beers. (4 *June* 1974)

Titrimetric determination of mercaptans with chloramine-T: Ram Chand Paul, Satish Kumar Sharma, Naresh Kumar and Ram Parkash. (4 *June* 1974)

Gas–liquid chromatography of monosubstituted benzaldehyde isomers—I. Separation and thermodynamic treatment of monosubstituted benzaldehyde isomers: Albertine E. Habboush and Ismail K. Al-Hitti. (4 *June* 1974)

Gas–liquid chromatography of monosubstituted benzaldehyde isomers—II. Substituent effects: Albertine E. Habboush and Ismail K. Al-Hitti. (4 *June* 1974)

The spectrophotometric determination of manganese(II) and zinc(II) with 4-(2-pyridylazo)resorcinol: Sten Ahrland and Richard G. Herman. (5 *June* 1974)

Precipitation of molybdenum(V) as hydroxide and its separation from rhenium: V. Yatirajam, Usha Ahuja and L. R. Kakkar. (18 *June* 1974)

Analytical applications of hydrazones: Mohan Katyal and Yag Dutt. (19 *June* 1974)

Spectrophotometric solvent-extraction studies of the uranyl 2-mercaptopyridine-1-oxide complex: M. Edrissi and A. Massoumi. (19 *June* 1974)

Mass spectra of metal chlorides by electron-impact mass-spectrometry: Kozo Matsumoto, Nobutoshi Kiba and Tsugio Takeuchi. (19 *June* 1974)

The complexometry of tin(IV): J. Kragten. (19 *June* 1974)

Direct photometric determination of tellurium: L. S. A. Dikshitulu and Dindi Satyanarayana. (19 *June* 1974)

Spectrophotometric and fluorometric determination of traces of molybdenum in soils and plants: P. R. Haddad, P. W. Alexander and L. E. Smythe. (21 *June* 1974)

The separation of molybdenum from technetium on di-2-ethylhexylphosphoric acid (D-2-EHPA) and kieselguhr: W. D'Olieslager, J. Indesteege and M. D'Hont. (21 *June* 1974)

Coulometric investigation of the drying methods for the standard reference materials potassium dichromate and sodium carbonate: Takayoshi Yoshimori and Noriyuki Sakaguchi. (21 *June* 1974)

Refractometric titrations: J. Alamo and J. Beltran. (24 *June* 1974)

A stable d.c. capillary arc plasma for solution analysis: H. Denton, B. L. Sharp and T. S. West. (24 *June* 1974)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—III. Verbrennungsvorgänge im leeren Rohr: Walter Walisch and Ottakar Jaenicke. (20 *May* 1974)

The anion-exchange behaviour of molybdenum, tungsten and uranium in presence of phosphoric acid in mixed solvent media: Lathika Devi Nair and P. K. Padmanabhan. (25 *June* 1974)

Extraction of metal complexes of ascorbic acid into trioctylmethylammonium chloride: J. Adam and R. Pribil. (25 *June* 1974)

Saccharin as an analytical standard: W. P. Hayes, I. A. Rashid, D. Thorburn Burns and J. S. Wragg. (17 *June* 1974)

Dispositif de prélèvement microanalytique de produits altérables: Bernard Cousin and Colette Muller. (26 *May* 1974)

Anwendung von Ionenaustauschverfahren zur Bestimmung von Spurenelementen in natürlichen Wassern—VII. Kupfer: J. Korkisch, L. Gödl and H. Gross. (27 *June* 1974)

Separation of platinum and palladium on dimethylglyoxime-treated silicone rubber foam: D. G. Gregoire and A. Chow. (8 *May* 1974)

A reinvestigation of the reaction between TiO^{2+} and salicylic acid in concentrated sulphuric acid: R. S. Ramakrishna, V. Paramasigamani and M. Mahendran. (28 *June* 1974)

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EDITORIAL

PRELIMINARY COMMUNICATIONS

In the interests of rapid publication and establishment of priority for new ideas and techniques in analytical chemistry, the Publisher and Editorial Board of *Talanta* have decided that from January 1975, Preliminary Communications will be printed direct from typescript instead of being typeset and proof-read. In this way it should be possible for an article to appear within 5–8 weeks from the date of receipt. Off-set printing direct from typescript requires both the writing and the typing to be done accurately, with strict adherence to the publisher's requirements, and any deviations will inevitably result in delay in appearance of the paper. Instructions to authors will be found at the end of this issue. Papers submitted for publication as Preliminary Communications should be sent direct to the Editor-in-Chief; they will be refereed as expeditiously as possible, but without relaxation of the standards that give *Talanta* its prestige, and to avoid disappointment authors are advised to consider their work critically before submitting it. Preliminary Communications are intended for the rapid publication of novel ideas likely to be useful in analytical chemistry or to initiate new lines of research. They are *not* intended for trivial applications of well-known techniques and reagents, and they must contain sufficient results to show that enough research has been done to establish the validity of the work. Acceptance of a Preliminary Communication will not bind the author(s) to submission of any follow-up papers to *Talanta*, nor will it commit *Talanta* to automatic acceptance of such papers (which would be refereed in the usual way).

This is the first of a number of developments the Publisher and Editorial Board have in mind for *Talanta*, and the others will be described in future Editorials.

PUBLICATIONS RECEIVED

Physics Reference Books: Vol. 1, **Motion and Units:** F. C. FLACK, K. E. GREW, T. W. PRIEST and W. G. V. ROSSER, Pp. 332; £1.40; Vol. 4, **Electricity and Electrons:** J. T. DAVIES, J. DUTTON and C. GREY-MORGAN, Pp. 196; £1.10; Vol. 6, **Interfaces of Physics:** E. F. SLADE, Pp. 218; £1.10; Penguin Books, Harmondsworth, 1973.

These three books constitute part of a six-volume series. This series is in the form of an extended dictionary of laws, phenomena and effects in physics. As such, it is suitable for students at second- and third-year sixth-form levels or first-year undergraduates. The items are included in each volume in alphabetical order and there is an extensive cross-reference system within and between the volumes. Additional information provided includes suggestions for further reading and lists of units and constants.

Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands: C. A. MCAULIFFE (ed.). Halsted Press, New York, 1973. Pp. xix + 428. £10.50.

The style of this book is similar to that of the Chemical Society Specialist Periodical Reports, although the title is a little misleading as the contents are devoted almost exclusively to phosphine, arsine and stibine ligands; others, such as phosphites, achieve only a passing mention. An introductory chapter (Pidcock) deals with Group VB element-transition metal bonds, with particular reference to platinum compounds and emphasizing the interpretation of experimental data. Subsequent chapters discuss phosphine complexes (Chow, Levason and McAuliffe), mono-tertiary arsine and stibine complexes (Lloyd and McAuliffe), multidentate ligands (Chiswell) and di-tertiary arsine complexes (Alyea). The literature references extend to 1971 and occasionally into 1972; the coverage generally is comprehensive rather than critical and the main value of the book will be as an initial source in a field where one has been badly needed.

The periodic Table: J. S. F. PODE. The Halsted Press Modern Chemistry Series, Halsted Press, New York, 1973. Pp. 157. Paperback £3.75.

This book is aimed at sixth-form and possibly first-year University students. The first half of the book assembles experimental and factual information on the chemistry of the elements and representative compounds, and is reinforced by an extensive series of well-chosen simple experiments. The second half interprets this information in terms of theoretical ideas of atomic structure, orbitals and chemical bonding. The two halves of the book are efficiently cross-referenced so that fact and theory are continuously correlated. The style is terse to the point of aggressiveness but in his anxiety to identify and deal with sacred cows the author sometimes succeeds only in substituting others of his own. In particular, his attachment to the concept of resonance leads to interpretations of the structures of LiF and BF_3 which many will find misleading. These reservations apart, the book provides a refreshing survey of elementary inorganic chemistry.

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TALANTA MEDAL

The Editorial Board of *Talanta* has pleasure in announcing that, with the approval of the Advisory Board, the Seventh Award of the Talanta Medal has been made to

PROFESSOR B. V. L'VOV

of the State Institute of Applied Chemistry, Leningrad.

Professor L'vov was the pioneer worker in the use of the graphite oven, instead of a flame, to provide the atom-reservoir in atomic-absorption spectroscopy. He was the first to apply it in chemical analysis, his first paper on the topic appearing in 1950 and being followed by several others. His work remained unnoticed in the West until about 1965, but since then many variants of the original idea have been extensively applied. The technique is versatile and extremely useful, especially for small samples. It is also readily adaptable for larger samples when sampling problems arise or when trace analysis is required.

Talanta, Vol 21, p 1 Pergamon Press. 1974 Printed in Great Britain

TALANTA ADVISORY BOARD

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

J. F. K. HUBER
J. INCZÉDY

They also wish to record their sincere thanks for the help given by

F. E. BEAMISH
G. GOTTSCHALK
YU. A. ZOLOTOV

who retire from the Advisory Board.

Professor J. Inczédy was born in 1923 in Budapest, Hungary. At school he was trained in classical languages and Latin and Greek literature. Afterwards he received tuition at the Technical University, Budapest, where he gained his diploma of Chemical Engineering in 1946. He then worked for 5 yr as an engineer in the leather industry. He came back as lecturer to the Technical University where he worked first on reaction kinetics and trace analysis, and later on analytical separation methods. His main research interest is the use of complex-formation reactions in ion-exchange chromatographic and extraction methods. His first book, ***Analytical Applications of Ion Exchangers***, was published in three languages. The book ***Analytical Applications of Complex Equilibria*** was published in Hungarian in 1970. In the year 1959 he received the Dr. Techn. degree from the Technical University, and in the year 1967 the D.Sc. degree. He is member of the Advisory Board of ***Ion Exchange and Membranes***, of IUPAC Commission V/1, and of the Presidium of the Hungarian Chemical Society. Since 1970 he has been professor of Analytical Chemistry at the University of Chemical Engineering, Veszprém.

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Extractions with long-chain amines—VII The colorimetric determination of chromium(VI) with diphenylcarbazide: J Adam and R Pribil (20 *November* 1973)

Sur le microdosage du soufre dans les composes organiques, en presence d'halogenes, par combustion et titrage coulometrique automatique de dioxyde de soufre: Daniel Fraisse and Suzanne Raveau (21 *November* 1973)

Thiomercurimetric determination of sulphur, aliphatic and aromatic thiols and disulphides in hydrocarbon solvents by reduction with sodium aluminium bis(2-methoxyethoxy) dihydride: Mieczyslaw Wronski (22 *November* 1973)

Formation of ferrocyanides—IV. Th(IV), Nd(III), UO_2(II) and Hg(II): Athos Bellomo, Domenico de Marco and Agatino Casale (23 *November* 1973)

Rapid determination of antimony in steel by flameless atomic-absorption: Wolfgang Frech (23 *November* 1973)

Forced-flow chromatography of the lanthanides with continuous in-stream detection: James N Story and James S Fritz (23 *November* 1973)

Analytical applications of thio- seleno- and telluro-ethers—III. Spectrophotometric determination of palladium with benzyl selenide: Luiz R M Pitombo and Elisabeth Q Cartaxo (23 *November* 1973)

Use of data processing in modern rapid methods of elemental analysis: Wolfgang Merz (26 *November* 1973)

Spectrophotometric determination of dissolved oxygen by using tris(4,7-dihydroxy-1,10-phenanthroline) iron(II): D P Poe and H Diehl (4 *December* 1973)

Redox indicator properties of some substituted chrysoidins: Ulrik J Larsen, Raymond A Bournique, Robert W Adler and George A Klaus (4 *December* 1973)

Oxidimetric determination of thiourea–xanthate and thiourea–dithiocarbamate mixtures: Balbir Chand Verma and Swatantar Kumar (5 *December* 1973)

Katalytische Bestimmung von Silberspuren in waßriger Losung und nach Extraktion: H Muller, H Schurig and G Werner (11 *December* 1973)

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Methyl Calcein Blue and other analogues of Calcein Blue: Geraldine M Huitink and Harvey Diehl (11 *December* 1973)

On the theory of the thermometric titration method: G O Piloyan and Yu V Dolinina (18 *December* 1973)

Dichromate titration of thallium(I). S R Sagi, G S Prakasa Raju and K V Ramana (18 *December* 1973)

Acidity scale in sulpholane: spectrophotometric determination of pK_a of picric acid: J D Czaban and L M Mukherjee (18 *December* 1973)

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Catalytic effect of copper on the hexacyanoferrate(III)–cyanide redox reaction: G Lopez-Cueto, J A Casado-Riobo and F Lucena-Conde (19 *December* 1973)

Formation of manganese(IV) in aqueous cyanide solution. Spectrophotometric and electroanalytical evidence: G Lopez-Cueto, A Alonso-Mateos, J Hernandez-Mendez and F Lucena-Conde (19 *December* 1973)

Polarographic end-point indication in chelometric titrations with triethylenetetraminehexa-acetic acid: M Kopanica and V Stara (19 *December* 1973)

Atomic-emission spectrometry with an induction-coupled high-frequency plasma source. A comparison with the inert gas shielded premixed nitrous oxide-acetylene flame for multi-element analysis: G F Kirkbright and A F Ward (19 *December* 1973)

An investigation of the potential uses of iodine monochloride as a titrant in thermometric titrimetry: L S Bark and J K Grime (19 *December* 1973)

Systèmes automatiques d'analyse par activation neutronique pour la mesure en ligne des procédés industriels: J Perdijon (20 *December* 1973)

The design and publication of work on stability constants: Hazel S Rossotti. (20 *December* 1973)

EDITORIAL

We wish to apologise to our Readers for the unusual and prolonged delay in publishing the last three issues of Talanta.

All our material went to press on the scheduled dates, but unfortunately the Printers have been experiencing some difficulties, the result being the belated appearance of the Journal. We hope that our readers will bear with us, and we expect to resume our normal schedule with the next issue. We have not been helped by recent events in the economy, and the imposition of the 3-day working week has caused delays over and above those due to the Printers problems.

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PAPERS RECEIVED

Recent problems and limitations in the analytical characterization of high purity material: Günther Tölg. (10 *October* 1973)

***p*-Methoxyphenyl pyruvic acid oxime: A reagent for the gravimetric estimation of iron(II), cobalt(II) and nickel(II):** A. Ahmad, Q. Haider, V. N. Melhotra and E. B. Singh. (11 *October* 1973)

Use of a liquid ion-exchanger in the solvent extraction and atomic-absorption determination of trace copper in waters: D. A. Tinsley and A. Iddon. (15 *October* 1973)

Separation and study of monosubstituted phenols by GLC: Albertine E. Habboush and Awni M. Amarin. (16 *October* 1973)

Anwendung der flammenlosen Atomabsorption in der messenden Komplexchemie: Verteilung von Cu(II) zwischen Chloroform und Wasser in Gegenwart von 8-Hydroxychinolin: B. Magyar and P. Wechsler. (18 *October* 1973)

Cathode ray polarography of rare earths: Determination of microgram quantities of gadolinium: M. L. Thakur. (18 *October* 1973)

Quantitative reflectometry—II. Precision and interferences: David Kealey. (19 *October* 1973)

Determination of cysteine and 3-mercaptopropionic and mercaptosuccinic acids with neutral hexacyanoferrate(III): Krishna K. Verma and Sameer Bose. (22 *October* 1973)

Spectrochemical determination of trace bismuth and lead in iron-base and high-temperature superalloys: G. L. Vassilaros. (22 *October* 1973)

Protolytic reactions of 3,3′-dimethylnaphthidine and 3,3′-dimethoxybenzidine: Stanisław Głab and Adam Hulanicki. (22 *October* 1973)

Effect of orthophosphate on the gravimetric determination of pyrophosphate: P. Bozadziev, M. Georgieva and L. Ilcheva. (8 *October* 1973)

Some important chromatographic separations on stannic antimonate papers: Mohsin Qureshi, Nighat Zehra and Syed Ashfaq Nabi. (24 *October* 1973)

Spectrophotometric determination of micro amounts of mercury with zephiramine: Shokichi Chaki. (25 *October* 1973)

Some misconceptions in the evaluation of efficiencies for solvent extraction–colorimetric techniques: Selman A. Berger. (29 *October* 1973)

Fluorometric determination of aromatic aldehydes with 1,2-diaminonaphthalene: Yosuke Ohkura and Kiyoshi Zaitsu. (30 *October* 1973)

Absorption characteristics of Xylenol Orange: B. L. Gupta. (1 *November* 1973)

New spot test for palladium(II) with acriflavine: G. S. Johar. (2 *November* 1973)

Extraktionsmethoden zur Trennung von Tellur(IV): I. Havezov and N. Jordanov. (2 *November* 1973)

Analysis of metals by solid–liquid separation after liquid–liquid extraction Spectrophotometric determination of some metals by extraction of metal chelates with molten naphthalene: Taitiro Fujinaga, Masatada Satake and Tatsuo Yonekubo. (2 *November* 1973)

Simultaneous analysis of gold, platinum and palladium by atomic-absorption spectroscopy: V. Eckelmans, E. Graauwmans and S. De Jaegere. (5 *November* 1973)

Analysis of petroleum streams by high-resolution mass spectrometry: Ian P. Fisher and Peter Fischer. (12 *November* 1973)

Some chelating ion-exchange resins: Milan Marhol and K. L. Cheng. (12 *November* 1973)

Chromatographic separation and determination of noble metals in Matte-Leach residues: C. Pohlandt and T. W. Steele. (12 *November* 1973)

Polarographic behaviour of thiotropolone: J. N. Srivastava, K. B. Pandeya and R. P. Singh (13 *November* 1973)

Studies on extraction of chromium–DCTA complex by methyltrioctylmammonium chloride (Aliquat-336): G. M. Kinhikar and S. S. Dara. (14 *November* 1973)

Comparison between amperometric and true potentiometric end-point detection in the determination of water by the Karl Fischer method: Anders Cedergren. (16 *November* 1973)

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PAPERS RECEIVED

Polarographic reduction of Methylene Blue in presence of clay minerals: S. K. Srivastava and Pushpati Razdan. (5 *September* 1974)

Ion-exchange properties of chromium ferrocyanide: W. U. Malik, S. K. Srivastava, V. M. Bhandari and Satish Kumar. (5 *September* 1974)

A rapid and sensitive determination of selenium, antimony and arsenic by atomic-absorption spectrophotometry by introduction of their hydrides into an argon–hydrogen flame: Yuroku Yamamoto, Takahiro Kumamaru, Yasuhisa Hayashi and Toshihiko Kamada. (5 *September* 1974)

Determination of soluble styphnate and nitrate in waste water from lead styphnate primer plants: George Norwitz and Herman Gordon. (6 *September* 1974)

Utilization of an Hg^{2+}-sensitive membrane-electrode in the complexometric determination of Bi^{3+}, Fe^{3+} and Cr^{3+}: Elena Hopîrtean, C. Liteanu and Rodica Vlad. (6 *September* 1974)

Metallsalzimprägnierung von Graphitrohren zur Verbesserten AAS-Siliziumbestimmung: H. M. Ortner and E. Kantuscher. (6 *September* 1974)

Direct complexometric determination of aluminium in "Alzinoy": Om P. Bhargava. (30 *July* 1974)

8-Quinolinol-5-sulphonic acid as both indicator and masking agent—I. The zinc–ferrocyanide titration: John A. Bishop. (3 *September* 1974)

8-Quinolinol-5-sulphonic acid as both indicator and masking agent—II. The precipitation titration of $LaPO_4$: John A. Bishop and Jacki Soler. (3 *September* 1974)

Multiparametric curve fitting—I. Data acquisition in the study of equilibrium systems by combined instrumental microtitration techniques: Milan Meloun, Václav Říha, Stanislav Kotrlý and Jan Pancl. (11 *September* 1974)

Colour changes of chemical indicators—VI. Metallochromic indicators for direct chelatometric titrations of zinc(II): Karel Vytras, Jarmila Vytřasová and Stanislav Kotrlý. (11 *September* 1974)

Solvent extraction of gallium(III) with 2-thenoyltrifluoroacetone: P. V. Dhond and S. M. Khopkar. (11 *September* 1974)

Anion-exchange behaviour of several elements in systems containing formic acid: S. Waqif Husain and M. D. Charandabi. (13 *September* 1974)

In defence of analytical chemistry: A. M. Wahbi. (16 *September* 1974)

Multiparametric curve fitting—II. Computer-assisted evaluation of chelatometric microtitrations with metallochromic indicators: Milan Meloun and Josef Čermák. (16 *September* 1974)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—IV. Kinetik der Verbrennung im leeren Rohr: Ottakar Jaenicke and Walter Walisch. (29 *August* 1974)

The interference of heteronuclear chromium(III) tartrate complexes in the EDTA titration of cobalt(II), copper(II), zinc(II) and cadmium(II): C. G. Ramsay and B. Tamhina. (19 *September* 1974)

Anion-exchange separation of plutonium in hydrochloric–hydrobromic acid media: R. P. Larsen and R. D. Oldham. (24 *June* 1974)

Multiple nucleation in the precipitation of nickel dimethylglyoximate from homogeneous solution: Abdolreza Salajegheh and Robert B. Fischer. (25 *July* 1974)

Determination of small amounts of mercury: S. Chilov. (25 *September* 1974)

Surface layer properties of sodium- and hydrogen-ion responsive glass electrodes: Anders Wikby. (27 *September* 1974)

Chelation of ter- and quadrivalent cerium with DCTA: Mohamed B. Hafez and Mourad A. Hanna. (30 *September* 1974)

Mechanistic interpretation of the redox behaviour of diphenylamine: K. Sriramam. (30 *September* 1974)

Iodometric determination of ascorbic acid by controlled potential coulometry: Ronald Karlsson. (1 *October* 1974)

Ein schneller kontinuierlicher Flüssigkeitseinlass zur Massenspektrometrie: WALTER WALISCH, GUNTHER BECKER and DIETER HEISE. (19 *September* 1974)

Eine spektrophotometrische Methode zur Bestimmung von Tokopherolen und Tokotrienolen mit Hilfe von Bis(diisopropyloxythiophosphon)disulfid als spezifisches Reagenz auf Kupfer(I): ST. D. STAMATOV, N K. NIKOLOV, A. N. SCHISCHKOV and ST. A. IVANOV. (2 *October* 1974)

Interference of mineral acids in the flame atomic-absorption determination of Cd, Co, Fe, Pb and Zn: HAIG AGEMIAN and A. S. Y. CHAU. (24 *September* 1974)

Nitron as a titrant in potentiometric determination of nitrate: ADAM HULANICKI and MAGDALENA MAJ. (3 *October* 1974)

Picolinaldehyde 4-phenyl-3-thiosemicarbazone as a spectrophotometric reagent for the selective determination of small amounts of cobalt in the presence of iron: J. L. GOMEZ ARIZA, J. M. CANO PAVON and F. PINO. (4 *October* 1974)

2'-Hydroxychalcone as an analytical reagent for beryllium: R. RAGHAVA NAIDU. (8 *October* 1974)

A measure for assessing certified reference ores and related materials: R. SUTARNO and G. H. FAYE. (8 *October* 1974)

New type of labile palladiazo–Pd(II) sandwich (?) compound formed in aqueous non-complexing media: J. A. PÉREZ-BUSTAMANTE. (9 *October* 1974)

Chelatometric determination of some bivalent metals with phenanthraquinone monothiosemicarbazone: A. K. SINGH, K. C. TRIKHA, R. P. SINGH and MOHAN KATYAL. (9 *October* 1974)

Estimation of glutathione with chloramine-T and dichloramine-T: D. S. MAHADEVAPPA and N. M. MADE GOWDA. (9 *October* 1974)

Determination of low-level carbon in tungsten wire by combustion gas chromatography: PETER CUKOR, CARMINE PERSIANI and ARTHUR RUSSELL. (3 *October* 1974)

Spectrophotometric investigation of the reaction between magnesium and Eriochrome Cyanin RC: N. G. ELENKOVA and EK. POPOVA. (10 *October* 1974)

A novel spray reagent for terpene derivatives on thin-layer plates: J. C. KOHLI. (10 *October* 1974)

Determination of manganese, cobalt and copper in whole blood and serum by hot-graphite atomic-absorption spectrometry: RICCARDO A. A. MUZZARELLI and ROBERTO ROCCHETTI. (14 *October* 1974)

A comparative kinetic study for rate-constant determination in the reaction of ascorbic acid with 2,6-dichlorophenolindophenol: M. I. KARAYANNIS. (15 *October* 1974)

Extraction titrimetric determination of mercury, silver and copper: A. L. J. RAO and CHANDER SHEKHAR. (21 *October* 1974)

The use of long-chain alkylamines for preconcentration and determination of traces of molybdenum, tungsten and rhenium by atomic-absorption spectroscopy—I. General studies: C. H. KIM, P. W. ALEXANDER and L. E. SMYTHE. (21 *October* 1974)

Anwendung von Ionenaustauschverfahren zur Bestimmung von Spurenelementen in naturlichen Wässern—VIII. Molybdän: J. KORKISCH, L. GÖDL and H. GROSS. (21 *October* 1974)

Ligand-exchange reaction between EDTA and Fe(III)–indicator complexes. Salicylic acid and 1,2-dihydroxy-3,5-benzenedisulphonic acid: EDOARDO MENTASTI and EZIO PELIZZETTI. (22 *October* 1974)

Thermodynamic study of Fe(III), Cr(III) and Ti(III) complexes with α-hydroxy acids: P B. CHAKRAWARTI and H. N. SHARMA. (22 *October* 1974)

Talanta Vol 21 pp i ii Pergamon Press 1974 Printed in Great Britain

PAPERS RECEIVED

X-Ray fluorescence spectrometry of copper intermediates. B W. Budesinsky. (18 *June* 1974)

Determination of selenium in some United States Geological Survey rocks by atomic-absorption spectroscopy. T J. Golembeski, V Lavrakas and E. F Barry (23 *June* 1974)

Ionic-transference numbers from Hall-effect measurements on electrolytic solutions. Leonard S. Levitt (15 *June* 1974)

Simultaneous determinations of total, non-carbonate and carbonate water hardness by direct potentiometry. I Sekerka and J. F Lechner (23 *June* 1974)

On the role of analytical chemistry in solvent extraction processing: A W. Ashbrook (29 *May* 1974)

Thiomercurimetric determination of carbon disulphide, carbonyl sulphide, thiols and hydrogen sulphide with 1,3-diaminopropane and tributyltin chloride· Mieczyslaw Wroński (15 *July* 1974)

Extraction of vanadium(II) as its pyridine thiocyanate complex and its separation from uranium, titanium, chromium and aluminium. V. Yatirajam and S. P. Arya (16 *July* 1974)

Spectrophotometric determination of nitrate by a difference method: Salah Shahine, M Fathy El-Shahat and Soad Khamis. (17 *July* 1974)

Microdetermination of metals in organometallic compounds by the oxine method with closed flask or open tube decomposition· A B Sakla, S W. Bishara and S A. Abu-Taleb. (17 *July* 1974)

Masking of iron with fluoride in the extractive atomic-absorption spectrometric determination of chromium in steel A G. Fogg, Miss S. Soleymanloo and D. Thorburn Burns (22 *July* 1974)

Metal and metalloid indicator electrodes for the non-aqueous potentiometric titration of weak acids—I. A comparative evaluation of group II, IV and V main group elements. E. J Greenhow and Miss B. F. Al-Mudarris. (22 *July* 1974)

Flotation of traces of silver and copper(II) ions with a methylcellosolve solution of dithizone: Masataka Hiraide and Atsushi Mizuike (23 *July* 1974)

Spectrophotometric determination of fluorides in water with zirconium–Pyrocatechol Violet lake: A. Devarajulu Naidu and V R Krishnan. (23 *July* 1974)

Determination of traces of oxygen in chalcogenide glasses: D L Swindle and E A. Schweikert. (23 *July* 1974)

Colorometric determination of N-substituted hydroxamic acids with vanadium (V): Dadu Ram Agrawal. (24 *July* 1974)

Acid-base equilibria in ethylene glycol—II. Autoprotolysis constants and acid-base properties of ethylene glycol and its mixtures P. Zikolov, A Astrug and O Budevsky. (24 *July* 1974)

Titrimetric study of the chloramine T–ammonia reaction: V. J Jennings and A. Dodson (24 *July* 1974)

Simple semiquantitative determination of trace metal ions with reagent gel columns—I. Determination of mercury with dithizone gel Yong Keun Lee, Kyu Ja Whang and Keihei Ueno. (15 *August* 1974)

Oxidation of organic substances by compounds of tervalent manganese—IV. The determination of the titre of the hydroquinone standard solution J Barek, A. Berka and P Hofmann. (15 *August* 1974)

Oxidation of organic substances by compounds of tervalent manganese—V. The preparation and basic analytical properties of standard solutions of tervalent manganese: J. Barek, A. Berka and J. Korečková. (15 *August* 1974)

Determination of organic substances by the oxidation with permanganate—XVIII. The oxidation of malonic acid. A Berka, M Kořínková and J. Barek (15 *August* 1974)

Studies with dithizone analogues—II. The preparation and characterization of 2,2′-dichlorodithizone and the investigation of its reactions with some metal ions A M Kiwan and A Y Kassim. (15 *August* 1974)

Trace metal analysis of rocks by flameless atomic-absorption spectrometry with a metal microtube atomizer· Kiyohisa Ohta and Masami Suzuki (15 *August* 1974)

Titrations of heterocyclic nitrogen bases in non-aqueous media K. C Mohan Rao and P R Naidu (16 *August* 1974)

Some aspects of the limits of applying a reagent for a spectrophotometric determination. *p*-Dimethylaminobenzilidenerhodanine as a spectrophotometric reagent for silver(I) and palladium(II): RAHILA BORISSOVA, MARIA KOEVA and ELENA TOPALOVA. (16 *August* 1974)

Study on the possibility of spectrophotometric determination of gold(III) with *p*-dimethylaminobenzilidenerhodanine in hydrochloric acid medium and 20% v/v ethanol: RAHILA BORISSOVA. (16 *August* 1974)

Synergic extraction of zinc, cadmium, and lead with hexafluoroacetylacetone and di-n-butylsulphoxide and tri-n-butylphosphate and the gas chromatography of the zinc adduct: JEROME W. O'LAUGHLIN and THOMAS P. O'BRIEN. (15 *July* 1974)

Determination of ruthenium and iridium in anode coatings by atomic-absorption spectroscopy: D. E. HARRINGTON and W. R. BRAMSTEDT. (1 *July* 1974)

3-Methyl-2-oxazolidone as a solvent for acid-base titrations: JOHN E. TAPHORN III, GARY M. DAVIS and JOSEPH A. CARUSO. (18 *July* 1974)

Lead content of evaporated milk as a function of time: HUGH L. HUFFMAN, JR and JOSEPH A. CARUSO. (18 *July* 1974)

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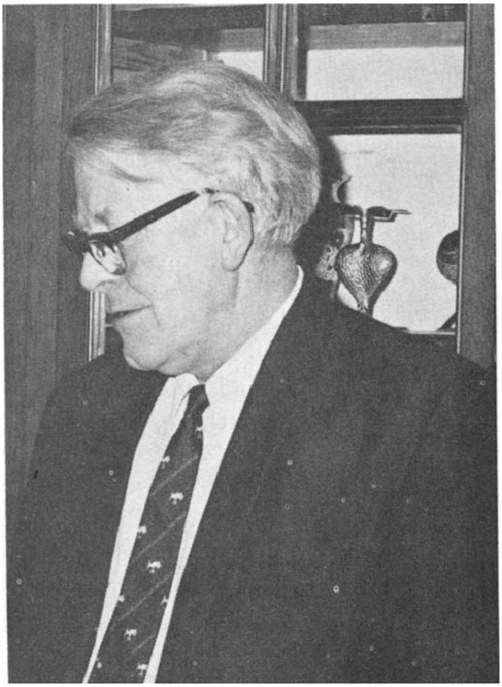
OBITUARY



PROFESSOR C. L. WILSON

Cecil L. Wilson, Professor of Analytical Chemistry in the Queen's University of Belfast, and the founder Editor of *Talanta*, died on Tuesday, 19th March, after a very brief illness.

Cecil Wilson obtained his first degree at Queen's University Belfast. He studied for his Ph.D., which he obtained in 1936, at the University of Glasgow and immediately returned to the Chemistry Department at Queen's as an Assistant Lecturer. Whilst he was at Glasgow, he attended lectures on microchemistry given by Dr. D. T. Gibson, who was one of the first microchemists in Britain. These lectures had a profound effect on Cecil Wilson, and there is no doubt, that although he became interested in other branches of analytical chemistry he never deviated from his first love and it was unquestionably in this area that his most notable contributions were made.

Although microchemical methods had been known since the turn of the century, at that time they were still much of a novelty in Britain. Cecil Wilson as fascinated by their elegance and the miniature apparatus that was used. When he returned to Queen's he organized a general course in microchemical methods; this was probably the first University course in *general inorganic microchemistry* in these Islands. Although organic microanalysis post-dated its inorganic counterpart, it was the first to become widely used; this subject was taught in British Universities more than a decade earlier. I had corresponded with Cecil Wilson and others during the early part of the war, but we did not meet until 1943 when we came together in Sheffield to try to form a microchemical society. Besides Cecil Wilson and myself were Dr. G. Ingram, Mr. C. Whalley, Dr. G. H. Wyatt and others.

Because of his great interest in microchemical apparatus, Cecil Wilson was always trying to devise new and improved forms of microequipment. During the war, as part of the Manhattan project, submicro methods of inorganic analysis had been developed in the U.S.A. Even after the war information on these methods was very restricted. However, from a very poor photograph of the submicrobalance that had been used, Wilson and his co-worker H. El Badry managed to construct a torsion balance that would weigh accurately at the levels required. They later developed a number of submicro methods for the detection, separation and determination of several elements.

Submicro methods of this kind proved to have a number of useful applications; they were not only of use for the analysis and the investigation of the chemistry of the trans-uranium elements but in many other areas where limited amount of sample was available, such as the composition of corrosion products, encrustations, the analysis of inclusions in minerals, meteorites and so on. Nowadays it is a simple matter to buy commercially specialized equipment of all kinds, but during the war period and even for some years afterwards, one had to make such equipment oneself, even sintered-glass microfilters. Cecil Wilson had that deft touch so rarely seen nowadays, which enabled him to make such equipment and to give it a professional appearance.

In 1958 Cecil Wilson was appointed to a Personal Chair in Analytical Chemistry at Queen's. Five years after, this was converted into an established Chair of Inorganic and Analytical Chemistry; in 1968 this was divided into two separate Chairs and Cecil Wilson retained the Chair of Analytical Chemistry until his death.

Cecil Wilson had many interests outside analytical chemistry, but the one for which we perhaps remember him most is his interest in the examination of written and printed documents. He became an authority in this field, and, in 1953, was appointed as Document Examiner to the Ministry of Home Affairs of Northern Ireland. He is well remembered for his entertaining lectures about his experiences in this field.

Cecil Wilson was a man who enjoyed life in all its aspects. He was a witty and entertaining companion and many of us are going to miss him at our meetings. He was a good friend, wise in counsel and of generous character. His passing is a great loss to British science.

He is survived by his wife, Grace, a daughter and a son.

RONALD BELCHER

Volume 21, 1974

January–June, Nos. 1–6

SUBJECT INDEX

PRINTED IN GREAT BRITAIN BY A. WHEATON & CO., EXETER **308**

Talanta. Vol. 21. p. ii. Pergamon Press. 1974. Printed in Great Britain

PUBLICATIONS RECEIVED

Analytical Chemistry of Silicon: L. V. MYSHLAEVA and V. V. KRASNOSHCHEKOV. Israel Program for Scientific Translations, Jerusalem, and Wiley, New York, 1974. Pp. VIII + 228. $30.00.

This translation of a volume in the Verdandsky Institute series on the analytical chemistry of the elements provides a somewhat uncritical guide to the literature up to about 1966, with a few later references but none more recent than 1971. The most useful feature is that many practical procedures are outlined, but the index does not list the materials to which the methods are applied, so the reader has to do some searching to find a particular application.

Ascorbinometric Titrations: L. ERDEY and G. SVEHLA, Akadémiai Kiadó, Budapest, 1973. Pp. 183. $8.50.

This may be regarded as a memorial to the work of the late Professor Erdey, who originated the technique in 1950 and followed this up with over 60 papers on applications. The text maintains the high standards one has come to expect from the authors and publishers and provides an authoritative guide to this interesting analytical technique. An interesting feature is that the publishers guarantee to replace faulty copies, without time limit, or to supply a book of equal value if the stocks have been exhausted at the time of claim.

Analytical Chemistry: ROBERT V. DILTS, Van Nostrand Reinhold, London, 1974. Pp. ix + 592. £7.50.

The subtitle of this book is Methods of Separation, and is a better guide to the contents, since nearly half the book is devoted to chromatography. Instrumental methods figure only insofar as they are ancillary to the techniques described. It is pleasant to see Ringbom's side-reaction coefficients used in an American text. The chapter on equilibria covers most aspects of the topic but omits redox equilibria. While this is understandable within the general framework of the book, it seems a curious oversight in view of the use of change of oxidation state as a means of avoiding interference by certain metal ions. The style is chatty, in the modern American manner, but not too obtrusively so. One wishes, however, that the author had not instructed the reader to filter precipitates *through* various types of receiver. The book will certainly prove a useful tool in undergraduate courses, though most teachers would want to use additional material not covered in this book.

Talanta, Vol. 21, p. II. Pergamon Press. 1974. Printed in Great Britain

LOUIS GORDON MEMORIAL AWARD

The Editorial Board and Publishers of *Talanta* have great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper appearing in *Talanta* during 1973 has been made jointly to J. van Gemert, of Kodak Ltd., Melbourne, for his paper "Automated wet chemical analysers and their applications" (November issue, p. 1045) and to A. Corsini and E. Nieboer, of McMaster University, Hamilton, Ontario, for their paper "2,2′-Dimercaptodiethylsulphide: a potential analytical reagent" (March issue, p. 291).

Talanta, Vol. 21, pp. ii–iii. Pergamon Press, 1974. Printed in Great Britain

PUBLICATIONS RECEIVED

Organic reagents in metal analysis: K. BURGER. Pergamon, Oxford, 1973. Pp. 266. £5.80

This is much more than just a catalogue of useful reagents. About a quarter of the book forms a very concise and readable account of chelate complexes and all the factors which affect their stability and selectivity. This is followed by the author's selection of the three dozen most important reagents, with detailed discussions of their applications. Over 100 additional reagents are then listed with brief data in tabular form, along with selected stability constants for 27 common organic reagents and their complexes. This book will be found both rewarding reading by teachers and students, and a useful reference volume for frequent consultation, as long as one can accept the archaic usage of γ for μg, which has been allowed to persist throughout the text.

Thermometric and enthalpimetric titrimetry: G. A. VAUGHAN. Van Nostrand Reinhold, London, 1973. Pp. xii + 255.

Here is a very readable introduction to an interesting branch of physical chemistry which has hitherto attracted rather little interest from analytical chemists. The author shows how success can be achieved with rather simple apparatus, and how increasing sophistication of technique and equipment can lead to remarkably good precision in analytical and thermochemical work. A comprehensive and critical coverage of the literature (with several references from 1972) quickly presents the reader with the present state of the technique as applied to a large range of samples and reactions.

Computers in chemistry—Topics in current chemistry, Vol. 39: Ed.: F. BOSCHKE. Springer Verlag, Berlin, 1973. Pp. 195. D.M. 62.

For a start one should make clear that this is not a library of programmes for the chemist, and does not even touch the topic of ionic equilibria in solutions. This collection of seven articles sets out instead to show some of the unexpected areas in chemistry which are now being looked at by groups of computer-oriented chemists. Some of the problems, such as "Retrieval of information from the literature," and "Computer-assisted comparison of spectra," are certainly very real to many chemists, and "Computer–gas chromatography" is a fact of life to the analyst. Whether the computer really offers so much help in planning organic syntheses or in teaching chemistry, only time will tell. Perhaps the theme is not so much "How to live with computers," as "How to make the most of computers in chemistry."

Analytical Chemistry: J. G. DICK, McGraw Hill, New York, 1973. Pp. viii + 696. £7.00

One of the author's objectives in writing this basic analytical text is to instil a respect for exact data and to demonstrate how they can be properly evaluated. There are many worked examples of basic calculations and detailed discussion of the procedures for evaluation of equivalence points. The exposition is clear and should prove of benefit to the weak or slightly confused student. Titrimetric methods are given most attention but equilibria, gravimetry, electroanalysis and spectrochemical methods are also dealt with. The treatment in many areas fails to take account of recent work, however, and this offsets its value.

IUPAC Analytical Chemistry-4: M. SENDA (Ed.); Butterworths, London, 1973. Pp. 170. £5.00

The plenary lectures presented at the IUPAC congress in Kyoto in 1972 cover diverse aspects of the subject and make interesting reading. A. J. P. Martin speculates on the possibilities for new methods of detection in chromatography. H. Kaiser theorizes on the proper definitions of trace, selectivity and sensitivity and the information value of an analysis. I. P. Alimarin points out ways in which the kinetics of complex formation might be exploited analytically. There are reviews of chelates in analytical chemistry (R. Belcher), developments in organic ultramicro analysis (W. J. Kirsten), precipitate-based ion-selective electrodes (E. Pungor and K. Tóth), non-dispersive systems in AAS (A. Walsh), analytical chemistry in Japan (T. Somiya) and the environment (P. W. West). There is also a very valuable account of pure and applied trace analysis by W. Meinke.

Technical Books and Monographs Sponsored by the United States Atomic Energy Commission. 1973 Catalog. Available free as TID-4582-R9 from U.S.A.E.C., P.O. Box 62, Oak Ridge, Tennessee 37820, USA.

Annual Reports on Analytical Atomic Spectroscopy 1972, Vol. 2: D. P. HUBBARD (ed.), Society for Analytical Chemistry, London, 1973. Pp. x + 216. £5.00

The high standard of Vol. 1 has clearly been maintained in the second volume of this valuable series. Volume 2 contains 1123 references, predominantly from 1972, but with a few from 1971 (omitted from Vol. 1) to maintain continuity. Its usefulness lies not only in the fact that it makes readily available the references to papers published in periodicals not normally scanned by analytical atomic spectroscopists and those presented at conferences and meetings throughout the world, but also in the presentation (often in tabular form) of the key facts contained within the references. Those responsible for these sections are to be congratulated for concentrating so much useful information into 135 pages of text. Although essentially comprehensive factual reports, rather than critical reviews, this series remains excellent value for money.

PUBLICATIONS RECEIVED

Problems in Chemistry: HENRY O. DALEY, JR. and ROBERT F. O'MALLEY. Dekker, New York, 1974. Pp. xvii + 490. $7.95.

This volume, which is very reasonably priced, will be a boon to those who feel that present-day students do not get nearly enough practice in calculations and problem solving. It will also save them the sheer hard labour of concocting their own set of problems. One criticism is that dissociation constants are used for complexes, although modern practice is to use association (stability) constants almost exclusively. The problems cover inorganic, physical and analytical chemistry.

Separation and Purification Methods, Vol. 2: edited by EDMOND S. PERRY, CAREL J. VAN OSS and ELI GRUSHKA. Dekker, New York, 1974. Pp. xi + 466. $25.50.

This volume continues the standard set by Vol. 1 in the series, and has chapters on applications of gas–solid chromatography, field flow fractionation, separation of latex particles according to size (by continuous electrophoresis), affinity chromatography, gel chromatography of oligosaccharides, free fluid particle electrophoresis on Apollo 16, application of the molecular sieve properties of zeolites, and high speed liquid chromatography. It is therefore of interest mainly to workers in chromatography and electrophoresis.

The "Practising Chemists": R. C. CHIRNSIDE and J. H. HAMENCE. Society for Analytical Chemistry, London, 1974. Pp. xvi + 225. £3.00.

This handsome volume will give pleasure to all those with an interest in the history of analytical chemistry and to those who take a pride in their craft. A history of the Society of Analytical Chemistry, it also sheds light on many facets of scientific and public life in the last century, and it is good to see this material set down before it disappears from memory. It is a bargain at the price and should be required reading for all those who affect to regard analysis as an inferior branch of chemistry instead of according it its proper place as the cornerstone of chemical knowledge.

Official, Standardised and Recommended Methods of Analysis: compiled and edited by N. W. HANSON, 2nd Ed., Society for Analytical Chemistry, London, 1974. Pp. xxiv + 897. £17.00; $42.50.

This handsome volume, published at a remarkably low price for these days of rapidly increasing costs, will be welcomed by all analysts in the industrial and public sectors of the profession. Full details are given of the methods developed by the Society's Analytical Methods Committee, and there is a comprehensive bibliography covering the methods accepted as standard by various bodies throughout the world. The extensive range of types of material dealt with ensures the book a place in every library used by analysts, and one can only marvel at the patience and industry shown by the compiler and his colleagues.

Osnovi na analitichnata khimiya (Principles of Analytical Chemistry: in Bulgarian): OMORTAG BUDEVSKY, Meditsina i Fizkultura, Sofia, 1974. Pp. 338 Lev 1.69.

This book gives a thoroughly modern treatment of the basic principles of analytical chemistry. A working knowledge of the Cyrillic alphabet would enable most Western analysts to appreciate the scope of the book.

Kachestvennii i kolichestvennii ultramikrokhimicheskii analiz (Qualitative and Quantitative Ultramicrochemical Analysis: in Russian): I. P. ALIMARIN and M. N. PETRIKOVA, Izdat. Khimiya, Moscow, 1974. Pp. 191. Kopeks 60.

The authors' names are themselves a guarantee of the quality and usefulness of this text. The impact of instrumental methods on trace analysis is reflected in the chronological distribution of the references, there being only a handful to work done in the 1970's, and none more recent than 1972, which implies that the purely chemical approach has had its day.

SUMMARIES FOR CARD INDEXES

Two-phase titration of organic ammonium ions with lauryl sulphate and Methyl Yellow as indicator: SVEN OLOF JANSSON, ROLF MODIN and GÖRAN SCHILL, *Talanta*, 1974, **21**, 905. (Department of Analytical Pharmaceutical Chemistry, University of Uppsala, Box 574, S-751 23 Uppsala, Sweden).

Summary—Conditions for determination of quaternary ammonium compounds and amines by two-phase titration have been calculated on the basis of extraction constants for the ion-pairs between the titrant (lauryl sulphate), the indicator (Methyl Yellow) and the sample. Methods for determination of extraction constants are presented. The precision and selectivity of the method are demonstrated by titrations of ammonium ions with different structures and degrees of substitution. The results are in agreement with the theoretical calculations.

Chromatographic separation and determination of noble metals in matte-leach residues: C. POHLANDT and T. W. STEELE, *Talanta*, 1974, **21**, 919. (Analytical Division, National Institute for Metallurgy, Johannesburg, South Africa.)

Summary—The practical application of various chromatographic methods to the analysis of residues obtained from the leaching of copper-nickel mattes is described. The procedure involves the separation of gold on a TBP-treated Porasil column, the separation of base metals by cation-exchange, the separation of tellurium from platinum-group metals, and the separation of the non-volatile platinum-group metals on one cellulose column.

Separation of monosubstituted phenols by gas–liquid chromatography: ALBERTINE E. HABBOUSH and AWNI M. AMARIN, *Talanta*, 1974, **21**, 927 (College of Science, University of Baghdad, Iraq.)

Summary—The factors influencing the separation of monosubstituted phenols on silicone oil, poly(ethylene glycol) (1500), Apiezon L + Bentone 34, squalane, Versamide and diethylhexyl sebacate are discussed. Specific retention volumes, height equivalent to a theoretical plate and thermodynamic quantities are reported. Diethylhexyl sebacate and Versamide are selective for quantitative separation of all the isomers studied.

Alkali- und Erdalkalispurenanalyse in Wolfram und Wolframverbingdungen nach Wolframmatrixabtrennung an DEAE-Sephadex: H. KRAINER, H. M. ORTNER, K. MÜLLER and H. SPITZY, *Talanta*, 1974, **21**, 933. (Institut für Allgemeine Chemie, Mikro- und Radiochemie, Technische Hochschule Graz, Technikerstraße 4, A-8010 Graz und Metallwerk Plansee AG, A-6600 Reutte, Österreich.)

Summary—A new column-chromatographic method is described, for the separation of tungsten on DEAE-Sephadex, enabling trace amounts of alkali and alkaline earth metals in tungsten to be determined quantitatively by AAS without matrix interference. Mean relative S.D. for <50 ppm Na, K, Mg are 5–10%, and for <50 ppm Ca 10–20%, and for >50 ppm, 2–5% and 5–10% respectively. Limits of detection in tungsten are 10 ppm Na and K, 1 ppm Mg, and 20 ppm Ca. Time for a determination is about 90 min. By appropriate changes in pH and other conditions, the method can be used for the separation of molybdenum from traces of alkali metal ions.

Controlled-potential iodometric titration of nitrite. Application to the determination of nitrite in meat products: RONALD KARLSSON and LARS-GUNNAR TORSTENSSON, *Talanta*, 1974, **21**, 945. (Department of Analytical Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden.)

Summary—A controlled-potential coulometric method using iodine as an intermediate has been devised for the determination of nitrite. Nitrite is reduced by iodide and the iodine formed is then reduced coulometrically. The reduction of nitrite in the pH range 0–6 has been studied and the optimum conditions for an accurate determination are stated. The time of analysis for a determination in the range 0·005–5 mg of nitrite is about 2–5 min and the error ± 0·1%. The method is applied to the determination of nitrite in some meat products.

Двухфазное титрование органических ионов аммония лаурилсульфатом с использованием метилового желтого в качестве индикатора: Sven Olof Jansson, Rolf Modin and Göran Schill, *Talanta*, 1974, **21**, 905.

Резюме—Вачислены условия определения соединений четвертичного аммония и аминов методом двухфазного титрования на основе констант экстракции для лар ионов между титрованным раствором (лаурилсульфат), индикатором (метиловый желтый) и пробой. Приведены методы определения констант экстракции. Воспроизводимость и селективность метода продемонстрированы на примере титрования ионов аммония различитой структуры и степени замещения. Результаты соглашаются с теоретическими данными.

Хроматографическое разделение и определение благородных металлов в остатках выщелачивания штейна: C. Pohlandt and T. W. Steele, *Talanta*, 1974, **21**, 919.

Резюме—Описано применение в практике различных хроматографических методов анализа остатков, полученных выщелачиванием штейна меди-инкеля. Метод состоится из отделения золота на колонке порасила, обработанного с ТбП, отделения матричных металлов катионообменным методом, отделения теллура от металлов платиновой группы и разделения нелетучих металлов платиновой группы на одной колонке целлюлозы.

Разделение однозамещенных фенолов методом газо-жидкостной хроматографии: Albertine E. Habboush and Awni M. Amarin, *Talanta*, 1974, **21**, 927.

Резюме—Рассмотрены факторы влияющие на разделение однозамещенных фенолов на силиконовом масле, полиэтиленгликоле (1500), апиезоне L + бентоне 34, сквалане, версамиде и диэтилгексилсебацате. Приведены удельные объемы удерживания, высоты, эквивалентные теоретической пщиты и термодинамические величины. Диэтилгексилсебалат и версамид являются селективными для количественного разделения всех изученных изомеров.

Определение следов щелочных и щелочноземельных элементов в вольфраме и соединениях вольфрама после отделения матрици вольфрама на колонке ДЕАЕ-Сефадекс: H. Krainer, H. M. Ortner, K. Müller and H. Spitzy, *Talanta*, 1974, **21**, 933.

Резюме—Описан новый хроматографический метод разделения вольфрама на колонке ДЕАЕ-Сефадекс, позволяющий определять количественно следовые количества шелочных и щелочноземельных елементов в вольфраме методом атомно-абсорбционной спектроскопии, без влияния матрицы. Средные относительные стандартные ошибки составляют 5–10% для < 50 ч. на миллион Na, K, Mg; 10–20% для < 50 ч. на миллион Ca; 2–5% и 5–10% для > 50 ч. на миллион, соответственно. Чувствительность определения в вольфраме—10 ч. на миллион Na и K, 1 ч. на миллион Mg и 20 ч. на миллион Ca. Продолжительность одного определения около 90 мин. Изменяя pH и другие условия, методом можно пользоваться для отделения молибдена от следов шелочных металлов.

Иодометриуеское титрование нитрита при контроллированном потенциале: Применение метода в определении нитрита в мясных продуктах: Ronald Karlsson and Lars-Gunnar Torstensson, *Talanta*, 1974, **21**, 945.

Резюме—Разработан кулонометрический метод определения нитрита при контроллированном потенциале, пользующийся иодом в качестве промежуточного продукта. Нитрит восстанавливается иодидом, а образованный иод восстанавливается кулонометрическим путем. Изучено восстановление нитрита в области pH 0–6 и приведены оптимальные условия для его аккуратного определепия. Продолжительность одного определения в рбласти 0,005–5 мг иитрита составляет 2–5 мин, а ошибка. ±0, 1%. Метод применен в определении нитрита в некоторвх мясных продуктах.

Determination of the oxidizing capacity of manganese ores: Ravindra Prasad, *Talanta*, 1974, **21**, 951. (Thomas Hill-Jones Ltd., 15 High Street, Stratford, London, E15 2QB).

Summary—An accurate method is described for determining the amount of active oxygen in manganese ores, based on the oxidation–reduction reaction between the ore and arsenic(III) in presence of ammonium molybdate, followed by the back-titration of excess of arsenic(III) with cerium(IV), using osmium tetroxide as catalyst and Disulphine Blue V as indicator. A survey has been made of the applicability of this method to various pyrolusite ores containing less than 0·2% phosphorus. Aluminium(III), copper(II), iron(III), manganese(II) and molybdenum(VI) do not interfere. Up to 30% phosphorus(V) causes no interference.

Coulometric determination of dissolved oxygen in water: Ronald Karlsson and Lars-Gunnar Torstensson, *Talanta*, 1974, **21**, 957. (Department of Analytical Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden.)

Summary—The oxygen content of air-saturated distilled water has been determined at between 10 and 40° by using a controlled-potential coulometric method based on an earlier published method for the iodometric determination of nitrite. The maximum error for the determinations was ±0·3% over the whole range, and the time of analysis about 3 min. An equation is given for the solubility in the measured range, and some thermodynamic functions are calculated.

Simultaneous determination of dimetridazole and furazolidone in feed-premixes by d.c. polarography: Marjan Slamnik, *Talanta*, 1974, **21**, 960. (Research-Development Institute, KRKA Pharmaceutical and Chemical Works, Nova Mesto, Yugoslavia.)

Summary—A polarographic method has been proposed by which dimetridazole and furazolidone can be determined in feed-premixes in a single determination. The sample is treated with DMF to facilitate the dissolution of dimetridazole and furazolidone. Britton–Robinson buffer of pH = 6·8 is added and the solution is polarographed at the dropping mercury electrode *vs.* SCE. The waves are sufficiently separated to allow quantitative determination. The standard-addition method is used. The method is simple and very fast.

Polystyrenes impregnated with ethers—A polymeric reagent selective for gold: A. Warshawsky, *Talanta*, 1974, **21**, 962. (National Institute for Metallurgy, Johannesburg, South Africa.)

Summary—A polymeric reagent selective for gold was obtained by impregnating XAD-2 polymeric absorbant with ethylene diglycol dibutyl ether, a gold-selective liquid. The reagent showed a high selectivity for gold over the platinum group metals, nickel(II) and copper(II), but the selectivity relative to iron(III) was pH-dependent.

Analytical applications of thio-, seleno- and telluro-ethers—III. Spectrophotometric determination of palladium with dibenzyl selenide: Luiz R. M. Pitombo and Elisabeth Q. Cartaxo, *Talanta*, 1974, **21**, 965. (Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, Brasil).

Summary—Palladium chloride is very efficiently extracted with a benzene solution of dibenzyl selenide. The extract can be used to determine palladium spectrophotometrically in the range 0·38–3·00 ppm. Determination of palladium in presence of platinum metals and many cations and anions, is reported.

Определение окитслительной способности руд марганца:
RAVINDRA PRASAD, *Talanta* 1974, **21**, 951

Резюме—Описан точный метод определения количества активного кислорода в рудах марганца, основывающийся на окислительно-восстановительной реакции руды с мышьяком (III) в присутствии молибдата аммония с последующим титрованием избытка мышьяка (III) раствором цера (IV), с использованием четирёхокиси осмия в качестве катализатора и дисульфинового синего V в качестве индикатора. Сделаи обзор применимости метода в анализе ряда пиролюзитовых руд содержащих меньше чем 0,2% фосфора. Алюминий (III), медь (II), железо (III), марганец (II), молибден (VI) и вплоть 30% фосфора не мешают определению.

Кудонометрическое определение растворенного кислорода в воде: RONALD KARLSSON and LARS-GUNNAR TORSTENSSON, *Talanta*, 1974, **21**, 957.

Резюме—Содержание кислорода в насыщенной воздухом дистиллированной воде определено в области температур 10–40° с помощью кулонометрического метода при постоянном потендиале, опубликованного раньше для иодометрического определения нитрита. Максимальная ошибка метода составляет ±0,3% в целом диапазоне концентраций, а продолжительность одного анализа—3 мин. Приведено уравнение для растворимости в области проведенных измерений и расчитаны некороые термодинамические функции.

Одновременное определение диметридазола и фуразолидона в продуктах питания методом полярографии постоянного тока: MARJAN SLAMNIK, *Talanta*, 1974, **21**, 960.

Резюме—Предложен полярографический метод одновременного определения диметридазола и фуразолидона в продуктах питания. Пробу обрабатывают с ДМф с целью облегчать растворение диметридазола и фуразолидона, добавляют буферный раствор Бриттона-Робинсона для pH 6,8 и раствор полярографируют на капельном ртутном электроде в сравнении с НКЭ. Волны довольно раздвинуты для количественного определения. Использован метод стандартных добавок. Метод является несложным и очень быстрым.

Пропитанный эфирами полистирол—полимерный реагент селективный для золота: A. WARSHAWSKY, *Talanta*, 1974, **21**, 962.

Резюме—Полимерный реагент селективный для золота приготовлен пропитыванием полимерного абсорбента XAD-2 этилендигликолдибутиловым эфиром—жидкостью селективой для золота. Реагент показывает высокую сепективность для золота в присутствии платиновых металлов, никеля (II) и мели IjI) но селективность в присутствии железа III) зависит от pH.

Применение тио-, селено- и теллурозфиров в анализе—III. Спектрофотометрическое определение палладия с дибензилселенидом: LUIZ R. M. PITOMBO and ELISABETH Q. CARTAXO, *Talanta*, 1974, **21**, 965.

Резюме—Хлорид палладия экстрагируется весьма эффективно раствором дибензилселенида в бензоле. Экстракт можно использовать для спектрофотометрического определения палладия в области 0,38–3,00 ч. на миллион. Описано определение палладия в присутствии платиновых металлов и ряпа катионов и анионов.

Titrimetric estimation of cysteine alone and in the presence of other amino-acids: PADAM SEN and KRISHNA BAHADUR, *Talanta*, 1974, **21**, 968. (Chemical Laboratories, University of Allahabad, Allahabad-211002, India.)

Summary—Cysteine has been determined alone and in the presence of other amino-acids by titration with mercury(II) at pH 6·2 or 9·2, and with lead at pH 9·2. In all three procedures, a 1:1 complex is formed.

Reaction between copper(I)–thiourea and bismuth(III)–thiourea complexes in presence of iodide. New spot-tests for copper(II) and bismuth(III): G. S. JOHAR, *Talanta*, 1974, **21**, 970. (Department of Chemistry, Vikramajit Singh Sanatan Dharma College, Kanpur (U.P.) 208002, India.)

Summary—New and very simple spot tests are described for the detection of Bi(III), Cu(II) and I^- ions with limits of detection of 3, 8, and 75 μg/0·05 ml respectively. Tests are also described for such combinations as Bi(III) + I^-; Bi(III) + Cu(II); and Bi(III) + Cu(II) + I^-. All the tests are based on the formation of an orange or red-orange precipitate of bismuth(III)–copper(I)–iodide–thiourea complex, for which the formula $[Bi(tu)_3I_3.Cu(tu)_3I]$ (where tu = thiourea) is proposed. This complex is produced in various ways by the interaction of Bi(III), Cu(II), and I^- ions with thiourea. Most cations and anions do not interfere, but Tl(I), Cs(I), SO_3^{2-}, $S_2O_3^{2-}$, EDTA, and oxidizing ions such as NO_2^-, IO_3^-, IO_4^-, BrO_3^-, and MnO_4 do. The complex hexakis(thioureato)sulphatomonoaquodicopper(I) $[Cu_2(tu)_6SO_4.H_2O]$ is proposed as a new spot-test reagent for Bi(III) and I^- ions, although the sensitivity for the latter is poor.

New spot-test for silver(I) based on double iodide formation with bismuth(III): G. S. JOHAR, *Talanta*, 1974, **21**, 973. (Department of Chemistry, Vikramajit Singh Sanatan Dharma College, Kanpur (U.P.) 208002, India.)

Summary—The formation of an intense brownish-maroon or maroon-red product by the interaction of silver(I) and bismuth(III) solution in the presence of iodide forms the basis of a new and specific spot-test procedure for silver. The test is conducted on a spot plate with 2 or 3 drops of 2% potassium iodide solution, 1 drop of 1% bismuth(III) nitrate solution, and 1 drop of test solution. Limit of detection is 0·01 μg; limit of dilution is $1:5 \times 10^6$. Most cations and anions do not interfere. Only Tl(I), Cs, $S_2O_3^{2-}$, EDTA, pyridine, excess of thiourea, oxidizing ions [NO_2^-. IO_3^-, IO_4^-. MnO_4^-: BrO_3^-, and $S_2O_8^{2-}$] and ions such as Cl^-, Br^-, I^-, SCN^-, and N_3^- which cause precipitation of silver, interfere. The product formed is most probably Ag_2BiI_5.

On the theory of thermometric titration: G. O. PILOYAN and YU. V. DOLININA, *Talanta*, 1974, **21**, 975. (The Institute for Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, U.S.S.R. Academy of Sciences, Staromonetny 35, Moscow 109017, USSR.)

Summary—The general equation defining the change in solution temperature ΔT during a thermometric titration is

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV}$$

where A and B are constants, V is the volume of titrant used to produce temperature T, and T_0 is the initial temperature. There is a linear relation between the inverse values of ΔT and V:

$$\frac{1}{\Delta T} = -\frac{a}{V} - b$$

where $a = 1/A$ and $b = B/A$, both a and b being constants. A linear relation between ΔT and V is usually a special case of this general relation, and is valid only over a narrow range of V. Graphs of $1/\Delta T$ *vs.* $1/V$ are more suitable for practical calculations than the usual graphs of ΔT *vs.* V.

Титриметрическая оценка цистеина самого и в присутствии других аминокислот: Padam Sen and Krishna Bahadur, *Talanta*, 1974, 21, 968.

Резюме—Определен самый цистеин и в присутствии других аминокислот титрованием с ртутью (II) при pH 6,2 или 9,2 и свинцем при pH 9,2. Комплекс 1:1 образуется во всех трех процедурах.

Взаимодействие комплексов тиомочевины с медбю(I) и тиомочевины с висмутом(III) в присутствии иодида. Новые капельные пробы для меди(II) и висмута(III): G. S. Johar, *Talanta*, 1974, 21, 970.

Резюме—Описаны новые весьма простие капельные пробы для обнаружения ионов Bi(III), Cn(II) и 1, с чувствительностью 3, 8 и 75 мкг (0,05 мл, соответственно. Также приведены пробы для комбинаций, как на пример Bi(III) + 1^-; Bi(III) + Cu(II); и Bi(III) + Co(II) + 1^-. Все пробы основаны на образовании оранжевого или красновато-оранжевого осадка комплекса висмут (III)-медь(I)-иодид-тиомочевина, для которого предложена формула $(\mathrm{Bi(TM)_3I^3.Cu(TM)_3I})$ где TM = тиомочевина. Этот комплекс образуется при взаимодействии Bi(III), Cu(II) и 1^- с тиомочевиной. Большинство катионов и анионов не мешают пробы; влияют только Tl(I), Cs(I), $\mathrm{So_3}^{2-}$, $\mathrm{S_2O_3}^{2-}$, ЭДТА и окислительные ионы, в том числе $\mathrm{NO_2}^-$, 10_3^-, 10_4^-, $\mathrm{BrO_3}^-$ и $\mathrm{MnO_4}^-$. Комплекс гексакис (тиоуреато) сульфатомоноакводимедь (I) $(\mathrm{Cu_2})$ TM $(_6\mathrm{SO_4.H_2O})$ предложен в качестве нового капельного реагента для B. (III) и I^-, хотя чувствительность для последнего но на плоха.

Новая капельная проба для серебра(I) основанная на образовании двойного иодида с висмутом(III): G. S. Johar, *Talanta*, 1974, 21, 973.

Резюме—Новая и специфическая капельная проба для серебра основана на образовании интенсивного коричневокаштанового или каштаново-красного продукта при взаимодействии растворов серебра (I) и висмута (III) в присутствии иодида. Пробу проводят на капельной плитке с 2–3 каплями 2%-ного раствора иодида калия, 1 каплей 1%-ного раствора нитрата висмута (III) и 1 каплей испытуемого раствора. Чувствительность метода 0,01 мкг, а предельное разбавление—1:5 × 10^6. Большинство катионов и анионов не мешают определению. Влияют только Tl(I), Cs, $\mathrm{S_2O_3}^{2-}$, ЭДТА, пиридин, избыток тиомочевины, окислительные ионв $(\mathrm{No_2}^-$, 10_3^-, 10_4^-, $\mathrm{MnG_4}^-$, $\mathrm{BrG_3}^-$ и $\mathrm{S_2O^-}_8{}^{2-})$ и ионы которые осаждают серебро, в том числе Cl^-, Br^- I^-, SCN^- и$\mathrm{N_3}^-$. Состав продукта вероятно $\mathrm{Ag_2BiI_5}$.

Доклад теории термометрической титрации: G. O. Piloyan and Yu. V. Dolinina, *Talanta*, 1974, 21, 975.

Резюме—Изменения температуры раствора ΔT в течение термометрической титрации даны общим уравнением

$$\Delta T = T - T_0 = -\frac{AV}{1 + BV}$$

где A и B—константы, V—объем титрованного раствора, расходованный для получения температуры T, а T_0—начельная тамлература. Существует линейное отношение между обратными величинами ΔT и V:

$$\frac{1}{\Delta T} = -\frac{a}{V} - b$$

где $a = 1/A$ и $b = B/A$, а a и b константы. Линейное отношение между ΔT и V обычно является специальным слуцаем этого общего отношения, а держит только в узкой области V. Графики $1/\Delta T - 1/V$ лучше применимы для практических рассчетов чем обыкновенные графики $\Delta T - V$.

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Analytical Data

Annotation

Talanta, Vol 21, p. iv. Pergamon Press, 1974. Printed in Great Britain

ERRATA

In the paper by J. M. Cano Pavon and F. Pino, *Talanta*, 1972, **19**, 1659, curves *B* and *C* in Fig. 1 were incorrectly labelled: curve *B* should be labelled curve *C*, and *vice versa*. The medium used for the p*K* measurements was 2% v/v ethanol in water.

AUTHOR INDEX

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SUMMARIES FOR CARD INDEXES

Analytical chemistry of the sulphur acids: László Szekeres, *Talanta*, 1974, **21**, 1, (Kapco, Inc., Kalamazoo, Michigan 49001, U.S.A.).

Summary—A comprehensive review is made of the analytical methods available for the inorganic acids derived from sulphur.

Application of the Davidon–Fletcher–Powell method to the calculation of stability constants: P. Gans and A. Vacca, *Talanta*, 1974, **21**, 45, (Laboratorio C.N.R., Istituto di Chimica Generale dell 'Università, Via J. Nardi 39, 50132 Firenze, Italy).

Summary—The Davidon–Fletcher–Powell method of function minimization has been modified and successfully applied to the calculation of stability constants of species of the type $H_pM_qL_r$ in solution. It is shown that the refinement with respect to the logarithms of the stability constants is intrinsically ill-conditioned, leading to convergence difficulties when poor initial parameters estimates are used, and to failures when one or more parameters are experimentally indeterminate.

Miniquad—a general computer programme for the computation of formation constants from potentiometric data: A. Sabatini, A. Vacca and P. Gans, *Talanta*, 1974, **21**, 53, (Laboratorio C.N.R., Istituto di Chimica Generale dell 'Università, Via J. Nardi 39, 50132 Firenze, Italy).

Summary—A new computer programme for the computation of formation constants of complex species in solution is presented. The programme can be applied to all kinds of potentiometric titration data, including multi-reactant and multi-electrode systems. A statistical analysis is made of the results in order to assess their validity, and to assist in hypothesis testing.

Formation constants of zinc(II) complexes with Semi-Xylenol Orange; Takashi Yoshino, Sadaaki Murakami, Megumi Kagawa and Takashi Araragi, *Talanta*, 1974, **21**, 79, (Department of Chemical Technology, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Japan).

Summary—A potentiometric and spectrophotometric investigation of the formation of zinc(II) complexes with Semi-Xylenol Orange (SXO or H_4L) is reported. In an aqueous solution ($\mu = 0{\cdot}1$), three 1:1 complex species, MH_2L, MHL^-, ML^{2-}, and a 1:2 complex, ML_2^{6-}, seem to exist. In a strongly alkaline medium (above pH 12·5) the complexes may dissociate to give zinc hydroxide and L^{4-}. The formation of a hydroxy complex is not observed. The absorption maxima are at 445 nm (MH_2L), 466 nm (MHL^-) and 561 nm (ML^{2-}), the molar absorptivities being $2{\cdot}34 \times 10^4$, $2{\cdot}42 \times 10^4$ and $3{\cdot}14 \times 10^4$ $1.mole^{-1}.cm^{-1}$ respectively. The formation constants are (at $25 \pm 0{\cdot}1°$) $\log K^{M}_{ML} = 11{\cdot}84$, $\log K^{M}_{MHL} = 7{\cdot}13$, $\log K^{M}_{MH2L} = 2{\cdot}70$, $\log K^{M}_{ML2} = 16{\cdot}60$.

Аналитическая химия сернистых кислот: László Szekeres, *Talanta*, 1974, **21**, 1.

Резюме — Дается исчерпывающий обзор имеющихся аналитических методов для неорганических кислот полученных из серы.

Применение метода Давидона-Флетчера-Пауелля в расчете констант устойчивости: P. Gans and A. Vacca, *Talanta* 1974, 21, 45.

Резюме — Метод Давидона-Флетчера-Пауелля для минимизации функций изменен и успешно применен в расчете констант устойчивости комплексов типа $H_pM_qL_r$ в растворе. Показано что усовершенствование логарифмов констант устойчивости в сущности неудовлетворительно; оно водит к проблемам конвергенции если используются плохие оценки начальных параметров и к неудачах в случае неопределенности однодо или двух параметров.

Miniquad — Общеприменимая программа для расчета констант образования на основе потенциометрических данных с помоью электронновычислительной машины: A. Sabatini, A. Vacca and P. Gans, *Talanta* 1974, **21**, 53.

Резюме — Предложена новая программа ЭВМ для расчета констант образования комплексов в растворе. Программа применима на все данные потенциометрического титрования, шключая системы с большим числом реагентов и электродов. Проведен статистический анализ результатов с целью оценивать их верность и в проверке гипотезов.

Образование комплексов цинка (II) с полуксиленол оранжевым: Takashi Yoshino, Sadaaki Murakami, Megumi Kagawa and Takashi Araragi, *Talanta*, 1974, 21, 79.

Резюме — Описываются потенциометрическое и спектрофотометрическое исследования образования комплексов цинка (II) с полуксиленол оранжевым (SXO или H_4L). В водном растворе ($\mu = 0{,}1$) кажется существуют три 1:1 комплекса группы MH_2L, MHL^-, ML^{2-} и 1:2 комплекса группы $ML_2{}^{6-}$. В очень щелочной среде (pH выше 12,5), комплексы могут подвергнуться диссоциации и образовать гидроокись цинка и L^{4-}. Не замечается образования комплекса гидрокси. Максимумом обсорбции являются: при 445 nm (MH_2L), при 466 nm (MHL^-) и при 561 nm (ML^{2-}) при чем молярные абсорбционности следующие: $2{,}34 \times 10^4$; $2{,}42 \times 10^4$ и $3{,}14 \times 10^4$ l.моль$^{-1}$ см$^{-1}$ соответственно. Константами образования являются (при $25 \pm 0{,}1°$): $\log K_L{}^M = 11{,}84$; $\log K^M_{MHL} = 7{,}13$; $\log K^M_{MH2L} = 2{,}70$; $\log K^M_{ML2} = 16{,}60$.

Solvent extraction–spectrophotometric determination of rare earths with chlorophosphonazo III: TOMITSUGU TAKETATSU, MASAMI KANEKO and NORIKO KONO, *Talanta*, 1974, **21**, 87. (College of General Education, Kyushu University, Fukuoka, Japan).

Summary—The rare-earth chlorophosphonazo III chelates are easily extracted from an aqueous solution (pH 1·1–1·5) into n-butanol. The absorbance at the absorption maximum (at 668 nm) is about 3 times that in aqueous solution. The spectrophotometric determination of rare earths has been investigated.

Adsorption of chlorinated pesticides from river water with XAD-2 resin; JOHN J. RICHARD and JAMES S. FRITZ, *Talanta*, 1974, **21**, 91. (Ames Laboratory-USAEC, Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.).

Summary—Pesticides in river water at levels as low as parts per billion (10^{12}), can be recovered by sorption on a column of XAD-2 resin, followed by elution with acetonitrile. Water is added to the acetonitrile and the pesticides are extracted by petroleum ether and determined by gas chromatography. The new procedure is more conventient to use than the solvent extraction procedure and gives comparable results for dieldrin.

Extraction-spectrophotometric determination of thallium in high-purity indium: Z. MARCZENKO, H. KAŁOWSKA and M. MOJSKI, *Talanta*, 1974, **21**, 93. (Department of Analytical Chemistry, Warsaw Technical University, Warsaw, Poland).

Summary—Trace amounts of thallium in high-purity indium are separated from the matrix by extraction from $6M$ hydrochloric acid by di-isopropyl ether. On shaking the extract with Brilliant Green in $0{\cdot}15M$ hydrochloric acid, an ion-association complex is formed in the organic phase. Interference of other elements is removed by their reduction with metallic copper and scrubbing. The proposed method permits determination of 10^{-5}–10^{-6}% thallium in high-purity indium with good precision and accuracy.

Evaluation of 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid as a metallochromic indicator: HIROKO WADA, OSAMU NAKAZAWA and GENKICHI NAKAGAWA, *Talanta*, 1974, **21**, 97. (Nagoya Institute of Technology, Laboratory of Analytical Chemistry, Showa-ku, Nagoya, Japan).

Summary—The acid dissociation constants of 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid (TAHN) and the formation constants of Cu(II), Ni(II) and Zn(II) chelates of this dye have been determined spectrophotometrically at 25° in a 5% v/v mixture of dioxan and water. The formation constants of the 1:2 chelates are smaller than those of other *o*-hydroxythiazolylazo compound chelates. TAHN is a satisfactory indicator for the tritration of Cu(II) and Ni(II) with EDTA.

Спектрофотометрическое определение редких землей путем экстрагирования хлорофосфоназом III: Tomitsugu Taketatsu, Masami Kaneko and Noriko Kono, *Talanta*, 1974, **21**, 87.

Резюме — Редкоземельные хлорофосфоназо III клешневидные соединения легко экстрагируются из водного раствора (pH 1,1–1,5) в n-бутанол. Поглащательная способность при максимальной абсорбции (668 nm) почти в три раза превышает абсорбцию водным раствором. Исследовалось спектрофотометрическое определение редкоземельных элементов.

Адсорбция хлорированных пестицидов из речной воды смолой XAD-2: John J. Richard and James S. Fritz, *Talanta*, 1974, **21**, 91.

Резюме — Сорбцией в колонне XAD-2 смолы можно экстрагировать пестициды из речной воды на таком низком уровне, как чст/блн. (10^{12}) с последующей элюцией ацетонитрилом. К ацетонитрилу добавляется вода, пестициды экстрагируются петролейным эфиром и определяются газовой хромотографией. Эта новая процедура более удобна при применении и дает результаты заслуживающие сравнение с диелдрином.

Экстракционно-спектрофотометрическое определение таллия в индии высокой чистоты: Z. Marczenko, H. Kałowska and M. Mojski, *Talanta*, 1974, **21**, 93.

Резюме — Малые количества таллия в индий высокой чистоты отделяется от матрицы экстрагированием из 6*M* хлористоводородной кислоты простым диизоприловым эфиром. При встряхивании экстракта бриллиантового зеленого с 0,15 *M* хлористоводородной кислоты, образуется комплекс ассоциации ионов в органической фазе. Интерференция других элементов отстраняется путем редукции металлической медью и очисткой. Предлагаемый метод допускает определение 10^{-5}–10^{-6}% таллия в высокочистом индии с удивительной точностью.

Оценка 1-(2-тиазолилаз)-2-окси-3-нафтойной кислоты металлохромовым индикатором: Hiroko Wada, Osamu Nakazawa and Genkichi Nakagawa, *Talanta*, 1974, **21**, 97.

Резюме — При температуре 25° в 5%ной смеси объем на объем диоксана и воды определили константу диссоциации кислоты 1-(2-тиазолилаз)-2-окси-3-нафтойная кислота (TAHN) и константы образования клешневидной формы Cu(II), Ni(II) и Zn(II) этого красителя. Константы образования 1:2 клешневидных форм менее, чем других клешневидных соединений о-окситиазолилазов. TAHN является удовлетворительным индикатором для титрирования Cu(II) и Ni(II) посредством EDTA.

Comparison of the ion-exchange behavior of zirconium, thorium, vanadium, uranium, stannic and titanium tungstates: MOHSIN QURESHI, JAI PRAKASH GUPTA and VEENA SHARMA, *Talanta*, 1974, **21**, 102. (Chemistry Department, Aligarh Muslim University, Aligarh (U.P.), India).

Summary—Zirconium, thorium, uranium, vanadium, stannic and titanium tungstates have been prepared and their properties such as ion-exchange capacity, K_d values of metal ions, chemical composition and stability have been compared. Titanium tungstate was found to be the most stable, and to have negligible capacity for tervalent cations.

Rapid EDTA determination of lead in binary alloys of lead and tin: MELVIN J. TSCHETTER and ROBERT Z. BACHMAN, *Talanta*, 1974, **21**, 106. (Ames Laboratory-USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Binary alloys of lead and tin were dissolved in nitric acid (1 + 1) containing 10% sodium fluoride. The tin(IV) was effectively masked by the fluoride. The lead was quickly and accurately titrated with EDTA in a hexamine-buffered solution, with Xylenol Orange as indicator.

A note on the determination of thorium in the presence of some bivalent metals ions: RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1974, **21**, 109. (Analytical Laboratory, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague 1, Jilská 16, Czechoslovakia.)

Summary—A new method for complexometric determination of thorium in the presence of bivalent metals without their masking is presented. Two aliquots of metal solution are necessary. In one the sum of thorium and other metals is determined by DTPA titration. The second aliquot is treated with Zn_2TTHA complex. Only thorium, forming a 1 : 1 complex with TTHA, displaces twice its molar amount of zinc from the complex, while other elements displace only an equimolar amount of zinc. The amount of thorium corresponds to the difference of consumption in the two titrations.

Extraction of metals into chloroform with some derivatives of phenylacetic acid: J. ADAM and R. PŘIBIL, *Talanta*, 1974, **21**, 113. (J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague 1, Jilská 16, Czechoslovakia).

Summary—A comparison has been made of phenylacetic, diphenylacetic, naphthylacetic and 2-naphthoxyacetic acids as extracting agents for metal ions. Phenylacetic acid is much superior to the others.

Сравнение ионообменных характеристик вольфраматов циркония, тория, ванадия, урана, олова(IV) и титана: Mohsin Qureshi, Jai Prakash Gupta and Veena Sharma, *Talanta* 1974, 21, 102.

Резюме — Приготовлены вольфраматы циркония, тория, урана, ванадия, олова(IV) и титана и сравнены их свойства, в том числе ионообменная мощность, величины *K* для ионов металлов, химический состав и устойчивость. Вольфрамат титана оказался наиболее устойчивым, с незначительной мощностью для трехвалентных катионов.

Быстрое определение свинца в двойных сплавах свинца и олова с помощью ЭДТА: Melvin J. Tschetter and Robert Z. Bachman, *Talanta*, 1974, 21, 106.

Резюме — Двойние сплавы свинца и олова растворяли в азотной кислоте (1 + 1) содержащей 10% фторида натрия. Олово(IV) эффективно маскировали фторидом. Свинец титровали быстро и точно с ЭДТА в растворе буферованном с гексамином, с использованием ксиленолоранжевым в качестве индикатора.

Заметка к определению тория в присутствии некоторых двувалентных ионов металлов: Rudolf Pribil and Vladimir Vesely, *Talanta*, 1974, 21, 109.

Резюме — Предложен новый метод комплексонометрического определения тория в присутствии двувалентных металлов без маскирования. Надо взять две аликвотных части раствора металлов. В одном из растворов определяют сумму тория и других металлов титрованием с ДТПА. Вторый раствор обрабатывают с комплексом Zn_2 ТТХА. Только торий, образующий комплекс 1 : 1 с ТТХА, вытесняет дважди его молярное количество цинка из комплекса, в то время как другие элементы вытесняют только эквимолекулярное количество цинка. Количество тория соответствует разници расходованных титрованных растворов в этих двух титрованиях.

Экстрагирование металлов в хлороформ с некоторыми производными фенилуксусной кислоты: J. Adam and R. Přibil, *Talanta*, 1974, 21, 113.

Резюме — Сравнивалось действие фенилуксусной, дифенилуксусной, нафтиуксусной и 2-нафтоксиуксусной кислот в качестве средств для экстрагирования ионов из металла. Нашли, что фенилуксусная кислота на много превосходит другие кислоты.

SUMMARIES FOR CARD INDEXES

On the properties of Calcein Blue: GERALDINE M. HUITINK, DONALD P. POE and HARVEY DIEHL, *Talanta*, 1974, **21**, 1221. (Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A. 50010).

Summary—A satisfactory method for the preparation of Calcein Blue has been devised. Elemental analysis, equivalent weight by neutralization, and the NMR spectrum show the compound to be 4-methylumbelliferone-8-methyleneiminodiacetic acid·$0{\cdot}25H_2O$. The ultraviolet absorbance and fluorescence have been studied as a function of pH and, combined with potentiometric titration and solubility data, have yielded for the acid dissociation constants the values $pK_1 = 3{\cdot}0$, $pK_2 = 6{\cdot}9$, and $pK_3 = 11{\cdot}3$. These acid functions are identified respectively as carboxyl, phenol, and ammonium ion, the free Calcein Blue being a zwitter-ion. Calcein Blue fluoresces in both acidic and basic solution when excited at a suitable wavelength. The fluorescence of the doubly-charged anion formed on the neutralization of the phenol group, when excited at 360 nm, reaches a maximum at pH 9, and decreases to zero with the neutralization of the ammonium ion; the wavelength of maximum emission is 455 nm. In the presence of calcium, the fluorescence increases with alkalinity up to pH 9 and then remains constant. The calcium derivative is a 1:1 compound, formation constant $10^{7{\cdot}1}$. The fluorescence of Calcein Blue at all pH values is quenched by copper(II). The calcium derivative is changed on standing in highly alkaline solution, presumably by ring opening, to another fluorescent material; thus Calcein Blue, although satisfactory as an indicator, is not useful for the direct fluorometric determination of calcium.

Plutonium and uranium determination in environmental samples: combined solvent extraction–liquid scintillation method: W. J. MCDOWELL, D. T. FARRAR and M. R. BILLINGS, *Talanta*, 1974, **21**, 1231. (Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.)

Summary—A method for the determination of uranium and plutonium by a combined high-resolution liquid scintillation–solvent extraction method is presented. Assuming a sample count equal to background count to be the detection limit, the lower detection limit for these and other alpha-emitting nuclides is 1·0 d.p.m. with a Pyrex sample tube, 0·3 d.p.m. with a quartz sample tube using present detector shielding or 0·02 d.p.m. with pulse-shape discrimination. Alpha-counting efficiency is 100%. With the counting data presented as an alpha-energy spectrum, an energy resolution of 0·2–0·3 MeV peak half-width and an energy identification to ±0·1 MeV are possible. Thus, within these limits, identification and quantitative determination of a specific alpha-emitter, independent of chemical separation, are possible. The separation procedure allows greater than 98% recovery of uranium and plutonium from solution samples containing large amounts of iron and other interfering substances. In most cases uranium, even when present in 10^8-fold molar ratio, may be quantitatively separated from plutonium without loss of the plutonium. Potential applications of this general analytical concept to other alpha-counting problems are noted. Special problems associated with the determination of plutonium in soil and water samples are discussed. Results of tests to determine the pulse-height and energy-resolution characteristics of several scintillators are presented. Construction of the high-resolution liquid scintillation detector is described.

Iodometric submicro determination of α-amino-alcohols by an amplification reaction: AMIR BESADA and Y. A. GAWARGIOUS, *Talanta*, 1974, **21**, 1247. (Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, Egypt (A.R.E.)

Summary—New methods are described for the iodometric submicro determination of α-amino-alcohols possessing primary, secondary or tertiary amino-groups which involve 6-, 12-, and 18-fold amplification reactions (relative to parent compound), respectively. The methods are based on reaction of the α-amino-alcohols with an excess of potassium periodate in a slightly alkaline medium, masking of the unreacted periodate with molybdate at pH 3·2 and, after addition of iodide, iodometric determination of the equivalent amounts of iodate released. In addition to being simple and rapid, the methods are sufficiently selective and specific and also highly accurate, being particularly siutable for the analysis of submicro amounts (50–150 μg); the average recovery is 99·9%.

Determination of gold in copper-bearing sulphide ores and metallurigcal flotation products by atomic-absorption spectrometry: B. STRONG and R. MURRAY-SMITH, *Talanta*, 1974, **21**, 1253. (Charter Consolidated Metallurgical Laboratory, Ashford, Kent, England).

Summary—A method is described which is specific for the determination of gold in sulphide copper ores and concentrates. Direct decomposition with *aqua regia* was found to be incomplete. A carefully controlled roasting stage followed by treatment with hydrochloric acid and then *aqua regia* was effective for dissolving all the gold. The gold is extracted into 4-methylpentan-2-one (methyl isobutyl ketone) then aspirated into a very lean air–acetylene flame and the gold determined by atomic-absorption spectrometry. No interferences were observed from large concentrations of copper, iron or nickel.

On the reduction of oxygen in aqueous solution by electrolytically precipitated cadmium: FOLKE NYDAHL, *Talanta*, 1974, **21**, 1259. (Department of Analytical Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden.)

Summary—The reduction of oxygen in aqueous solution by electrolytically precipitated cadmium, used in a reductor column, has been studied in two ways. First, by analysis of the effluent for the hydrogen peroxide formed as a reaction intermediate, the conditions for quantitative reduction have been found. Attention is called to the fact that an effluent free from hydrogen peroxide also implies quantitative reduction of all dissolved oxygen. The practical consequences are pointed out. A comparison is also made with some other reductors. Secondly, the oxidation of electrolytically precipitated cadmium by hydrogen ion is strongly inhibited, so at pH 7 it is possible to determine oxygen as the equivalent amount of cadmium ion produced in the reductor column. The conditions of quantitative reduction of oxygen are determined and found to be in agreement with those obtained by the first method. From the results the solubility of oxygen in water in equilibrium with air is estimated and found to agree with a published result considered as reliable. An outline is given of a method for determination of oxygen in aqueous solution by measurement of the amount of cadmium ions produced.

Titrations using an apparatus for recording the antilogarithm of pH or pM: AXEL JOHANSSON, *Talanta*, 1974, **21**, 1269. (Royal Institute of Technology, Stockholm, Sweden).

Summary—A titration apparatus plotting either the concentration of sample ion or the concentration of titrant ion has been tested. An antilog apparatus, converting measured e.m.f. values into concentrations is connected to ordinary titration equipment. The instrument has been tested by means of acid–base titrations (titrations of mixtures of weak acids and of a weak and a strong acid), precipitation titrations (determination of the chloride concentration in tap-water, titration of mixtures of halides), titrations with ion-selective electrodes (determination of the fluoride content of toothpaste) and complexometric titrations (determination of copper with EDTA, using mercuric ion as indicator ion and amalgamated silver rod as indicator electrode, or using a copper-selective indicator electrode). The method considerably simplifies the evaluation of the results as compared to conventional potentiometric titrations.

Preconcentration and determination of cadmium in water by reversed-phase column chromatography and atomic absorption: JOSEPH J. TOPPING and WILLIAM A. MACCREHAN, *Talanta*, 1974, **21**, 1281. (Chemistry Department, Towson State College, Towson, Maryland 21204, U.S.A.).

Summary—Studies were made of the solvent extraction of cadmium(II) from hydrochloric acid into a tri-n-octylamine–cyclohexene mixture. Distribution ratios, as a function of amine and acid concentration, were determined and this information was used to establish optimum extraction conditions and the probable nature of the extracted species. This system was used as the basis for the development of a reversed-phase column chromatographic technique for preconcentrating Cd(II). The amine–cyclohexene phase was coated on an inert macroreticular resin (XAD-2) to provide a stable column. With this system, Cd(II) in acidified water samples as large as 3 l. may be concentrated to 10 ml and determined by conventional atomic absorption. Interferences were studied, and the method was applied to the analysis of fresh-water streams for Cd(II).

Dispositif de prélèvement microanalytique de produits altérables: Bernard Cousin and Colette Muller, *Talanta*, 1974, **21**, 1287. (Service Central de Microanalyse du Centre National de la Recherche Scientifique, 2, rue Henry Dunant 94320 Thiais, France).

Summary—A small glass device is described for microanalytical or submicroanalytical sampling of unstable solid or liquid substances, in an argon atmosphere.

New type of blue ternary complex of arsenazo I with plutonium(IV) in the presence of hydrogen peroxide: J. A. Pérez-Bustamante, *Talanta*, 1974, **21**, 1291. (Departamento de Quimica Analitica, Facultad de Ciencias, Universidad Complutense, Ciudad Universitaria, Madrid-3, Spain).

Summary—The preparation and spectrophotometric properties of a new type of complex compound of arsenazo I with Pu(IV) in the presence of H_2O_2 are described. The new compound has a blue colour, derived from a wide absorption band with a maximum at 610 nm, and a corresponding molar absorptivity of 4×10^4 l. $\text{mole}^{-1}.\text{cm}^{-1}$. From 2 hr after its preparation this curious new compound undergoes for several days a steady decomposition accompanied by decolorization. The formation of similar peroxy Pu(IV) complexes has not so far been shown to take place with arsenazo III or with any other "arsenazo-type" reagent.

***Ortho*-effects of carboxyl, sulpho and arsono groups on the protonation and dissociation constants of mono-azo and bis-azo chromotropic acid derivatives:** A. A. Muk, V. N. Nikolić and T. V. Petrova, *Talanta*, 1974, **21**, 1296. (Boris Kidrič Institute of Nuclear Sciences–Vinča, Beograd, Yugoslavia.)

Summary—The effect of carboxyl, sulpho and arsono groups on the protonation and dissociation constants of mono-azo and bis-azo chromotropic acid derivatives has been investigated. From the value obtained for the effect of the substituents, the equation

$$\textit{ortho}\text{-effect} = \log K_{ortho}\text{-}\log K_{para}$$

has been derived. The causes of the effect are discussed.

Precipitation of lead as lead sulphate by destructive oxidation of EDTA: J. Rajagopala Rao, A. Suryanarayana and B. R. Sant, *Talanta*, 1974, **21**, 1300. (Regional Laboratory, Bhubaneswar-4, India.)

Summary—Gravimetric determination of lead (5–100 mg) by homogeneous precipitation of lead sulphate from a solution containing lead(II), EDTA and sulphate by destructive oxidation of EDTA with hydrogen peroxide or sodium bromate is described. Aluminium(III), iron(III), zinc(II), manganese(II), copper(II), nickel(II), tin(II) and antimony(III) do not interfere in the method. The method can successfully be applied to the analysis of type metal.

Eléments de fluorimétrie organique fonctionnelle—IX. Fluorimétrie de dérivés nitrés aromatiques: J. Bartos, *Talanta*, 1974, **21**, 1303. (Centre de Recherches Roussel-Uclaf, 93-Romainville, France).

Summary—Aromatic nitro compounds are reduced to aromatic amines by iron(II) in alkaline medium. The dye obtained by reacting the amine with 1,2-naphthoquinone-4-sulphonic acid is extractable into methylene chloride. Reduction by potassium borohydride yields a fluorescent *o*-diphenol, thus allowing the fluorimetric estimation of aromatic nitro compounds on the microgram scale.

Sur une colorimétrie d'aldéhydes aromatiques par l'intermédiaire de leurs thiosemicarbazones: J. Bartos and M. Pesez, *Talanta*, 1974, **21**, 1304. (Centre de Recherches Roussel-Uclaf, 93-Romainville, France).

Summary—The thiosemicarbazone obtained by reacting an aromatic aldehyde with thiosemicarbazide in acidic medium is extracted into methylene chloride. The colour developed by adding 2,3-dichloro-1,4-naphthoquinone to the organic extract allows the colorimetric determination of a few micrograms.

Sur une colorimétrie des acides carboxyliques par hydroxamation directe: M. Pesez and J. Bartos, *Talanta*, 1974, **21**, 1306. (Centre de Recherches Roussel-Uclaf, 93-Romainville, France).

Summary—Carboxylic acids react with hydroxylamine hydrochloride in the presence of dicyclohexylcarbodi-imide to give the corresponding hydroxamic acid which is developed with iron(III), thus allowing colorimetric determinations on the tenths of a milligram scale. Esters do not react, and acetic acid can be determined in butyl acetate at a concentration of about 0·1%.

Spectrophotometric determination of molybdenum by extraction of its thiosulphate complex: V. Yatirajam and Jaswant Ram, *Talanta*, 1974, **21**, 1308. (Chemistry Department, Kurukshetra University, Kurukshetra, 132119, India.

Summary—A simple and rapid spectrophotometric determination of molybdenum is described. The molybdenum thiosulphate complex is extracted into isoamyl alcohol from 1·0–1·5*M* hydrochloric acid containing 36–40 mg of $Na_2S_2O_3 \cdot 5H_2O$ per ml. The absorbance at $\lambda_{max} = 475$ nm obeys Beer's law over the range 0–32 μg of Mo per ml of solvent phase. Up to 5 mg/ml of Ti(IV), V(V), Cr(VI), Fe(III), Co(II), Ni(II), U(VI), W(VI), Sb(III), 1 mg/ml of Cu(II), Sn(II), Bi(V) and 10 μg/ml of Pt(IV) and Pd(II) do not interfere. Large amounts of complexing agents interfere. The method has been applied to analysis of synthetic and industrial samples.

Dissociation constants of carboxymethyloxysuccinic acid: C. E. Rodriguez and C. D. Devine, *Talanta*, 1974, **21**, 1313. (Lever Brothers Company Inc., Research and Development Division, 45 River Road, Edgewater, New Jersey 07020, U.S.A.)

Summary—The dissociation constants of carboxymethyloxysuccinic acid (CMOS) have been measured at 25° and an ionic strength of 0·1*M* in sodium perchlorate. The values found were: $pK_1 = 2·52$, $pK_2 = 3·77$ and $pK_3 = 5·00$. CMOS is thus seen to be rather stronger than its isomer citric acid.

Comparison of an instrumental and a modified Kjeldahl technique for determination of nitrogen in niobium and tantalum alloys: Emery J. Merkle, Judson W. Graab and Warren F. Davis, *Talanta*, 1974, **21**, 1317. (Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio, U.S.A.)

Summary—Results obtained for the determination of nitrogen in two tantalum alloys and six niobium alloys by modified Kjeldahl and Leco TC-30 nitrogen–oxygen determinator are compared. In the 5–25 ppm range, for tantalum alloys, the relative standard deviation was 3–9% by the Kjeldahl procedure and 9–11% by the instrumental technique. In the range 30–80 ppm, for niobium alloys, the relative standard deviation was 2–8% by the Kjeldahl procedure and 5–7% by the instrumental technique