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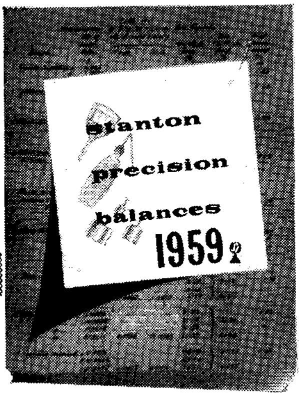
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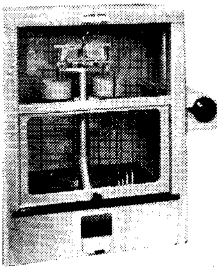

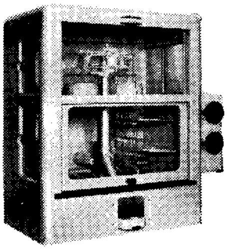

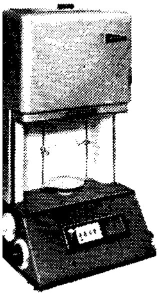

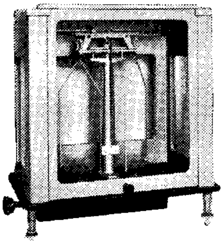

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A CRITICAL REVIEW OF THE VOLUMETRIC METHODS FOR THE PLATINUM METALS

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The following review deals with the volumetric methods for the determination of the platinum metals which have been recorded up to January 1958. Undoubtedly some will have escaped the author's attention, particularly where their applications have been integrated within a larger scheme of separation and determination. It is hoped that even these will receive attention during subsequent reviews on methods of separation. In any case there is ample evidence for a marked deficiency of acceptable volumetric methods for most of the platinum metals. Furthermore, one cannot escape the conclusion that a more careful and detailed examination of many of the methods now available, made in the light of the increase in knowledge of the behaviour of acid solutions of the metals, will suggest the elimination of some and improvement in others.

It is a surprising fact that the number of recorded volumetric methods for the determination of the platinum metals is only a small fraction of those presented for gravimetric determinations. Furthermore many of the proposed volumetric methods can be considered useful only when applied to the isolated platinum metal constituent and applied under carefully controlled conditions. The analytical researcher in the field of the platinum metals seems not always to have realized the degree of complexity of the equilibria existing in mineral acid solutions of these metals. This is made evident by the general failure to deal adequately with methods of dissolution prior to the application of the volumetric methods. These, like colorimetric, are sometimes peculiarly sensitive to changes in identity of the dissolved metal constituent. This is particularly true of some of the proposed potentiometric titrations where one may encounter almost totally different valence states in various acid concentrations. Indeed, there are recorded volumetric methods which claim quantitative application in weak acids for one valence, and for a second valence in strong acids. One cannot avoid concern about procedures whose successful application is dependent upon either the enforcement of a practically complete equilibrium through control of acidity, prior oxidation, etc. or upon the development of an equilibrium mixture of constant composition.

Regarding the general status of volumetric methods for the platinum metals there is much to be desired. There is a paucity of acceptable methods for all of these metals and for some no really acceptable method is available.

PALLADIUM

About a dozen methods have been recorded for the volumetric determination of palladium. Many of these involve the formation of insoluble palladium compounds and incorporate some physical process for ascertaining the stoichiometric end-point. Several of the methods require the addition of an accurately measured excess of a standard complexing reagent with the excess determined by a back titration. None of the methods can be applied indiscriminately for the analysis of even simple platinum metals systems. A few of the procedures are useful for routine analysis of simple alloys whose constituents vary little in proportions and identity.

Turbidimetric titrations

Perhaps the first volumetric method for palladium was described by KERSTING[1] who titrated a palladium solution directly with potassium iodide to the disappearance of the brown iodide in the supernatant liquid. Obviously this method can be subject to considerable error. A potentiometric titration of palladium with potassium iodide was used by PSHENITSYN and co-workers[2,3]. When hydroquinone was used initially as a reducing reagent there was no interference from platinum(IV), rhodium(III), and iridium(IV). The interference from quadrivalent platinum could also be avoided by the addition of potassium salt to form potassium hexachloroplatinate[3]. One of the most satisfactory iodide procedures is that proposed by ATKINSON and associates[4-6]. One method[4] involved the treatment of a palladium–ruthenium alloy with hydrochloric acid containing a small amount of nitric acid. Subsequent to dissolution ferrous sulphate solution was added to eliminate any oxidizing effect on the potassium iodide which is used at 0.01 molar strength as the titrant. The end-point was determined with the assistance of a centrifuge which encouraged coagulation and settling. The method produced an accuracy of 0.5% or better in the presence of 5% of nickel, iridium, platinum, rhodium, tungsten, molybdenum, copper and tin. For alloys containing gold or silver a modified technique was used. In the case of samples containing gold the mixture was allowed to stand for 1 h following addition of ferrous sulphate. With silver, the chloride was precipitated and aliquots of the supernatant liquid were removed from the measured volume. The error due to the volume of silver chloride presumably fell within the 0.5% expected from the method. In a second paper[5] the iodide method was extended to apply to a series of binary alloys of palladium with platinum, rhodium, iridium, silver, gold, copper, tin, molybdenum, tungsten and nickel. A slight modification was required to remove the increased amount of nitric acid used to dissolve the alloys. For the analysis of palladium–silver alloys the hydrochloric acid concentration was adjusted to dissolve the silver chloride, in which case the titer included both silver and palladium values, with the former determined separately by iodide titration in an ammoniacal solution. This modification will have very limited application. The authors[6] also recorded a general discussion of their procedures. Improvements in the technique of detecting end-points were described; the application of a potentiometric end-point was eliminated by the presence of ferrous sulphate. Reduction to palladium by ferrous sulphate occurred at elevated temperatures, low acidity, or large excess of the ferrous ion. Under the prescribed conditions this cloud method was shown to have an end-point corresponding to the stoichiometric value and to be free of any interference from adsorption or solubility effects.

As might be expected, other well known precipitating reactions have been adapted to volumetric determinations. Those thus applied are: sodium thiosulphate, dimethylglyoxime, 1-nitroso-2-naphthol, β-furfural dioxime, cupferron and diethyldithiocarbamate. The general difficulty of course is associated with ascertaining the stoichiometric end-point. Sodium thiosulphate was used by RYABCHIKOV[7] to titrate palladium potentiometrically in a neutral solution at 80°. The end-point corresponded to complete precipitation of palladium sulphide. Dimethylglyoxime was used by KARABASH[8] for samples of 1–50 mg of palladium in less than $0.2N$ hydrochloric or sulphuric acids and containing no gold or divalent platinum. A small amount of quadrivalent platinum was permissible. The ethanol solution of the titrant was standardized against pure palladium. Carbon tetrachloride or chloroform was added to the palladium solution and the extracted precipitate was periodically removed during the titration. As one approached the end-point care was taken to ensure the presence of a fresh carbon tetrachloride layer whose freedom from colour was taken as indicating the stoichiometric end-point.

A more ingenious application of dimethylglyoxime was proposed by BOBTELSKY and associates[9] who have applied "heterometric" determinations to a wide variety of volumetric analyses. The method involves a continuous measurement of optical densities of the precipitating medium during the course of the titration. These data are plotted against the volume of the titrating liquid with the stoichiometric end-point taken as the straight line intersection of the horizontal curve of maximum density and the titrating curve. Undoubtedly there is much of value in this approach to volumetric methods but it should be recognized, particularly for unfamiliar titrations, that the degree to which the titrating curve requires extrapolation to the intersection of the maximum density curve there is the possibility of a corresponding error. In experienced hands this source of error can often become insignificant. There is also the limitation that the method would hardly be applicable to other than very dilute solutions. From this point of view extractive methods, or the "cloud method" used by ATKINSON can offer desirable advantages. Furthermore, within this area of small concentrations there are competitive colorimetric or spectrophotometric procedures. For the direct microheterometric determination of palladium, BOBTELSKY used palladium contents of the order of a few milligrams or less and $0.01M$ dimethylglyoxime. The authors included a discussion of the effects of various buffers, complexing reagents, acidity and foreign dissolved constituents. Precipitation was complete at pH's less than 5 but at pH 11 there was complete dissolution. The examination of the effects of associated materials involved many cations which are not usually associated with the platinum metals and, inexplicably, included none of the associated platinum metals. However, with the exception of platinum and gold one would not expect a significant influence on the accuracy of the method. By a similar procedure BOBTELSKY and associates applied 1-nitroso-2-naphthol[10] and diethyldithiocarbamate[11] as titrants. Ethanol solutions of the former were used for quantities of palladium of the order of 0.2 mg or less. In the presence of uncoloured cations a red filter must be used, whereas with most coloured impurities a filter is not recommended. While chlorides should be absent, a large number of foreign cations as nitrates were without significant effect. The method is considered to be about three times more sensitive than the dimethylglyoxime procedure, although with the latter method copper did not interfere. It should be noted that the value of these heterometric investigations is not necessarily limited to the area of analytical chemistry. Interesting data concerning the compositions of precipitates corresponding to maximum density have been forthcoming. With α-nitroso-β-naphthol the rather surprising ratio of 1 palladium to 3 precipitant was recorded. With diethyldithiocarbamate[11] both palladium and gold could be determined from a single solution whose pH was close to that of pure acetic acid and which contained large excesses of ammonium chloride. Two points of maximum density were obtained, the first corresponding to the gold complex and the second to the sum of the gold and palladium complexes. If platinum is also present the second maximum density value corresponds to the sum of the three metal complexes. Determinations could be be made also in weakly basic solution by a modified and less desirable procedure. The methods are applicable to amounts of metals of the order of a milligram. Diethyldithiocarbamate had previously been used as a titrant by POLLARD[12] for weights of palladium between 0.01 to 1.0 mg. Approximately 50% hydrochloric acid must be present and sulphates, iodides and metallic impurities absent. The method involved prolonged heating in the presence of tin and tin(II) chloride, a filtration, and addition of benzene as an extractant. The carbamate titrant was added to an almost colorless solution and then the titration was continued in the presence of mercuric chloride which intensified the brown colour.

Back titrations

A variety of back titrations have been proposed for volumetric determinations of palladium. Perhaps the most generally suitable is the method recorded by MACNEVIN AND KREIGE[13]. These authors added a slight excess of EDTA to the palladium chloride solution adjusted to pH 10 ± 1, and back titrated with a standard zinc nitrate solution to the pink end-point of Eriochrome Black T. Of importance is the finding that platinum does not interfere. The fact that the method is not applicable in the presence of rhodium and osmium and that iridium and ruthenium may interfere at higher concentrations is not a particularly serious criticism of the method. These more insoluble platinum metals are often present in small proportions. The applicable range of concentration of palladium is a useful one.

An earlier EDTA titration was recorded by FLASCHKA[14]. In this method an excess of concentrated dipotassium tetracyano nickelate was added to the palladium solution which resulted in an exchange of metal to set free a stoichiometric amount of nickel ion. The latter was titrated in ammoniacal medium with EDTA to the violet of murexide indicator. The range of application was 0.3 to 3.0 mg of palladium. This method can also be a useful one.

KINNUNEN AND MERIKANTO[15] stated that the EDTA back titration, with murexide as the indicator, produced only approximate results. Alternative procedures were suggested. One method, applicable to the determination of palladium in platinum salts, involved the addition of the potassium nickel cyanide to a hydrochloric acid solution, followed by an ammonium chloride buffer, a measured excess of EDTA, ascorbic acid, and Eriochrome Black T. The excess of EDTA was titrated with manganous sulphate solution to the red colour, and then with standard EDTA to the blue colour. A second procedure, although less accurate, involved a simpler technique. With this method the excess EDTA was titrated in an acid medium with bismuth nitrate solution in the presence of pyrocatechol violet. In the author's opinion both methods are laborious and the data provided by the authors indicate neither high accuracy nor precision.

Back titrations involving prior isolation of palladium by some of the usual organic precipitants have been proposed. SYROKOMSKIĬ AND GUBEL'BANK[16] precipitated palladium by dimethylglyoxime, cupferron or furfural dioxime, then dissolved the purified complex with sulphuric acid, added a standard solution of the organic precipitant, and an excess of $V_2O_4(SO_3)_3$. The excess of the latter was titrated with standard ammonium ferrous sulphate. The method is cumbersome and is not recommended. A second procedure recorded by the authors[16] involved the isolation of palladium by precipitation as potassium or ammonium chloropalladate. Excess of ammonium ferrous sulphate was added, followed by a back titration with an oxidizing reagent. Neither the method nor the claim of non interference from small proportions of platinum is acceptable. A back titration method was proposed by GAHIDE[17]. This author worked with 12N sulphuric acid solutions containing 5 to 40 mg of palladium and precipitated the latter by a measured excess of standard salicylaldoxime. Subsequent to filtration the excess of reagent in the filtrate was hydrolyzed to form the hydroxylamine. Ferric sulphate was added and the resulting ferrous salt was titrated with standard potassium permanganate. The results recorded indicated indifferent accuracy and precision. Presumably there was little or no interference from gold or platinum. Attempts to use dimethylglyoxime and various other oximes failed.

An unusual type of back titration was proposed by BURRIEL AND PÉREZ[18] who treated a neutral palladium solution with an excess of standard potassium cyanide, then decomposed the free potassium cyanide by mercury(II) oxide and titrated the resulting hydroxide rapidly with sulphuric acid solution to a phenolphthalein endpoint.

PLATINUM

The volumetric determination of platinum remains a fertile field for the analytical researcher. Very few methods have been recorded and none is recommended for other than the most restricted application. This dearth of methods finds a partial explanation in the few really satisfactory precipitating reagents, the most efficient of which have only recently been recorded. In the author's opinion, there are now available, sufficient data to encourage those investigators who entertain an interest in the development of useful volumetric methods for platinum.

About the earliest volumetric methods for platinum were recorded by HINTZ[19]; DE KONINCK[20]; and by RUPP[21]. In general, the first methods required the isolation of platinum as the potassium or ammonium salt, reduction to metal, and subsequent titration of the released chloride by silver nitrate[19,20]. RUPP[21] used a measured excess of thallous nitrate to precipitate the platinum salt which was then filtered and the excess thallous salt determined by a sodium thiosulphate titration subsequent to the addition of dichromate and potassium iodide.

As might be expected one of the earliest known reactions of platinum suggesting the possibility of a volumetric application is that with potassium iodide. This approach has occupied the attention of a number of researchers but nothing of analytical application has been forthcoming. PETERSON[22] over a half century ago claimed success with a sodium thiosulphate titration of the iodine set free by treating a platinum salt with excess potassium iodide. It was assumed that the iodide reacted with the platinum salt to produce stoichiometric quantities of platinum(II) iodide and iodine. Although the author claimed that the results were accurate this claim may be disregarded. GRINBERG and co-workers[23] who have recorded a variety of volumetric methods for the platinum metals investigated the efficiency of the iodide method applied by a number of techniques. While the use of alcoholic solutions of iodine was inadmissible under all conditions, aqueous potassium iodide solution of iodine could be used to produce reasonably satisfactory results, *e.g.* 94–98% of the theoretical value. It was assumed that the reaction involved a complete exchange of iodine for chlorine in dipotassium tetrachloro platinate to produce the hexaiodo platinate. The method is slow, inaccurate, and is not recommended. GRINBERG and associates recorded also a series of procedures in which permanganate was used for the direct titration of platinum and of platinum together with iridium and iron[24–31]. The mechanism of the oxidation reaction was discussed and the product of the reaction with bivalent platinum was stated as an addition of two hydroxyl groups to form $K_2PtCl_4(OH)_2$[29]. In dilute sulphuric acid solutions bivalent platinum and trivalent iridium were oxidized by permanganate to $K_2PtCl_4(OH)_2$ and K_2IrCl_6. By potentiometric titration at 80–90°, it was possible to determine platinum in the presence of iridium. By a modified procedure the end-point could also be determined visually[31]. Quadrivalent platinum could also be determined by reducing with copper(I) chloride, oxidizing the excess of the latter in air and titration with permanganate to form $(PtCl_6)^{-2}$[25]. In a second paper[28] the author and associates recorded an application of this method for the determination of total platinum and iridium. The results indicated an accuracy of about 1%. For solutions of bivalent iron, trivalent iridium and bivalent platinum two volumetric methods were discussed[24,26]. The potentiometric titration resulted in a distribution of the platinum between the iron transition and the iridium transition[26]. With the second method the iron was determined potentiometrically by a cerous sulphate titration and the sum of the three constituents was similarly determined by a permanganate titration. Methods such as these are of theoretical interest but of little practical value. GRINBERG[27] also proposed a potentiometric titration for quadrivalent platinum and iridium which involved a reduction by copper(I) chloride. Separately, platinum was determined at 70° in solutions acidified to $0.05N$ HCl; iridium at 50° and $0.1N$ HCl. In determining the sum of the two quadrivalent metals, the nature of the titration curve depended upon the temperature, acidity, and the relative quantities of the metals. By control of these factors the curve showed either one or two breaks, one subsequent to reduction of iridium and the second, after the reduction of platinum. A number of investigators had devised volumetric methods based on this principle of reduction to the bivalent state. STELLING[32] reduced platinum by hydrazine and subsequently titrated potentiometrically with permanganate or bromate. MULLER AND TANZLER[33] used copper(I) chloride which had been standardized against potassium dichromate to titrate platinum made quadrivalent by chlorine. RYABCHIKOV AND NERSESOVA[34] titrated quadrivalent platinum and iridium potentiometrically with copper(I) chloride in an atmosphere of carbon dioxide. In a later procedure the platinum was reduced by excess copper(I) chloride and subsequently oxidized with standard ceric sulphate[7]. Similarly SYROKOMSKIĬ AND PROSHENKOVA[35] reduced platinum by ferrous sulphate and titrated the excess with ammonium metavanadate in the presence of phenylanthranilic acid as indicator. Ferric ion was complexed by either phosphate or fluoride. Again an atmosphere of carbon dioxide was required throughout the titration. Ascorbic acid has also been used for the quantitative reduction of quadrivalent platinum[36]. With 0.2N hydrochloric acid solutions of platinum the excess of ascorbic acid was titrated potentiometrically with ferric chloride[36]. Diethyldithiocarbamate was used as a titrant by POLLARD[37] for the determination of 1 to 0.01 mg of platinum in the presence of gold. Applied to silver assay beads, the latter were parted in a minimum of nitric acid. Strong hydrochloric was added to prevent the precipitation of silver chloride and to dissolve platinum and gold. The addition of tin(II) chloride resulted in the precipitation of gold and the formation of the coloured platinum constituent. The mixture was shaken with benzene and titrated with diethyldithiocarbamate to form a platinum complex which passed into the benzene layer along with the precipitated gold. The end-point was indicated by a colourless aqueous-acid layer. An adaptation allowed the determination of both gold and platinum.

In order to avoid interference from palladium, POLLARD[38] substituted tin(II) bromide for the chloride to precipitate both palladium and gold. This method was also applied to silver-assay beads. Subsequent to parting by nitric acid the silver, platinum and gold were dissolved in a strong hydrobromic acid solution. The resulting nitrosyl bromide and bromine were destroyed by hydroxylamine hydrochloride. Any of the insoluble platinum metals were removed at this stage; tin(II) bromide was added to produce the yellowish-brown platinum complex and to isolate metallic gold and palladium. The addition of benzene and subsequent titration with the carbamate to a colourless end-point permitted the direct determination of platinum. The data provided indicated very satisfactory accuracy and in the opinion of the present author the method is a useful one. There is here one of the few instances when the investigator has not ignored the difficulties incident to the methods of dissolution and separation encountered in analytical practice.

RHODIUM

Only two acceptably complete volumetric procedures for rhodium have been recorded. SYROKOMSKIĬ AND PROSHENKOVA[39] used a sodium bismuthate oxidation of rhodium in a previously fumed sulphuric acid solution. Subsequent to a filtration the quinquevalent rhodium was titrated with Mohr's salt to the yellow-green end-point of phenylanthranilic acid. The authors reported no interference from other platinum metals. However, MCBRYDE AND CLUETT[40] found that in the presence of iridium the reduction of sodium bismuthate was accelerated and rhodium values were low. The oxidation of iridium proceeded to an indefinite stage. These data suggest a very restricted area of application and furthermore, one can expect difficulty with the slowly developing end-point. The precipitating reagent thionalide was applied volumetrically by KIENITZ AND ROMBOCK[41]. The rhodium solution was fumed to remove chloride ion which interfered by producing a precipitate of the rhodium thionalide mixed with rhodium chloride. The method involved the precipitation of rhodium by excess of thionalide, and titration of the latter by standard iodine to a slight excess of the latter, and back titration with sodium thiosulphate. The method requires a simple technique but is less accurate than existing gravimetric methods. Ascorbic acid has also been used as a titrant for quadrivalent rhodium.

PSHENITSYN AND PROKOF'EVA[42] applied this reagent to the volumetric determination of both rhodium and iridium.

IRIDIUM

Approximately one dozen volumetric methods for iridium have been recorded. Most of these are potentiometric titrations which involve the oxidation of iridium from the trivalent state or the reduction of iridium from the quadrivalent state. In a few cases visual observation of the end-point was considered feasible. None of these latter procedures is recommended.

SHOW-CHOW AND YOST[43] claimed good results from a sodium thiosulphate titration of the iodine liberated from a hydrochloric acid solution containing quadrivalent iridium and excess of potassium iodide. This procedure was unacceptable to GRINBERG and co-workers[28,31] and this decision would seem to be the more acceptable. GRINBERG used copper(I) chloride to produce trivalent iridium. The solution was air oxidized to eliminate the cuprous copper and titrated potentiometrically with potassium permanganate[28]. The results were accurate to about 1%. RYABCHIKOV AND NERSESOVA[34] titrated quadrivalent iridium potentiometrically with copper(I) chloride in an atmosphere of carbon dioxide. The method is relatively unsatisfactory due to the sensitivity to oxidation of the titrant. Various authors have used hydroquinone or related compounds as reducing reagents[7,44-47]. RYABCHIKOV[7,47] standardized hydroquinone against an iridium solution of known value. Chlorine was used to ensure the initial quadrivalent state. MILAZZO AND PAOLONI[45] used hydroquinone as a titrant with *o*-dianisidine as an indicator. PSHENITSYN AND PROKOF'EVA[46] used diphenylamine as an indicator. Hydroquinone was used by POLLARD[48] for the determination of quantities of iridium of the order of 0.1 to 0.001 mg. Subsequent to the isolation of iridium by methods, some of which are not consistently reliable, the solution of iridium was treated with a lithium sulphate–sulphuric acid reagent, perchloric acid, and dichlorobenzidine indicator, and heated according to an accurately measured time schedule to produce the usual mauve iridium constituent. This solution was titrated with hydroquinone, previously standardized against pure iridium, to the disappearance of the yellow colour of the dichlorobenzidine indicator, a drop of which was added near the completion of the titration. A confirming determination should always be made by re-oxidation and a second titration. The authors' data indicate a surprising degree of accuracy and precision. The mauve colour development recommended is comparable to that which found later application in spectrophotometric methods and the experience with this method gained by the author and co-workers does not encourage a recommendation for this volumetric method. The susceptibility of colour intensity to the various factors which influence the equilibria involved in the production of this mauve colour suggest the need for further data. Until these data are provided the method will remain suspect.

Titanium(III) chloride[40,46] and tetrapotassium hexacyanoferrate[45,49] have also been applied as titrants. Ferrous sulphate and Mohr's salt have also been used frequently for the volumetric determination of iridium. GRINBERG AND PTITZUIN[31] were able to follow potentiometrically the reduction of sulphuric acid solutions of quadrivalent iridium by Mohr's salt, and also quantitatively to re-oxidize the trivalent iridium with potassium permanganate.

Both of these methods were recommended by KOZYAR[50] to produce an accuracy of 0.2%. There was no interference from quadrivalent platinum, trivalent rhodium and divalent palladium. MCBRYDE AND CLUETT[40] used the ferrous sulphate reduction of solutions of iridium previously fumed with sulphuric acid and then oxidized with ceric sulphate for a period of about 10 h. A direct oxidation of iridium(III) was unsuccessful due probably to the slowness of the reaction. Titanium(III) chloride could also be used for the reduction titration. Platinum and rhodium did not interfere. Ruthenium and osmium could be removed by prior oxidation; with the latter metal, nitric acid was added to produce the volatile octovalent oxide. In addition to the end-point indicated by the reduction of cerium(IV) sulphate there were two end-points involved in the complete reduction of iridium to the trivalent state. The first represented a one equivalent reduction and the second step a 1/2 equivalent reduction. Of advantage is the fact that just prior to the final end-point the solution becomes colourless. The method was applicable to quantities between 2 and 20 mg and the accuracy for the larger samples was of the order of 1%.

PSHENITSYN and co-workers[42,46] also used ferrous sulphate as a titrant with *o*-phenanthroline as an indicator. In a later publication[42] ascorbic acid was used although the errors were as high as 5%. Platinum and rhodium did not interfere.

Of the volumetric methods available for iridium the author recommends the reduction by ferrous sulphate. With all of the methods a degree of isolation is required. While no reference to the influence of gold is included for the methods it is probable that all of the recorded reducing reagents will precipitate this metal. Prior treatment of the solution by fuming with sulphuric acid would probably remove both gold and platinum as metals with the possibility of some slight dissolution of the latter metal. Of interest in this volumetric method is the fact that rhodium is not generally an interfering element and the advantage of this factor lies in the frequent association of rhodium and iridium in somewhat comparable proportions.

RUTHENIUM

Very few methods for the determination of ruthenium have been recorded. Until recently no reliable method for the quantitative recovery of the metal was known. Simultaneously with improvement in the precipitation as a hydrated oxide there appeared a volumetric method which involved a titration with tin(II) chloride. The procedure entailed a reduction of ruthenium to the trivalent state by an excess of standard tin(II) chloride which was back titrated with iodine in the presence of starch. HOWE[51] used this method but reported a tendency toward low values for which no satisfactory explanation was available. CROWELL AND YOST[52] used two volumetric methods during their investigation of the various oxidation states of dissolved ruthenium halides. In one procedure an excess of potassium iodide was added to ruthenium chloride in hydrochloric acid solution and the liberated iodine was titrated with sodium thiosulphate. The second method required a potentiometric titration of quadrivalent ruthenium with titanium(III) chloride. Their data indicate a quantitative reduction from the quadrivalent to the trivalent state with solutions previously oxidized with chlorine. In the absence of the latter the discontinuity in the titration curve suggested the existence of both the trivalent and quadrivalent states. Since this publication was not directed toward the analytical field, few of the necessary techniques were discussed. The titanium(III) chloride titration was also examined by PSHENITSYN AND GINZBURG[53], who stated that two potential jumps were present in their titration curve. The first, corresponding to a change of one half an equivalent weight of ruthenium, and resulting from an intermediate equilibrium mixture of constant proportions of quadrivalent and trivalent ruthenium, made possible by a high rate of equilibrium. The second break corresponded to the formation of trivalent ruthenium. Comparable results were obtained from both discontinuities.

OSMIUM

One of the first volumetric methods for the determination of osmium was developed by KLOBBIE[54] who added potassium iodide to a sulphuric acid solution of the octavalent oxide and titrated the liberated iodine with sodium thiosulphate. The author claimed an accuracy of 0.01%. This claim is unacceptable. The end-point in the green solution cannot be determined with good precision. For small amounts of osmium the usual modification of reducing the strength of the sodium thiosulphate is ineffective because of the considerable decrease in the time of reaction. With large amounts of osmium the detection of the end-point becomes increasingly difficult because of the deeper colour of the reduced osmium. CROWELL AND KIRSCHMAN[55] modified the method to avoid air oxidation of the potassium iodide. SAITO[56] proposed the use of benzene as an aid in ascertaining the end-point. RYABCHIKOV[47,57] used the iodide method in a potentiometric titration. This author[7] also titrated directly, by a potentiometric method, an alkaline solution of octovalent osmium to produce a sexivalent state. The drop in potential at the equivalence point, while not large, was quite distinct. CROWELL *et al.*[55,58,59] applied this approach to develop a number of volumetric methods for osmium. Hydrazine sulphate[55] was used a titrant resulting in a reduction of octovalent osmium to the quadrivalent state in a hydrobromic acid solution whose final acidity was 1.5*N*. To avoid the error due to the volatility of osmium in an acid medium the authors prepared sealed glass tubes containing the osmium added as an alkaline solution, together with hydrobromic acid, and a slight deficiency of hydrazine sulphate determined by a prior titration. The reaction was induced by a boiling period after which the tube was broken, washed out with hydrobromic acid solution and titrated potentiometrically at 70°. The method was applied satisfactorily to amounts of osmium of the order of 2 mg. Compared to a gravimetric and the volumetric iodide method the results from three methods agreed within 0.3%. In later publications CROWELL[58-60] reported a volumetric method for octovalent and for quadrivalent osmium based on the difference in equilibria of osmium salts in dilute and concentrated solutions of hydrobromic acid. In 8*N* hydrobromic acid the reaction was practically complete in the direction of formation of quadrivalent osmium and bromine. Potentiometric titration with hydrazine sulphate of the bromine produced permitted the determination of octovalent osmium with an accuracy of about 0.2%. The octovalent oxide in an alkaline medium was sealed into a pyrex tube containing an ice-cold solution of concentrated hydrobromic acid; the tube was heated, cooled and broken into a slight deficiency of hydrazine sulphate solution and the titration of the residual bromine was then completed potentiometrically. With solutions of osmium containing about 0.1*N* hydrobromic acid, quadrivalent osmium reacted in the direction opposite to that in 8*N* acid. The osmium could then be determined by a similar measurement of the bromine consumed. In this procedure the sealed tube contained a measured volume of standard bromine solution. Titanium(III) chloride was also used as a titrant[60] to produce quadrivalent and trivalent osmium, but its relative instability makes it a lesser desirable standard than hydrazine sulphate. Furthermore this method is quite inaccurate. All of these techniques are cumbersome and since the accuracy depends upon forcing equilibria to practical completion, one cannot use these methods with confidence. They will find little application in general practice. In the author's opinion this is also true of the chromous sulphate method recorded by CROWELL AND BAUMBACH[59]. The titrant is exceedingly sensitive to oxidation and the technique involved in the procedure, while capable of yielding acceptable results in the hands of an experienced operator, will not encourage any extensive application.

A back titration method was recorded by SYROKOMSKIĬ[61]. The octovalent osmium dissolved in 4 – 6N sulphuric acid was reduced to the quadrivalent state by passing the solution over bismuth granules. Quantitative oxidation to the sexivalent state was accomplished by the addition of a measured excess of ammonium *meta*vanadate. This excess was determined by a ferrous sulphate titration with phenylanthranilic acid. Any lack of accuracy by this procedure finds some compensation in relative simplicity of operation.

SUMMARY

The published methods for the volumetric determination of the six platinum metals have been appraised. The lack of generally applicable and accurate methods is emphasized. No volumetric method has been recorded for the direct application to solutions of platinum metals, ores, concentrates or natural alloys, and only a few for determinations in synthetic alloys such as fire assay beads. Volumetric methods for the platinum metals are characterized by the absence of data concerning methods of dissolution.

RÉSUMÉ

L'auteur passe en revue les méthodes volumétriques publiées pour le dosage des six métaux de la mine de platine. On constate un manque de méthodes générales et précises, ainsi que de données concernant les mises en solution.

ZUSAMMENFASSUNG

Die bekannten volumetrischen Methoden zur Bestimmung der 6 Metalle der Platingruppe werden einer kritischen Betrachtung unterzogen. Es wird das Fehlen von genauen, allgemein anwendbaren Methoden sowie Vorschriften zur Auflösung dieser Metalle hervorgehoben.

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THE DETERMINATION OF TITANIUM WITH EDTA

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The work of SCHWARZENBACH and co-workers has led to many applications of EDTA* in analytical chemistry. A large number of publications have appeared in the literature presenting useful data and methods for the application of EDTA to analytical problems.

This work was initiated to clarify some conflicting opinions on the conditions under which EDTA could be used for the determination of titanium. A method has been proposed[1] for the determination of titanium in which an excess of EDTA is added to a titanium solution and the excess determined by a back titration with standard copper. Pyrocatechol violet is used as an indicator, and the solution is buffered at a pH of 5.3–6.0 with pyridine acetate. It was reported that the indicator color change was irreversible.

The author has tried this procedure as well as buffering at pH of 4–5 with sodium acetate–acetic acid[2] with little success. The failure of the method can be attributed to the formation of a hydrous oxide precipitate which results in a release of EDTA from the titanium–EDTA complex. This was quite evident from the appearance of a precipitate or cloudiness in the solution and from the values obtained on a standard titanium solution. The results shown in Table I demonstrate the unsatisfactory values obtained by back titration with copper over the pH range of 4–6.

The condition mentioned above is even more serious in the actual analysis of a metallurgical sample. In this laboratory the methods of separation of titanium from interfering elements usually finish with the titanium present in strong hydrochloric or hydrofluoric acid. In either case the acid must be removed. This is usually done by the

TABLE I

TITRATION OF Ti WITHOUT PEROXIDE

Sample No.	*Cu used*	*Cu required*	*Error mg Ti*
1	3.99	2.94	1.5
2	3.99	2.94	1.5
3	3.77	2.94	1.2
4	4.30	2.94	2.0
5	3.73	2.94	1.1
6	3.74	2.94	1.1
7	3.77	2.94	1.2

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* Ethylenediaminetetraacetic acid.

addition of a few ml of sulfuric acid followed by evaporation to copious fumes. Attempts to use the previously mentioned procedure invariably resulted in more severe precipitation of titanium because of the necessity of neutralizing the excess acid.

PECSOK AND MAVERICK[3] have studied the titanium-EDTA complex polarographically. They suggest that at a pH greater than 2, the complex contains oxygen. The half-wave potential is pH-dependent over the pH range of 2-8, and the solutions were often visually cloudy.

It is apparent that the interference in the method is caused by a side reaction, namely, the precipitation of hydrous titanium oxide. A possible mechanism for this side reaction is the initial formation of a titanium-EDTA-oxygen (or hydroxy) complex followed by polymerization through oxygen bridges. This process would continue by the formation of sufficiently large aggregates to form colloidal hydrous titanium oxide and finally result in a precipitate. This would release EDTA in solution and produce an error in the back-titration.

If this mechanism is correct, the reaction could be inhibited by substituting some other group in the complex in place of oxygen or hydroxy ions.

In order to conform to the stipulation that the titanium would be present in a concentrated sulfuric acid after its separation, a substituent group was desired which would allow neutralization of the titanium solution from concentrated sulfuric acid to a pH of approximately 4.8 without interfering with the 1:1 relationship between EDTA and titanium. Tartaric acid and hydrogen peroxide were selected for a preliminary investigation. Tartaric acid masked titanium almost completely, which made its use in the titration impossible. Hydrogen peroxide proved promising and was investigated further. It has been reported that hydrogen peroxide does not interfere in the titration[1,2], but in both papers the recommended procedures do not include hydrogen peroxide in the method. SWEETSER AND BRICKER[4] determined titanium with EDTA by means of a back titration with an iron solution, using a spectrophotometric end-point. The titration was performed at a pH of 1.7 but the results were 0.7-1.5 % low. They suggest that the error is caused by the displacement of titanium from its EDTA complex by iron[4]. They also found that the titanium is not displaced by the iron when peroxide is present at a pH of 1.7 and that a 1:1 titanium-EDTA complex is formed.

EXPERIMENTAL

To aliquots of the standard titanium in a 250-ml beaker were added 3 drops of 30 vol. % hydrogen peroxide, an excess of EDTA, and 10 ml of sodium acetate-acetic acid buffer. The resulting orange solution was diluted to approximately 100 ml and, while stirring with a magnetic stirrer, the solution was neutralized to a pH of 4-5 by the addition of a 50 % sodium hydroxide solution from a polyethylene wash bottle. After neutralization, eight drops of PAN [1-(2-pyridylazo)-2-naphthol; 0.05% in ethanol] were added and the solution back-titrated with a standard copper solution. The color change at the end-point was from orange to orange-red. The results of analysis of the standard solution are shown in Table II. The method was applied to alloy samples (after separation of titanium) by the method below.

PROCEDURE

To the hydrofluoric or hydrochloric acid titanium fraction in an appropriate vessel add 10 ml of 1 : 1 sulfuric acid and evaporate to copious fumes. Cool to room temperature, add 10-15 g of ice (from distilled water) followed immediately by 3 drops of 30 volumes hydrogen peroxide. (At this point, for large amounts of titanium, transfer the solution to a volumetric flask, dilute to volume with water and take an appropriate aliquot.) Add a 5–10 ml excess of EDTA solution, dilute to approximately 100 ml with water, neutralize with 50% sodium hydroxide (to pH of 4–5) and add 8 drops of PAN indicator. Back-titrate with standard copper solution to color change from orange to orange-red.

TABLE II

TITRATION OF Ti WITH PEROXIDE

Sample No.	*mg Ti present*	*mg Ti found*	*Error mg Ti*
1	10.28	10.26	0.02
2	10.28	10.25	0.03
3	10.28	10.25	0.03
4	10.28	10.26	0.02
5	10.28	10.27	0.01
6	10.28	10.23	0.05
7	10.28	10.20	0.08
8	10.28	10.20	0.08
9	10.28	10.20	0.08

DISCUSSION

The addition of peroxide to the titanium solution containing EDTA before adjusting the pH definitely inhibits the precipitation of hydrous titanium oxide. This is evident by the fact that the solution remains clear throughout the titration. One would normally expect a hydrogen complex, such as TiHY, in strong acid solution; however, in view of the orange color present in strong acid (with hydrogen peroxide present) it appears that the titanium complex contains one or more peroxide molecules in place of the hydrogen ion. The orange color present in the titanium-EDTA-peroxide system at a pH of 4-5 indicates that one or more peroxide molecules also are present in the complex under these conditions. Furthermore, since precipitation occurs in the absence of hydrogen peroxide but does not occur in its presence, it is suggested that the hydroxy (or oxygen) ion is displaced by peroxide, which inhibits the mechanism of precipitation.

The indicator color is reversible when peroxide is used. In experiments without peroxide, in which precipitation invariably took place, the color change with pyrocatechol violet was irreversible. This phenomenon can be explained by the formation of colored lakes by the indicator and hydrous titanium oxide or by the irreversible adsorption of the copper indicator complex on the surface of hydrous titanium oxide.

It is well known that with PAN and pyrocatechol violet the color change during a back titration with copper is reversible. In determinations in which an irreversible color change occurs during a back-titration with copper, it should be taken as evidence that some side reaction is taking place and the method should be investigated more thoroughly before applying it to analytical problems in the laboratory.

SUMMARY

The determination of titanium EDTA by means of a back-titration with standard copper has been investigated. The phenomenon of an irreversible color change has been eliminated by the addition of hydrogen peroxide prior to the addition of EDTA and adjustment of pH.

It is theorized that peroxide displaces the hydroxyl (or oxygen) ion in the hydroxy-EDTA-titanium complex and thus inhibits precipitation.

References p. 116

RÉSUMÉ

L'auteur étudie le dosage du titane par l'acide éthylènediaminotétracétique par titrage indirect au moyen d'une solution étalon de cuivre. Une addition de peroxyde d'hydrogène permet d'éviter le phénomène du changement de coloration irréversible. Le peroxyde déplace l'ion hydroxyle (ou l'oxygène) du complexe hydroxy-EDTA-titane et empêche ainsi la précipitation.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Titan mit EDTA durch indirekte Titrierung mit einer Standard-Kupfersalzlösung beschrieben. Ein Zusatz von Wasserstoffsuperoxyd verhindert das Auftreten eines irreversiblen Farbumschlages. Vermutlich wird das OH-(oder Sauerstoff) Ion des Hydroxy-EDTA-Ti Komplexes durch das Peroxyd verdrängt, wodurch die Bildung eines Niederschlages verhindert wird.

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THE DETERMINATION OF LITHIUM IN LITHIUM-MAGNESIUM ALLOYS

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As would be expected from the similarity in the size to charge ratio of lithium and magnesium, the separation of these two elements by gravimetric methods is difficult. The methods generally used for the determination of lithium are based on precipitation as an insoluble aluminate, fluoride, or phosphate. Magnesium interferes with these procedures.

Lithium is conveniently determined in many materials by flame photometry; however, it has been reported that the characteristic emission of lithium is quenched by magnesium[1]. In view of the unfavorable ratio of magnesium to lithium in the alloys under consideration, the application of the flame photometer was not investigated.

Recent advances in the applications of ion exchange resins in analytical chemistry have shown excellent results in the separation of elements with closely related properties. The separation of rare earth elements best illustrates this fact.

Samuelson and Schramm[2] have suggested a method for the separation of sodium and potassium from the transition elements by using an anion exchange resin in the citrate form to absorb the heavy metals. The alkali metals in the form of their citrates are passed through a second column, coupled to the first, to convert the alkali metal salts to hydroxides. The hydroxides were determined by titration with a standard acid. Magnesium accompanies the alkali metals[3].

In a subsequent publication[4], EDTA was substituted for citrate in order to separate calcium and magnesium from the alkali metals. Lithium and magnesium could not be separated in aqueous solution. By lowering the pH in the resin phase and by eluting with a 60% ethyl alcohol solution, the separation of lithium and magnesium was accomplished.

The favorable relationship in the absorption of lithium and hydrogen by a strongly acidic cation exchange resin indicated that a suitable separation of lithium and magnesium could be attained on a cation exchange resin. The separation on a cation exchange resin, by eluting the lithium with dilute acid, would simplify the regeneration of the column and provide a rapid separation.

EXPERIMENTAL

Initial experiments were conducted with synthetic samples. These samples consisted of aliquots from a standard lithium solution to which were added sufficient magnesium carbonate to approximate the magnesium content in the alloys of interest. Excess hydrochloric acid was added to each sample to dissolve the magnesium carbonate and the samples taken to dryness on a hot plate. The samples were redissolved in water and sufficient dilute hydrochloric acid added to give a clear solution. The sample solution was then transferred to an ion exchange column (1 cm I.D. × 50 cm long) containing a strongly acidic ion exchange resin (H^+ form, 100–150 mesh) with water. After all the sample was rinsed onto the resin with water, the lithium was eluted with 0.5N hydrochloric acid. The eluate was checked frequently for lithium by catching a drop on a platinum wire and applying the flame test for lithium. It was observed that the eluate from washing the sample into the resin with water never contained lithium and that the first 150-ml fraction of 0.5N hydrochloric acid contained all the lithium. This was determined with several different columns.

The eluate containing the lithium was evaporated to dryness, dried for 1 h in an oven at 110° and dissolved in 50 ml of water. The lithium was determined by titration of the chloride from the lithium chloride residue with silver nitrate. The results of eight synthetic samples are shown in Table I.

TABLE I

Sample No.	*Li present* *mg*	*Li found* *mg*	*Mg present* *mg*
1	10.14	10.12	90
2	10.14	10.11	90
3	10.14	10.23	90
4	10.14	9.97	90
5	10.14	10.19	90
6	10.14	10.05	90
7	10.14	10.18	90
8	10.14	9.95	90
	average	10.10	

PROCEDURE

Dissolve a 0.5-g sample in dilute hydrochloric acid and evaporate to dryness. Dissolve the residue in water and sufficient hydrochloric acid to give a clear solution. Transfer to a 100-ml volumetric flask and dilute to volume with water. Transfer a 10-ml aliquot to the ion exchange column and wash the sample into the resin with water. Discard the eluate from the washings and elute the lithium with 150 ml of 0.5N hydrochloric acid into a 250-ml beaker. Evaporate the solution containing the lithium to dryness and dry the beaker in an oven at 110° for 1 h. After cooling, dissolve the residue in water and titrate the chloride with silver nitrate.

$$\% \text{ Li} = \frac{(\text{vol. of AgNO}_3)\ (N \text{ of AgNO}_3)\ (\text{mol. wt. of Li}) \times 100}{(\text{sample wt.})\ (1/10)}$$

The column is prepared for the next sample by eluting the magnesium with $4N$ hydrochloric acid (2 column volumes) followed by washing with water until neutral.

DISCUSSION

The volume used for the elution of lithium was suitable for the columns and the resin used in this work. Since the particle size of resins varies somewhat from one lot to the next, it is necessary to determine the volume of eluate which contains the lithium when a different lot of resin is used as well as for columns with different dimensions. The resin was supported in the columns in this investigation by means of a coarse glass frit. The flow rate was restricted only by the normal back pressure in the column and varied from 10 to 11 ml per min for the columns used.

A precaution which must be taken into account is the calculation of per cent lithium. Some caution is needed in the analysis of lithium today since the lithium routinely available may consist of an unusual mixture of isotopes. With elements of low atomic weight, such as lithium, variations from the normal isotopic mixture may cause significant errors.

In the analysis of alloys small amounts of heavy metals will remain in the column with magnesium provided the solution is acidified slightly before diluting to volume. Failure to add sufficient acid to obtain a clear solution may result in colloidal aggregates which may pass through the column.

SUMMARY

An ion exchange method has been developed for the determination of lithium in lithium–magnesium alloys. Lithium is separated from magnesium by eluting lithium from a strongly acidic cation exchange resin with $0.5N$ hydrochloric acid. Attention is drawn to the fact that considerable quantities of unusual mixtures of lithium isotopes are in existence, and may cause significant errors if their composition is unknown to the analyst.

RÉSUMÉ

Une méthode par échange d'ions est proposée pour le dosage du lithium dans des alliages lithium–magnésium. Le lithium est séparé du magnésium par élution au moyen d'acide chlorhydrique $0.5N$.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Lithium in Lithium–Magnesium Legierungen mit Hilfe von Ionen-Austauschern beschrieben. Die Trennung vom Magnesium erfolgt durch Eluieren mit $0.5N$ Salzsäure.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES. II

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Antimonates

In earlier publications[1-3] from this laboratory dealing with the behaviour of insoluble substances, a number of substances have been reported that become resistant towards the action of acids on heating to a high temperature. None of the antimonates has so far been reported as being insoluble in acids but our investigations have shown that the antimonates of many metals if heated to 900° for two hours in a muffle furnace become very difficultly soluble in concentrated acids.

With regard to the preparation of antimonates the general method followed consisted in adding an aqueous solution containing the chloride or sulphate of the metal to a hot dilute aqueous solution of potassium dihydropyroantimonate. An aqueous solution of potassium dihydropyroantimonate is regarded as potassium dihydroantimonate[4], KH_2SbO_4 and the precipitates obtained by precipitation may thus be regarded as dihydroantimonates which on heating to a high temperature change into metantimonates.

$$NiCl_2 + 2\ KH_2SbO_4 \rightleftharpoons Ni(H_2SbO_4)_2 + 2\ KCl$$

$$Ni(H_2SbO_4)_2 \xrightarrow{\text{Heat}} Ni(SbO_3)_2$$

The precipitated antimonates were filtered and washed with water. All the antimonates prepared by the above method were found to be soluble in acids but were rendered insoluble on heating to 900° for two hours in a muffle furnace. Of course, before they were subjected to the standard acid treatment, all of them were treated with dilute hydrochloric acid to extract any impurity that may be present.

To measure the extent of insolubility of the heated antimonates, the procedure outlined in an earlier paper[3] of this series was followed. After the acid treatment the heated antimonates should be washed with dil. HCl and not with pure water as some of them tend to form a suspension with pure water.

The heated antimonates were also analysed to determine their percentage composition. Weighed amounts of the substances were fused with caustic potash, potassium nitrate being added when chromium was present and potassium carbonate in the case of calcium, strontium or barium. Sodium salts alone or in combination with potassium salts cannot be used for fusion because of the precipitation of sodium antimonate which is much less soluble than the potassium salt in water. Antimony was estimated in the filtrate as antimony pentasulphide[5] and the other metals by well-known methods. Percentage composition of the heated antimonates was calculated and found to be the same as that of the metantimonates (without the combined water) reported in the literature. Only in the case of aluminium did the composition of the heated substance correspond to a mixture of ortho- and metantimonates, and in the case of zirconium to that of zirconyl pyroantimonate.

TABLE I

ANTIMONATES

Name of the compound	*Two hours ignition at 900°*		*Nine hours additional ignition at 900°*		*0.01 g of the substance in one standard acid treatment*	*Formula given in literature*	*Formula found*
	Percentage left undissolved in		*Percentage left undissolved in*				
	one standard acid treatment	*five standard acid treatments*	*one standard acid treatment*	*five standard acid treatments*			
1. Beryllium metantimonate	94.6	86.6	96.8	92.3	Does not dissolve completely	$Be(SbO_3)_2$	$Be(SbO_3)_2$
2. Magnesium ,,	99.3	98.4	—	—	,,	$Mg(SbO_3)_2$	$Mg(SbO_3)_2$
3. Zinc ,,	99.5	99.4	—	—	,,	$Zn(SbO_3)_2$	$Zn(SbO_3)_2$
4. Cadmium ,,	98.4	93.8	98.8	95.3	,,	$Cd(SbO_3)_2$	$Cd(SbO_3)_2$
5. Chromium ,,	97.4	93.4	98.0	94.9	,,	$Cr(SbO_3)_3$	$Cr(SbO_3)_3$
6. Manganese ,,	99.7	98.0	—	—	,,	$Mn(SbO_3)_2$	$Mn(SbO_3)_2$
7. Cobalt ,,	99.3	99.0	—	—	,,	$Co(SbO_3)_2$	$Co(SbO_3)_2$
8. Nickel ,,	99.8	99.7	—	—	,,	$Ni(SbO_3)_2$	$Ni(SbO_3)_2$
9. Copper ,,	99.8	99.0	—	—	,,	$Cu(SbO_3)_2$	$Cu(SbO_3)_2$
10. Calcium ,,	99.2	99.0	—	—	,,	$Ca(SbO_3)_2$	$Ca(SbO_3)_2$
11. Strontium ,,	99.6	99.4	—	—	,,	$Sr(SbO_3)_2$	$Sr(SbO_3)_2$
12. Barium ,,	68.4	66.0	95.8	83.1	,,	$Ba(SbO_3)_2$	$Ba(SbO_3)_2$
13. Aluminium antimonate	99.9	99.6	—	—	,,	$\begin{bmatrix} AlSbO_4 \\ Al(SbO_3)_3 \end{bmatrix}$	$\begin{bmatrix} AlSbO_4 \\ Al(SbO_3)_3 \end{bmatrix}$
14. Thorium metantimonate	98.6	96.2	99.5	98.0	,,	—	$Th(SbO_3)_4$
15. Zirconyl pyroantimonate	98.4	97.6	98.5	97.6	,,	$Zr_2Sb_2O_9$	$Zr_2Sb_2O_9$
16. Uranium antimonate	86.4	76.5	91.4	80.6	,,	$UO_2 \cdot 1.22Sb_2O_5$	$UO_2 \cdot 1.22Sb_2O_5$

Stannates and arsenates

The behaviour of the corresponding arsenates and stannates was also investigated but though the difficultly soluble salts are precipitated on mixing the solution of sodium stannate and disodium hydrogen arsenate with the metallic salt solution, unlike antimonates, they are not rendered insoluble in acids on heating to a high temperature. The stannates decompose leaving a residue of stannic oxide, while arsenates form pyroarsenates which are soluble in acids. The only exceptions are the arsenates of the three metals reported in the previous paper[3] and that of tin which also becomes insoluble to the extent of about 99%.

To see how far these insoluble compounds would be affected when preparing the sodium carbonate filtrate for the detection of the anions, the heated compounds were boiled with about 10% sodium carbonate solution for ten minutes. It was found that most of the heated compounds were not at all affected by this treatment. The exceptions were the arsenates of zirconium, titanium and tin, which are attacked to a slight extent and manganic metaphosphate which is completely decomposed.

SUMMARY

The antimonates of Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr and U when heated to 900° were found to become sufficiently resistant to the standard acid treatment to be considered insoluble. The corresponding stannates do not become insoluble on being subjected to this treatment. The corresponding arsenates with the exception of those of Zr, Ti, Cr and Sn also do not become insoluble on being heated.

RÉSUMÉ

Les antimoniates de Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr et U, chauffés à 900° résistent suffisamment au traitement par un acide pour être considérés comme insolubles, contrairement aux stannates et aux arsénates correspondants (à l'exception de ceux de Zr, Ti, Cr et Sn).

ZUSAMMENFASSUNG

Die Antimonate von Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr und U werden durch Erhitzen auf 900° genügend säure-unempfindlich, dass sie als „unlöslich" bezeichnet werden können. Die entsprechenden Stannate and Arsenate (letztere mit Ausnahme von Zr, Ti, Cr und Sn) bleiben nach dieser Behandlung säure-löslich.

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SEPARATIONS INVOLVING PALLADIUM

SEPARATION OF LEAD, BISMUTH, CADMIUM, THALLIUM, COPPER, COBALT AND NICKEL FROM PALLADIUM

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In the new and more comprehensive scheme of qualitative analysis[1], the use of 1% dimethylglyoxime to separate palladium from other metals of the copper group has been recommended. In the present investigation an attempt has been made to carry out this separation on a quantitative basis and quite satisfactory results have been obtained. The quantitative separation of palladium from rhodium with dimethylglyoxime is already well-known and has been omitted.

EXPERIMENTAL

Separation of palladium from lead

Measured volumes of standard solutions of palladium chloride[2] and lead acetate[3] were mixed, treated with 20 ml of 12*N* hydrochloric and diluted to 100 ml to adjust the concentration of acid to 2-3*N*. The mixture was treated with 20 ml of 1% dimethylglyoxime solution in alcohol and allowed to stand for an hour with occasional shaking to complete the precipitation of palladium. The precipitate of palladium complex was filtered through a weighed sintered glass crucible (porosity 4), washed with hot water containing a few drops of 2*N* hydrochloric acid (the filtrate being reserved for the estimation of lead), then with 50% alcohol, dried at 110° for an hour and weighed.

The filtrate was concentrated to a small volume and organic matter destroyed by evaporating to fumes with sulphuric acid and concentrated nitric acid. The solution was diluted to 25 ml and again evaporated to fumes to destroy nitroso-compounds which may interfere in the subsequent precipitation of lead as sulphide. The free acid was neutralized with ammonia (sp.gr. 0.88) and the precipitate of lead sulphate dissolved by adding ammonium acetate (solid). The solution was cooled in ice and treated with 20-30 ml of 2*N* sodium sulphide reagent[4] followed by enough 6*N* acetic acid to render the mixture acid. The mixture was heated to boiling to completely precipitate lead as sulphide. The precipitate of lead sulphide was weighed after suitable treatment.

In the filtrate from palladium, lead can also be estimated as sulphate, but the procedure of evaporating to fumes with H_2SO_4-HNO_3 has to be repeated 2-3 times in order to remove hydrochloric and acetic acids completely.

45-58 mg of palladium could be separated from 49-62 mg of lead. The metals were recovered with an accuracy of: Pd 0.0 to —0.27% and Pb 0.0 to —0.29%.

Separation of palladium from bismuth and cadmium

Standard solutions of palladium chloride and bismuth chloride[5] or cadmium sulphate[5] were used. The procedure given for the separation of palladium from lead was followed. Palladium was estimated as the dimethylglyoxime complex. In the filtrate bismuth and cadmium were estimated as sulphides. The precipitate of cadmium sulphide was washed thoroughly with alcohol and ether successively, dried at 105° for 1 h and weighed.

45-58 mg of palladium could be separated from 46-59 mg of bismuth or 44-56 mg of cadmium. The metals were recovered with an accuracy of:

Pd 0.0 to —0.26% and Bi +0.06 to —0.3%;
Pd 0.0 to —0.28% and Cd 0.0 to —0.36%.

Separation of palladium from thallium, copper, cobalt or nickel

Standard solutions of palladium chloride, thallium sulphate[6], copper sulphate, cobalt sulphate[7], and nickel sulphate[8] were used. The procedure given for the separation of palladium from lead was followed. Palladium was estimated as the dimethylglyoxime complex.

In the case of thallium, copper and cobalt, the filtrate was treated with H_2SO_4-HNO_3 to destroy the organic matter. Thallium was estimated as Tl_2CrO_4, copper was estimated volumetrically with sodium thiosulphate and cobalt as the pyridine complex. In the case of nickel, the metal was directly estimated as the dimethylglyoxime complex.

25-47 mg of palladium could be separated from 92-116 mg of thallium or 40-51 mg of copper. 25-58 mg of palladium could be separated from 19-35 mg of cobalt or 16-20 mg of nickel. The metals were recovered with an accuracy of:

Pd 0.0 to —0.27% and Tl 0.0 to —0.16%;
Pd 0.0 to —0.28%, Cu + 0.25 to —0.37%,
Co +0.04 to —0.16%, and Ni 0.0 to —0.15%

SUMMARY

It has been shown that 1% dimethylglyoxime solution in alcohol can be efficiently used to separate quantitatively palladium from other metals of the copper group, as indicated in the new and more comprehensive scheme of qualitative analysis.

RÉSUMÉ

Une solution de diméthylglyoxime à 1% dans l'alcool peut être utilisée pour effectuer la séparation quantitative du palladium d'avec d'autres métaux du groupe du cuivre.

ZUSAMMENFASSUNG

Eine 1%ige alkoholische Lösung von Dimethylglyoxim kann zur quantitativen Abtrennung des Palladiums von den Metallen der Kupfergruppe verwendet werden.

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HIGH FREQUENCY TITRATIONS

I. THE SILVER-THIOCYANATE REACTION

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High frequency (oscillometric) methods are particularly useful for measuring the dielectric strength of a system and for detecting the end-point in a titration. By far the most ingenious application of oscillometry has been the direct determination of percentage composition of two-component single-phase mixtures by employing the use of standard curves[1]. WEST *et al.*[2-4] illustrated this procedure by the analysis of a water-benzene-methyl ethyl ketone system. They further employed the high frequency technique for the determination of small amounts of water in oils and various organic liquids. HARA AND WEST[5] used the high frequency instrument for studying the EDTA chelation of several metal ions and for the determination of organic functional groups such as imine, amine, oxime and carboxyl, both in aqueous and non-aqueous solutions. BLAEDEL AND MALMSTADT[6] demonstrated the general suitability of high frequency titrimeters for acid-base, precipitation, soluble complex formation and redox reactions. The end points were at times found to be superior to the conventional electrometric end-points. The chief advantage of all these procedures is the isolation of the system from electrodes and other active parts of the instrument without impairing their response to slight changes in the composition of the system.

The purpose of the present work was to investigate with the aid of a high frequency instrument the reactions involving the precipitation or soluble complex formation of simple and complex metal thiocyanates, and to assess the accuracy of the method for analysis of mg quantities of material in highly dilute solutions. Data presented in this communication refer to a study of the silver-thiocyanate precipitation reaction.

EXPERIMENTAL

Apparatus

A Sargent model V Oscillometer, operating at 110-120 V and 60 cycles, was used in the present series of experiments. High frequency titrations were carried out in the large 100-ml cell.

Reagents

One-tenth molar aqueous solutions of reagent-grade silver nitrate, ammonium thiocyanate, and potassium thiocyanate were prepared and standardized by the usual methods.

Procedure

Prior to its use, the oscillometer was thermally equilibriated for 30-60 min. The clean dry cell was placed in position and the needle pointer adjusted to center zero scale position. A measured volume of silver nitrate solution was transferred into the cell and the total volume brought to 100 ml with water. After the initial instrument (capacitance) reading was taken, small increments of ammonium or potassium thiocyanate solution were added from the buret. After each addition of the reagent, the system was stirred by means of a thin glass rod. As far as possible, the time and method of stirring were duplicated. The titration was continued beyond the stoichiometric end-point and the experimental value obtained by plotting a graph. The same procedure was adopted for reverse titrations *viz.*, thiocyanate ion against silver nitrate.

Typical curves are shown in Figs. 1–4 and representative data for silver estimation are compiled in Table I.

TABLE I

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF SILVER WITH THIOCYANATE

Final molarity of $AgNO_3$ solution, M	*Silver (mg)*		*Diff. (mg)*
	actual	*found*	
1/1613	6.703	6.505	0.198
1/1336	8.082	7.842	0.240
1/2672	4.016	4.056	0.040
1/3343	3.232	3.393	0.161

DISCUSSION

During the course of a straight or a reverse titration, the instrument (capacitance) reading remains initially almost constant (*cf.* Figs. 1–4) and then rises steadily. The end-point is located at the intersection of the two straight lines. Since the initial level of the solution is above (about 1 cm) the upper edge of the electrodes, dilution effects will be negligible, the more so as the present work concerns conducting samples[1]. Furthermore, the concentration of the reagent has been adjusted in such manner that the total change in volume after titration does not exceed 3% of the original. This

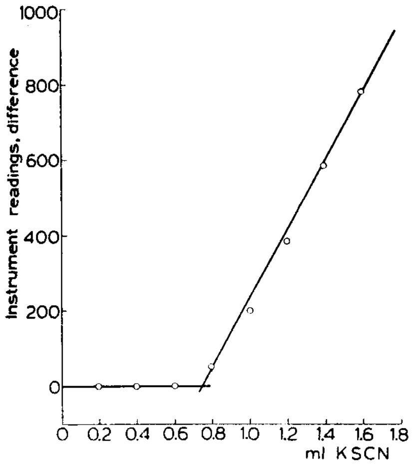

Fig. 1. Titration of 1/2672M $AgNO_3$ with 1/20M KSCN. End-point: theory: 0.745 ml; from graph: 0.75 ml.

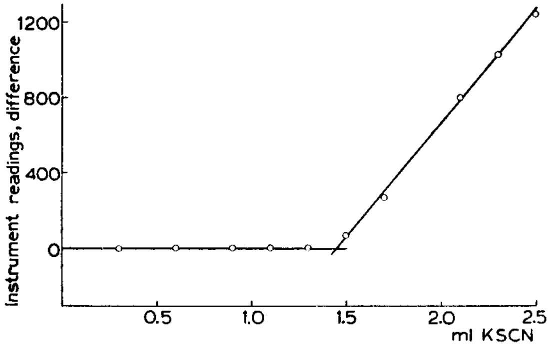

Fig. 2. Titration of 1/1336M $AgNO_3$ with 1/20M KSCN. End-point: theory: 1.49 ml; from graph: 1.45 ml.

References p. 127

is easily accomplished by starting with solutions of approximately equal strength and diluting with water in the titration vessel (*cf.* EXPERIMENTAL). The silver nitrate or thiocyanate solution up to 1/4000*M* could be titrated within a maximum deviation of about 5%. At still greater dilutions, the changes in the instrument reading result in a rather flat curve making it diffucult to obtain a clear end-point. The principal advantage of the present method is that comparatively large volumes can be handled and mg quantities of silver or thiocyanate can be determined at dilutions at which the indicator or other conventional electrometric methods do not usually yield satisfactory results.

Further work on the high frequency study of mercuric thiocyanate and zinc tetracyanatomercuriate(II) is in progress.

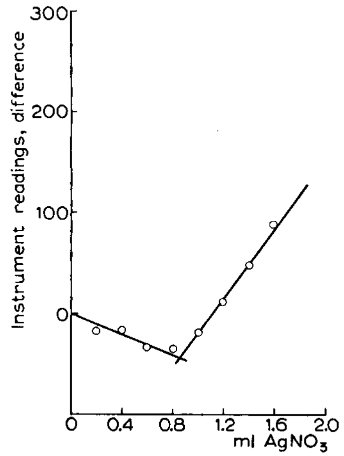

Fig. 3. Titration of 1/3982*M* KSCN with 1/33.4M $AgNO_3$. End-point: theory: 0.833 ml; from graph: 0.86 ml.

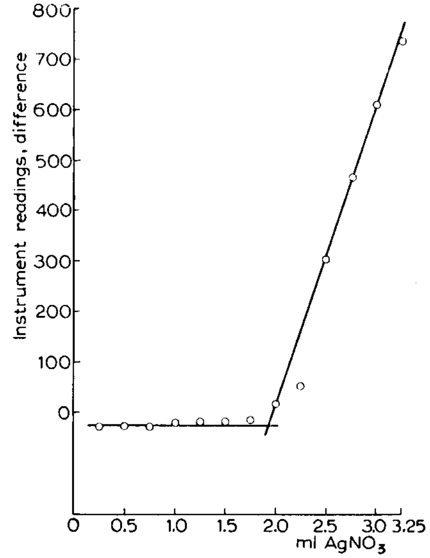

Fig. 4. Titration of 1/1680*M* NH_4SCN with 1/33.4*M* $AgNO_3$. End-point: theory: 1.983 ml; from graph: 1.925 ml.

ACKNOWLEDGEMENTS

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SUMMARY

A high frequency (oscillometric) method for the titrimetric determination of small amounts of silver at dilutions down to 1/4000*M* with ammonium or potassium thiocyanate is described. Reverse titrations in the same order of dilution are also feasible. Oscillometric studies on the formation of soluble mercuric thiocyanate and of the sparingly soluble zinc tetracyanatomercuriate(II) are in progress.

References p. 127

RÉSUMÉ

Une méthode à haute fréquence (oscillométrique) est proposée pour le dosage titrimétrique de faibles teneurs d'argent, au moyen de thiocyanate d'ammonium ou de potassium.

ZUSAMMENFASSUNG

Es wird eine Hochfrequenzmethode (oszillometrisch) zur titrimetrischen Bestimmung von sehr geringen Mengen von Silber mit Ammonium oder Kaliumthiocyanatlösung beschrieben.

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THE REDUCTION OF MICRO AND SEMIMICRO WEIGHINGS TO A NORMAL TEMPERATURE AND A NORMAL PRESSURE

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As long ago as 1936[1,2] we pointed out that the accuracy of micro and semimicro weighings can be considerably increased by always reducing the balance readings to the same — but arbitrary — normal values of temperature and atmospheric pressure. The problem is essentially very simple. We know that in gravimetric determinations the correction for the buoyancy of the air for the precipitate itself is generally negligible, *viz.* in the neighbourhood of 0.1%. The buoyancy for the receptacle — crucible, weighing bottle, absorption tube, etc. — is of course far greater if expressed in % of the amount of precipitate weighed, but it is generally taken for granted that this is of no importance since the upward force on the receptacle is the same for the empty as for the full crucible. Now it is evident that this only holds good so long as the density of the air has not changed in the mean time because of changes in temperature and atmospheric pressure (and even relative humidity); and a very simple calculation shows that this can easily lead to quite considerable errors, particularly with micro and semi-micro weighings, where as a rule the ratio, weight of the receptacle : weight of the precipitate, etc., is so much more unfavourable than with macro procedures.

Example: Weight semimicro glass filtertube 7.5 g. Density of the air 1.205 mg/cm^3. Sp. gr. glass 2.5. Sp. gr. brass weights 8.4. Volume filtertube 3.0 cm^3. Volume weights 0.9 cm^3. Resulting buoyancy: (3.0–0.9) 1.205 = 2.52 mg. Therefore, if we want to weigh the precipitate exactly to 0.01 mg (semimicro), this resulting buoyancy must not change more than 0.01 mg, that is about 0.4% of its value. This implies that between the two weighings the density of the air must not change more than 0.4%. Conclusion: Changes of the atmospheric pressure of $0.004 \times 760 = 3$ mm, and changes of the temperature of $0.004 \times 293 = 1.2°$ are inadmissible!

For micro weighings in six decimal places the limits are even about ten times narrower. Changes of 50–60 μg from one day to the next are no exceptions. To carry out the weighings in a room at a constant temperature is certainly feasible and even to be recommended. But a weighing room so completely air-conditioned that even the pressure remains constant, is hardly within the limits of practicability. Thus the evident solution of the problem is to reduce all weighings to an arbitrary normal temperature and a normal pressure. Of course this can be done by reading the temperature and the barometric pressure and calculating the desired correction. However, even when nomographs are used for this purpose, it takes so much time that hardly anybody ever does it.

There is indeed a simpler way. The buoyancy is determined by the difference in volume between the receptacle and the weights, and by the density of the air. The first factor can easily be calculated, for semimicro weighings in one's head in whole cm^3, for micro weighings with weights and specific gravities to one decimal place. So the only datum we need is the density of the air, or rather the deviation of this density from that under the chosen normal conditions. Apparatus exist from which this value can be read directly with great accuracy (Lux, Stock, Aston balance, etc.) but they are rather expensive and fragile.

For our purpose, where considerably less accuracy is required, we described[1,2] an apparatus, consisting of a barometer tube into the vacuum space of which a liquid had been brought (55 vol. % toluene, 45 vol. % benzene), which fulfils the requirement that 1 % increase of the absolute temperature increases its vapour pressure by 7.60 mm (*i.e.* 1 % of the normal atmospheric pressure). The readings of the lower mercury level are then a direct measure of changes in the density of the air.

This apparatus has rendered us excellent service in the course of the last twenty years. It considerably improved the accuracy of our micro and semimicro gravimetric determinations. However it had one very serious drawback: it was difficult to transport and therefore quite unattractive for manufacturers of laboratory instruments.

When devising means to improve it in this respect, we came to the conclusion that from the very beginning we had been on the wrong road. It is not necessary at all to make use of a true barometer tube with a vacuum at the top. A quite simple apparatus as shown in Fig. 1 will do just as well. It consists of two connecting tubes, one, A, wide and closed, the other, B, narrow and open, partly filled with mercury. The stopcocks C and D have no other use than to facilitate transport. When the apparatus is in use both should be open.

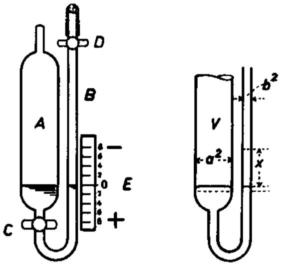

Fig. 1.

References p. 129

We can now bring a scale at E, divided in such a way that it shows with how many units of the fifth decimal place (0.01 mg) the weight found must be increased per cm^3 difference in volume between the receptacle and the weights, in order to reduce it to 760 mm Hg and 20°. The calculation of the length of one scale division is quite easy when the dimensions of the tubes are known.

Let us assume that in the initial state both mercury levels are at the same height. Let V (in mm^3) be the volume of the enclosed air at 760 mm and 20°, a^2 (in mm^2) the cross surface of the wide tube, b^2 (in mm^2) the same for the narrow tube; the density of the air at 760 mm and 20° is 1.205 mg/cm^3. Then we know that for a decrease of the atmospheric pressure of 1%, *i.e.* 7.60 mm, the density of the air also decreases by 1%; buoyancy per cm^3 difference in volume is also decreased by 1% of 1.205 mg per cm^3, *i.e.* 0.01205 mg. Hence for a decrease of atmospheric pressure of

$$7.60 \frac{0.01}{0.01205} = 6.33 \text{ mm},$$

the buoyancy is decreased by 0.0100 mg. The only calculation we have to make is how much (x mm) the mercury in tube B rises, when the atmospheric pressure changes from 760 to 760—6.33 mm Hg at a constant temperature of 20°. The value of x we found is the length of one scale division.

It is evident that x is given by the formula:

$$760\ V = \left[760 - 6.33 + x\left(1 + \frac{b^2}{a^2}\right)\right]\left[V + xb^2\right]$$

in which V = volume enclosed air in mm^3 at 760 mm and 20°;
a^2 = cross surface of the wide tube in mm^2;
b^2 = cross surface of the narrow tube in mm^2.

In exactly the same way the value of x must be known for an increase of temperature equal to $\frac{0.01}{0.01205} \cdot 2.93 = 2.43°$ at a constant atmospheric pressure. In this case the formula for x is

$$\frac{760\ V}{293} = \frac{\left[760 + x\left(1 + \frac{b^2}{a^2}\right)\right]\left[V + xb^2\right]}{293 + 2.43}$$

It is easy to see that both formulas give practically the same value for x, and this is exactly why the changes in the mercury level in tube B are proportional to the changes in the density of the air.

In our first apparatus V was 22700 mm^3, a^2 199 mm^2 and b^2 14.9 mm^2. From the two formulas we found x = 4.02 mm.

A decrease of atmospheric pressure (or an increase of temperature) means a decrease of the density of the air, *i.e.* a decrease of the buoyancy. Hence the weight we find is higher than that found under normal conditions. This means that the correction we have to apply is negative. Therefore the negative readings of the scale are above the zero mark, the positive readings below it.

SUMMARY

An apparatus is described, essentially simpler than the one previously described by the author, which makes it possible to reduce all micro and semimicro weighings to a normal atmospheric pressure and a normal temperature.

RÉSUMÉ

L'auteur décrit un appareil simple permettant de ramener toutes les micro- et semimicropesées à une pression et à une température normale.

ZUSAMMENFASSUNG

Es wird ein einfacher Apparat zur Reduzierung von Halbmikro- und Mikrowägungen auf einen Normaldruck und eine Normaltemperatur beschrieben.

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NEUES VERFAHREN ZUR BESTIMMUNG DER ACETYLGRUPPE

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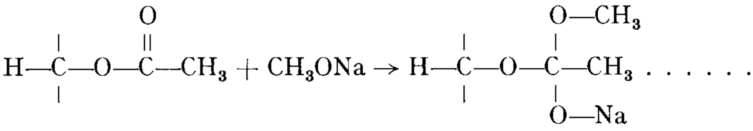
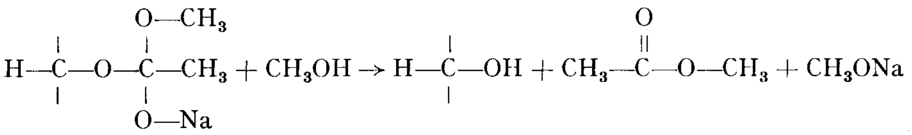
Das Wesen der sowohl in Makro- als auch in Semimikro- und Mikromengen durchgeführten und am häufigsten angewandten Verfahren zur Bestimmung der Acetylgruppe besteht in Verseifung mit Hilfe von Säure oder Lauge, Freisetzung der Essigsäure und deren Trennung durch Destillation, und schliesslich in der acidimetrischen oder jodometrischen Bestimmung der gewonnenen Essigsäure. Die Fehler dieses Verfahrens sind dem Analytiker wohl bekannt, da die Methode nicht nur langwierig, sondern in Mikromengen auch ungenau ist. Es zeigen sich ausserdem Schwierigkeiten nicht nur in der Auswahl des geeignetesten Verseifungsmittels, sondern auch zufolge jenes Umstandes, dass die Verseifung in heterogener Phase nicht vor sich geht, sondern nur im Falle solcher Verbindungen zustandekommt, die in Wasser, Säure oder Lauge bzw. Alkohol löslich sind. Andere Verfahren, wie z.B. jenes, bei welchem die Verseifung in acetonhaltiger Lösung mit überschüssiger Lauge vorgenommen und der Laugeüberschuss rücktitriert wird[1,2], oder ein anderes, bei welchem die Verseifung in Anwesenheit von Äthylalkohol mit *p*-Toluolsulfonsäure durchgeführt und das gewonnene Äthylacetat abdestilliert wird[3,4], können nur zur Analyse einiger, über O-Acetylbindung verfügender Verbindungen herangezogen werden.

Zemplén und Mitarbeiter[5-7] entwarfen eine präparative Methode für die Herstellung desacetylierter Kohlenhydraten, bei welcher die acetylierten Kohlenhydrate in absoluter methyl-alkoholischer Lösung mit Natriummethylat reagierten und auf diese Weise im ersten Schritt das Natriumsalz des Essigsäurediesters entstand:



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + CH_3ONa \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}O{-}\overset{\overset{O-CH_3}{|}}{\underset{\underset{O-Na}{|}}{C}}{-}CH_3} \quad \ldots\ldots \quad (I)$$

Dieses setzte sich auf Einwirkung von Methylalkohol zu Kohlenhydrat und Methylacetat um, wobei sich das Natriummethylat regenerierte:



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O{-}\overset{\overset{O-CH_3}{|}}{\underset{\underset{O-Na}{|}}{C}}{-}CH_3 + CH_3OH \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}OH + CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + CH_3ONa} \quad (II)$$

Zemplén und Mitarbeiter stellten dabei fest, dass das Natriummethylat den Vorgang katalysiert.

Im Laufe unserer Untersuchungen fanden wir, dass diese Reaktion nicht nur zur

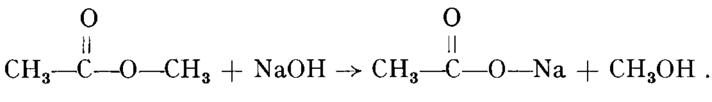
Literatur S. 133

Desacetylierung von Kohlenhydraten geeignet ist, sondern dass mit Natriummethylat auch andere Verbindungen reagieren, falls die Acetylgruppe durch ein Sauerstoffatom an das Molekül gebunden ist. Dieses Reaktionsprinzip schien also zur schnellen und einfachen Bestimmung der Acetylgruppe mit Hilfe des im Laufe der Reaktion entstehenden Methylacetats geeignet zu sein.

Wird nämlich das an Reaktionen (I) und (II) beteiligte Natriummethylat mit Wasser zersetzt, so entstehen Methylalkohol und Natriumhydroxyd in der zum Gleichgewicht führenden, doch stark nach rechts verschobener Reaktion:

$$CH_3ONa + H_2O \rightarrow CH_3OH + NaOH \quad \ldots\ldots\ldots \quad (III)$$

Das Natriumhydroxyd verseift sodann das Methylacetat, wodurch Natriumacetat und Methylalkohol entstehen:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + NaOH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-Na + CH_3OH \quad \ldots\ldots \quad (IV)$$

Da wir aber das Kaliummethylat wirkungsvoller fanden als das Natriummethylat, benützten wir im weiteren ausschliesslich Kaliummethylat zu unseren Versuchen.

Nach Beendigung der Reaktionen (I) und (II) zersetzt sich das Kaliummethylat also quantitativ laut Reaktion(III). Wird jedoch das Kaliummethylat als Masslösung in überschüssiger Menge angewandt, so wird das daraus entstandene Kaliumhydroxyd nicht vollständig in der Reaktion(IV) verbraucht; die überschüssige Menge lässt sich mit Säure rücktitrieren. Kennt man den Wirkungswert der Kaliummethylatlösung, d.h. die Menge des aus ihr durch Hydrolyse freisetzbaren Kaliumhydroxyds und bestimmt man die Menge des nach der Reaktion zurückgebliebenen Kaliumhydroxyds, so ist die Differenz der beiden Bestimmungsergebnissen mit dem aus der Verbindung gebildeten Methylacetat, folglich mit der Acetylgruppe äquivalent. Voraussetzungen sind dabei jedoch der vollständige Ablauf der Desacetylierung und der Hydrolyse, weiterhin, dass das Kaliummethylat bzw. das daraus entstehende Kaliumhydroxyd ausschliesslich auf Einwirkung der Acetylgruppe eine Änderung erleiden, und dass keine andere Nebenreaktionen sich abspielen.

Bezüglich der Brauchbarkeit des Verfahrens ist also die Stabilität der Kaliummethylatlösung entscheidend und zwar nicht nur bei Zimmertemperatur, sondern auch bei Siedetemperatur. Es wurde gefunden, dass der Wirkungswert, falls die Lösung in gut verschlossener Flasche aufbewahrt wurde, drei Wochen hindurch unverändert blieb. Die Lösung war titerbeständig auch bei drei Stunden langern Kochen in einem, mit Rückflusskühler versehenem Destillierkolben.

Wir bewiesen ausserdem, dass bei der Analyse von nicht-Zuckerderivaten, sondern z.B. von Triacetylcellulose oder Diacetylmorphin, die Reaktion ebenfalls durch katalytische Desacetylierung und nicht durch einfache alkalische Hydrolyse vor sich geht. Falls wir nämlich nach der Verseifung den Inhalt des Kolbens abdestillierten, fanden wir das Methylacetat quantitativ im Destillat vor. Im Falle einer einfachen alkalischen Hydrolyse hätte Natriumacetat entstehen müssen, das selbstverständlich ohne Ansäuern nicht destilliert werden kann. Die Hydrolyse vollzieht sich nicht plötzlich sondern nimmt etwa 10 min in Anspruch.

Die Bestimmung der Acetylgruppe durch direkte Titration kann jedoch nur dann erfolgen, wenn das Molekül keine saure oder basische Gruppen enthält und auch keine mit Laugenverbrauch verbundene Zersetzung zustandekommt, wie z.B. im Falle der Acetate der reduzierenden Zuckersorten. Ist die Lösung der Substanz schon ursprünglich farbig oder nimmt sie im Laufe der Desacetylierung Farbe an, so wandten wir zur Titration statt Phenolphthalein chemilumineszierende Indikatoren an. Das Lucigenin[8] bewies sich z.B. sehr dazu geeignet.

Falls aus den oben erwähnten Gründen die Titration nicht direkt auszuführen wäre, so destillieren wir das in Reaktion(II) entstandene Methylacetat in einem geschlossenem Apparat ab, und fangen das Destillat in einem mit Rückflusskühler versehenen Kolben in Laugelösung von bekannter Menge und bekanntem Titer auf. Das Methylacetat wird mit Lauge hydrolysiert und der Laugenüberschuss wird sodann titriert. Um den raschen und quantitativen Verlauf der Reaktion zu befördern, wird in solchen Fällen zur Desacetylierung 1*N* Kaliummethylatlösung im Überschuss angewandt.

Diese letztere modifizierte Form des Verfahrens führt im Falle sämtlicher Verbindungen des O-Acetyl Types zu genauen Ergebnissen, mit Ausnahme jener Verbindungen, bei denen im Laufe der Desacetylierung destillierbare Säure oder Lauge als Zerfallsprodukt zustandekommt. Beide modifizierte Formen des Verfahrens liefern einwandfreie Ergebnisse, sogar wenn die Verbindung in Methylalkohol unlöslich ist. Die Desacetylierung geht daher auch in heterogener Phase mit genügender Geschwindigkeit und quantitativ vor sich.

Mit Hilfe direkter Titration bestimmten wir die Acetylgruppengehalt von Oktaacetylsaccharose, Pregnenolonacetat, Triacetylcellulose, 3α-Acetoxy-5β-ergost-22-en, Diacetylmorphin und β-Naphtholacetat. Substanzmengen von 45–300 mg wurden mit 10 ml 0.1*N* Kaliummethylatlösung desacetyliert. Bei der Rücktitration des überschüssigen Natriumhydroxyds ergab sich der Verbrauch an 0.1*N* Salzsäurelösung zu 0.73–7.7 ml. Die in Prozentsatz ausgedrückte Abweichung vom theoretischen Acetylgruppengehalt bewegte sich zwischen + 0,41 und — 0.41 %.

Bei der Titration von β-Naphtholacetat wurde als Indikator Lucigenin angewandt.

Zu indirekter, nach Destillation erfolgender Bestimmung des Acetylgruppengehalts wurden folgende Substanzen herangezogen: Pentaacetyl-D-glucose, Oktaacetylcellobiose, Oktaacetylsaccharose, β-Naphtholacetat, 3α-Acetoxy-5β-ergost-22-en, Diacetylmorphin, Triacetylcellulose und Polyvinylacetat. In 5–8 Parallelversuchen wurden Substanzmengen von 39.2–184.0 mg eingewogen und das Methylacetat-Destillat wurde im Rezipienten in 10.0 ml 0.1*N* NaOH-Lösung aufgefangen. Bei der Rücktitration bewegte sich der Verbrauch an 0.1*N* HCl zwischen 1.66 und 7.89 ml. Die in Prozentsatz ausgedrückte Abweichung vom theoretischen Wert bewegte sich zwischen — 0.44 und + 0.52 %.

DANK

Herrn Prof. ERDEY, der unsere Arbeit von Anfang an verfolgte und durch seine wertvollen Ratschläge beförderte sprechen wir hiermit unseren Dank aus.

ZUSAMMENFASSUNG

Der O-Acetylgruppenhalt organischer Verbindungen kann einfach und genau bestimmt werden, indem in abs. methylalkoholhaltiger Lösung oder Suspension mit bekannter Menge einer Kaliummethylatlösung verseift und danach das nichtverbrauchte Kaliummethylat nach Hydrolyse als Kaliumhydroxyd titriert wird. Als Indikator dient Phenolphthalein, oder, falls die Lösung farbig ist, Lucigenin. Ist die Titration in der Lösung nicht direkt ausführbar, so wird das bei der Verseifung entstehende Methylacetat abdestilliert, in Laugenlösung aufgefangen und der Laugenüberschuss nach Hydrolyse rücktitriert.

Das Verfahren wurde mit gutem Erfolg bei Acetylbestimmungen in reduzierenden und nichtreduzierenden Zuckeracetaten, Celluloseacetaten, Polyvinylacetaten, β-Naphtholacetat, Pregnenolonacetat, 3α-Acetoxy-5β-ergost-22-en, weiterhin in Diacetylmorphin erprobt. Ein Vorteil des Verfahrens gegenüber den bekannten Methoden ist seine schnelle Ausführbarkeit und der Umstand, dass die Verseifung sich auch in heterogener Phase vollzieht.

Literatur S. 133

SUMMARY

A simple and accurate method is described for the determination of acetyl groups in various organic compounds. The compound is dissolved or suspended in absolute methanol and saponified with a known quantity of potassium methylate solution. The excess potassium methylate is then hydrolysed and determined as potassium hydroxide by titration, an appropriate indicator being used.

RÉSUMÉ

Une méthode pour le dosage du groupement acétyle dans divers composés organiques est proposé. On traite la solution, ou la suspension, à analyser par une solution de méthylate de potassium, dont l'excès est ensuite hydrolysé en hydroxyde de potassium, que l'on titre en présence d'un indicateur approprié.

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METOMEGA CHROME CYANINE BLL AS A METAL INDICATOR IN EDTA TITRATIONS

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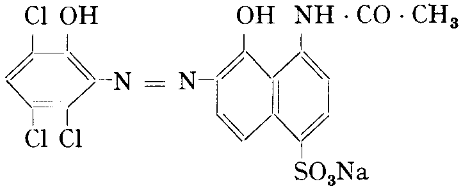
Since the introduction of Eriochrome Black T by SCHWARZENBACH AND BIEDERMANN[1] as a metal indicator, many workers have introduced other azo dyes for the same purpose.

The present work describes the use of Metomega Chrome Cyanine BLL for analytical purposes. This dye was used as an indicator by BELCHER, CLOSE AND WEST[2] under the I.C.I. trade name Solochromate Fast Blue B for the ethylenediaminetetraacetic acid (EDTA) titrations of Cd and Mn at pH 10 with a colour change from purple to red. According to the entry in the second edition of the Colour Index[3], it is known as C. I. Mordant Blue 7. The structural formula of the dye is as follows:



Properties of Metomega Chrome Cyanine BLL

Cyanine BLL is a blue-black powder with a faint metallic lustre, soluble in water and ethanol giving a sky-blue solution. The colour of the dye is very sensitive to pH variations. In the pH range from 5.7 to 7.9 the dye solution is blue, while it changes to violet at higher or lower pH ranges. Thus it seems that Cyanine BLL will find no application in highly acedic or alkaline pH ranges. The aqueous and ethanolic solutions of the dye are stable for a few days; however, if the solution is kept for a period of more than a week the colour gradually changes and after about 10 days it turns completely to brown-red because of polymerisation.

Cyanine BLL metal complexes

The metal complexes of Cyanine BLL are readily prepared by adding a few drops of a freshly prepared aqueous solution of the dye to solutions of heavy metals. The results obtained indicated that red chelate compounds were formed, regardless of the nature of the anion present, when the pH of the solution was maintained within the range 5.7 to 7.9. The cations that caused a colour change are listed in Table I.

TABLE I

COLOUR REACTIONS AND SENSITIVITY LIMITS OF METALLIC IONS WITH CYANINE BLL

Ion	*Colour*	*Identification limit µg*	*Dilution limit*
Al	pink	0.22	$1:1.36\cdot10^5$
Ba	pink		
Ca	wine red	0.20	$1:1.5\cdot10^5$
Cd	red	0.56	$1:5.3\cdot10^4$
Co	red	0.12	$1:2.5\cdot10^5$
Cu	red	0.13	$1:2.3\cdot10^5$
Fe^{+3}	pink	0.17	$1:1.8\cdot10^5$
Pb	wine red	2.07	$1:1.4\cdot10^4$
Mn	wine red	0.33	$1:9\cdot10^4$
Hg	red	1.40	$1:2.1\cdot10^4$
Ni	wine red	0.18	$1:1.7\cdot10^5$
Sr	pink		
Th	pink	0.71	$1:4.3\cdot10^5$
U	pink	0.71	$1:4.2\cdot10^4$
Zn	wine red	0.13	$1:2.3\cdot10^5$
Zr	wine red	1.37	$1:2.1\cdot10^4$

Spot tests were performed by mixing a micro drop (0.03 ml) of the metal solution with a micro drop of an aqueous 1% solution of the dye at pH 6.8. These tests were also carried out with a solution of known concentration of the metal ion. Solutions with lower concentrations were prepared by progressive dilution and were tested in the same manner. A blank experiment was carried out for comparison. In this way the detection limits of the cations were estimated and the corresponding dilution limits were computed.

Results and remarks on spot tests

The results in Table I show that the blue colour of Cyanine BLL turns to pink or wine red on the addition of the ions indicated in Table I.

From the sensitivity limits of the reactions causing colour change it can be seen that the presence of Al^{+3}, Ca^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}, Fe^{+3}, Pb^{+2}, Mn^{+2}, Hg^{+2}, Ni^{+2}, Th^{+4}, U^{+4}, Zn^{+2}, and Zr^{+4} can easily be detected when small amounts of these ions are present in solutions and that the reaction may be applied for the detection of the end-points of titrations of these metals with EDTA.

APPLICATIONS

The use of Cyanine BLL as a metal indicator in EDTA titrations has been investigated. The results obtained show that the indicator is particularly suitable for the titration of Zn^{+2}, Cd^{+2}, Mn^{+2} and Pb^{+2} because of the reversibility and sensitivity of the colour change of the indicator. Copper gave a reversible colour change with the dye but the amounts of EDTA required are much more than the equivalent amounts. Ba^{+2}, Ca^{+2}, Mg^{+2}, and Sr^{+2} gave weak complexes with the dye. The rest of the metals gave an irreversible colour change.

Reagents

Indicator powder: 0.1 g of Metomega Chrome Cyanine BLL (Sandoz) was ground with 10 g of sodium chloride (A.R.).

EDTA solution 0.01*M:* Dissolve 3.722 g of reagent grade disodium ethylenediaminetetraacetate dihydrate in water; dilute to 1 l with bidistilled water.

Buffer solution (pH 6.8): Mix 522 ml of 0.1*M* sodium diethylbarbiturate with 478 ml of 0.1*N* HCl.

Metal salt solution: Prepare 0.01*M* solutions of the various metals from analytical grade reagents. Standardize these solutions against EDTA using Eriochrome Black T or murexide as indicator according to the usual procedure for the determination of the appropriate cation.

Other reagents: Ascorbic acid, Eriochrome Black T indicator powder.

Procedure for the determination of Zn, Cd, Mn and Pb

To an aliquot portion of the sample solution in a conical flask, add 5 ml of the buffer and a few mg of the indicator until the solution becomes clearly coloured red or pink. When of determining manganese add a few crystals of ascorbic acid. Titrate with 0.01*M* EDTA until the colour changes to clear blue.

1 ml of the titrant corresponds to 653.8 μg of Zn, 1124.1 μg of Cd, 549.4 μg of Mn or 2072.1 μg of Pb.

Results and remarks

The results given in Table II show the slight differences between the amounts of zinc taken and found, as well as the calculated volume of EDTA required and that consumed in titrations. These data are those of representative samples of a large number of determinations, the calculated standard deviation was found to be 7.0 μg and therefore the probable error was 4.6 μg when 0.01*M* EDTA solution was used. Similar data are shown in Table II for the determination of cadmium, manganese, and lead. The standard deviations and probable errors of determination of these metals were 12.5 μg and 8.1 μg for cadmium; 8.1 μg and 5.4 μg for Mn; and 19.5 μg and 13 μg for lead.

The end-points of titrations of zinc, cadmium, manganese and lead were very sharp and could be easily detected. It is therefore concluded that Metomega Chrome Cyanine BLL is a suitable indicator for the titration of these metals.

TABLE II

EDTA TITRATIONS OF SOME METALS USING CYANINE BLL AS INDICATOR

Metal ion	*mg metal*			*ml 0.01 M EDTA*		
	present	*found*	*error*	*calculated*	*consumed*	*error*
Zn	0.968	0.968	0.00	1.48	1.48	0.00
	1.412	1.406	0.006	2.16	2.15	0.01
	2.066	2.079	0.013	3.16	3.18	0.02
	3.530	3.530	0.00	4.14	4.14	0.00
Cd	1.124	1.124	0.00	1.00	1.00	0.00
	2.068	2.057	0.011	1.84	1.83	0.01
	3.182	3.200	0.023	2.92	2.94	0.02
	4.541	4.563	0.022	4.04	4.06	0.02
	6.362	6.396	0.034	5.66	5.69	0.02
Mn	1.099	1.109	0.010	2.00	2.02	0.02
	1.318	1.301	0.017	2.4	2.37	0.03
	2.560	2.565	0.005	4.66	4.67	0.01
	3.457	3.457	0.00	6.22	6.22	0.00
Pb	1.202	1.243	0.041	0.58	0.60	0.02
	3.067	3.067	0.00	1.48	1.48	0.00
	11.272	11.334	0.062	5.44	5.47	0.03
	13.717	13.759	0.042	6.62	6.64	0.02

SUMMARY

A study was made of the suitability of Metomega Chrome Cyanine BLL as a metal indicator for the EDTA titration of zinc, cadmium, manganese and lead. Spot tests for the determination of the sensitivity limits are described.

RÉSUMÉ

Le „Metomega Chrome Cyanine BLL" est proposé comme indicateur pour le titrage du zinc, du cadmium, du manganèse et du plomb, au moyen d'EDTA. Les limites de sensibilité des réactions de ce réactif avec divers cations ont été déterminées.

ZUSAMMENFASSUNG

„Metomega Chrome Cyanin BLL" wird als Metall-Indikator für die EDTA Titration von Zink, Cadmium, Mangan und Blei vorgeschlagen. Die Empfindlichkeit des Indikators gegenüber den einzelnen Kationen wurde mit Hilfe von Tüpfelproben bestimmt.

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A QUALITATIVE AND QUANTITATIVE COLOR REACTION FOR PYRIDOXAL WITH SULFURIC ACID*

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INTRODUCTION

Many color reactions utilized qualitatively and quantitatively in biological chemistry are based upon the aldehyde–phenol–acid reaction system. One component of this system may be determined if the reagents furnish the other two components. The aldehyde and the phenol condense to form a chromogenic complex in the presence of a condensing agent such as concentrated hydrochloric or sulfuric acid[1–3].

The aldehyde–phenol–acid reaction system has furnished analytical procedures for a large variety of compounds:

1. Phenols
2. Phenologenic compounds, such as quinones, which on reduction produce phenols.
3. Aldehydes
4. Aldehydogenic compounds, among which may be mentioned the following compounds:
   (a) Primary alcohols, which yield aldehydes on oxidation.
   (b) Carbohydrates, which in themselves contain a free or combined aldehyde group, and which on treatment with hydrochloric acid or sulfuric acid of sufficient concentration, disrupt to form the aldehyde, furfural or its derivatives, methylfurfural and hydroxymethylfurfural.
   (c) Glycol, glycerol, and higher polyalcohols, sugars, and α-amino alcohols, which yield aldehydes on oxidation with periodate (Malaprade reaction).
   (d) Amino acids, which react with ninhydrin to liberate carbon dioxide and ammonia, and to produce an aldehyde. Glycine, proline and hydroxyproline produce aldehydes with ninhydrin.
   (e) Carboxylic acids, such as citric acid, succinic acid, malic acid, tartaric acid, glycolic acid or lactic acid, which react with concentrated sulfuric acid to yield an aldehyde. Glycolic acid produces formaldehyde, and lactic acid yields acetaldehyde.
   (f) Alkaloids, such as narcotine and hydrastine, which on oxidative hydrolysis, yield the aldehyde, opianic acid (3,4-dimethoxy-*o*-aldehydo-benzoic acid.)

5. Inorganic acids, such as hydrochloric acid or sulfuric acid.

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In the aldehyde-phenol-acid reaction system a ketone may be substituted for the aldehyde, since both types of compounds possess a common group, the C=O or carbonyl group. Not only ketones and ketoses, but ketogenic compounds, such as secondary alcohols, may be determined by means of the ketone-phenol-acid reaction system. Certain sugars, such as the hexoses, in addition to forming derivatives of furfural on treatment with acid, may also produce at the same time the ketonic acid, levulinic acid, which is 3-keto-*n*-valeric acid.

As illustrations of the aldehyde-phenol-acid reaction system a few well-known analytical procedures will be cited. The *Marquis reaction* for the detection of morphine and other phenolic alkaloids requires the Marquis reagent, which is formaldehyde in sulfuric acid. Acetaldehyde is determined qualitatively or quantitatively by the characteristic coloration formed by the interaction of the phenolic compound, *p*-hydroxydiphenyl and sulfuric acid[4]. This method can be employed for the determination of paraldehyde and of lactic acid, both of which on treatment with sulfuric acid can be converted to acetaldehyde[5].

The *Molisch test* for carbohydrates uses the phenol, α-naphthol, in the presence of sulfuric acid. The *Günzberg test* is considered one of the most satisfactory tests for free hydrochloric acid in gastric contents. The test requires the Günzberg reagent, which contains the triphenol, phloroglucin, and the aldehyde, vanillin, in 95% alcohol. A similar test for free hydrochloric acid in gastric contents is the *procedure of Boas*. Gastric contents are evaporated together with the reagents, the diphenol, resorcinol and sucrose. In the presence of free hydrochloric acid, a rose-red color is produced. The acid hydrolyzes the sucrose to form glucose and fructose, which on further action of the acid produces the aldehyde, hydroxymethylfurfural, which may eventually yield the ketonic acid, levulinic acid.

We were attempting to develop a color reaction for pyridoxal (2-methyl-3-hydroxy-4-aldehydo-5-hydroxymethyl pyridine). This vitamin contains a phenolic hydroxyl and an aldehyde group. Pyridoxine, pyridoxamine and pyridoxic acid, contain a phenolic hydroxyl but no aldehyde group. We know that many organic compounds, such as sterols, bile acids and corticosteroids, though not phenolic aldehydes or phenolic ketones, yield reactions with more or less concentrated sulfuric acid. Nevertheless we advanced, in consideration of the carbonyl-phenol-acid reaction system, the hypothesis that an aromatic compound containing within its structure an aldehyde or ketone group as well as an hydroxyl group should yield a characteristic color reaction when the reagent consists solely of sulfuric acid. We were encouraged to advance this hypothesis when we found that certain compounds possessing both a phenol and a carbonyl group reacted with concentrated sulfuric acid. Salicylaldehyde (*o*-hydroxybenzaldehyde) yields a yellow color with concentrated sulfuric acid, while salicylic acid (*o*-hydroxybenzoic acid) does not react chromogenically with sulfuric acid. Colchicine is a phenolic ether with one ketone group. It possesses three methoxy groups which are potential phenolic hydroxyls. With concentrated sulfuric acid, colchicine develops a yellow color. Heliotropine (dihydroxymethylene protocatechuic aldehyde) and veratryl aldehyde (3,4-dimethoxybenzaldehyde) also develop yellow colors with sulfuric acid. Estrone is a phenolic ketone yielding with sulfuric acid a characteristic color reaction utilized in the quantitative estimation of this hormone[6]. The phenolic glycosides, salicin, containing the phenolic aglucon, *o*-hydroxybenzyl alcohol and phlorhizin, containing the phenolic and ketonic aglucon, *p*-dihydroxyphenyl propiophenone, yield characteristic color reactions with sulfuric acid. Salicin produces a bright red color, and phlorhizin a light yellow color changing to light orange.

If our hypothesis has any merit, anisaldehyde which is an aldehydic phenolic ether, and vanillin, which contains a phenolic hydroxyl, a methoxy group and an aldehyde group, should yield a color complex with concentrated sulfuric acid. On the other hand, anisic acid and vanillic acid, both of which contain a phenolic or phenolic ether group only should not react chromogenically with concentrated sulfuric acid. Pyridoxine is a pyridine derivative with one hydroxyl group at carbon 3. This hydroxyl group reacts like a phenolic hydroxyl. Pyridoxine reacts with ferric chloride to yield a red-brown or orange-red color[7,8]. We have found pyridoxal also to react with ferric chloride. Pyridoxine, pyridoxal and pyridoxamine have been reported to couple with diazonium compounds. Pyridoxal, which possesses both an aldehyde group and a phenolic hydroxyl, should yield a chromogenic complex with concentrated sulfuric acid. Pyridoxine, pyridoxamine and pyridoxic acid, possessing a phenolic hydroxyl but not an aldehyde group, should not yield a color reaction with sulfuric acid.

EXPERIMENTAL

The phenolic aldehydes and phenolic ketones investigated were dissolved in absolute alcohol. The alcohol was heated with silver acetate and sodium hydroxide and subsequently subjected to distillation. With one compound, *p,p'*-dimethoxybenzophenone, benzene had to be used as the solvent because the compound was insoluble in alcohol. The compounds were made up in two solutions. Solution A contained one mg/ml (0.1% by weight) and solution B, 5 mg/ml (0.5% by weight). In the case of liquid compounds, *o*-methoxybenzaldehyde, *p*-methoxybenzaldehyde (anisaldehyde), *o*-ethoxybenzaldehyde, *o*-hydroxybenzaldehyde (salicyl aldehyde)and *o*-hydroxyacetophenone, two solutions were made up, one representing 1% by volume (Solution C) and the other 5% by volume (Solution D)*. One set of experiments was designed for a zone test. For this set we employed 2 ml of each of these four solutions and 2 to 3 ml concentrated sulfuric acid. To avoid side reactions and possible charring, the tubes containing the solutions were kept in ice water before, during, and after the addition of sulfuric acid. In a second set of experiments varied quantities of the compounds in definite concentrations were mixed with 2.5 ml of concentrated sulfuric acid. The mixture was shaken to diffuse the color which developed. This set of experiments was also performed with the aid of ice water.

The phenolic aldehydes, anisaldehyde and vanillin, gave positive reactions with concentrated sulfuric acid. The phenolic acids, anisic acid and vanillic acid, yielded no color with sulfuric acid. We have also tested aesculin with concentrated sulfuric acid and found it to give a yellow color or a yellow color with a greenish tinge at higher concentrations. Aesculin is a glycoside in which the aglucon is the diphenolic compound aesculetin (6,7-dihydroxycoumarin). Aesculetin reacts with ferric chloride to yield a green color. The aesculetin furnishes the phenolic hydroxyls, while the glucose portion of the molecule on treatment with acid disrupts to produce the aldehyde, hydroxymethylfurfural, which may in turn be converted to the ketocarboxylic acid, levulinic acid. We have also investigated two phenolic glycosides, arbutin (Table I and III) and rutin (Tables II and IV).

We have tested the four compounds related to vitamin B_6 (pyridoxine, pyridoxamine, pyridoxal and pyridoxic acid). Pyridoxal hydrochloride or phosphate is the only compound that gave an intense yellow color with concentrated sulfuric acid. While

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* The liquid compound, *p,p'*-dimethoxybenzophenone, dissolved in benzene, was made up in concentrations of 1% and 5% by volume.

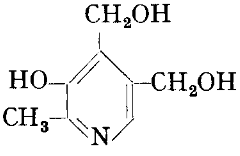
TABLE I

REACTIONS OF PHENOLIC ALDEHYDES WITH SULFURIC ACID; ZONE TESTS REACTIONS AT INTERFACE

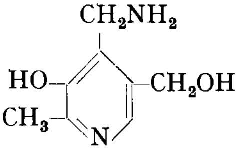
Compound	*Concentration of compound (by weight)*	
	2 ml of 1.0% solution	*2 ml of 5.0% solution*
1. *p*-Hydroxybenzaldehyde	yellow ring	yellow ring
2. Sodium-4-hydroxybenzaldehyde-3-sulfonate	yellow ring	yellow ring
3. 2-Hydroxy-5-chlorbenzaldehyde	yellow ring	deep yellow ring
4. 2-Hydroxy-5-brombenzaldehyde	yellow ring	deeper yellow ring
5. 2,4-Dihydroxybenzaldehyde	light yellow ring; very light violet above ring	yellow ring; distinct violet above ring
6. 2-Hydroxy-3-methoxybenzaldehyde	golden yellow ring	orange ring
7. 4-Hydroxy-3-ethoxybenzaldehyde	yellow ring	deep yellow ring
8. 2,3-Dimethoxybenzaldehyde	yellow orange ring	deep orange ring
9. 4-Hydroxy-3-methoxybenzaldehyde (vanillin)	deep yellow ring	deep greenish brown ring
10. Hydroquinone-glucose (arbutin)	faint yellow ring	yellowish brown ring
	Concentration of compound (by volume)	
	2 ml of 1.0% solution	*2 ml of 5.0% solution*
11. *o*-Hydroxybenzaldehyde [a] (salicylaldehyde)	reddish orange ring	deep red ring
12. *o*-Methoxybenzaldehyde [a]	purplish ring	purplish ring
13. *p*-Methoxybenzaldehyde [a] (anisaldehyde)	greenish brown ring	greenish purple ring
14. *o*-Ethoxybenzaldehyde [a]	dark reddish brown ring	dark reddish brown ring
15. 3,4-Diethoxybenzaldehyde [a]	deep reddish orange violet ring	reddish violet ring

[a] The compounds are liquids.

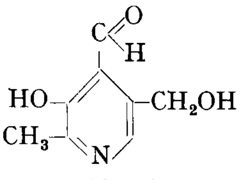
all the four compounds related to vitamin B_6 possess a phenolic hydroxyl, pyridoxal is the only one that possesses a phenolic hydroxyl as well as an aldehyde group.



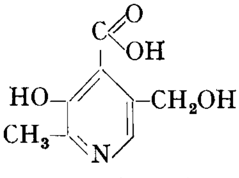
pyridoxine



pyridoxamine



pyridoxal



pyridoxic acid

TABLE II

REACTION OF PHENOLIC KETONES WITH SULFURIC ACID; ZONE TESTS REACTIONS AT INTERFACE

Compound	*Concentration of compound*	
	2 ml of 0.1% solution	*2 ml of 0.5% solution*
1. *o*-Hydroxyacetophenone [a]	yellow ring	deep yellow ring
2. *p*-Hydroxyacetophenone	no color	faint golden yellow ring
3. *p*-Hydroxypropiophenone	no color	light green and yellow rings
4. 4-(*o*-Hydroxyphenyl)-3-butene-one	orange ring	red ring
5. 2,4-Dihydroxyacetophenone (resacetophenone)	no color	light yellow ring
6. Anisalacetone	orange ring	deep orange ring
7. Vanillalacetone	orange ring	red ring
8. 4-Hydroxybenzophenone	yellowish green ring	yellowish green ring
9. 4,4′-Dihydroxybenzophenone	yellow ring	deep yellow ring
10. *p,p*′-Dimethoxybenzophenone [a]	yellow	deep yellow
11. Hydroxy-2-acetonaphthone	yellow ring	golden yellow ring
12. Quercetin [b]	yellow ring	orange ring
13. Rutin	yellow ring	yellow ring

[a] The compound is a liquid. The quantities used in the test are 2 ml of 1% and 2 ml of 5% by volume.

[b] Quercetin (pentahydroxyflavone) is a polyphenolic quinone with a C = O group at position 4 in the molecule. It crystallizes in yellow needles and gives an intense green color with ferric chloride. Rutin is a flavone glycoside, the carbohydrate rutinose, which is 6-D-glucose-β-L-rhamnoside, being linked to quercetin at carbon 3.

The color reaction with pyridoxal is sensitive to 1 μg when 2 drops of 0.5% copper sulfate are added and the reaction mixture heated on the water bath for 10 to 15 min. The color reaction is sensitive to 10 μg without the addition of copper sulfate and without the aid of heat.

QUANTITATIVE DETERMINATION

The absorption spectrum of pyridoxal hydrochloride was determined by means of the DU Beckman spectrophotometer, using 100 μg of the compound dissolved in 1 ml of distilled water and 4 ml of concentrated sulfuric acid (Mallinckrodt-A.C.S. specifications) (Fig. 1). The reaction was carried out at room temperature. The absorption

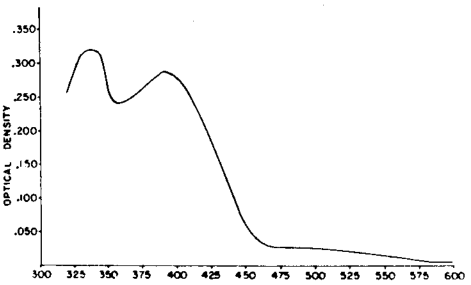


Fig. 1.

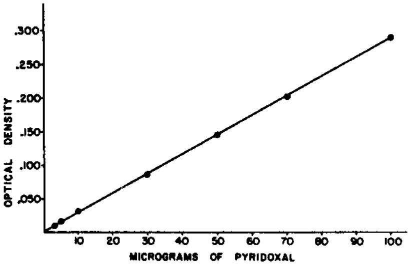


Fig. 2.

TABLE III REACTIONS OF PHENOLIC ALDEHYDES WITH SULFURIC ACID; DIFFUSION TESTS

Compound	*Concentration of compound*					
	0.1% by weight			*0.5% by weight*		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
1. *p*-Hydroxybenzaldehyde	colorless	colorless	yellow tinge	yellow tinge	light orange brown	deeper orange brown
2. Sodium-4-hydroxybenzaldehyde-3-sulfonate	colorless	colorless	colorless	light yellowish pink	yellowish pink	deeper yellowish pink
3. 2-Hydroxy-5-chlorbenzaldehyde	strong yellow color	strong yellow color	deeper yellow color	deep yellow	deep yellow with slight greenish tinge	deeper yellow with slightly greener tinge
4. 2-Hydroxy-5-brombenzaldehyde	yellow	yellow	golden yellow	dark golden yellow	greenish yellow	greenish yellow
5. 2,4-Dithydroxybenzaldehyde	colorless	very light yellow	yellow with pinkish tinge	pink	reddish violet	reddish violet
6. 2-Hydroxy-3-methoxybenzaldehyde	yellowish orange	light orange	orange	reddish brown	reddish	reddish brown
7. 4-Hydroxy-3-methoxybenzaldehyde	light yellow	yellow	deep yellow	dark yellow with brown tinge	amber	dark amber
8. 2,3-Dimethoxybenzaldehyde	dark yellow	light orange	dark orange	strong reddish orange	reddish brown	dark reddish brown
9. 4-Hydroxy-3-methoxybenzaldehyde (vanillin)	light yellow	light greenish yellow	greenish yellow	strong greenish yellow	strong greenish brown	deep greenish brown
10. Hydroquinone-glucose (arbutin)	no reaction	no reaction [a]	yellow	yellow-brown	light brown	brown
	Concentration of compound					
	1.0% by weight			*5.0% by volume*		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
11. *o*-Hydroxybenzaldehyde	deep yellow	orange	reddish orange	cherry red	cherry red	cherry red
12. *o*-Methoxybenzaldehyde	reddish orange	dark cherry color	reddish purple	deep reddish purple	very deep reddish purple	very dark reddish purple
13. *p*-Methoxybenzaldehyde	light yellow	yellow	olive yellow	deep reddish purple	very deep reddish purple	very deep reddish purple
14. *o*-Ethoxybenzaldehyde	deep yellow	reddish brown	reddish purple	deep reddish purple	very deep reddish purple	very deep reddish purple
15. 3,4-Diethoxybenzaldehyde	red	cherry red	reddish violet	deep reddish violet	very deep reddish purple	very deep reddish purple

[a] Yellow on standing.

TABLE IV

REACTIONS OF PHENOLIC KETONES WITH SULFURIC ACID; DIFFUSION TESTS

Compound	*Concentration of compound*					
	0.1%			0.5%		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
1. *o*-Hydroxyacetophenone [a]	pale yellowish green	yellowish green	yellowish green	amber yellow	amber yellow	yellowish green
2. *p*-Hydroxyacetophenone	colorless	colorless	colorless	light yellow tinge	very light yellow	light golden yellow
3. *p*-Hydroxypropiophenone	colorless	colorless	colorless	greenish blue tinge	very light yellow	very light yellow
4. 4-(*o*-Hydroxyphenyl)-3-butene-2-one	deep yellow	orange	orange red	red	deep red	deep red
5. 2,4-Dihydroxyacetophenone (resacetophenone)	colorless	colorless	colorless	very light yellow	very light yellow	very light yellow
6. Anisalacetone	yellow tinge	light orange	orange	red	deep red	deep red
7. Vanillalacetone	deep yellow	orange	deep orange	deep red	reddish violet	deep reddish violet
8. 4-Hydroxybenzophenone	very pale green	light green	light green	yellow green	greenish yellow	lemon color
9. 4,4′-Dihydroxybenzophenone	very light yellow	light yellow with greenish tinge	yellowish green	lemon color	lemon color	lemon color
10. *p,p*′-Dimethoxybenzophenone [a]	pale yellow	light yellow	light yellow	yellow green in acid layer; green in benzene layer	yellow green in acid layer; green in benzene layer	yellow green in acid layer; green in benzene layer
11. Hydroxy-2-acetonaphthone	bright yellow	deep yellow	deep yellow	golden yellow	golden yellow	golden yellow
12. Quercetin	greenish	greenish	greenish	orange yellow	orange yellow	orange yellow
13. Rutin	light yellow	light yellow	light yellow	golden yellow	orange yellow	orange yellow

[a] This compound is a liquid. The concentrations represent per cent by volume for this compound, and for the others per cent by weight. The compounds, *o*-hydroxyacetophenone and *p,p*′-dimethoxybenzophenone, were made up in concentrations of 1.0% and 5.0%.

spectrum shows two peaks, one at 335 mμ and the other at 390 mμ. With the latter wave length a graph constructed with varying quantities of pyridoxal hydrochloride tested (10 to 100 μg) indicated that the color reactions followed the Beer-Lambert law. (Fig. 2). The color proved to be stable for at least 2 days when kept in the refrigerator at 40°F.

DISCUSSION

The vitamin B_6 group consists of pyridoxine, pyridoxal, and pyridoxamine. Pyridoxic acid constitutes a metabolic product eliminated by the kidneys. The first analytical procedures were developed when pyridoxine was believed to be the only compound that possessed the biologic characteristics of vitamin B_6. The colorimetric methods developed were based upon two chemical properties of pyridoxine. This compound possesses a phenolic hydroxyl and is a pyridine derivative.

The phenolic nature of pyridoxine gave rise to the development of colorimetric procedures typical of phenols. KERESZTESY AND STEVENS[7] and also GREEN[8] utilized ferric chloride as an analytical reagent with the resulting production of a red-brown color. KUHN AND LÖW[9] employed the phenol reagent of FOLIN AND DENIS[10] for the determination of pyridoxine. Several analytical procedures involve a coupling reaction with a diazo compound, a reaction characteristic of most phenolic compounds. SWAMINATHAN[11,12] employed diazotized sulfanilic acid and also diazotized *p*-nitroaniline, and BROWN, BINA AND THOMAS[13] employed diazotized *p*-aminoacetophenone. According to GIBBS[14], a phenol with an unsubstituted *para* position can form a blue indophenol compound. Pyridoxine is a phenol with an unsubstituted *para* position. STILLER, KERESZTESY AND STEVENS[15] showed that pyridoxine yielded a positive GIBBS reaction with 2,6-dichloroquinone chloroimide, and SCUDI and his collaborators[16–19] devised an analytical procedure based upon the finding of KERESZTESY AND STEVENS.

Two analytical procedures depend upon the fact that pyridoxine is a pyridine derivative. KUHN AND LÖW[9] developed the cyanine dye test, which is specific for α-picoline (2-methyl pyridine) and its derivatives. Pyridoxine is a 2-methyl pyridine derivative. The final product of the cyanine dye test is a violet complex, which shows absorption maxima at 599 mμ and at 555 mμ. SWEENEY AND HALL[20] developed the cyanogen bromide procedure. This procedure is based upon the fact that cyanogen bromide reacts with pyridine compounds to rupture the ring. The resulting compound is coupled with a diazotized aromatic amine. Although pyridoxine is a pyridine derivative, it does not react with cyanogen bromide because of the interference arising from the presence of the 2-methyl group. This methyl group is removed by oxidation to a carboxyl group, which on heating, is decomposed with the evolution of carbon dioxide. The demethylated pyridoxine reacts with cyanogen bromide, and the resulting compound is coupled with diazotized sulfanilic acid.

It is interesting to note whether various methods can be applied to differentiate the three vitamins (pyridoxine, pyridoxal and pyridoxamine) and the metabolite, pyridoxic acid. Pyridoxine forms a complex which does not react with 2,6-dichloroquinone chloroimide, while pyridoxal and pyridoxamine do react to form the blue dye. MELNICK *et al.*[21] observed that pyridoxal and pyridoxamine on an equimolar basis were about 15% and 31% as reactive as pyridoxine. ORMSBY, FISHER AND SCHLENK[22] observed that the three members of the vitamin B_6 group yielded different colors with diazotized sulfanilic acid. Pyridoxine gave an orange color, pyridoxamine an orange pink, and pyridoxal a bright yellow color. These colors were not very stable. With each compound the maximum intensity was reached one minute after the addition of the diazotized sulfanilic acid. The color developed with pyridoxine began to fade rapidly within 3 min, and the color developed with pyridoxal after about 5 min. Although the stability of the colors was limited in time, the investigators were able to obtain characteristic absorption spectra. According to METZLER AND SNELL[23] pyridoxal in alkaline solution exhibited a characteristic absorption band at about 390 mμ The color intensity varied with temperature and in the presence of pyridoxamine or amino acids. The reaction was not suitable for analytical purposes. Addition of an excess of ethanolamine, however, converted pyridoxal to a more highly colored complex, presumably a Schiff base, suitable for an analytical procedure.

Pyridoxic acid, according to SHIROISHI, FUKAI AND SAKURAI[24], yielded a dye with diazotized sulfanilic acid, but not with 2,6-dichloroquinone chloroimide. HUFF AND PERLZWEIG[25] developed for pyridoxic acid or its lactone a specific quantitative method based upon its characteristic fluorescent effects in the presence of hydrochloric acid. The sulfuric acid method is a quantitative procedure specific for pyridoxal.

SUMMARY

The carbonyl–phenol–acid reaction system yields color reactions with phenols, carbonyl compounds (aldehydes and ketones), and inorganic acids. To test for one of the components of this reaction system, the remaining two components constitute the specific reagents.

The four related compounds, pyridoxine, pyridoxamine, pyridoxal, and pyridoxic acid each possess a phenolic hydroxyl. Pyridoxal possesses an aldehyde group in addition to the phenolic hydroxyl. Pyridoxal yields an intense yellow color on treatment with concentrated sulfuric acid. Pyridoxine, pyridoxamine and pyridoxic acid prove not to be chromogenic on treatment with concentrated sulfuric acid. Pyridoxal can therefore be differentiated by means of the sulfuric acid reaction from the other three compounds related to vitamin B_6.

The colored product obtained by the interaction of pyridoxal and concentrated sulfuric acid yields a characteristic absorption spectrum and follows the Beer-Lambert law in the concentrations of pyridoxal tested (10–100 μg).

RÉSUMÉ

Le système carbonyl–phénol–acide permet d'obtenir des réactions colorées avec les phénols, les aldéhydes, les cétones et les acides inorganiques. On peut donc déterminer l'un des composés de ce système à l'aide des deux autres. Le pyridoxal, renfermant un groupe aldéhydique et un hydroxyle phénolique, donne avec l'acide sulfurique une coloration jaune; il peut ainsi être différentié de la pyridoxine, de la pyridoxamine et de l'acide pyridoxique. Le produit coloré obtenu par l'interaction du pyridoxal avec l'acide sulphurique concentré donne un spectre d'absorption caractéristique et suit la loi de Beer-Lambert dans les concentrations de pyridoxal étudiées, de 10–100 μg.

ZUSAMMENFASSUNG

Die Farbbildung des Systems: Carbonyl (Aldehyde und Ketone)–Phenole–Mineralsäuren kann zum Nachweis einer dieser Komponenten mit Hilfe der beiden anderen verwendet werden. Pyridoxal, das neben der phenolischen Hydroxylgruppe noch eine Aldehydgruppe besitzt, gibt mit Schwefelsäure eine intensive gelbe Farbe im Gegensatz zu Pyridoxin, Pyridoxamin und Pyridoxinsäure, die hierbei farblos bleiben. Das farbige Produkt der Reaktion von Pyridoxal mit konz. Schwefelsäure ergibt ein characteristisches Absorptions-spektrum und folgt dem Beer-Lambertschen Gesetz in den untersuchten Pyridoxal Konzentrationen von 10–100 μg.

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DETERMINATION OF POTASSIUM AND SODIUM IN MIXTURES OF THEIR SALTS BY MEANS OF CATION EXCHANGERS

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INTRODUCTION

This paper deals with some simple analytical applications of ion-exchange methods which, to judge from the available literature, have not previously been described. These methods are useful for the analysis of aqueous solutions (or water-soluble mixtures) of two substances if the qualitative composition of the solution or the mixture is known. The analyses described in this paper were performed with solutions of potassium chloride and sodium chloride. The methods are therefore illustrated by descriptions, of the determination of these two salts.

METHOD

In an aqueous solution containing potassium chloride and sodium chloride, the amounts of these salts (or of potassium and sodium) are to be determined. The analysis is performed in the following way:

A sample of the solution is evaporated, dried and accurately weighed. Another sample of equal volume is passed through a cation exchanger in the potassium or the sodium form. After washing with distilled water the combined effluent and wash-water are evaporated, dried and weighed. From these two weighings the content of potassium chloride and sodium chloride (and hence of potassium and sodium) are computed. The calculation is simple.

Suppose that, before the ion-exchange passage, the sample contains

$$a \text{ g KCl} + b \text{ g NaCl}$$

giving a total salt content of S_1 g. After the ion-exchange passage the following amounts are present in the combined effluent and wash-water, depending on whether the resin is in the potassium or the sodium form:

$$a \text{ g KCl} + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b \text{ g KCl},$$

giving a total salt content of S_2 g, or

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a \text{ g NaCl} + b \text{ g NaCl},$$

giving a total salt content of S_3 g.
From the above we find:

$$a + b = S_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$a + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b = S_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a + b = S_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

in which M_{KCl} and M_{NaCl} denote the molecular weights of KCl and NaCl respectively. From eqn. (1) and eqn. (2) it follows that:

$$S_2 - S_1 = a + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b - a - b = b \cdot \left(\frac{M_{\text{KCl}}}{M_{\text{NaCl}}} - 1 \right) \quad . \; . \; . \quad (4)$$

and from eqn. (1) and eqn. (3):

$$S_1 - S_3 = a + b - \frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a - b = a \cdot \left(1 - \frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \right) \quad . \; . \; . \quad (5)$$

In these equations only a and b are unknown.

This method thus comprises the evaporation and drying of two samples of the solution to be analysed, one of the samples first being passed through a cation exchanger saturated with one of the ions present. Of course the salts must not be decomposed during the drying and should not be deliquescent. If necessary, the solution can be passed through an anion exchange resin, saturated with a suitable ion, in order to fulfil this condition.

The solution passed through the cation exchanger must not be acid, as in this case the hydrogen ions would, of course, also be exchanged. The solution must then be evaporated to drive off the acid, if volatile, or percolated through an anion exchanger in the hydroxyl form and then through another anion exchanger in, for instance, the chloride form.

The analysis may be performed in an alternative manner. The sample, containing potassium and sodium chloride, is dried and weighed as before. A sample of the same volume is passed through a strongly acid cation exchanger in the hydrogen form. The combined effluent and wash-water are titrated with standard alkali. The amounts of the salts in the solution are calculated as follows.

As before, suppose that the sample contains

$$a \text{ g KCl} + b \text{ g NaCl}$$

with a total salt content of S_1 g. Further let it be assumed that on titration after the ion-exchange passage c ml 1N alkali hydroxide are consumed; then there are

$$\frac{1 \cdot c}{1000} = E \text{ equivalents}$$

in the sample. We then have:

$$a + b = S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{a}{M_{\text{KCl}}} + \frac{b}{M_{\text{NaCl}}} = E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where M_{KCl} and M_{NaCl} as before denote the molecular weights of potassium chloride and sodium chloride respectively. From eqn. (1) and eqn. (6) it follows that:

$$\frac{S_1 - b}{M_{\text{KCl}}} + \frac{b}{M_{\text{NaCl}}} = E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$S_1 \cdot M_{\text{NaCl}} - b \cdot M_{\text{NaCl}} + b \cdot M_{\text{KCl}} = E \cdot M_{\text{KCl}} \cdot M_{\text{NaCl}}$$

$$b = \frac{E \cdot M_{\text{KCl}} \cdot M_{\text{NaCl}} - S_1 \cdot M_{\text{NaCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} = \frac{M_{\text{NaCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} \cdot (E \cdot M_{\text{KCl}} - S_1)$$

$$a = \frac{M_{\text{KCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} \cdot (S_1 - E \cdot M_{\text{NaCl}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This method thus comprises the evaporation and drying of a sample of the solution to be analysed, and titrating another sample of the same volume with standard alkali, after it has passed a cation exchanger in the hydrogen form.

Estimation of the error

With the first method decsribed above, the ion that is present in excess may conveniently be exchanged in order to get optimum accuracy in the analysis; this is shown by the following example.

The mixture to be analysed contains 90 mole% potassium chloride and 10 mole% sodium chloride. If the sample taken contains 9 mequiv. of KCl and 1 mequiv. of NaCl we have:

Before the ion exchange: 0.67095 g KCl + 0.05845 g NaCl = 0.7294 g total salt $= S_1$.
After exchange against potassium ions: 10 mequiv. of KCl = 0.7455 g $= S_2$.

$$S_2 - S_1 = 0.7455 - 0.7294 = 0.0161 \text{ g}$$

After exchange against sodium ions: 10 mequiv. of NaCl = 0.5845 g $= S_3$.

$$S_1 - S_3 = 0.7294 - 0.5845 = 0.1449 \text{ g}$$

Suppose that the error in the weighings is 1.0 mg. The maximum error in both cases is therefore 2.0 mg. The % error in the first case is 200/16.1 = 12.4%, whereas in the second case the maximum relative error is 200/144.9 = 1.4%.

If we suppose that the solution contains the same amount of potassium chloride and sodium chloride then a sample of 1 g salt contains:

$$0.5 \text{ g KCl} + 0.5 \text{ g NaCl} = 1.0 \text{ g} = S_1$$

After exchange against potassium ions:

$$0.5 + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot 0.5 = 1.1377 \text{ g} = S_2$$

$$S_2 - S_1 = 1.1377 - 1.0 = 0.1377 \text{ g}$$

The maximum relative error is $\dfrac{200}{137.7} = 1.46\%$

After exchange against sodium ions:

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot 0.5 + 0.5 = 0.8920 \text{ g} = S_3$$

$$S_1 - S_3 = 1.0000 - 0.8920 = 0.1080 \text{ g}$$

The maximum relative error is $\dfrac{200}{108.0} = 1.86\%$

From these simple calculations it can be seen that, if the total salt content in the sample is about 1 g and the error in the weighings 1.0 mg, the maximum relative error is $<2\%$, when the analysis is performed in the most suitable way.

In a similar manner the maximum relative error in the second way of performancing the analysis may be estimated. In this case, however, the differences $(S_1 - E \cdot M_{\text{NaCl}})$ or $(E \cdot M_{\text{KCl}} - S_1)$ respectively, occur in the formula and these are generally small. Even small errors in the weighings therefore give relatively large errors in the calculations. The maximum relative error in this case is therefore larger but ought in every case to be $< 6\%$.

EXPERIMENTAL

Apparatus

The cation exchanger used was Amberlite IR-120 (Rohm & Haas Co., Philadelphia, U.S.A.), which is of sulfonic acid type. The particle size was 0.15–0.30 mm in air dry condition. Ion-exchange columns of ordinary type were used, the diameter and height of the resin layer being 10 mm and 160 mm respectively.

The resin was transformed into the desired form by passing 100 ml of 3–4*N* solution of the corresponding chloride through the column, followed by subsequent washing with distilled water, until no traces of chloride could be detected in the filtrate. In order to transform the resin to the hydrogen form 100 ml 2*N* HCl was passed through the ion-exchange layer, afterwards washing the resin with distilled water until neutral reaction of the effluent. The flow-rate during regeneration and washing was about 5 ml/min.

Procedure

Solutions containing varying amounts of potassium and sodium chloride were used in the experiments. The solutions were prepared from salts of analytical reagent grade, which were dried at about 150° and accurately weighed. Samples of 10 ml were percolated through the ion-exchange layer; after washing with 50 ml distilled water the combined effluent and wash-water were dried and the residue accurately weighed; when the resin was in the hydrogen form the combined effluent and wash-water were titrated with 1*N* NaOH. 10 ml of the original solution were also evaporated and dried and the salt residue accurately weighed. The potassium and sodium chloride in the solutions were then calculated as described above. The results are presented in Tables I and II.

TABLE I

Added, g/l		*Found, g/l*							
		After passage through K-saturated resin				*After passage through Na-saturated resin*			
NaCl	*KCl*	*NaCl*	*% relative error*	*KCl*	*% relative error*	*NaCl*	*% relative error*	*KCl*	*% relative error*
0.2502	0.7505	0.2360	—5.68	0.7638	+1.77	0.2523	+0.84	0.7475	—1.03
0.3641	0.6366	0.3768	+3.46	0.6260	—1.66	0.3721	+0.25	0.6480	+1.76
0.4577	0.5430	0.4533	—0.92	0.5402	—0.52	0.4601	+0.52	0.5397	—0.61
0.5003	0.5004	0.5022	+0.34	0.4944	—1.20	0.5060	+1.10	0.4916	—1.76
0.6862	0.3145	0.6832	—0.44	0.3180	+1.11	0.6913	+0.74	0.3083	—1.97
0.7508	0.2499	0.7523	+0.20	0.2558	+1.44	0.7354	—2.04	0.2657	+6.32
0.8419	0.1588	0.8410	—0.16	0.1580	—0.51	0.8023	—4.70	0.1703	+7.02

TABLE II

Added, g/l		*Equivalents added*	*Equivalents found after passage through H-saturated ion exchanger*	*Found, g/l*			
NaCl	*KCl*			*NaCl*	*% relative error*	*KCl*	*% relative error*
0.2502	0.7505	0.01435	0.01440	0.2643	+5.65	0.7362	—1.90
0.4577	0.5430	0.01511	0.01515	0.4672	+2.08	0.5334	—1.77
0.6862	0.3145	0.01596	0.01591	0.6730	—1.92	0.3278	+4.23
0.8419	0.1588	0.01653	0.01656	0.8491	+0.86	0.1519	—4.35

As can be seen from Table I the errors in this type of analysis, which involves two weighings, are larger the smaller the weight-differences before and after ion-exchange passage. This is in accordance with the estimation of the error given above. It is, however, always possible to perform the analysis in such a manner that the error in the determination is less than 2%. In most cases it is, of course, impossible to know which constituent is present in larger amount, and it is therefore advisable to percolate the solution through both the sodium and the potassium form of the cation exchanger. The analysis then comprises 3 weighings, with a maximum relative error of 2%.

Table II shows that the maximum relative error in this case is larger, which agrees with the above estimation. This analysis is, however, simpler, since it involves only one weighing and one standard titration.

DISCUSSION

Of the methods described in this paper the first one, comprising only weighings, is obviously very suitable for the analysis of a mixture of two difficultly separable salts. Besides solutions of potassium and sodium salts, solutions of two alkaline earth metal salts or of nickel and cobalt salts may be mentioned. Of course the method may also be applied to the determination of negative ions, if the cation exchanger is replaced by an anion exchanger. The points discussed are likewise valid in this case.

As has been stated above the second method, comprising weighing and titration, is not so accurate as the first one. The method is, however, simple, but it is probably not sufficiently accurate for most analyses.

SUMMARY

Methods for the determination of two substances in aqueous solutions (or water-soluble mixtures) are described. A sample of the solution is dried and the residue accurately weighed. Another sample of the same volume is passed through a cation exchanger (when cations are to be determined), saturated with one of the ions in the solution. After washing with distilled water the combined effluent and wash-water are dried and the residue carefully weighed. From these weighings the composition of the solution is determined by simple calculations, the maximum relative error being $< 2.0\%$. The method may be used for the determination of anions, if an anion exchanger is used instead of the cation exchanger.

A variation of the method consists in passing the solution through a cation exchanger in the hydrogen form. The number of equivalents is determined by standard alkali titration and from this and the weight before the ion-exchange passage the composition of the solution can be determined. In this case, however, the maximum relative error is larger. This method is directly applicable to the determination of anions.

RÉSUMÉ

Des méthodes sont décrites pour le dosage de deux substances en solution aqueuse. On procède d'abord par évaporation d'un volume déterminé de l'échantillon à analyser et pesée du résidus. On traite ensuite un volume égal de cette solution à analyser par un échangeur d'ions approprié. On évapore l'éluat et on pèse; par un simple calcul, on peut alors déterminer la composition recherchée. On peut également utiliser un échangeur de cations (forme hydrogène) et titrer par une solution étalon d'hydroxyde alcalin.

ZUSAMMENFASSUNG

Es werden Methoden zur Bestimmung von zwei verschiedenen Substanzen (z.B. Kationen) in wässriger Lösung beschrieben. Ein bestimmtes Volumen der Lösung wird zur Trockne gedampft und der Rückstand gewogen. Ein gleiches Volumen der Lösung wird mit einem Kationenaustauscher Harz, das mit einem der Kationen beladen ist, behandelt und das Eluat ebenfalls zur Trockne gedampft und der Rückstand gewogen. Aus der Gewichtsdifferenz lässt sich dann die Zusammensetzung der ursprünglichen Lösung berechnen. Man kann die Lösung auch mit einem Kationenaustauscher in der H-Form behandeln und das Eluat mit einer Standard-Alkalilauge titrieren.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXV. DOSAGE DE L'IRIDIUM*

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Nous avons relevé[1] dans un article récent, les modes de dosage gravimétrique proposés jusqu'ici pour l'iridium. On peut faire la pesée sous forme de métal en précipitant soit par l'acide formique, soit par le mercapto-2 benzothiazole, ou encore à l'état de sulfure.

1. *En metal par l'acide formique*

La précipitation se fait, comme d'habitude, en présence du tampon d'acétate d'ammonium. Toute la difficulté se présente lorsqu'il s'agit de rassembler le précipité qui prend facilement une nature colloïdale. C'est pourquoi, nous avons utilisé le mode opératoire suivant que nous croyons recommandable.

Nous prenons un des creusets filtrants de verre déjà décrits[2] et garnissons le fond de soie de quartz qui retient bien l'iridium colloïdal en son centre. Après lavage soigné, la petite pastille est décollée avec soin puis transférée dans l'un des creusets adaptables sur l'anneau de la thermobalance. On pourrait aussi prendre, naturellement, un petit vase de silice percé à sa base de trous et garni de soie de silice. En effet, après chauffage, pesée, on a toute latitude pour attaquer cette soie par l'acide fluorhydrique et récupérer ainsi l'iridium; autrement il n'est guère possible de nettoyer un creuset de verre ou de silice frittés. Il n'est pas question non plus d'effectuer la filtration sur papier.

Ceci posé, l'iridium ainsi précipité nous a donné par inscription sur la thermobalance, une droite parfaitement horizontale jusqu'à 879°. Nous croyons donc parfaitement inutile de compliquer ce dosage en effectuant le chauffage, puis le refroidissement dans l'hydrogène, puis dans l'azote, comme on le fait encore à l'heure actuelle. Cette droite horizontale ne sera pas reproduite.

2. *Avec le mercapto-2 benzothiazole*

Le précipité volumineux, orangé, préparé comme l'indiquent BAREFOOT, MCDONNELL ET BEAMISH[3], ne présente pas de palier de poids constant quoique la courbe s'infléchisse assez nettement entre 135 et 250°. Cela correspond sensiblement à un atome d'iridium pour 3.8 molécules de mercaptobenzothiazole (poids moléculaire

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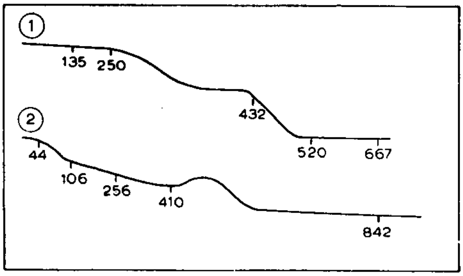
* Pour LXIV (Rhodium), voir[5].

calculé: 837) (Fig. 1). La matière organique se détruit ensuite et à 520°, on obtient le poids constant en iridium métal, qui se maintient au moins jusqu'à 980°.



Figs. 1 et 2

3. *Précipitation en sulfure*

En utilisant le sulfure de sodium, TAIMNI ET SALARIA[4] obtiennent un précipité qu'ils séchent à 85° et auquel ils attribuent la formule $Ir_2S_3 \cdot 10H_2O$. Nous avons reproduit cette expérience, ce qui nous a donné la courbe de thermolyse (Fig. 2) montrant nettement que ce précipité ne présente pas de palier dans la région de 85° où la courbe descend d'une manière abrupte. La perte de poids a lieu dès la température ordinaire et au-dessus de 410°, il se produit une légère réoxydation qui pourrait être attribuée à un passage de sulfure en sulfate. Après quoi, il y a de nouveau perte de poids pour arriver vers 800° à l'iridium métal. On ne peut donc pas faire entrer cette méthode en ligne de compte.

RÉSUMÉ

Nous avons enregistré la courbe de thermolyse des précipités contenant de l'iridium et obtenus respectivement avec l'acide formique, le mercapto-2 benzothiazole et le sulfure de sodium.

SUMMARY

Thermolysis curves have been recorded of precipitates containing iridium, obtained with formic acid, 2-mercapto-benzothiazole and sodium sulphide respectively.

ZUSAMMENFASSUNG

Es wird der Verlauf (Kurven) der Thermolyse von Iridium-haltigen Niederschlägen, die mit Ameisensäure, Mercapto-2-benzothiazol oder Natriumsulfid erhalten wurden, beschrieben.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES LXVI. DOSAGE DU HAFNIUM*

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OBTENTION DE LA MATIÈRE PREMIÈRE

L'oxychlorure de hafnium $HfOCl_2 \cdot 8H_2O$ nécessaire pour effectuer ce travail, a été obtenu par la méthode STREET ET SEABORG[1] en faisant usage de la résine Dowex-50, passée sur tamis à 100 trous. On ajoute peu à peu 150 mg d'oxychlorure de zirconium du commerce, produit Merck, à une suspension de 2 ml de Dowex dans 45 ml d'acide perchlorique 2*N* et, au bout d'un quart d'heure, le petit paquet de résine obtenu est disposé au sommet d'une colonne neuve, préalablement permutée en ions H^+ par une liqueur d'acide chlorhydrique *N*. On élue ensuite par l'acide chlorhydrique 6*N*. On sait que l'on obtient dans les 60 premiers ml isolés, 66% de l'oxyde de hafnium primitif ne contenant plus que 1% d'oxyde de zirconium.

La pureté définitive du produit a été contrôlée spectrographiquement et comparée à celle d'un échantillon d'oxychlorure de hafnium pur mis gracieusement à notre disposition par Monsieur le Professeur C. J. VAN NIEUWENBURG (Delft), que nous sommes heureux de remercier ici.

Dans le LIe mémoire de cette série[2], on trouve une étude sur les courbes de thermolyse effectuées avec de l'oxychlorure de zirconium brut et de l'oxychlorure de zirconium exempt de hafnium. Nous n'avons pas reproduit toutes ces courbes dans le cas du hafnium pur; nous nous sommes limités à l'étude de 6 précipités que nous croyons caractéristiques et utiles pour le dosage du hafnium, c'est-à-dire la formation d'hydroxyde (par l'ammoniaque, par l'ammoniac, par le tannin), de sélénite (basique et neutre), de mandélate, de *p*-hydroxyphénylarsinate, de phosphate et de cupferronate.

Chaque fois nous avons comparé la courbe de thermolyse due au hafnium et celle due au zirconium, les précipitations étant faites dans les mêmes conditions.

A. Par l'ammoniaque

On observe d'abord (Fig. 1) une rapide perte d'eau jusqu'à 199° dans le cas d'un chauffage linéairement croissant, à raison de 300°/h et pour un poids d'oxyde de hafnium résiduel correspondant à 45.9 mg. Ensuite, la perte de poids est plus lente et l'eau de constitution s'échappe à partir de 270° environ. On n'observe aucun accident sensible correspondant aux compositions $HfO(OH)_2$ et $Hf(OH)_4$; on obtient le palier de l'oxyde HfO_2 à partir de 350° (dans les mêmes conditions il faut chauffer jusqu'à 400° pour obtenir l'oxyde de zirconium anhydre). Ainsi donc, cette méthode permet

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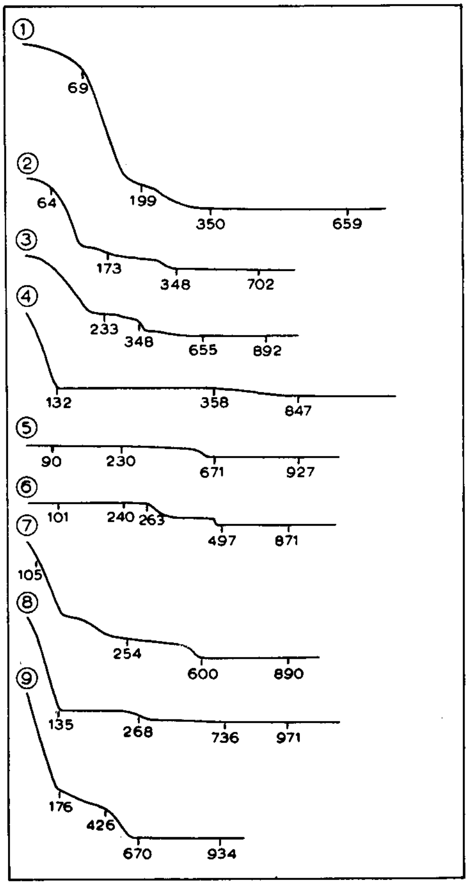
* Pour LXV (Iridium) voir[14].

Bibliographie p. 159

d'opérer à température relativement basse, mais le manque de sélectivité est le gros inconvénient.

B. Par l'ammoniac

La précipitation est effectuée avec un lent courant d'air chargé de gaz ammoniac suivant la méthode de TROMBE[3] que nous avons utilisée bien des fois au cours de cette étude. La courbe de thermolyse obtenue (Fig. 2) ressemble beaucoup à la précédente. La déshydratation se poursuit lentement jusqu'à 350° où l'on atteint le palier de l'oxyde tout au moins avec les poids indiqués ci-dessous. Un dosage de hafnium exécuté par cette méthode fournit 5.3 ± 0.5 mg d'après la mesure sur le papier graphique, pour une quantité d'oxyde de hafnium de 5.272 ± 0.001 mg mesurée sur la microbalance.



Figs. 1–9.

Bibliographie p. 159

C. Par le tannin

Nous avons utilisé la méthode de SCHOELLER[4]. La courbe obtenue (Fig. 3) est tout à fait identique à celle du zirconium. On obtient l'oxyde de hafnium à partir de 655° et celui de zirconium à partir de 880°. Nous n'avons pas observé la légère remontée de la courbe signalée dans le cas du zirconium et attribuée à une réduction, puis à une réoxydation de la zircone.

D. Précipitation en sélénite basique

Nous avons utilisé la méthode proposée par CLAASSEN pour le zirconium[5]. Le palier observé sur la Fig. 4 ne correspond à aucun composé défini, comme le montre le calcul et comme nous l'avions déjà constaté d'ailleurs pour le précipité homologue de zirconium.

E. Précipitation en sélénite neutre

Mais par la technique de CLAASSEN, si on laisse digérer le précipité de sélénite de hafnium pendant plusieurs heures à 80°, on obtient un précipité cristallin correspondant bien à la composition $Hf(SeO_3)_2$. La courbe de thermolyse de ce précipité est représentée sur la Fig. 5. Le sélénite de hafnium se décompose à température nettement inférieure à celle du sélénite de zirconium:

$Hf(SeO_3)_2$ à partir de 230°

$Zr(SeO_3)_2$ à partir de 537°

La méthode peut servir pour le dosage du hafnium et de deux manières: soit en pesant le sélénite, soit en pesant l'oxyde:

Poids d'oxyde de hafnium pesé	10.060 ± 0.001 mg
Poids d'oxyde de hafnium mesuré sur la courbe	10.8 ± 0.5 mg
Poids de sélénite de hafnium pesé	22.750 ± 0.001 mg
Poids de sélénite de hafnium mesuré sur la courbe	23.8 ± 1 mg

Le facteur analytique est très favorable: $HfO_2/Hf(SeO_3)_2 = 0.4869$.

F. Précipitation en mandélate

En généralisant la méthode de KUMINS[6] et de HAHN ET BAGINSKY[7], nous avons obtenu le précipité de tétramandélate de hafnium dont la composition correspond à la formule $Hf(C_6H_5CHOHCO_2)_4$; celui-ci est stable jusqu'à 240° comme le prouve la courbe de thermolyse de la Fig. 6. Il commence alors à se décomposer très lentement, puis plus rapidement à partir de 263° et à 497° commence le palier horizontal de l'oxyde. Comme dans le cas du zirconium, il y a sans doute une légère réduction de cet oxyde à cause de l'atmosphère réductrice qui règne dans le four.

Ce réactif est très spécifique et possède aussi un facteur analytique avantageux: $HfO_2/Hf(C_8H_7O_3)_4 = 0.2689$.

G. Précipitation en p-hydroxyphénylarsinate

Nous avons suivi les indications de CLAASSEN[8], ce qui donne un précipité blanc, floconneux et très sélectif. Les courbes de thermolyse des *p*-hydroxyphénylarsinates de hafnium et de zirconium (Fig. 7) sont tout à fait semblables; il ne semble pas y avoir de composé défini; pour le hafnium la courbe est constamment décroissante jusqu'à 600°; on obtient le palier de l'oxyde à partir de 770°.

Là encore, depuis 600°, on constate une augmentation de poids du corps chauffé; on l'attribue à une réoxydation du hafnium, consécutive à la réduction exercée dans le four par l'anhydride arsénieux et l'oxyde de carbone. Il s'agit d'une excellente méthode de dosage. En effet, l'un de nos essais nous donne:

Poids d'oxyde de hafnium pesé	11.85 ± 0.01 mg
Poids d'oxyde de hafnium mesuré sur la courbe	11.9 ± 0.6 mg

H. Précipitation en phosphate

En suivant la méthode proposée pour le zirconium par STUMPFER ET METTELOCK[9] utilisant le phosphate diammonique, nous avons obtenu un précipité riche en eau dont il perd une grande partie jusqu'à 135° (Fig. 8). Le palier intermédiaire ne s'adapte avec aucune formule simple. A partir de 350°, on obtient un phosphate correspondant à la formule $(HfO)HPO_4$ qui se déshydrate lentement puis, on aboutit au composé HfP_2O_7 ou pyrophosphate vers 700°. Les résultats sont tout à fait d'accord avec ceux obtenus pour le zirconium. La précision est bonne puisque un dosage nous donne:

HfP_2O_7 calculé 5.221 mg

HfP_2O_7 mesuré 5.30 mg

mais il est difficile de récupérer ensuite le hafnium combiné au phosphore.

I. Précipitation en cupferronate

La précipitation effectuée avec le cupferron suivant la méthode de SCHRÖDER[10], FERRARI[11] conduit à un précipité très instable, aussi bien pour le hafnium que pour le zirconium, qui perd du poids constamment jusqu'à 745° pour le zirconium et 670° pour le hafnium (Fig. 9). Ce précipité n'est pas spécifique; il faut peser en oxyde. Cependant, on peut y avoir recours si l'on effectue la précipitation en milieu très acide ou si l'on fait un entraînement.

Tableau I donne les réactifs étudiés pour le dosage gravimétrique du hafnium, les formes de pesée et les limites de température.

PREMIÈRE NOTE

Sur la récupération du hafnium

Nous voulons indiquer, à toutes fins utiles, comment se fait la préparation de l'oxychlorure de hafnium à partir des résidus du chauffage dans la thermobalance.

a) Au départ de l'oxyde de hafnium. On l'attaque par fusion avec le pyrosulfate de sodium ou par l'acide sulfurique concentré, au bain de sable. On reprend le résidu par l'acide sulfurique au demi et chaud, filtre, précipité l'hydroxyde par l'ammoniaque,

Bibliographie p. 159

TABLEAU I

Réactif	*Forme de pesée*	*Limites de températures*
Ammoniaque	HfO_2	>350°
Ammoniac	HfO_2	>500°
Tannin	HfO_2	>655°
* Acide sélénieux	$Hf(SeO_3)_2$	90–220°
	HfO_2	>680°
* Acide mandélique	$Hf\ (C_6H_5\text{-CHOH-}CO_2)_4$	90–260°
	HfO_2	>500°
Acide *p*-hydroxyphénylarsinique	HfO_2	>660°
Phosphate diammonique	HfP_2O_7	>750°
Cupferron	HfO_2	>670°

* Nous avons indiqué par un astérisque celles des méthodes que nous proposons pour la gravimétrie automatique.

filtre de nouveau, lave le précipité avec de l'eau ammoniacale jusqu'à disparition des ions SO_4^{-2} dans la liqueur filtrée; on dissout alors l'hydroxyde dans l'acide chlorhydrique, évapore au bain-marie. Parfois, le corps cristallisé possède une coloration jaune pâle due à la fois à des traces de fer et à du tétrachlorure de hafnium. On peut, naturellement, séparer des traces de fer en appliquant la méthode d'extraction mise au point par SWIFT[12] et DODSON, FORNEY ET SWIFT[13]; on dissout l'oxychlorure brut dans 20 ml d'acide chlorhydrique 8*N* puis, on fait l'extraction par 50 ml d'éther isopropylique et on fait cristalliser la phase aqueuse sous vide.

b) Au départ du pyrophosphate. On fait une fusion de ce dernier en creuset de platine, avec le carbonate neutre de sodium. On reprend par l'acide chlorhydrique et précipite le hafnium par le cupferron, seul réactif usuel permettant une précipitation en présence de phosphate; on chauffe à 900° pour obtenir l'oxyde, que l'on met en solution comme ci-dessus.

DEUXIÈME NOTE

Essai par spectrographie infrarouge

Nous avons tenté d'obtenir à l'état solide, les spectres d'absorption infrarouge des oxychlorures de hafnium et de zirconium, en vue de trouver les fréquences propres des groupes prétendus HfO et ZrO. L'expérience a été négative; avec différentes épaisseurs de cuve, nous n'avons pu observer de bandes entre 6 et 38 μ. On peut donc conclure que ou bien les fréquences caractéristiques sont à rechercher au-dessus de 38 μ, ou bien que ces deux groupements n'existent pas.

RÉSUMÉ

Les auteurs ont préparé de l'oxychlorure de hafnium exempt de zirconium et tracé les courbes de thermolyse des précipités permettant de doser gravimétriquement le hafnium. Leur attention se porte surtout sur le séléniate neutre, le *p*-hydroxyphénylarsinate et le mandélate. Les courbes obtenues ont été comparées à celles que l'on peut former avec les dérivés homologues du zirconium.

SUMMARY

A zirconium-free oxychloride of hafnium was prepared. The hafnium can be determined gravimetrically from the thermolysis curves of the precipitate. In particular, the neutral selenate, the *p*-hydroxyphenylarsinate and the mandelate were studied, and the curves obtained were compared to those plotted of the homologous zirconium derivatives.

Bibliographie p. 159

ZUSAMMENFASSUNG

Es wird die Herstellung eines zirkoniumfreien Hafniumoxychlorides beschrieben. Aus dem Verlauf der Thermolyse (Kurven) der Niederschläge lässt sich das Hafnium gravimetrisch bestimmen. Hervorgehoben werden das neutrale Selenat, das *p*-Hydroxyphenylarsenat und das Mandelat. Die erhaltenen Kurven werden mit denjenigen der entsprechenden Zirkoniumverbindungen verglichen.

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THE DETERMINATION OF THE SOLUBILITY OF ORGANIC SOLVENTS IN MINERAL ACIDS

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INTRODUCTION

Thermodynamic or mass-action treatments of the partition of mineral acids between aqueous solutions and organic solvents[1-3] tacitly assume that the equilibrium can be represented by an equation such as

$$R_2O_{(org)} + HX_{(aq)} \rightleftharpoons R_2O{\cdot}HX_{(org)}$$

where the subscripts indicate the phase in which the species exist. It is important in this respect to be certain that the aqueous phase contains no significant amount of either the solvent or the acid-base complex, both of which are assumed to be completely insoluble in the mineral acid. This point has been discussed by Sutton[4] with reference to the system H_2O/HNO_3/di-ethyl ether, where the solvent is appreciably soluble in the aqueous phase. This type of solubility is of further interest in relation to the solvation of mineral acids in aqueous solution[5,6].

The methods available for the determination of such solubilities have been discussed by Campbell, Laurene and Clark[6]. These authors examined changes of sur-

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face tension, refractive index, viscosity and density and found that only the density variation was suitable for use in comparative measurements of the ether concentration in aqueous hydrochloric acid. The method described below depends on the direct determination of the amount of solvent thrown out of an aliquot of the aqueous phase on neutralization; it has been tested by a series of experiments on the iso-propyl ether/HCl system, for which results are already available from the work of CAMPBELL *et al.*

EXPERIMENTAL

Materials

Pure iso-propyl ether was shaken with aqueous sodium carbonate, washed several times with water, dried over anhydrous magnesium sulphate, and treated with chromatographic alumina to remove peroxides[7].

Analytical grade hydrochloric acid was suitably diluted some time before use; acid concentrations were determined by titration with standard alkali.

Centrifuge tubes

The centrifuge tube used in this work is that designed for the Babcock test (fat content of human milk), and shown in Fig. 1. The total volume to the bottom of the narrow neck is approximately 7.5 ml; the neck is ∿ 4.5 cm long. The tubes were calibrated by measuring the increase in weight due to the addition of a small amount of water to a tube already almost completely filled. The increase in the height of the liquid in the neck was measured with a travelling microscope.

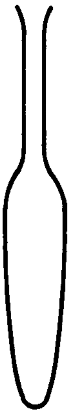

Fig. 1. Centrifuge tube for Babcock test.

Procedure

As an illustration of the experimental technique, measurements on the H_2O/HCl/iso-propyl ether system will be described. All experiments were carried out at room temperature, which remained constant throughout at 23°.

Equal volumes of aqueous hydrochloric acid and iso-propyl ether were shaken together for 30 min in a stoppered bottle. The (upper) organic phase was then completely removed and an aliquot of the aqueous phase titrated to determine the acid concentration. A suitable aliquot (generally 1-3 ml) of the aqueous solution was placed in the centrifuge tube and neutralized with strong (25% w/w) caustic soda solution. The use of an indicator during neutralization is not recommended, since this tends to precipitate and subsequently collect at the liquid–liquid interface, making the meniscus obscure and difficult to measure. Cooling of the centrifuge tube was required to dissipate the heat of neutralization and to prevent evaporation of the ether. Mechanical stirring of the liquid was not found to be necessary.

Sufficient caustic soda and/or water were added to bring the ether into the calibrated neck of the tube which was then centrifuged for a few minutes. The tube was left to reach room temperature, after which the height of the column of ether was measured with a travelling microscope. It was found advisable to cork the neck of the tube before centrifuging; this prevents both evaporation of the ether and accumulation of dust at the liquid–liquid interface.

RESULTS AND DISCUSSION

Reproducibility and calibration

The accuracy of the method was initially tested simply by measuring the height of the column of iso-propyl ether obtained from equal aliquots of the same solution.

Two such series gave

$$1.37,\ 1.36,\ 1.35\ \text{cm}$$
$$\text{and } 0.43_0,\ 0.42_5,\ 0.41_5\ \text{cm}$$

showing that the results are reproducible to within 1% for identical conditions. It soon became clear however, that the results obtained from different aliquots varied systematically with the volume of solution taken. The results of three such experiments are shown in Fig. 2.

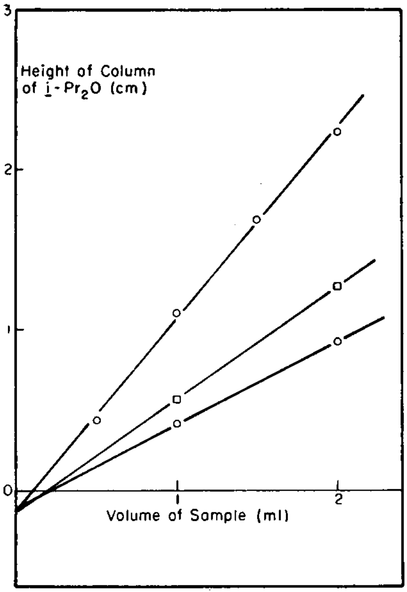

Fig. 2. Variation of height of column of iso-propyl ether with volume of sample.

The intercept from these three experiments is reasonably constant at 0.13 ± 0.01 cm, and corresponds to a solubility of 0.15 g iso-propyl ether per 100 ml of the final aqueous solution of caustic soda and sodium chloride. In making a correction for this effect it is assumed that the volume and composition of the final neutralized solution in the centrifuge tube are constant. This is not strictly true, but the errors introduced by the small variations in these factors are certainly negligible for any but the most refined measurements. The zero correction needs to be determined separately, of course, for each organic solvent.

Calibration of five tubes by the method already described gave the capacity of the cylindrical neck as

$$0.120,\ 0.119,\ 0.117,\ 0.120,\ 0.119 \text{ ml/cm}$$

yielding as the mean value for any individual tube 0.119 ± 0.002 ml/cm. From this one can calculate the calibration factor for iso-propyl ether (density 0.726 g/ml, molecular weight 102) as

$$[\text{i-Pr}_2\text{O}] = \left(\frac{h + 0.13}{V}\right) \cdot \frac{0.119 \times 0.736 \times 10^3}{102}$$

where [i-Pr$_2$O] is the molar concentration of iso-propyl ether in the solution under examination, h the height of the ether column in the tube (in cm) and V the volume of sample taken (in ml). This equation reduces to

$$[\text{i-Pr}_2\text{O}] = \left(\frac{h + 0.13}{V}\right) \times 0.847$$

Any errors arising from differences in the shape of the ether-air and ether-aqueous solution menisci are certainly negligible.

Solubility of iso-propyl ether in aqueous hydrochloric acid

The results of a series of determinations of the solubility of iso-propyl ether in aqueous hydrochloric acid are shown in Fig. 3. This diagram also shows the results reported by CAMPBELL, LAURENE AND CLARK[6] for this system at 20°, based on measurements of the density of the solution.

Two main points emerge immediately from Fig. 3. One is the sharp rise in the solubility at about $7M$ hydrochloric acid; this effect has been discussed in terms of the solvation of the proton[6]. Similar (but larger) changes have been noted by LEJEUNE[5] for the solubility of di-ethyl ether in perchloric acid. The other interesting feature is the marked temperature coefficient of the solubility in this region; the behaviour of the di-ethyl ether–perchloric acid system is very similar[8]. It is also worth noting that the present method apparently gives results whose reproducibility is as good as, or better than, those found from the density measurements.

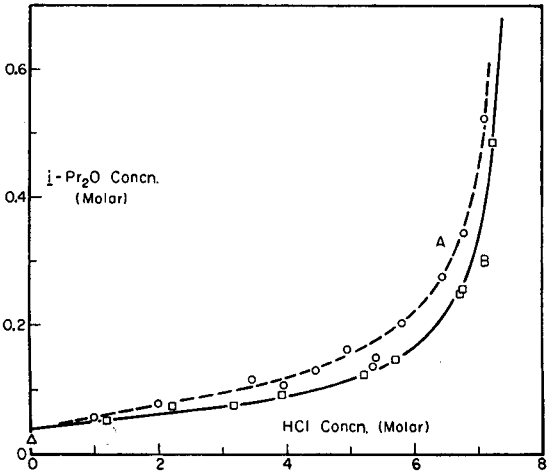

Fig. 3. Solubility of iso-propyl ether in aqueous hydrochloric acid; A. CAMPBELL, LAURENE AND CLARK[6] at 20°; B. present work at 23°.

One should point out that both curves in Fig. 3 extrapolate to a solubility for iso-propyl ether in water of ∿ 0.4 g/100 ml, which is appreciably higher than the value

References p. 163

quoted by CAMPBELL *et al.*, (shown in the diagram at zero HCl concentration). This effect may be due to a deviation from linearity below approx. 1*M* hydrochloric acid.

Advantages and limitations of method

The method as described is rapid and easy to use, and gives reproducible results with an overall accuracy, for columns of ether over 1 cm in height, estimated at ± 2%. For smaller amounts of organic solvent this figure becomes larger due to the uncertainty in the correction for the solubility of the solvent in the final neutralized solution. The lower limit of the method is set by this factor and by the necessity to precipitate significant amounts of solvent out of a reasonably small amount of the aqueous phase. One could of course use tubes of much larger total volume to get over this difficulty. The upper limit of the method has not been investigated but will probably be determined by the size of sample necessary to give a column of liquid less than about 4 cm in height. Here again one could no doubt produce a modified centrifuge tube if necessary.

The method is being currently used in solvent extraction investigations and appears especially applicable to the analysis of the third phase which has been found to appear in certain concentrated acid–ether systems[9].

ACKNOWLEDGEMENT

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SUMMARY

A knowledge of the solubility of organic solvents in aqueous solutions of mineral acids is shown to be important in solvent extraction studies. The method described depends upon the direct measurement of the amount of solvent thrown out of the aqueous phase on neutralization. The results of experiments on the solubility of iso-propyl ether in aqueous hydrochloric acid are given. The accuracy, limitations, and uses of the method are discussed.

RÉSUMÉ

Il est important de connaître la solubilité des solvants organiques dans des solutions aqueuses d'acides minéraux, pour l'étude d'extractions au moyen de solvants. Les résultats expérimentaux sur la solubilité de l'éther isopropylique dans l'acide chlorhydrique sont donnés.

ZUSAMMENFASSUNG

Die Kenntnis der Löslichkeit organischer Lösungsmittel in wässrigen Mineralsäuren is wichtig für Untersuchungen über Extraktionsverfahren. Es werden Angaben über die Löslichkeit von Isopropyläther in wässriger Chlorwasserstoffsäure gemacht.

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COLORIMETRIC URANIUM DETERMINATION WITH ARSENAZO*

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Although a large number of reagents have been proposed for the colorimetric determination of uranium, most of these are non-selective and rather insensitive. In several of the methods a preliminary reduction to uranium(IV) is required[1–5]. The reduction step lengthens the procedure and introduces a possible source of error.

Dibenzoylmethane is a sensitive chromogenic reagent for uranium(VI) (the molar absorptivity is around 20,000) and is probably the best of the existing reagents. Although numerous metal ions interfere[6,7], dibenzoylmethane can be made more selective through the use of masking agents. PRIBIL AND JELINEK[8] determine uranium after extracting uranyl dibenzoylmethane from an aqueous EDTA (ethylenediaminetetraacetic acid) solution. Three extractions are required; each involves considerable shaking. BLANQUET[9] has proposed a highly selective method for uranium based on a carbonate precipitation of impurities followed by colorimetric measurement of uranyl dibenzoylmethane in homogeneous solution containing tartrate and EDTA. He does not indicate clearly which of the foreign ions are removed by precipitation and which are masked by the tartrate and EDTA.

Many of the published methods for the determination of small amounts of uranium employ a liquid–liquid extraction, chromatographic separation, electrolysis with a mercury cathode, or other type of preliminary separation. The success of the subsequent colorimetric determination thus depends upon the efficiency of separation. EBELE AND LERNER have reviewed these separative methods[10]. Very recently several other methods have been published that deal with liquid–liquid extractions[11,12] or with ion exchange separations[13].

There are many occasions where a direct, rapid colorimetric determination of uranium without a preliminary separation would be a distinct advantage. The method described in this paper largely fills this need. Arsenazo, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, is used as the chromogenic reagent for uranium(VI). This reagent has previously been used for the qualitative detection of several elements[14,15] and for the quantitative determination of aluminum, beryllium, rare earths and zirconium[15–17]. Our determination is carried out entirely in aqueous solution; the color develops rapidly and is stable. The method is applicable to the determination of low concentrations of uranium, and the analysis can be carried out successfully in the presence of moderate quantities of most metal ions. If thorium

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* Contribution No. 637. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

is present, however, the uranium must be separated by extraction of uranyl diethyldithiocarbamate.

THE URANIUM-ARSENAZO COMPLEX

In Figs. 1 and 2 the spectral curves of arsenazo and the uranium-arsenazo complex are shown as a function of pH. At pH 8 and below, the wavelength of maximum absorbance is at 595 mμ; at pH 9 and 10 the maximum is shifted toward shorter wavelengths. This wavelength shift, along with the fact that the reagent absorbance at 595 mμ increases significantly above pH 8.5, indicates that the pH for quantitative colorimetric determination of uranium should be below 8.5. In order to establish more precisely the optimum pH range, the absorbance of a uranium-arsenazo solution was measured at 595 mμ as a function of pH. The resulting plot, shown in Fig. 3, indicates that pH 7.0-8.0 is the best for determining uranium with arsenazo.

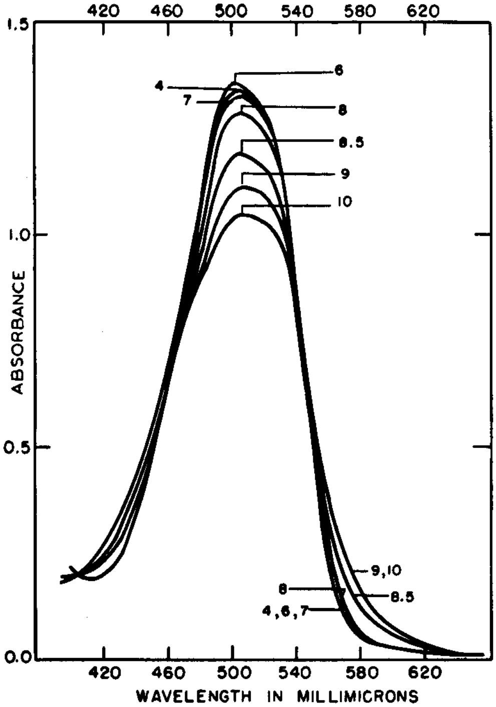

Fig. 1. Spectral curves for arsenazo at pH 4, 6, 7, 8, 8.5, 9 and 10. Solution contained $2 \cdot 10^{-3}$ millimole arsenazo made up to 50 ml. A 1-cm cell was used for spectra.

The ratio of ligand to metal in a metal-organic complex is always of interest. A photometric titration of uranium with arsenazo gave a definite inflection at a mole ratio of arsenazo to uranium of 0.98:1 (see Fig. 4), assuming that the arsenazo was pure acid monohydrate, molecular weight 566. This indicates clearly that a 1:1 complex formed. No evidence was found for any higher complexes. Previously a single 1:1 complex species was found for lanthanum-arsenazo[18].

References p. 171

The absorbance of uranium solutions complexed with excess arsenazo was measured at pH 7.5, 595 mμ. Beer's law is followed with good precision up to at least 10 ppm of uranium. The solutions were found to be stable for at least 11 days. Accurate determination of the molar absorptivity is complicated by the fact that uncomplexed arsenazo absorbs somewhat at 595 mμ. This can be corrected for by using a measured amount of arsenazo and taking into account the fact that a 1:1 complex is formed.

$$A = A_c + A_r = \varepsilon_c c_c + \varepsilon_r c_r \qquad (1)$$

$$c_r = c_r^{\circ} - c_c \qquad (2)$$

$$A = (\varepsilon_c - \varepsilon_r) c_c + \varepsilon_r c_r^{\circ} \qquad (3)$$

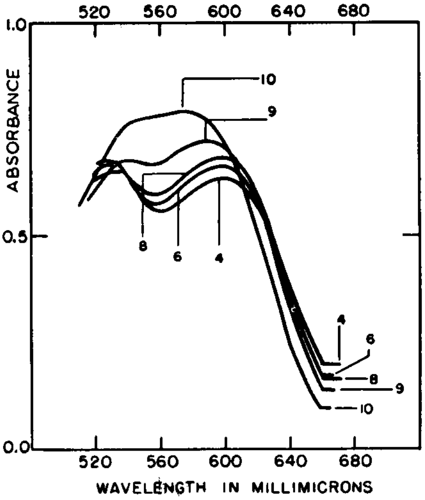

Fig. 2. Spectral curves of uranium–arsenazo complex at pH 4, 6, 8, 9 and 10. Solution contained $7.5 \cdot 10^{-4}$ millimole $UO_2(NO_3)_2$ and $1 \cdot 10^{-3}$ millimole arsenazo made up to 50 ml. A 2-cm cell was used for spectra.

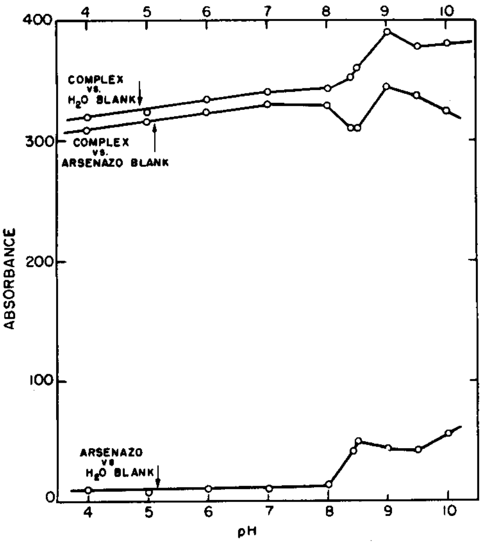

Fig. 3. Absorbance of arsenazo and uranium–arsenazo as a function of pH. Solutions were (1) $7.5 \cdot 10^{-4}$ millimole $UO_2(NO_3)_2$ diluted to 50 ml and (2) $2 \cdot 10^{-3}$ millimole arsenazo diluted to 50 ml. A 1-cm cell was used for all readings.

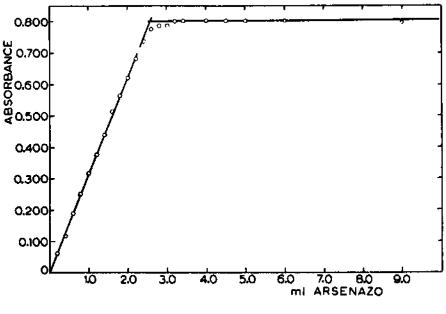

Fig. 4. Photometric titration of uranium with arsenazo $7.5 \cdot 10^{-4}$ millimole of $UO_2(NO_3)_2$ was used. Arsenazo was $2.87 \cdot 10^{-4} M$.

where subscript c refers to the complex and r to the free reagent; $c_r{}^\circ$ is the concentration of reagent before complex formation. Plotting A against concentration of uranium gives a straight line with slope equal to $(\varepsilon_c - \varepsilon_r)$ and intercept at zero uranium concentration equal to $\varepsilon_r c_r{}^\circ$. By this method the molar absorptivity for uranium–arsenazo at 595 mμ and pH 7.5 was found to be 22,900.

INTERFERENCE STUDY

It quickly became apparent that many metal ions would interfere with the simple colorimetric determination of uranium with arsenazo. Thorium and rare earths form an intense violet color with arsenazo over a wide pH range. Iron(III), zirconium(IV) and several divalent metal cations also interfere seriously.

To avoid these interferences, several complexing agents were tried as masking agents. The most widely applicable complexing agent found was EDTA. The addition of EDTA permits the accurate determination of uranium in the presence of at least 35:1 mole ratio of many foreign metal ions to uranium. The data obtained are summarized in Table I.

TABLE I

DIRECT COLORIMETRIC DETERMINATION OF URANIUM IN THE PRESENCE OF ADDED IONS

Ion added	*Masking agent*	*% Uranium recovery*	
		0.005 millimole added ion	*0.025 millimole added ion*
Ag^+	None	—	99·7
Al^{+3}	EDTA	—	98.8
	Acetylacetone	96.9	98.7
Ba^{+2}	EDTA	—	99·1
Be^{+2}	Acetylacetone	102.0	120
Bi^{+3}	EDTA	98.5	100.1
	EDTA	100.4	—
	Thioglycerol	—	100.0
Ca^{+2}	EDTA	98.5	99·1
	EDTA	100.4	—
Cd^{+2}	EDTA	99·0	99·1
	EDTA	99.6	—
Co^{+2}	EDTA	100.0	100.0
	EDTA	104·3	—
Cr^{+3}	EDTA	55·4	—
Cu^{+2}	EDTA	100.0	99·1
	Thioglycerol	101.2	100.0
Dy^{+3}	EDTA	—	101.7
Fe^{+3}	EDTA	98.5	99·4
	EDTA	100.4	—
Hg^{+2}	EDTA	—	99·7
La^{+3}	EDTA	—	97·1
Mg^{+2}	EDTA	—	99·1
Mn^{+2}	EDTA	98.5	99·7
	EDTA	101.2	——
$MoO_4{}^{-2}$	Tartaric acid	100.0	99·3
Ni^{+2}	EDTA	98.5	100.6
	EDTA	100.4	—

TABLE I (continued)

Ion added	*Masking agent*	*% Uranium recovery*	
		0.005 millimole added ion	*0.025 millimole added ion*
Pb^{+2}	EDTA	100.0	99.7
	EDTA	103.2	—
Sb^{+3}	Thioglycerol	100.3	100.3
Sc^{+3}	EDTA	—	100.0
Sn^{+4}	EDTA	—	88.3
Sr^{+2}	EDTA	—	99.7
Ti^{+4}	EDTA	100.0	102.6
VO^{+2}	EDTA	—	100.0
VO_3^-	EDTA	99.2	—
WO_4^{-2}	Tartaric acid	100.0	98.7
Y^{+3}	EDTA	—	101.5
Zn^{+2}	EDTA	100.0	100.3
Zr^{+4}	EDTA	101.5	99.7
	EDTA	104.3	—

Uranium taken: 142–178 g
Average recovery (eliminating results more than 10% in error): 99.9%
Standard deviation: ± 1.40%.

The chief limitation of EDTA as a masking agent is that only a slight *excess* of EDTA can be permitted. Up to 0.005 millimoles of EDTA per 50 ml affects the results by an amount that is no greater than the average error in making a colorimetric measurement on the spectrophotometric instrument used. A higher concentration of EDTA causes low results in the uranium determination. Uranium can be determined accurately in the presence of foreign metal ions provided the foreign ions are complexed trongly by EDTA and that the excess EDTA is not greater than 0.005 millimoles per 50 ml. Uranium solutions containing 0.005 millimoles of EDTA per 50 ml follow Beer's law, and we recommend the inclusion of that concentration of EDTA when preparing the standard working curve for uranium.

Complexing agents other than EDTA are useful for masking certain metals. Molybdenum(VI) and tungsten(VI) are effectively masked by tartrate, and titanium(IV) causes only slightly high results in tartrate solution. Uranium can be determined in the presence of aluminum if sulfosalicylate is present. Thioglycerol permits determination of uranium in the presence of antimony, bismuth or copper. A moderate excess of any of these masking agents does not affect the uranium results.

Of the anions studied only phosphate was found to interfere seriously. No interference is caused by $0.2M$ nitrate, chloride, perchlorate or acetate, or by $0.01M$ fluoride, oxalate or sulfate. A $0.2M$ sulfate concentration made the results for uranium only 2.4% low.

EXTRACTION OF URANIUM

Although the direct colorimetric determination of uranium is made selective through the use of masking agents, thorium constitutes a serious interference. For this reason, the preliminary separation of uranium from interfering ions was investigated.

The liquid–liquid extraction of uranyl diethyldithiocarbamate has been reported[19]. If EDTA is added, uranium still extracts quantitatively but the extraction of several

References p. 171

other metal diethyldithiocarbamates is prevented. In the presence of EDTA only bismuth, cobalt, copper, mercury, silver and tin diethyldithiocarbamates are extracted along with uranium. The chief value of this extraction, however, is the separation of uranium from metals such as thorium and iron.

After extraction, the problem exists of getting the uranium into a medium suitable for colorimetric determination. Direct measurement of the color of uranyl diethyldithiocarbamate in nonaqueous solution has been employed[19], but this is a rather insensitive method. We have found that back-extraction of uranium into a dilute, aqueous carbonate solution is very quick and satisfactory. The pH of the aqueous solution is then adjusted, arsenazo is added and the absorbance is measured at 595 mμ. Data obtained by this method are presented in Table II.

TABLE II

DETERMINATION OF URANIUM USING EXTRACTION PROCEDURE

Ion added *(0.05 millimole)*	*% Uranium recovery* *0.0023 millimole U*	*0.0030 millimole U*
Ag^{+}	98.8	97.6
Al^{+3}	98.0	—
Bi^{+3}	—	95.8
Ca^{+2}	96.8	98.2
Cd^{+2}	99.6	97.6
Co^{+2}	97.6	96.7
Cu^{+2}	99.6	97.0
Fe^{+3}	100.0	98.8
Hg^{+2}	94.8	83.1
Mg^{+2}	100.0	99.1
Mn^{+2}	101.2	97.0
Ni^{+2}	99.2	96.1
Sb^{+3}	96.4	95.8
Sc^{+3}	104.0	100.0
Sn^{+4}	52.4	55.6
Th^{+4} [a]	98.0	100.0
Y^{+3}	98.0	102.0
Yb^{+3}	103.6	97.6
Zn^{+2}	99.6	99.1
Zr^{+4}	99.2	99.1

[a] 0.25 m. mole added.

REAGENTS, SOLUTIONS AND APPARATUS

Arsenazo, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid. Purify the Eastman Organic Chemicals product by slowly dropping a saturated aqueous solution of arsenazo into an equal volume of concentrated hydrochloric acid. Filter off the orange precipitate, wash with acetonitrile and dry at 110° for 1-2 h. Prepare a 0.001M aqueous solution from the purified product.

Diethyldithiocarbamate. Prepare a 2% aqueous solution from pure sodium diethyldithiocarbamate. A fresh solution should be prepared every day or two.

EDTA. Prepare a 0.01M solution from reagent grade disodium or diammonium dihydrogen ethylenediaminetetraacetate.

Sodium carbonate. Prepare a 0.02% solution and adjust the pH to 8.0.

Triethanolamine buffer. Mix equal volumes of 1M triethanolamine and 0.5N nitric acid.

References p. 171

Uranyl nitrate. Dissolve an accurately weighed portion of pure U_3O_8 in dilute nitric acid and dilute to the desired volume. A $5 \cdot 10^{-5}M$ solution is convenient for preparing uranium standards.

All other chemicals used were of reagent grade. Metal nitrates or perchlorates were used in the interference study. Demineralized distilled water was used throughout this investigation.

Spectral curves were carried out on a Cary model 12 recording spectrophotometer. All other measurements were made on a Beckman model B spectrophotometer.

PROCEDURES

A. General Colorimetric Procedure

This procedure is for a sample or aliquot containing 5–500 μg of uranium. Dilution and cell size can be adjusted to handle greater or smaller quantities of uranium.

If the sample is highly acidic, adjust the pH to approximately 2 or 3 with sodium or ammonium hydroxide. Add sufficient $0.01M$ EDTA to complex foreign metal ions that react with EDTA; do not add more than a 0.5-ml excess of EDTA. If the amount of foreign metal ions present is negligible, add 0.5 ml of $0.01M$ EDTA. Add 2 ml of $0.001M$ arsenazo solution. Add 5 ml of triethanolamine buffer and dilute to approximately 40 ml. Adjust the pH to 7.5 with dilute nitric acid or ammonium hydroxide, transfer to a 50-ml volumetric flask and dilute to volume. Measure the color against a reagent blank (a water blank may be used) at 595 mμ in a 1-cm cell. Calculate the uranium concentration with the aid of a Beer's law plot previously prepared using this same procedure.

If aluminum may be present, it is advisable to heat the solution to boiling after adding the EDTA. If molybdenum (VI), tungsten(VI) or titanium(IV) may be present, add 1 ml of $0.1M$ tartaric acid to the acidic sample before continuing with the rest of the procedure. These metals are not complexed by EDTA under the conditions of the determination.

B. Extraction Procedure

To a sample containing not more than 0.08 millimole of foreign metal, add 2 ml of $0.05M$ EDTA and approximately 1 ml of pyridine. Dilute to approximately 20 ml, add 3 ml of 2% diethyldithiocarbamate and adjust the pH to 7–8.* Transfer without delay to a separatory funnel and extract with 25 ml of chloroform. A few ml of a saturated solution of $NaNO_3$ may be added to clear up the layers. Drain the chloroform layer into another separatory funnel which contains 50 ml of 0.02% sodium carbonate. Add 1 ml of additional diethyldithiocarbamate solution to the aqueous layer and re-extract with 15 ml of chloroform. Drain this chloroform layer into the same sodium carbonate solution, then shake the carbonate and combined chloroform extracts for 30 seconds to back-extract the uranium. Drain the chloroform from this back-extraction into another separatory funnel and back-extract with a second 25-ml portion of sodium carbonate solution. To combined carbonate solutions, add 1 ml of concentrated perchloric acid to destroy the carbonate. Then add 5 ml of triethanolamine buffer, 5 ml of $0.001M$ arsenazo and adjust the pH to 7.5. Dilute to exactly 200 ml and measure the color at 595 mμ.

SUMMARY

A rapid and sensitive method is described for the quantitative colorimetric determination of uranium(VI). Masking agents such as EDTA, tartaric acid or thioglycerol make possible the determination of uranium in the presence of many foreign metal ions. If thorium is present, a preliminary extraction of uranium as the diethyldithiocarbamate is required.

RÉSUMÉ

Une méthode rapide et sensible est décrite pour le dosage colorimétrique de l'uranium(VI). Des réactifs de masquage permettent le dosage en présence de nombreux ions étrangers. En présence de thorium, on doit procéder à une extraction préliminaire de l'uranium sous forme de diéthyldithiocarbamate.

ZUSAMMENFASSUNG

Es wird eine empfindliche Schnell-Methode für die colorimetrische Bestimmung von Uran-(VI) beschrieben. Fremdmetalle können mit EDTA usw. maskiert werden. Bei Gegenwart von Thorium muss das Uran als Diäthyldithiocarbamat durch Extraktion abgetrennt werden.

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* If thorium is the interfering ion, let the solution stand for 15–30 min at pH 7–8 before adding the diethyldithiocarbamate solution.

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RESORCINOL AS AN ANALYTICAL REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

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In recent years a number of organic reagents have been suggested for the colorimetric estimation of uranium(VI), for example, dibenzoylmethane[1], salicylic acid[2], sulphosalicylic acid[3], salicylamide[4], salicylamidoxime[5], etc. Of these dibenzoylmethane is claimed to be the most sensitive reagent known so far, but it has the disadvantage of being insoluble in water. Resorcinol produces an orange-red coloration with uranyl salts, which colour reaction was first observed by SEIMSSEN[6]. Resorcinol is extremely soluble in water, easily available and cheap. In view of these advantageous properties, resorcinol was tested as a reagent for the spectrophotometric determination of uranium, and the results are described in this paper.

EXPERIMENTAL

Absorption measurements were made on Coleman's Universal Spectrophotometer, Model 14. A Marconi pH meter was employed for pH measurements, a glass electrode and a saturated calomel reference electrode being used. A freshly prepared solution of resorcinol (Merck's pure quality) was always used for the measurements. A stock solution of uranyl acetate ($UO_2(CH_3COO)_2 \cdot 4H_2O$, a Swiss pure sample) was made by dissolving about 10 g per litre; the uranium content was standardised gravimetrically by precipitating with ammonia and igniting the precipitate to U_3O_8.

DISCUSSION

The absorption spectra of the coloured species ($M/70$ uranyl acetate and $M/7$ resorcinol in water) in presence of excess of resorcinol at pH 4.72 is shown in Fig. 1, along with that of pure reagent of the same concentration at pH 5.68. It follows from the graph that the coloured product has high absorption between 400 mμ and 450 mμ, whereas the reagent has comparatively negligible absorption. Therefore the wavelength 400 mμ was selected for the absorption measurements to investigate the various factors mentioned below.

Colour intensity

Solutions containing the same concentrations of uranium, and resorcinol (in excess), were made at different pH values and their absorption was measured at 400 mμ. The results, which are shown in Fig. 2, indicate that the colour intensity reaches a maximum at pH 4.72 and then decreases at higher pH values. It can further be observed that excess of reagent, even more than a ten-fold excess, has no influence on the colour intensity.

Beer's law

The validity of Beer's law for the system was investigated by the usual method at 400 mμ. The plot of the values of log T against concentration is shown in Fig. 3. This figure indicates that the system obeys Beer's law in the concentration range from $1.125 \cdot 10^{-3} M$ to $0.25 \cdot 10^{-3} M$.

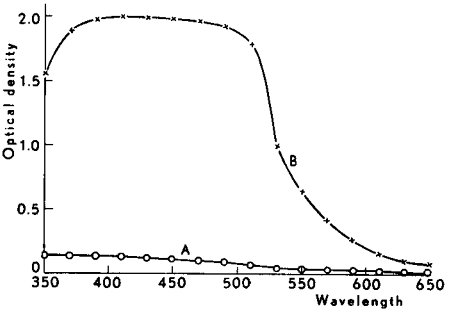

Fig. 1. Curve A: Absorption of an aqueous solution of resorcinol $M/7$. Curve B: Absorption of a mixture of uranyl acetate $M/70$ and resorcinol $M/7$ in water.

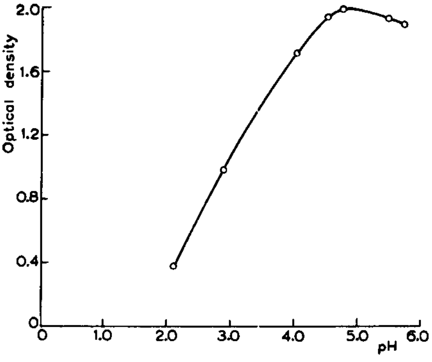

Fig. 2. Variation of optical density with pH of a mixture of uranyl acetate $M/70$ and resorcinol $M/7$ in water.

Stability of the colour and the sensitivity of the reagent

The coloured product remained stable at room temperature and there was no change in the optical density even after 48 h. The sensitivity of the reagent is approximately $M/32,000$ (7.43 p.p.m.) of UO^{+2} ion in excess of resorcinol.

References p. 174

Composition

The composition of the product was determined by following JOB's continuous variation method as modified by VOSBURGH AND COOPER[7]. For this investigation uranyl acetate $M/40$ and resorcinol $M/20$ were used. These solutions were mixed in different proportions keeping the total volume the same (20 ml). The results of the optical density measurements are plotted against $\frac{[R]}{[R] + [UO_2^{+2}]}$ in Fig. 4. The curve shows that maximum optical density (1.2) is obtained when $\frac{[R]}{[R] + [UO_2^{+2}]}$ equals 0.66, indicating the formation of a 1:2 product between UO_2^{+2} ion and the reagent. An attempt was made to determine the composition of the coloured product by conductivity and pH titration methods, but these failed to give any conclusive results, possibly owing to the fact that the uranyl resorcinolate formed is highly dissociated in solution and that one of the constituents of the reaction product is a free acid:

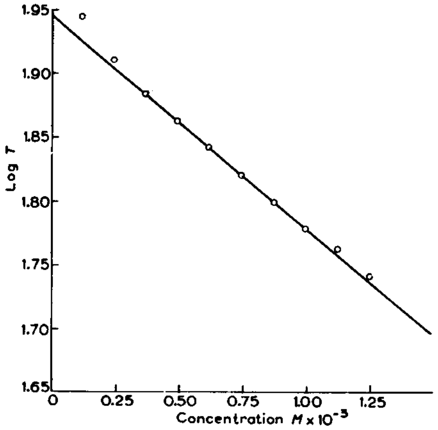

Fig. 3. Curve showing the validity of Beer's law for the system uranyl acetate and resorcinol.

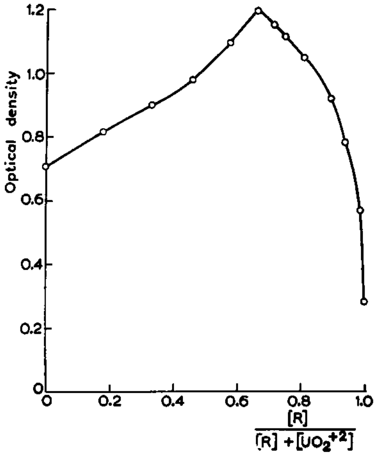

Fig. 4. Curve showing the composition of the coloured product formed from uranyl acetate and resorcinol.

$$UO_2(CH_3COO)_2 + 2C_6H_4(OH)_2 \rightleftharpoons UO_2(C_6H_5O_2)_2 + 2CH_3COOH$$

Interference of other ions

The effect of certain cations and anions that are likely to interfere with the estimation of uranium was investigated and the results are summarised in Table I. The amount of an ion (in p.p.m.) that will produce ± 2% change in optical density was taken as the tolerance limit.

ACKNOWLEDGEMENT

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References p. 174

TABLE 1

EFFECT OF SOME CATIONS AND ANIONS

10.0 ml $M/800$ uranyl acetate + 8.0 ml $M/64$ resorcinol + 2.0 ml water; total volume 20.0 ml.

Salts	*Ions*	*p.p.m.*	*% change*	*Tolerance limit p.p.m.*
K_2SO_4	SO_4^{-2}	10,000	no change	large excess
KNO_3	NO_3^-	20,000	−2	20,000
KCl	Cl^-	10,000	−1.5	15,000
CH_3COONa	CH_3COO^-	3	+4	7
		9	+1.3	
NaF	F^-	10	−25	—
		8	−8	
NaK tartrate	$C_4H_4O_6^{-2}$	24	−22	—
$NaBO_2$	BO_2^-	4	+3	2
		8	+12	
Na_2CO_3	CO_3^{-2}	5	+2	5
		12	+6	
Na citrate	$C_6H_5O_9^{-3}$	20	−32	—
Na_2WO_4	WO_4^{-2}	62	−1.4	72
		37	+6	
NH_4 molybdate	MoO_4^{-2}	18	+8	—
		2	+5	
NH_4VO_3	VO_3^-	1	+48	13
		5	+1	
$K_2Cr_2O_7$	$Cr_2O_7^{-2}$	10	+12	—
Na_2HPO_4	PO_4^{-3}	6	−1.5	8
		15	−5	
$CoCl_2$	Co^{+2}	1	+2	1
$MnCl_2$	Mn^{+2}	1	−12	—
$Ce(NO_3)_4$	Ce^{+4}	1	−9	—
$FeCl_3$	Fe^{+3}	2	+3	1
		3	+5	
$Th(NO_3)_4$	Th^{+4}	1	+2	1
		2	+4	
$CuCl_2$	Cu^{+2}	1	−1	—
		2	+1	
$CrCl_3$	Cr^{+3}	1	−1.8	1
		2	−21	

SUMMARY

A spectrophotometric study of the reaction of uranyl acetate and resorcinol shows that an orange-red coloured resorcinolate of composition 1:2 is formed. This colour reaction can be conveniently used for the spectrophotometric estimation of uranium at pH 4.72.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage de l'uranium au moyen de résorcinol. Le composé obtenu est rouge orange.

ZUSAMMENFASSUNG

Uranylacetat gibt mit Resorcin eine orangerot gefärbte Verbindung, die zur spektrophotometrischen Bestimmung des Urans verwendet werden kann.

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THE SPECTROPHOTOMETRIC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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Until the microgram method[1] of separation of polycyclic aromatic hydrocarbons by elution chromatography on alumina columns was devised, the presence of this class of compound in small proportions could not readily be demonstrated; but since that time, improvements in separation methods and in ultra-violet and fluorescence spectrophotometry have made possible more rapid qualitative and quantitative analyses. The object of the present paper is to describe some recent advances and improvements in technique and to present tabulated essential information covering a wider range of compounds than has previously been given. This should be of use in the analysis of combustion or pyrolysis products such as smokes and soots and tars.

The proportions of polycyclic aromatic hydrocarbons in such products is usually small; very often only a few parts per million. It follows therefore that a satisfactory analytical method must comprise (*i*) a quantitative separation process of extremely small amounts of the wanted material from the rest of the very complex mixture and (*ii*) a sensitive method of identification and determination in the separated fraction.

The use of elution chromatography from alumina columns followed by ultraviolet and fluorescence spectrophotometry has been previously shown in this Department to fulfil these requirements and to be suitable for a wide range of combustion products[2-5]. Earlier workers on chromatographic separation of polycyclic aromatic hydrocarbons[6-11] were more interested in preparative separations and purifications than analysis and had no need to standardize the activity of the alumina or to ensure complete recovery of their products. In the first quantitative work carried out in this laboratory it was customary to select partially de-activated alumina and to employ this material for the separations. Such materials were not wholly satisfactory as they could be standardized only for the duration of the supply of de-activated alumina and thus the methods were not repeatable when the supply had been used. Throughout this paper the separations described were effected on alumina previously brought into equilibrium with water vapour over 75% sulphuric acid[12] in order to ensure reproducible conditions.

The method used by COOPER[13] has given good service for relatively "clean" specimens such as soots and air solids, but has frequently failed to reveal suspected constituents in complex materials such as condensed tobacco smoke. With such samples it is almost always necessary to recombine chromatographic fractions in groups and to pass them through additional columns. In these circumstances the use of an automatic recording spectrophotometer (such as the Beckman D.K. 2) is of great advantage because of its rapid working; and it is now customary to prepare with this apparatus a spectrum of every chromatographic fraction to assist in preliminary identification of constituents and thus to aid the choice of fractions for subsequent re-chromatography. Manual plotting of complete spectra, as was done in the original method[2], for each fraction is impossibly time consuming when many samples have to be analysed.

EXPERIMENTAL

As the method is so sensitive (as little as 0.01 μg of pyrene in 1 ml of solution can be recognised) special care has to be taken to clean all apparatus and to purify all materials.

Cleaning of glassware

All glassware was cleaned by immersion in chromic acid solution, washing with water and drying in an electric oven. This cleaning was completed just before use to avoid possible contamination by atmospheric pollutants.

Preparation of solvents

Spectrophotometrically pure solvents for this work were prepared by distilling the purest commercially available material through glass apparatus using a short column of glass marbles to prevent contamination of the distillates by spray. When cyclohexane was required free from benzene, it was allowed to flow through a column of silica gel (150 × 5 cm) freshly activated by heating to 300°.

Preparation of alumina columns

Active alumina (Peter Spence, type H, 100 to 200 mesh) was used for all this work. It was brought to standardized activity and used by the method previously described[12].

Chromatographic sequence

The most complete list of polycyclic aromatic hydrocarbons with their chromatographic sequence for elution from alumina columns was published by COOPER AND WEDGWOOD[14]. This list and that in Table I, were the result of experiments with mixed solutions of pure hydrocarbons in cyclohexane and they hold for quantities of the order of several micrograms of each compound per ml of solution. In the presence of other compounds and with considerably different amounts of the hydrocarbons this order may be disturbed. It has sometimes been found profitable to employ displacement carriers to space out the hydrocarbons in the chromatographic sequence[3].

Determination of absorption spectra

Standard solutions were prepared by weighing the pure hydrocarbon dissolving in cyclohexane and diluting to a known volume. Absorption peak wavelengths were determined by direct reference to the wavelength scale of the instrument which was calibrated by means of the hydrogen lines at 4861 Å and 6536 Å, and by means of the spectrum of pure benzene in cyclohexane. In Table I also are listed the wavelengths of these absorption maxima to the nearest mμ. To assist in identification of compounds in spectra of unknown mixtures these compounds could be listed against the wavelengths.

Quantitative analysis

For the determination of compounds in solution by means of their absorption spectra a number of empirical techniques have been employed. All these depend upon the solution obeying Beer's law over the range of concentrations employed. COOPER[13] used a "base line" technique in which he drew a tangent to the minima at each side of the maximum absorption and measured the height from this line. GILBERT[15] and others used to measure the absorbance at the maximum and at a fixed wavelength difference above and below the maximum. The difference between the mean of these and the maximum absorbance was regarded as being proportional to the quantity of compound under investigation. These techniques have been tested on a number of compounds but are of necessity less accurate than absorbance measurements because smaller heights are measured. In GILBERT's method errors may be introduced by the asymmetry of absorption peaks. Fig. 1 shows that for serial dilutions of cyclohexane solutions of anthracene, pyrene and 3:4-benzpyrene all three techniques are useful. Similar results are given with other hydrocarbons.

For quantitative determinations it is best to calibrate the spectrophotometer with standard solutions and to prepare a table of factors (absorbances per microgram per ml) to convert the absorbances of the test solution into concentrations. Any of the arbitrary methods described above may be used for this purpose but total absorbance measurements are the most accurate. Table I gives a list of these calibration factors, and wavelengths recommended for quantitative work (underlined).

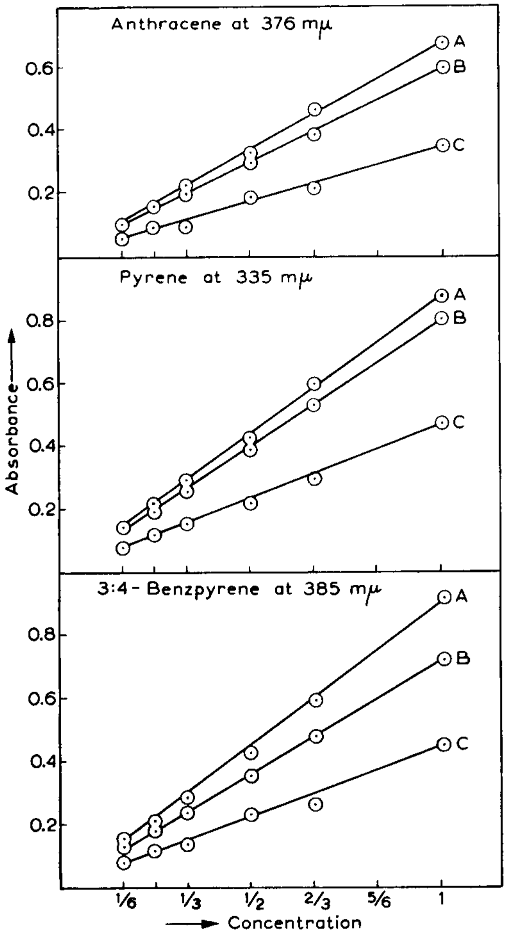

Fig. 1. Concentrations–calibration relationship for anthracene, pyrene and 3:4-benzpyrene, 13.32, 2.95 and 7.22 μg/ml respectively, each diluted to 2/3, 1/2, 1/3, 1/4 and 1/6 of the original concentration. A = total absorbance, B = absorbance measured from base of peak, C = absorbance from base line + or — 3mμ from peak.

TABLE I

CHROMATOGRAPHIC SEQUENCE OF ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ACTIVE ALUMINA COLUMNS WITH CYCLOHEXANE

Compound	*Wavelength of peaks*	*Absorbance (µg/ml)*
Naphthalene	297	0.00283
	301	0.00239
	304	0.00179
	306	0.00168
	311	0.00212
	320	0.000135
Azulene	296	0.0365
	315	0.0171
	322	0.0236
	327	0.0275
	337	0.0348
	341	0.0413
	353	0.00816
2-Methylnaphthalene	305	0.00315
	312	0.00193
	320	0.00326
Acenaphthene	280	0.0398
	288	0.0445
	300	0.0287
	307	0.0189
	310	0.000907
	314	0.000544
	321	0.0110
Acenaphthylene	276	0.0200
	311	0.0504
	323	0.0627
	335	0.0304
	340	0.0307
Fluorene	221	0.109
	265	0.129
	290	0.0423
	294	0.0348
	301	0.0661
Phenanthrene	252	4.13
	275	0.883
	282	0.681
	293	0.897
Anthracene	253	1.24
	325	0.00704
	340	0.0122
	357	0.0264
	376	0.0358
Pyrene	273	0.295
	306	0.588
	320	0.161
	335	0.302
Fluoranthene	237	0.281
	254	0.0815
	259	0.0653
	263	0.0747
	272	0.0602
	277	0.127
	282	0.0965
	288	0.265
3-Methylpyrene	233	0.214
	243	0.373
	254	0.0491
	260	0.0552
	266	0.129
	276	0.268
	313	0.0569
	327	0.136
	344	0.214
	355	0.00869
1:2-3:4-Dibenzanthracene	323	0.0328
	333	0.0260
	350	0.0123
	375	0.00222
1:2-Benzanthracene	250	0.241
	255	0.279
	260	0.205
	269	0.183
	278	0.354
	289	0.460
	300	0.0435
Chrysene	269	0.755
	282	0.0617
	294	0.0612
	306	0.0661
	320	0.0664
Naphthacene	270	1.08
	294	0.133
	374	0.00465
	393	0.105
	413	0.0228
	441	0.0443
	471	0.0495

TABLE I (Continued)

Compound	*Wavelength of peaks*	*Absorbance (μg/ml)*
Perylene	253	0.195
	339	0.0150
	355	0.0228
	388	0.0461
	409	0.0993
	437	0.139
1:2-Benzpyrene	257	0.109
	267	0.130
	278	0.179
	290	0.246
	317	0.104
	332	0.167
3:4-Benzpyrene	266	0.213
	273	0.134
	285	0.201
	297	0.297
	331	0.0240
	347	0.0584
	364	0.107
	385	0.126
	404	0.0173
1:12-Benzperylene	249	0.0747
	255	0.0883
	261	0.0823
	276	0.0895
	289	0.151
	300	0.210
	313	0.0174
1:12-Benzperylene (continued)	392	0.0232
	345	0.0346
	363	0.0743
	384	0.0985
Anthanthrene	233	0.312
	259	0.138
	294	0.142
	307	0.325
	380	0.0445
	401	0.115
	406	0.132
	422	0.160
	430	0.284
Coronene	302	0.818
	317	0.0667
	324	0.0797
	334	0.0670
	339	0.195
	345	0.0424
3:4-9:10-Dibenzpyrene	223	0.136
	234	0.149
	242	0.319
	272	0.124
	283	0.181
	295	0.285
	314	0.0913
	330	0.0799
	354	0.0723
	372	0.194
	394	0.298

APPLICATION OF THE METHOD

The procedure adopted in the analysis of combustion products for polycyclic aromatic hydrocarbons depends very much upon the type of specimen. The method has been successfully used for materials of many kinds including carbon blacks, soots, urban air solids, condensible smokes in which the disperse phase is a liquid or semi solid (tobacco smoke, wood smoke and coal tar are examples of this), thermal decomposition or pyrolysis products (which may vary from dry soots to dark mobile liquids) and other materials which have through accident or design been subjected to the action of smokes or other combustion products (in this category can be included urban vegetation, soil, tobacco, snuff, smoked foods and surface drainage water containing no industrial effluents). It has also been used in the investigation of carbon formation in flames, especially reversed hydrocarbon flames.

In some cases a great deal of the specimen is either aqueous or hydrophilic (tobacco smoke and wood smoke are in this class). Such materials are easily dissolved in acetone, the solution is then mixed with an equal volume of cyclohexane and the mixture distilled until the temperature of the vapour reaches 70°. The cooled solution is then poured off from the aqueous layer (often semi-solid at this stage) and the process repeated several times. Smoked foodstuffs, especially meats may give considerable difficulty because of the presence of fats. These are best hydrolysed with alcoholic sodium hydroxide and then extracted with cyclohexane. Stubborn emulsions may be formed at this stage but in most cases can be broken by adding quantities of calcium chloride.

When a clear cyclohexane solution has been prepared it is extracted in turn with several quantities of dilute sulphuric acid, water and sodium hydroxide. It may then be submitted to chromatographic separation as described earlier. Solutions in cyclohexane for chromatography should be dry. In most cases a single column treatment is enough, but with tobacco smoke a preliminary separation is necessary.

The degree of adsorption of the hydrocarbons from cyclohexane solution upon alumina varies very much from the least strongly held, naphthalene, to coronene. This results in a very slow elution of the hydrocarbons later in the sequence and consequently very dilute later fractions. The use of a solution of benzene in cyclohexane for eluting later fractions increases the concentration but introduces strong light absorption below 260 mμ. As an alternative method, it has been found useful to employ two columns for separate aliquots of the solution in cyclohexane; one, brought to equilibrium with 70% sulphuric acid for the upper members of the sequence and the other in equilibrium with 50% sulphuric acid for the remainder. With heavy general light absorption the use of the calibration factors given in Table I may be inaccurate. In such cases and indeed in any work which needs confirmation of identity and quantity, the addition of a standard solution of one of the constituents as an internal standard is a great advantage.

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SUMMARY

The determination of polycyclic aromatic hydrocarbons by elution chromatography from alumina columns followed by ultra-violet spectrophotometry has been elaborated for a more extended range of substances than has been published previously. The methods have been standardised and tables of absorption peaks are provided for easy identification of a number of compounds commonly found as traces in combustion products. Recommendations are given for the preparation of samples for determinations by this method, which has been successfully employed for the analysis of carbon blacks, soots, urban air solids, condensible smokes such as tobacco smoke, wood smoke and coal tar, thermal decomposition or pyrolysis products and other substances, such as urban vegetation, soil, tobacco, snuff, smoked food, and surface drainage water, which have been subjected to the action of smokes or other combustion products.

RÉSUMÉ

Une méthode est proposée pour le dosage des hydrocarbures aromatiques polycycliques par chromatographie et spectrophotométrie dans l'ultra-violet. Ce procédé a pu être appliqué avec succès à l'analyse de suies, de poussières, de fumées, de produits de décomposition thermique et d'autres substances exposées à des fumées ou à d'autres produits de combustion.

ZUSAMMENFASSUNG

Es wird eine chromatographische und UV-spektrophotometrische Methode zur Bestimmung von mehrkernigen aromatischen Kohlenwasserstoffen beschrieben. Diese Methode wurde mit Erfolg

bei der Untersuchung von Russ, Rauch und sonstigen Verbrennungsprodukten, oder bei Substanzen, die mit Verbrennungsprodukten in Berührung kamen, angewandt.

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THE DETERMINATION OF MAGNESIUM IN THE PRESENCE OF LARGE AMOUNTS OF ZINC

A SPECTROPHOTOMETRIC METHOD

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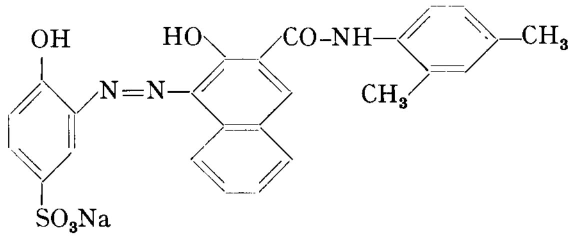
INTRODUCTION

The aim of the investigation, described in this paper, was to develop a method for the determination of 100–1000 μg of magnesium in the presence of 1 g of zinc and small amounts of other metals, such as manganese, iron, nickel, aluminium, lead and calcium.

It is advantageous to keep the amount of zinc as small as possible, since it may be expected that in the case of a large amount of zinc with respect to magnesium the first metal will have to be removed in order to eliminate interference of the magnesium determination. It is then desirable to use a spectrophotometric method for the determination of magnesium. This method should have a high sensitivity.

For this spectrophotometric determination some methods have already been described in the literature. A reagent widely used for this purpose is titan yellow, which forms a colour lake when adsorbed on colloidal magnesium hydroxide[1,2,3]. Other reagents that can be used are Eriochrome Black[4,5] and 8-hydroxyquinoline[6]. Recently, MANN AND YOE have described procedures based on the formation of coloured compounds of magnesium with sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene-5-sulphonate)[7] and with 1-azo-2-hydroxy-3-(2,4-dimenthylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene)[8].



The coloured complex of magnesium and the second reagent is formed in ethanolic medium. Although calcium does not form a coloured complex with the reagent, it may interfere owing to precipitation of its salts in the ethanolic solution. When the second reagent is used there is a greater tolerance for water than when the first one is used. It is obvious that when more water is tolerated the possibility of precipitation of calcium salts decreases. For this reason the authors mentioned prefer the second reagent to the first one. Of course, the possible interference of calcium depends upon the anions present. The sensitivity of the method is high. According to MANN AND YOE[8] a solution of the coloured magnesium complex containing 20 μg of magnesium per litre has an absorbance of 0.020 when measured in 1-cm cells at 505 mμ. The coloured complex is formed at pH = 8.95. A disadvantage of the method is that it is necessary to prepare a new calibration graph for each freshly prepared reagent solution.

Because of this high sensitivity, it was decided to study the applicability of the method to the determination of magnesium in the presence of large amounts of zinc. The fact that heavy metals in amounts of the same order of magnitude as that of magnesium or larger, interfere with the method should not be considered as a specific disadvantage, since these metals also interfere in other procedures.

MANN AND YOE[7] found that a chloroform extraction with 8-hydroxyquinoline can be used for the removal of these metal ions. However, the amounts of metals that can be removed in this way are limited to about one milligram. This means that in our case where so much zinc must be removed, another method of separation had to be found.

A known method for the removal of several heavy metal ions from an aqueous solution is mercury cathode electrolysis. WIBERLEY AND BASSET[9] used this separation technique in the determination of aluminium in steel. These authors used a cell according to MELAVEN[10] which was slightly modified. After this electrolysis, aluminium, calcium and magnesium remain in the solution. Besides these metals titanium, zirconium and vanadium are not removed.

This method of separation was thought to be attractive and it was therefore decided to investigate this separation method combined with the procedure proposed by MANN AND YOE[8], in order to solve our problem.

EXPERIMENTAL

Preliminary experiments

A calibration graph was prepared according to the procedure recommended by MANN AND YOE[8], starting from solutions that contained known amounts of magnesium. All other metals were absent. Five different amounts of magnesium were taken and for each three separate determinations were carried out. The graph, which is not a straight line, is given in Fig. 1.

The numerical values are given in Table I. In this Table the amount of magnesium is the amount in the final solution of which the absorbance is measured.

TABLE I

Magnesium present *µg*	*Absorbance*		
2	0.065	0.067	0.067
4	0.114	0.115	0.112
6	0.162	0.160	0.161
8	0.196	0.194	0.192
10	0.219	0.220	0.220

In order to establish the precision of the method, the equation of the calibration graph was calculated from the absorbances by the method of least squares. A quadratic relationship was supposed to hold. With the aid of this equation the standard deviation of a single determination, *i.e.* the standard deviation of an amount of magnesium predicted from a measured absorbance using the graph, was calculated. We found $s = 0.16$ µg of magnesium and therefore conclude that the precision of the method is fair.

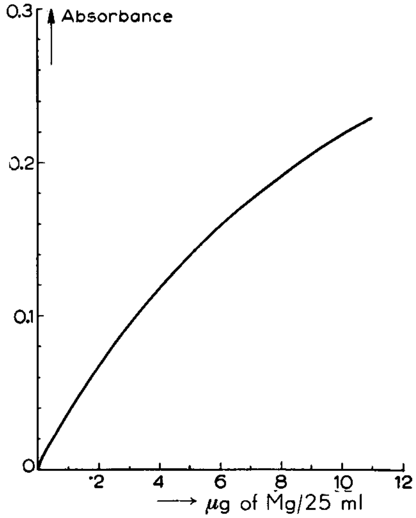


Fig. 1. Calibration graph for the determination of magnesium according to MANN AND YOE[8].

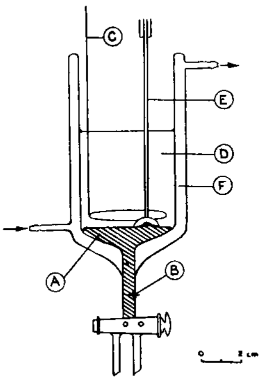


Fig. 2. Modified MELAVEN cell. A: mercury cathode; B: platinum wire; C: anode, platinum wire 1.5 mm ø; D: sample solution; E: stirrer; F: cooling water.

The removal of zinc from an aqueous solution by mercury cathode electrolysis was also studied. In these experiments we started from zinc sulphate, to which small amounts of magnesium, aluminium and calcium were added. A modified MELAVEN cell, as shown in Fig. 2, was used.

From a few experiments it followed that 400 mg of zinc can be quantitatively removed from an acidified solution by electrolysis for 30 min, using a current of 5 A.

After this period no zinc could be detected in the solution by means of the reaction with potassium ferrocyanide. During the electrolysis the solution was stirred with an air-driven stirrer according to STOCK AND FILL[11].

The solution obtained in this way is strongly acid. According to MANN AND YOE[8] the solution in which magnesium is to be determined should be slightly acid. A large amount of acid must therefore be removed from the solution. It was established that this could not be done by a simple neutralization with alkali hydroxide, since the alkali salt so formed unfavourably influences the results of the magnesium determination. Therefore, the acid had to be eliminated in another way. The usefulness of some anion exchangers for this purpose was studied. The slightly basic anion exchanger Dowex 3 was found to be quite suitable. After passing the electrolysed solution through a column packed with this exchange resin it was established that no magnesium was retained by the resin. The solution to be passed through the column must be dilute with respect to magnesium, in order to prevent losses by precipitation of magnesium hydroxide in the column. Poor results were obtained with the anion exchangers Dowex 2 and Amberlite IR4B, because part of the magnesium present was retained by the resin. This phenomenon could not be decreased by heating the solution and the washing water to about 50°.

It proved to be necessary to treat the solution obtained after anion exchange with 8-hydroxyquinoline in chloroform as proposed by MANN AND YOE[7], in order to remove aluminium. Use is then made of the fact that aluminium 8-hydroxyquinolate can be quantitatively extracted from an aqueous solution with chloroform at pH between 5 and 6.7, while magnesium 8-hydroxyquinolate is not formed at pH values under 6.7. Based on these experiences the following procedure was developed.

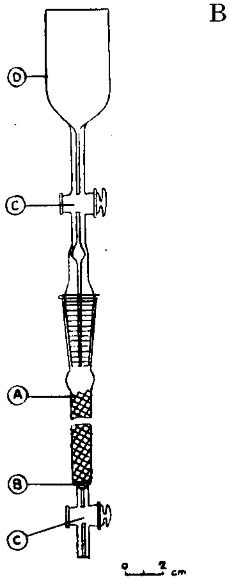


Fig. 3. Ion-exchange apparatus. A: resin column; B: glass wool plug; C: 1-mm capillary stopcocks; D: introductory funnel.

Procedure

Transfer 25 ml of a neutral zinc solution containing 400 mg of zinc as zinc sulphate and 40–400 μg of magnesium into the electrolysis cell (Fig. 2), which contains 15 ml of mercury. Acidify with 3 ml of $4N$ sulphuric acid and dilute with water to about 50 ml, so that the solution is about $0.25N$ in sulphuric acid. Cool the cell with running water, start the stirrer, which is positioned so that only the top layer of mercury is agitated, cover the cell with a split watch-glass to prevent spray losses and electrolyse the solution for 30 min, using a current of 5 A for which 12–18 V is required. Draw off the mercury layer without interrupting the current, and pass the aqueous solution through a column (Fig. 3) packed with Dowex 3 at a rate of one drop per second, collecting the effluent in a 200-ml volumetric flask.

Wash the column with 100 ml of water, and combine washings and effluent. Make this solution just acid to neutral red (pH: 6, 7) and dilute with water to the mark. From this solution pipette 50 ml into a separatory funnel, add 5 ml of 5% 8-hydroxyquinoline in chloroform, shake vigorously and draw off the chloroform layer. Repeat this extraction four times and finally extract the aqueous solution with two 2-ml portions of chloroform. Transfer the aqueous solution to a 100-ml volumetric flask and dilute with water to the mark.

From this solution pipette 10 ml into a 25-ml volumetric flask containing 5 ml of a 0.01% solution of 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene) in 95% ethanol. Add 0.5 ml of $0.08M$ sodium tetraborate solution, in order to adjust the pH to 8.95 and make up to the mark with 95% ethanol. Measure the absorbance of this solution in a 1-cm cell at a wavelength of 505 mμ against a blank. Prepare the blank by adding 10 ml of water and 0.5 ml of $0.08M$ sodium tetraborate solution to 5 ml of the reagent solution and making up to volume with 95% ethanol. Calculate the amount of magnesium with the aid of a calibration graph, prepared by carrying 10-ml aliquots of standard magnesium solutions through the last part of the procedure in which the coloured magnesium complex is formed.

RESULTS

In order to check the procedure described above, solutions of zinc sulphate of analytical grade, containing 400 mg of zinc per 25 ml, to which known amounts of magnesium had been added, were analysed. The results are listed in Table II. The amounts of magnesium are given in p.p.m. with respect to zinc.

TABLE II

Mg present p.p.m.	*Mg found p.p.m.*	*Δ = present — found p.p.m.*	*Recovery %*
198	203	— 5	102.5
198	203	— 5	102.5
396	376	+20	95.2
396	380	+16	96.0
594	579	+15	97.5
594	595	— 1	100.2
792	785	+ 7	99.1
792	818	—26	103.3
990	970	+20	98.0
990	976	+14	98.6
	mean	+ 6	99.3
	st. dev.	10	2.8

Magnesium was also determined in zinc sulphate containing other impurities, *viz.* 150 p.p.m. of manganese, 100 p.p.m. of iron, 40 p.p.m. of nickel, 150 p.p.m. of aluminium, 75 p.p.m. of lead and 250 p.p.m. of calcium, all with respect to zinc. The results are given in Table III.

TABLE III

Mg present p.p.m.	*Mg found p.p.m.*	*Δ = present — found p.p.m.*	*Recovery %*
200	205	— 5	102.5
200	192	+ 8	96.0
400	385	+15	96.2
400	409	— 9	102.2
600	586	+14	97.7
600	590	+10	98.3
	mean	+ 6	98.8
	st. dev.	10	2.9

DISCUSSION

From Tables II and III it can be seen that the method yields precise and accurate results. The mean recovery percentages do not differ significantly from 100% and the standard deviations of the difference between „present" and „found" are satisfactory.

An advantage of the method over that using Eriochrome Black T as a reagent, is that the method is applicable to solutions containing amounts of calcium of the same order of magnitude as those of magnesium. In the Eriochrome Black T method a correction must be applied when calcium is present[12].

Finally, it should be remarked that the procedure has the additional advantage of allowing the determination of aluminium, as this has to be removed by extraction of the 8-hydroxyquinolate with chloroform, which, according to GENTRY AND SHERRINGTON[13], can be determined spectrophotometrically.

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SUMMARY

The spectrophotometric determination of magnesium in the presence of large amounts of zinc is described. Zinc as well as some other interfering metals are removed by mercury cathode electrolysis and aluminium is removed by a chloroform extraction with 8-hydroxyquinoline.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du magnésium en présence de grandes quantités de zinc. Le zinc et quelques autres métaux interférents sont séparés par électrolyse avec une cathode de mercure; l'aluminium est éliminé par extraction au chloroforme avec le 8-hydroxyquinoline.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Magnesium neben grossen Mengen Zink beschrieben. Zink sowie einige andere störenden Metalle werden entfernt mittels Elektrolyse an einer Quecksilberkathode und Aluminium wird entfernt mittels einer Chloroform-extraktion mit 8-Hydroxychinolin.

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APPLICATION DE LA DIPHÉNYL-ACROLÉINE À L'ANALYSE FONCTIONNELLE

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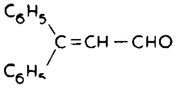
C'est souvent par le jeu de structures conjuguées que l'on interprête le mécanisme de nombreuses réactions colorées. La formation de cycles insaturés ou de structures quinoniques en sont des exemples classiques, de même que l'entrée en conjugaison de systèmes insaturés préexistants. A cet égard, la diphényl-acroléine, I, non encore utilisée en analyse, laisse prévoir, par sa structure, l'obtention facile de dérivés colorés.



$(C_6H_5)_2C{=}CH{-}CHO$

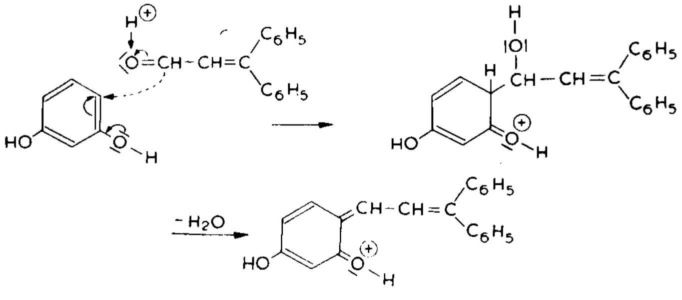
I

Nous décrivons ici sommairement plusieurs condensations intéressant l'analyse organique fonctionnelle.

(1) En milieu alcoolique fortement acide, la diphényl-acroléine développe à froid, avec les composés ayant au moins *deux hydroxyles phénoliques en méta*, une coloration rouge.

A 2 ml de solution méthanolique d'un *m*-diphénol, on ajoute 2 ml de solution à 1% de diphényl-acroléine dans le méthanol et 1 ml d'acide chlorhydrique concentré. Après 20 min à température ordinaire, le maximum d'absorption est situé à 4850 Å (résorcinol, phloroglucinol, orcinol) ou 5000 Å (naphtorésorcinol, pyrogallol).

La vitesse d'apparition de la coloration varie avec le solvant. Le méthanol permet d'obtenir une sensibilité de 1 µg, que l'on n'atteint pas en éthanol. L'addition d'eau fait disparaître la coloration. Enfin, cette réaction liée à la position *méta* des deux hydroxyles permet d'effectuer des dosages. La loi de Beer est satisfaite au maximum d'absorption pour des prises d'essai généralement comprises entre 2 et 10 µg.

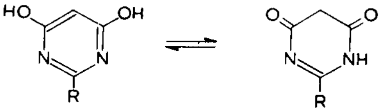


II

Le mécanisme de la réaction n'a pu, jusqu'à présent, être établi, le colorant n'ayant pas été isolé à l'état pur. Par analogie avec les autres condensations décrites ici et en raison de la sélectivité de la réaction, nous croyons cependant pouvoir suggérer une attaque électrophile du *m*-diphénol par la diphényl-acroléine qui aboutit à une structure *o*-quinonique, II.

Cette hypothèse est en accord avec le fait que l'acide résorcinol 4,6-disulfonique ne développe aucune coloration, et que cette coloration est, par contre, observée avec le *m*-diméthylamino phénol.

(2) Dans les mêmes conditions que précédemment, les *méthylènes en α du carbonyle* des cyclanones sont également réactifs. Les colorations sont jaune à jaune-vert avec les cyclopentanone et cyclohexanone. La cyclohexane 1,3-dione et son dérivé 5,5-diméthylé ou dimédone réagissent toutefois assez peu. Les 4,6-dihydroxy pyrimidines fournissent, par contre, des colorations rouges ou orangées. La sensibilité atteint le μg avec la 2-éthyl-4,6-dihydroxy pyrimidine, III*, la 2-carbamylméthyl-4,6-dihydroxy pyrimidine, IV, et l'acide barbiturique, V.

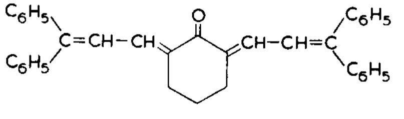


III R = C_2H_5-

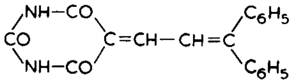
IV R = H_2N-CO-CH_2-

V R = -OH

Les dérivés formés à partir de la cyclohexanone et de l'acide barbiturique ont été isolés. Nous leur avons attribué les structures VI et VII:



VI



VII

La réaction n'est pas fournie par les méthylènes activés rencontrés en série aliphatique: malonate et cyanacétate d'éthyle, acétylacétone et acétylacétate d'éthyle. Par contre, l'indole non carbonylé, mais existant sous une forme méthylénique en β de l'azote développe une coloration rouge.

(3) Les *amines aromatiques* primaires offrent, par action de la diphényl-acroléine en milieu acide, des colorations jaune orangé qui ne sont pas fournies par les amines aliphatiques ou aromatiques substituées. Au maximum d'absorption, vers 4000 Å, la loi de Beer est satisfaite pour des prises d'essai inférieures à 20 μg.

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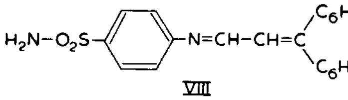
* Ce composé a été préparé selon HULL[1] et BROWN[2] par action du propionate de méthyle sur le diamide malonique.

Il s'agit là d'une formation de bases de Schiff. Nous avons isolé une de ces bases, VIII, à partir du *p*-amino benzènesulfonamide, en raison de la faible solubilité de son chlorhydrate.



VIII

PARTIE EXPÉRIMENTALE

(avec Mlle G. CLÉMENT)

2,6-Bis-diphénylallylidène cyclohexanone, VI.

On ajoute 1 ml d'acide chlorhydrique concentré à 0.5 g de cyclohexanone et 1.0 g de diphényl-acroléine en solution dans 7 ml de méthanol puis abandonne pendant 3 jours à température ordinaire. Le cristallisat jaune-vert obtenu est isolé puis lavé au méthanol et à l'éther (0.7 g). F.inst.: 207°.

Analyse: $C_{36}H_{30}O = 478.6$

Calculé:	C	90.3	H	6.3	O	3.3
Trouvé:		90.1		6.5		3.8

Diphénylallylidène malonylurée, VII.

Dans 35 ml de méthanol, on dissout 0.5 g d'acide barbiturique et 0.82 g de diphényl-acroléine, puis ajoute 5 ml d'acide chlorhydrique concentré. Après amorçage et quelques heures de repos, on essore, lave au méthanol et à l'éther (1.0 g). F.inst.: 330° (déc.).

Analyse: $C_{19}H_{14}O_3N_2 = 318.3$

Calculé:	C	71.7	H	4.4	O	15.1	N	8.8
Trouvé:		71.7		4.4		15.3		8.8

p-(Diphénylallylidène-amino) benzènesulfonamide, VIII.

À la solution de 0.5 g de *p*-amino benzènesulfonamide et 0.6 g de diphényl-acroléine dans 15 ml de méthanol, on ajoute 2 ml d'acide chlorhydrique concentré. Après 2 heures au repos, on essore, lave au méthanol et à l'éther (0.9 g). F.inst.: 230–235°.

Analyse: $C_{21}H_{18}O_2N_2S{\cdot}HCl = 398.9$

Calculé:	C	63.2	H	4.8	O	8.0	S	8.0
Trouvé:		63.3		4.7		7.9		7.7

RÉSUMÉ

En milieu alcoolique fortement acide, la diphényl-acroléine développe, à froid, avec les *m*-diphénols une coloration rouge. Cette réaction, qui permet d'effectuer des dosages, offre une sensibilité de 1 μg. Dans les mêmes conditions, on obtient des colorations jaunes avec les méthylènes situés en α d'un carbonyle ou avec les groupes aminés aromatiques primaires. Plusieurs produits de condensation ont pu être isolés.

SUMMARY

In highly acid alcoholic medium, diphenyl-acrolein develops a red colour with *m*-diphenols, in the cold. This reaction, which makes it possible to carry out determinations, has a sensitivity of one μg. Under the same conditions, yellow colouring is obtained with methylenes in the α position of a carboxyl or with primary aromatic amino groups. Various condensation products have been isolated.

ZUSAMMENFASSUNG

Diphenyl-acrolein gibt mit *m*-Diphenolen in stark saurer, alkoholischen Lösung in der Kälte eine rote Färbung. Empfindlichkeit der Reaktion: 1 μg. Methylengruppen, in α Stellung zu einer Carbonylgruppe oder primäre aromatische Aminogruppen geben unter den gleichen Bedingungen eine gelbe Färbung. Einige der Kondensationsprodukte konnten isoliert werden.

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Reçu le 23 mai 1958

POLAROGRAPHIC REDUCTION OF HEXAVALENT URANIUM IN SODIUM TRIPOLYPHOSPHATE

II. ESTIMATION OF URANIUM

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An acid supporting electrolyte is generally used for the polarographic estimation of uranium. The reduction of UO_2^{+2} can be carried to the penta- or even tetravalent stage by controlling the acidity[1,2,3]. The $E^1/_2$ (around —0.3 V *vs.* S.C.E.) for the reduction of the uranyl ion is inconveniently close to the reduction potentials of several common ions. STRUBL[4] avoided the interference from ferric iron by using hydroxylamine hydrochloride. It has been reported that a 50% solution of ammonium citrate[5] adjusted to pH 4–5 eliminates the interference caused by small amounts of copper and lead. Reduction in ascorbic acid medium at pH 3.5–4, recommended by ŠUŠIĆ *et al.*[6], also offers certain advantages.

Alkaline supporting electrolytes have not been much used in the polarographic estimation of uranium, though there is the probable advantage that many elements such as tungsten, molybdenum, titanium, tin, antimony and niobium might cease to interfere. Alkaline solutions of uranyl complexes undergo a one-electron reduction with an $E^1/_2$ around —0.7 to —1.1 V. The uranium waves in alkali carbonate[7] and in alkali citrate/tartrate[8] are regarded unsuitable for analytical work, but PŘIBIL AND BLAŽEK[9] have used a combination of EDTA and sodium carbonate for uranium estimation with some success. The present paper reports a method for the estimation of uranium based on the reduction of the uranyl tripolyphosphate complex in an alkaline medium.

EXPERIMENTAL

The experimental set-up was substantially the same as described in a previous communication[10]. Uranyl nitrate was used as the standard.

Uranyl concentration vs. diffusion current

All polarograms were taken in presence of 0.005% camphor in the solution, which was observed to improve the shape of the reduction wave considerably, without materially affecting the diffusion current. The height of the wave was corrected for the residual current by graphical extrapolation. The proportionality between *id* and *c* is shown in Table I.

Interferences

In addition to those anionic radicals which are polarographically inactive in the alkaline medium (WO_4^{-2}, MoO_4^{-2} etc.), several cations, *e.g.*, Cr^{+3}, Co^{+2}, Ni^{+2}, Mn^{+2}

TABLE I

id VERSUS URANYL ION CONCENTRATION

Electrolyte composition: uranyl nitrate, 1*M* KNO_3, 0.1*M* $Na_5P_3O_{10}$, 0.005% camphor (m = 1.68 mg/sec, t = 4.204 sec/drop)

Uranyl ion (mM)	*id (µa × 100)*	*id/c*
0.2	56	280
0.5	142	284
1.0	280	280
2.0	556	278
3.0	830	277
5.0	1370	274

and Zn^{+2} were found not to interfere. By complexation with tripolyphosphate, the reduction potentials of these cations became too negative to give cathodic steps in the accessible potential range. Among ions which undergo reduction in an alkaline tripolyphosphate medium, Pb^{+2} and Bi^{+3} have $E^1/_2$ values that are fairly well in advance of the uranyl wave (Pb^{+2} —0.65, Bi^{+3} —0.63, UO_2^{+2} —1.05 V)[10], and do not interfere in low concentrations. Uranium estimations in a few synthetic mixtures containing these non-interfering ions are reported in Table II. The method of standard addition[11] was used throughout to compute uranium concentrations from the polarograms, because the *id* for this reduction varies somewhat with pH, total ionic strength type and concentration of maximum suppressor used, etc.[10]

TABLE II

ESTIMATION OF URANIUM IN SYNTHETIC MIXTURE

Addition to electrolyte (mM)	*UO_2^{+2} taken (mM)*	*UO_2^{+2} found (mM)*
MoO_4^{-2} 10 WO_4^{-2} 10 Ti^{+4} 5	0.50	0.52
ditto	1.00	1.06
ditto	2.00	2.02
Cr^{+3} 10 Ni^{+2} 10 Zn^{+2} 10 Mn^{+2} 10 Co^{+2} 10	0.50	0.54
ditto	1.00	1.03
ditto	2.00	1.96
Pb^{+2} 2 Bi^{+3} 2	1.00	1.04

Separation of uranium with orthophosphate

While the estimation of uranium is thus possible in the presence of many impurities, a method of general applicability will almost always involve a preliminary separation of the uranium from some interfering elements. MILNER AND EDWARDS[12] have recently reported that uranium can be separated from a host of elements by precipitating as uranyl ammonium phosphate in presence of EDTA. A few, *e.g.*, tin, molybdenum, tungsten, titanium and beryllium co-precipitate with uranium since they do not form sufficiently stable complexes with EDTA. But, fortunately, their removal is not essential for the present method of estimating uranium.

The following EDTA–phosphate procedure was, therefore, adopted as the general method for estimating uranium in complex mixtures:

The acidic solution containing uranium is rendered faintly alkaline with ammonia, 3 g disodium salt of EDTA (Merck's Reagent) are added, and the solution boiled for 5 min to facilitate complexation. The solution (not exceeding 200 ml in volume) is buffered with an equimolar mixture of ammonium acetate–acetic acid, about 10 mg beryllium (as chloride) and 2 g solid diammonium phosphate are added, and the solution is boiled for 10 min. After further digesting on the water-bath for 30 min, the precipitate is filtered, washed with a solution containing 2% ammonium nitrate and 1% disodium salt of EDTA, and dissolved in dilute nitric acid (1:4).

TABLE III

ESTIMATION OF URANIUM IN SYNTHETIC MIXTURES

(Before polarographing, the uranium was separated by the EDTA–phosphate procedure).

Synthetic sample[a] *composition (mg)*	*Uranium taken (mg)*	*Uranium found (mg)*
Fe^{+3} 50 Cu^{+2} 50 V^{+5} 50	2.38	2.46
ditto	4.76	4.83
ditto	7.14	7.05
Pb^{+2} 70 Bi^{+3} 70 Cr^{+3} 80	2.38	2.32
ditto	4.76	4.84
ditto	7.14	7.00
Ti^{+4} 20 WO_4^{-2} 50 MoO_4^{-2} 50	2.38	2.47
ditto	4.76	4.86

[a] All the samples contained 10 mg Be^{+2} as the chloride.

References p. 194

The acidic solution is neutralised with ammonia to pH 3–5 with the help of indicator paper, 2 g anhydrous sodium tripolyphosphate and 1 ml of 0.25% camphor solution are added, mixed and the solution is made up to 50 ml. (While making a stock solution of the sparingly soluble camphor, addition of a little alcohol helps to bring about easy dissolution). Aliquots are then transferred to the electrolytic cell and polarographed.

Table III shows some of the results obtained by the above procedure. Incomplete recovery of uranium was indicated in the absence of beryllium coprecipitant, particularly when the uranium taken was below a few mg. Below 1 mg level, uranium recoveries were erratic. All the polarograms were free from any steps other than the one for uranyl ion. The EDTA–phosphate procedure, therefore, gives a complete separation from interfering elements such as cadmium, copper, bismuth, lead, vanadium and ferric iron.

Estimation of uranium in minerals

A few samples of uraniferous ores were analysed for their uranium contents by the new method. Two samples of tantalo-niobate taken for analysis contained as major constituents Nb, Ta, Ti, Fe, Mn and Ca. The only other sample analysed was a Travancore monazite.

Procedure for tantalo-niobate

The sample (2 g, ground to 100 mesh) is weighed into a platinum basin, decomposed with a mixture of nitric and hydrofluoric acids and taken to fumes with sulphuric acid. The fumed mass is transferred with a jet of water to a 500-ml beaker, almost neutralised with ammonia and then re-acidified with 2 ml of nitric acid. On diluting to about 300 ml and boiling, practically all the tantalum and niobium along with most of the titanium precipitate out leaving the uranium in solution. After filtration, the precipitate is washed with 1 : 5 nitric acid. The filtrate is boiled down to about 200 ml and subjected to the EDTA–phosphate procedure. The analysis is completed polarographically by the method of standard addition as already described.

Procedure for monazite

The sample (2 g, ground to 100 mesh) is weighed into 250-ml pyrex beaker and

TABLE IV

ANALYSIS OF URANIFEROUS ORES

Sample	*Uranium content*	
	Procedure under test (%)	*Alternative procedure* (%)
Tantalo-niobate (I)	0.36	0.37
Tantalo-niobate (II)	0.52	0.54
Travancore monazite	0.32	0.34

decomposed with concentrated sulphuric acid. The pasty mass is diluted and boiled with 200 ml of 15% sodium carbonate. It is filtered and the residue boiled with sodium carbonate once again to ensure quantitative extraction of uranium. The combined filtrates are neutralised with dilute nitric acid, boiled down to about 200 ml and subjected to the EDTA-phosphate procedure. The polarographic analysis is then completed as before.

Results of analyses of the minerals are shown in Table IV. The alternative procedure indicated in the Table refers to the conventional colorimetric method with peroxide after extracting the uranium with ether from an aqueous nitrate solution.

For accurate work with complex materials, the sample taken for analysis should contain not less than 2-3 mg of uranium. When interfering elements, *viz.* copper, cadmium, iron, vanadium and large amounts of lead and bismuth are absent, and a preliminary separation of the uranium by the EDTA-phosphate procedure is not indicated, even fractions of a mg of uranium can be estimated, since solutions as dilute as $10^{-4}M$ with respect to uranyl give measurable diffusion currents in an alkaline tripolyphosphate medium.

SUMMARY

A polarographic method of estimating of uranium, based on the reduction of its tripolyphosphate complex at the dropping mercury electrode, has been developed and applied to uraniferous tantaloniobates and monazite. In the presence of elements such as copper, iron and vanadium which interfere with the cathodic step of the uranyl complex, a preliminary separation as uranyl ammonium phosphate in presence of EDTA is necessary.

RÉSUMÉ

Une méthode polarographique est proposée pour le dosage de l'uranium; elle peut être appliquée à l'analyse de tantalo-niobates uranifères et de la monazite.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode zur Bestimmung des Urans beschrieben. Sie lässt sich für die Analyse uran-haltiger Tantal-niobate und Monazit anwenden.

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A SIMPLE APPARATUS FOR THE DETERMINATION OF MERCURY BY AMALGAMATION WITH GOLD

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INTRODUCTION

Difficulty had been experienced in one of our laboratories in obtaining consistent results for the estimation of mercury in charcoal which had been activated by treatment with mercuric chloride. The method used was essentially that of ESCHKA[1] which involves heating the sample with iron powder and quicklime[2] (or zinc oxide) in a silica crucible and amalgamating the mercury, liberated as vapour, on a weighed gold lid. The gold lid is placed on top of the crucible and is cooled by water. The main disadvantage of this procedure is the possible leakage of mercury vapour between the gold lid and the top of the crucible. It was considered, therefore, that the design of an apparatus which would eliminate this difficulty would result in more consistent and accurate results.

EXPERIMENTAL

The apparatus used is shown in Fig. 1. It consists of a straight silica column about 10 cm long and 0.6 cm in diameter loosely packed with gold foil. The bottom of the column fits into a small silica flask containing a mixture of the sample and iron powder which is covered with a thin layer of zinc oxide. On heating, the mercuric chloride is reduced to mercury and the mercury content of the sample is calculated from the increase in weight of the column containing the gold foil.

The apparatus was first tested on AnalaR mercuric chloride, and then on mixtures of charcoal and known amounts of mercuric chloride. The effect of small amounts of impurities was also tested.

Analyses were also carried out by different operators on actual samples of charcoal which had been activated by treatment with mercuric chloride. Three of the operators were applying the method for the first time. The results obtained are shown in Tables I and II.

It is evident, therefore, that the precision is good and that no operator bias is likely to arise in the application of the method. The procedure cannot be applied, of course, in the presence of metals which are volatile at the temperature of the determination and which alloy with gold.

Apparatus

As in Fig. 1.

Cut the gold foil (about 0.0025 cm thick) into strips about 0.3 cm × 2.5 cm. Bend two of these strips at right angles at both ends and place them diagonally across each other inside the silica column. Crumple other strips lightly with the fingers and place them in the column. The column should be filled to a height of about 5–6 cm; this usually requires about 5–6 g of gold foil.

TABLE I

ANALYSIS OF MIXTURES CONTAINING KNOWN AMOUNTS OF MERCURY

Sample	*Mean % Hg[a] recovered*	*No. of determinations*	*Estimated standard deviation*	*Impurities added*
Pure $HgCl_2$	98.9	10	1.20	Nil
Mixtures of charcoal and $HgCl_2$	98.9	12	1.34	
	99.8	4	0.62	1% Na_2S
	98.8	6	0.73	0.1% As_2O_3 0.2% KH_2PO_4 0.15% Na_2SO_3

[a] The amount of mercuric chloride per determination ranged from 50–100 mg.

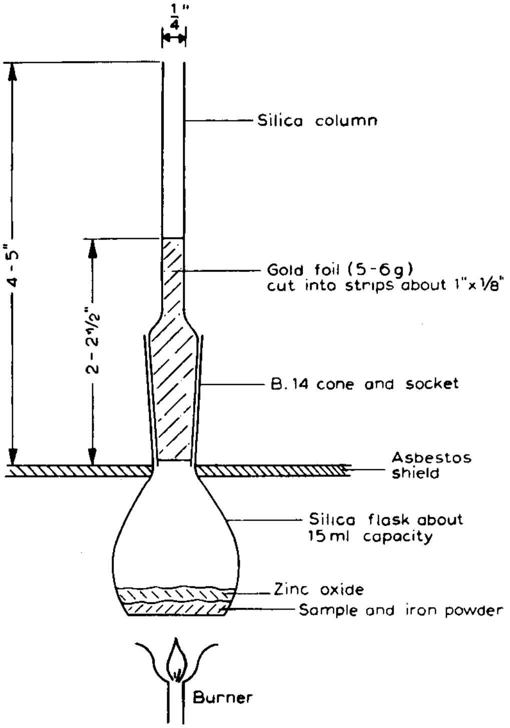

Fig. 1. Apparatus for the determination of mercury.

TABLE II

ANALYSES CARRIED OUT BY DIFFERENT OPERATORS ON ACTUAL SAMPLES

Operator	*Mean % mercury (as Hg)*	*No. of determinations*	*Estimated standard deviation*
1	3.00	10	0.08
2	3.00	5	0.04
3	2.97	6	0.05
4	2.98	4	0.05

Reagents

Iron powder: A.R. grade; to pass 100-mesh sieve; Zinc oxide: A.R. grade; Acetone.

Procedure

Weigh accurately about 1 g of the sample into the silica flask. The sample should contain not more than 70 mg of mercury. Add about 1 g of fine iron powder and mix by gently swirling the flask. Cover the mixture with about 0.3-cm layer of zinc oxide and insert the column, which has been previously rinsed with acetone, dried and weighed, into the silica flask. Place a shield of asbestos, with a hole in the middle, round the neck of the silica flask and heat the bottom of the flask, first with a low flame for 10 minutes and then at a dull red heat for 20 minutes. Allow the apparatus to cool, remove the column, rinse it with acetone, dry and weigh. After each determination, the column can be regenerated by heating it in a bunsen flame and passing air through it to remove the mercury.

ACKNOWLEDGEMENTS

Thanks are due to Mr. V. R. CONRADI who carried out most of the experimental work and to African Explosives and Chemical Industries, Limited, for permission to publish this paper.

SUMMARY

The method of ESCHKA for the determination of mercury by amalgamating with gold has been modified by using a simple apparatus which eliminates errors caused by loss of mercury vapour. The method does not require a skilled operator and it is suitable for routine analysis. For a sample containing 3% mercury, the estimated standard deviation is 0.06.

RÉSUMÉ

L'auteur propose une modification de la méthode d'ESCHKA pour le dosage du mercure par amalgamation de l'or, en utilisant un appareil simple qui permet d'éliminer des erreurs par perte de vapeur de mercure.

ZUSAMMENFASSUNG

Es wird eine Modifikation der Methode nach ESCHKA zur Bestimmung von Quecksilber als Gold-Amalgam beschrieben, wobei ein einfacher Apparat verwendet wird, der Fehler durch Verlust von Quecksilberdampf verhindert.

REFERENCES

1 A. ESCHKA, *Dinglers Polytech. J.*, 204 (1872) 47.
2 G. T. HOLLOWAY, *Analyst*, 31 (1906) 66.

Received June 10th, 1958

Short Communications

The use of 4-amino-4′-chlorodiphenyl as reagent for the determination of sulphate

The original estimation of the solubility of the dried amine sulphate led us to believe that 4-amino-4′-chlorodiphenyl sulphate was only slightly more soluble than barium sulphate[1], but after the reagent had been in routine use for some time it became apparent that the freshly precipitated sulphate was considerably more soluble[2].

Redetermination of the solubility of samples of the *freshly* precipitated salt were made by two methods. The evaporation to dryness and constant weight of 100 ml of a saturated solution of the amine sulphate gave a residue of 8 mg, corresponding to an apparent solubility of 80 mg. Titration of 20-ml aliquots of the same solution with 0.025*N*-sodium hydroxide gave a mean value for the acidity as equal to 0.614 ml of *N*-sodium hydroxide per l. Taking the equivalent weight of the amine sulphate as 254, the solubility becomes 155 mg/l.

BENGTSSON[3] has recently advanced an interesting explanation for the contradictory values for the solubility, based on the equilibrium conditions for the system amine sulphate–water. Because of the sparing solubility of the amine itself in water, its solubility is exceeded before final equilibrium is reached, and thus it precipitates. Determination of the solubility of a saturated solution of the amine salt then gives erroneous results when the solution is evaporated to dryness and the residue is weighed. This possible source of error had been overlooked because earlier determinations on benzidine derivatives involved amines which were all more soluble in water than their corresponding sulphates[4]. This is an extremely important point which has never been adequately appreciated.

The fact that the solubility of the amine sulphate is higher than was originally believed does not affect the use of the reagent under the recommended conditions[2]. Sensitivity data show that a much smaller amount of sulphate ion is detectable in solution in the presence of excess reagent than is present in a saturated solution of the amine sulphate (prepared by shaking the amine sulphate with water for three days). The reagent can readily detect 10 μg of sulphate ion (formed as a precipitate) in a total volume of 50 ml which corresponds to a dilution of 1 : $5 \cdot 10^6$. The amount of sulphate ion present in 1 l of saturated solution of the amine sulphate is approximately 30 mg. From the sensitivity data, 1 ml of saturated amine sulphate should give a definite turbidity with the reagent solution and this can readily be verified. But 1 ml of the amine sulphate solution contains approximately 30 μg of SO_4^{-2}, therefore the amount of sulphate ion remaining in solution must be considerably less than this for an observable precipitate to be obtained.

BENGTSSON concluded on purely theoretical grounds that the reagent is unsuitable for sulphate determinations on the micro-scale because of the solubility of the amine sulphate. He has found by spectrophotometric methods (*cf.* JONES AND LETHAM[5]) that 1 l of the saturated solution of 4-amino-4′-chlorodiphenyl sulphate contains 31.2 mg of sulphate ion and 40.8 mg of amine, which corresponds to a deficiency of amine of 91.8 mg. BENGTSSON's values for the solubility are in close agreement with our results, namely, 80 mg/l for the apparent solubility (BENGTSSON, 72 mg/l and 155 mg/l for the theoretical solubility (BENGTSSON, 164 mg/l).

We can only conclude from BENGTSSON's remarks that he has not appreciated the remarkable sensitivity of the reagent towards sulphate ions. He considers that solubility is the prime factor which can influence the suitability of an analytical reagent, whereas we accept FEIGL's view that the sensitivity of the reagent is the more important criterion.

References p. 199

BENGTSSON's suggestion for improving the use of the reagent by halving the amount of free hydrochloric acid in the reagent solution thus, in his words, 'favouring the completeness of the precipitation by a factor of two or three owing to the increased pH and lower ionic strength of the solution' offers no advantage over the original reagent, and in fact, has the disadvantage of crystallising out the amine hydrochloride more readily on standing, thus decreasing the already limited strength of the reagent solution.

BENGTSSON states that 'since the solubility product of the amine sulphate is $0.8 \cdot 10^{-11}$, the amount of sulphate left in solution is *calculated* to be 30 µg. But this cannot be reconciled with the fact that the reagent will under quite standard conditions give an observable precipitate not only with 31 µg of sulphate ion in 1 ml of a saturated solution of the amine sulphate (BENGTSSON's figure), but with as little as 10 µg.

4-Amino-4′-chlorodiphenyl is the most sensitive reagent known for the precipitation of the sulphate ion. This can readily be shown by adding to three 50-ml Nessler glasses 10 ml of a solution containing 5 µg/ml of SO_4^{-2} and diluting each glass to the mark with equivalent solutions of barium chloride, benzidine hydrochloride and 4-amino-4′-chlorodiphenyl hydrochloride respectively. Only with the last reagent does a well-defined turbidity develop which is still apparent when the test solution of sulphate is diluted 5 times. Hence precipitation of sulphate is even more complete than with barium.

Provided that the proper care (which we have always stressed) is taken in the washing procedure, the reagent is capable of giving very accurate results over a wide range of sulphate concentrations. BENGTSSON's arguments against the suitability of 4-amino-4′-chlorodiphenyl as an analytical reagent could be applied equally well to a great number of analytical precipitants, for example, the double uranyl acetate reagents for sodium. Nevertheless, such reagents are extensively used in quantitative analytical procedures with satisfactory results.

During the years following the proposal of the present reagent, considerable interest has been aroused by its many possible applications. Successful procedures have been adopted in a number of laboratories and sufficient published data exist for the reagent to be the subject of a forthcoming review.

The University, Edgbaston, Birmingham (Great Britain) R. BELCHER
W. I. STEPHEN

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Solubility products of gadolinium bicarbonate

Although this compound has not been previously reported, the bicarbonate of calcium and other alkaline earths are well known. SÖRENSEN[1], in reporting on the Winkler method[2] for caustic alkalies, states that in the addition of barium chloride to a carbonate solution appreciable bicarbonate is coprecipitated. In this study a preweighed amount of gadolinium oxide was dissolved in perchloric acid. This solution was then titrated in increments with standard sodium carbonate and the pH was observed by means of a model #2 Beckman pH meter. A curve of the type shown in Fig. 1 was obtained by plotting pH as a function of solution added. The portion A′ —C represents the precipitation of the bicarbonate. The portion A —A′/2) represents the titration of excess perchloric acid. The pH at point B(B = C —A′/2) was used to obtain the hydrogen ion concentration resultant from the bicarbonate equilibrium. From the equivalents of carbonate consumed in the portion A′ —C it was found that the ratio of gadolinium to carbonate was 1:3, which has a variance of 0.12. The precipitate was dried over dehydrate and when analyzed gave 55.2% ignited oxide (R_2O_3). This compared with 50.6% for the bicarbonate compound. Oven drying caused thermal decomposition and conversion to the carbonate.

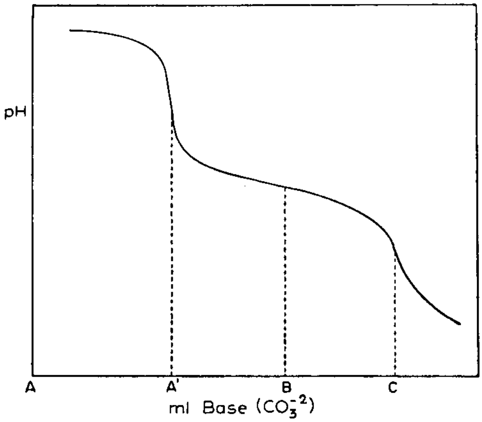

Fig. 1. Typical titration curve.

The solubility product was evaluated from the known hydrogen ion concentration at point B, and the fact that at B the concentration of the gadolinium ion is about one-half of that at A′. The hydrogen ion concentration coupled with the carbonate equilibrium ($K = 4.5 \cdot 10^{-11}$) gave the bicarbonate concentration[3]. Table I gives the pertinent data for the observed solubilities of this material. The normally expected result is rising solubility with increasing temperature.

References p. 201

TABLE I

SOLUBILITY PRODUCT DATA FOR GADOLINIUM BICARBONATE

Temperature	*pH at B*	*$Gd(HCO_3)_3$*
10	5.26	$9.7 \cdot 10^{-3}$
20	5.24	$13 \cdot 10^{-3}$
30	5.14	$20 \cdot 10^{-3}$
40	4.95	$340 \cdot 10^{-3}$

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C. C. MELOCHE**

1 S. P. L. SÖRENSEN AND A. C. ANDERSON, *Z. anal. Chem.*, 45 (1906) 220.
2 I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. 2, Interscience, New York, 1947, p. 10.
3 I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. 1, Interscience, New York, 1947, p. 151.

Received August 30th, 1958

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REVUE DE LIVRE

Manual of Analytical Methods Recommended for Sampling & Analysis of Atmospheric Contaminants, publié par le Committee on Recommended Analytical Methods – American Conference of Governmental Industrial Hygienists, Cincinnati 2, Ohio, 1958, Prix $ 5.00.

L'ouvrage que nous avons en mains est un recueil de méthodes concernant le dosage de divers poisons dans l'atmosphère. Il est le résultat d'un travail collectif et critique, travail dû à un Comité désigné par l',,American Conference of Governmental Industrial Hygienists''.

Présenté sous forme de classeur avec des feuilles interchangeables, il permet au lecteur d'y joindre les méthodes que le Comité fera paraître ultérieurement et dont les neuf premières sont comprises dans le prix indiqué plus haut.

Bien que soumises à un contrôle sévère, les marches à suivre proposées souffrent d'un certain manque de détails, ce qui pourrait quelque peu étonner un lecteur habitué aux publications américaines de ce genre (celles de l'A.S.T.M., par exemple). De même, à notre avis, les références bibliographiques pourraient être plus riches, spécialement dans le cas du plomb. (Comparer au rapport de l'American Public Health Association Inc.: *Methods for Determining in Air and in Biologic Materials*).

En dépit de ces remarques, nous nous faisons un plaisir de reconnaître que les exposés sont très clairs et les modes opératoires proposés, en général, suffisamment simples pour qu'ils puissent être appliqués dans un laboratoire ordinaire.

Les rapports parus jusqu'à présent traitent successivement: l'arsenic, les hydrocarbures chlorés, le formaldéhyde, l'hydrogène sulfuré, le plomb, le manganèse, le mercure, les oxydes de l'azote, le parathion et l'anhydride sulfureux. Ils sont classés par ordre alphabétique, la pagination étant propre pour chaque élément.

En terminant, nous tenons à recommander cet ouvrage, tout particulièrement aux analystes de l'industrie chimique, persuadés qu'ils y puiseront des méthodes fort utiles pour le contrôle de l'air dans leurs établissements.

I. KAPÉTANIDIS (Genève)

BUCHBESPRECHUNG

GMELINS *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, GmbH, Weinheim, 1958.

Fortlaufend erscheinen die neuen Bände der achten Auflage des obgenannten Werkes. Mit diesen Neuerscheinungen behauptet das Werk seinen hervorragenden Platz im Schrifttum der Chemie, baut diesen sogar weiter aus. Soeben sind vier neue Bände dieses umfassendsten Werkes der anorganischen Chemie erschienen:

Sauerstoff, System-Nummer 3 (Lieferung 3), 518 Seiten (Elementarer Sauerstoff) Kart. DM 283.–.

Das Buch behandelt auf den ersten 17 Seiten die Herstellung des Sauerstoffes im Laboratorium und in der Technik. Ein spezieller Abschnitt befasst sich mit der Anreicherung und Trennung der Sauerstoffisotopen. Der grösste Teil des Bandes behandelt die physikalischen Eigenschaften des Elementes, in erster Stelle die atomaren und molekularen Grössen. Eingehend werden die Löslichkeit, die Allotropien, sowie die optischen Eigenschaften des Sauerstoffes behandelt. Abschliessend finden wir auf 196 Seiten eingehende Ausführungen über die Eigenschaften der Sauerstoff – Wasserstoff Gemische und Luft – Wasserstoff Gemische. Explosionsfähige Gemische, Schwellentemperaturen, Explosionskatalysatoren sind im letzten Abschnitt ausführlich besprochen.

Zirconium, System-Nummer 42, 448 Seiten, Kart. DM 266. – .

Mit der Entwicklung der Technik kommen immer mehr Elemente zur Geltung, die bis anhin eine untergeordnete Stellung einnahmen. Eines von diesen Elementen ist das Zirkon. Seinem neuen Rang ist im vorliegenden Bande gebührend Rechnung getragen.

Ein kurzer geschichtlicher Überblick ist gefolgt von den Abschnitten: Vorkommen, und Gewinnung von Zirkoniumverbindungen aus Erzen. Dieses letztere Kapitel behandelt ausführlich die Aufbereitung der Erze, der bei der Gewinnung und Trennung des Zirkons eine ganz besondere Bedeutung zukommt. Die folgenden 112 Seiten sind dem Elemente Zirkonium gewidmet. Seine Herstellung im Laboratorium und in der Technik, die physikalischen Eigenschaften des Metalles, das chemische und elektrochemische Verhalten und die Legierungen sind mit sehr viel Fachkenntnis und Ausführlichkeit behandelt. Dabei werden auch die Verwendungsmöglichkeiten des Metalles und seiner Eigenschaften als Werkstoff besprochen. Der letzte, grösste Abschnitt befasst sich mit den Verbindungen des Elementes wobei die technisch wichtigen Körper eingehend besonders besprochen werden.

Hafnium, System-Nummer 43, 23 Seiten, Kart. DM 22. – (Ergänzungsband).

Das Werk umfasst die Forschungsergebnisse der Jahre 1940 bis 1949. Die Geochemie des Elementes zeigt naturgemäss eine sehr grosse Verbundenheit mit dem Zirkon. Besondere Sorgfalt und Ausführlichkeit sind den Abschnitten über die analytische und technische Trennung des Elementes von Zirkon gewidmet. Die Kapitel über die Verwendung und den Eigenschaften des Metalles und die Besprechung seiner Verbindungen beschliessen das Werk.

Germanium, System-Nummer 45, 576 Seiten, Kart. DM 332. – (Ergänzungsband).

Das Werk umfasst die Jahre 1931 bis 1953/4. In dieser Zeitspanne hat das Element Germanium eine technische Wichtigkeit erlangt, die mit seiner Bedeutung zur Zeit des Erscheinens des ersten Bandes nicht verglichen werden kann. Der Umfang des Bandes hat sich demgemäss auch vervielfacht. Die ersten 27 Seiten behandeln das Vorkommen und die Geochemie des Elementes. Das folgende Kapitel ist der Gewinnung der Germaniumverbindungen aus den Erzen gewidmet. Besondere Aufmerksamkeit erhielt dabei die Herstellung reinstes Germaniums. Die physikalischen Eigenschaften, in erster Stelle die so wichtige Elektronenkonfiguration des Atoms, sind mit der charakteristischen Sorgfalt des Handbuches beschrieben. Dieser Abschnitt, der über 400 Seiten des Bandes einnimmt, ist weitaus der wichtigste Teil. Die elektrischen und lichtelektrischen Eigenschaften sind im Inhaltsverzeichnis separat gehalten was ihre Wichtigkeit wohl unterstreicht, jedoch beim ersten Durchblättern des Buches etwas irreführend sein kann.

Die Chemie des Germaniums, seine analytischen Nachweis- und Bestimmungsmethoden sind ebenfalls ausführlich behandelt. Die Legierungen und Verbindungen des Elementes–dessen besonderer Übergangscharakter auch diesem Abschnitt einen besonderen Ton verleiht, wobei es nicht zu vergessen ist, dass Germanium zu der Kohlenstoffe-Gruppe gehört–beschliessen das Werk.

H. KELLER (Genf)

SOME RECENTLY PUBLISHED BOOKS

E. BRODA, *Radioaktive Isotope in der Biochemie*, Bd III, Verlag Franz Deuticke, Wien, 1958, viii + 326 S., in Ganzleinen, öst. S. 294.—, DM 49.—

M. HUDLICKÝ, *Chemie organických sloučenin fluoru, Chemie der organischen Fluorverbindungen*, Verlag der Tschechoslowakischen Akademie der Wissenschaften, Praha, 1958, 360 S., Kcs 38.50

B. JIRGENSONS, *Organic Colloids*, Elsevier Publishing Company, Amsterdam, 1958, xiv + 625 pp., £ 4.5.—

F. KLAGES, *Lehrbuch d. organischen Chemie*, Bd III, Walter De Gruyter und Co, Berlin, 1958, xix + 766 S., geb. DM 98.—, bei Einzelbezug DM 104.—

J. MAURIN, *Les piles atomiques à neutrons lents*, Dunod, Paris, 1958, xii + 197 pp., relié toile souple, 980 Frs.

S. S. PENNER, *Chemistry Problems in Jet Propulsion*, Pergamon Press Ltd, London, 1957, xiv + 394 pp., 90 s. net

E. H. RODD, *Chemistry of Carbon Compounds*, Vol. IV A, Elsevier Publishing Company, Amsterdam, 1958, xxvi + 808 pp., £ 7.7.—

K. SAGEL, *Tabellen zur Röntgenstrukturanalyse*, Bd VIII, Springer-Verlag, Berlin, 1958, viii + 204 S., Steif geheftet DM 28.—

H. BREDERECK UND E. MULLER, *Organische Chemie in Einzeldarstellungen*. VI. Bd, *Präparative organische Photochemie*, Ankündigung des Springer-Verlages, Berlin, 1958, Etwa 288 S., Ganzleinen etwa DM 58.—

SCHULZE, *Molekülbau*, Slg. Göschen Bd 786, Walter de Gruyter und Co., Berlin, 1958, 123 S., geh. DM 2.40

H. SIRK, *Einführung in die Vektorrechnung für Naturwissenschaftler und Chemiker*, Verlag Dr. Dietrich Steinkopff, Darmstadt, 1958, x + 124, DM 16.—

Anon., *Analyse-Voorschriften*, Kunststoffeninstituut T.N.O., Delft, 1958, loose-leaf publication (in Dutch), Dutch guilders 75,—.

Announcements

26e CONGRES INTERNATIONAL DE FONDERIE

L'INSTITUTO DEL HIERRO Y DEL ACERO, chargé par le Comité International des Associations Techniques de Fonderie de l'organisation du 26e Congrès International de Fonderie et par le Conseil Supérieur des Recherches Scientifiques d'Espagne, de sa IVe Assemblée Générale, a l'honneur de vous inviter à prendre part à ces deux actes.

Ce congrès aura lieu à Madrid du 4 au 10 octobre 1959. Le thème des mémoires scientifiques est libre. Le programme provisoire comprend:

> Séances solennelles d'ouverture et de clôture; Inauguration des nouvelles installations de l'INSTITUTO DEL HIERRO Y DEL ACERO à la Cité Universitaire; Présentation et discussion de mémoires; Réunions des Commissions Internationales de Fonderie; Conférences techniques; Réceptions officielles; Visites de fabriques; Soirées artistiques; Programme spécial pour dames; Voyage post-Congrès d'intérêt technique et touristique, avec deux itinéraires: Espagne du Nord; Espagne du Sud et Méditerranée.

Nous espérons vous souhaiter la bienvenue à Madrid en 1959 et votre rendre séjour en Espagne agréable et instructif.

L'Agence Wagons-Lits/Cook, a été chargée officiellement de l'organisation de voyages et de logements.

Toute information sera fournie avec plaisir par l'INSTITUTO DEL HIERRO Y DEL ACERO, 13 Villanueva, à Madrid.

PRELIMINARY NOTICE
of the
2nd INTERNATIONAL CONGRESS OF POLAROGRAPHY
Organised by the
POLAROGRAPHIC SOCIETY

to be held in Cambridge 24th—29th August 1959.

The Congress will be held in the University of Cambridge and will consist of Scientific Sessions (original papers, reviews and discussions) and Exhibition of Commercial Equipment, Demonstrations of Laboratory Apparatus, visits to local industry and places of interest and social functions.

A supporting programme for ladies is being arranged.

The scientific programme will be divided into the following Sections:

1. Instrumentation.
2. Theory and Kinetics.
3. Analytical and Industrial Applications.
4. Fundamental Studies.
5. Biological and Medical Applications.
6. Miscellaneous.

There will also be four Plenary Lectures by World Authorities and six Section Lectures. Contributions will be welcome and details should be submitted to: G. F. REYNOLDS, M.Sc., F.R.I.C., Chemical Inspectorate, Ministry of Supply, C. 36. Royal Arsenal, Woolwich, London, S.E.18, (Great Britain)

Notification of intention to submit a communication should be made as soon as possible and in anycase not later than 31st, March 1959, by which date a summary not exceeding 200 words is also required. Preprints of all papers will be issued and final manuscripts must therefore be received not later than 31st, May 1959. There will be an exhibition of commercial equipment and ancilliary materials.

Requests for application forms and further details should be sent to: Mrs. B. LAMB B.Sc., F.R.I.C., Chemistry Laboratory, Evershed and Vignoles, Corner of Iveagh Avenue, North Circular Road, London, N.W.10 (Great Britain).

VOL. 20 NO. 2 ANALYTICA CHIMICA ACTA FEBRUARY 1959

CONTENTS

Short Communications: