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A CRITICAL REVIEW OF METHODS OF ISOLATING AND SEPARATING THE SIX PLATINUM METALS

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Summary—This review covers pertinent publications up to January 1960. While relatively little of the early literature is discussed, certain procedures which remain potentially useful have been included. All published information related to the efficiency of fire-assay recovery is discussed from the point of view of flux composition, button and bead collections, and methods of parting the latter. The character and usefulness of a wet selective extraction before fire-assay fusion are critically examined. The wet methods of separating the six platinum metals are reviewed, and the application of exchange resins and chromatographic separations are discussed.

THE recognition of indebtedness to the early platinum metals researcher with which this review was initiated was not lessened by the detailed examination of the great accumulation of pertinent literature. Within these early reports one finds the foundation for almost all of the major improvements in the analytical chemistry of the platinum metals. Indeed, here and there, one encounters neglected procedures which may yet provide new methods of separation and determination. Reluctantly the author has done his best to adhere to the purpose of a critical review and toward this end only those references have been selected which suggest potentially useful analytical applications.

The older methods of *en masse* separation involved a combination of solvent extractions from aqueous and fused media. In general, the descriptions of these separations do not provide quantitative data and too frequently depend upon the incorrect inference that acid extractions of complex mixtures are similar in character to those of single metals. One cannot over-emphasise the fact that even to-day too few authors have recognised the potential complexity of equilibria in platinum metal solutions, the character of which may well affect all methods of separation as well as methods of determination. In some instances these deficiencies may have resulted in unmerited criticisms and the author can only hope that this presentation will serve to identify the more firmly established separational procedures and to provide assistance to the analyst in his efforts to recognise unprofitable techniques.

While, from a practical point of view, very little would be gained by a detailed discussion of the very early literature, there is salutary value in the fact that the intervening century and a half of researches has added little to our knowledge of analytical extractions from natural sources, nor do we know much more than Deville and Debray concerning the character of the minerals of the platinum group. The long continued ignorance of the identity of the final "insoluble" in the assay extraction was obscured then, even as it is to-day, by the terms osmide of iridium or iridosmine. The mineralogy of the latter[1] is incomplete and potentially misleading. To the best of the present author's knowledge no acceptable chemical examination of the assay "insoluble" has been recorded. Presumably Berzelius separated "grains" or "scales" to which he ascribed the term "osmurate of iridium".[2] With some justification the expression osmiridium of iridosmine was applied in early reports of composition but without good reason has been used continually to the present day. Fortunately the proportion of the "insolubles" in platinum assays is practically always very small, and this fact alleviates the moral responsibility of reporting as available platinum metals a substance which in some cases does not readily yield the individual platinum metals.

The methods of *en masse* extraction will be discussed under the headings "Selective Extractions" and "Fire Assay." The latter division will include a selected summary of wet and fire treatments, a discussion of the efficiency of fluxes, lead-alloy collection and silver-bead collection.

SELECTIVE AQUEOUS EXTRACTIONS

While it is a fact that no proved wet procedure, as applied to ores and concentrates, has ever been recorded, it remains true that wet methods theoretically will make available for accurate determination each of the platinum metals. The problem is a practical one since with ores one is dealing with a dilution of about 200–400 μg of total platinum metals in about 30 g of ore, a ratio which represents some of the good grade Northern Ontario sources.

Early attempts at wet selective extractions were generally made on rich concentrates or minerals. The initial processes usually involved some type of caustic oxidising fusion or chlorination in the presence of sodium chloride. A critical survey of the procedure is made particularly difficult because of the confused interpretation of the dissolved constituents, which situation is particularly applicable to the period before Claus's discovery of ruthenium. After dissolution, the most generally useful separatory reagent was ammonium chloride which was used by Claus[3] and by Gibbs[4] and by Elsner[5] to separate platinum, iridium, ruthenium and rhodium. Lea[6] modified Claus's methods by the addition of oxalic acid to reduce and thus dissolve the ammonium chloroiridate. Ruthenium salts were removed by washing with saturated ammonium chloride. Gibbs[7] recorded in great detail the preferred analytical methods used in the later 19th century. Potassium nitrite was used to dissolve the iridium salt selectively. The general scheme involved the addition of sodium nitrite and sulphide to precipitate rhodium, platinum, ruthenium and iridium. The mixed sulphides were dissolved, and the metals were then precipitated by zinc and subsequently chlorinated and treated with nitrite. The ruthenium was extracted with ethanol, and the rhodium was separated from platinum by the precipitation of the rhodium nitrite complex. Deville and Debray[8,9] selectively isolated platinum and iridium from the minerals by *aqua regia*, converted the two metals to the ammonium chloride complexes, reduced with turpentine, and extracted platinum selectively with dilute *aqua regia*. The mineral extract was evaporated, and was fused with sulphur to form sulphides of base metals, rhodium and palladium. The mixture was then treated with nitric acid to isolate the insoluble rhodium and gold. The methods of Deville and Debray were improved significantly by Leide and coworkers, to whom insufficient credit has been given for the initiation of the most generally useful wet procedure for the separation of platinum metals from associated base metals.

This improved procedure, refined by the Bureau of Standards at Washington, involves the development of stable nitrite complexes in a basic medium from which the base metals may be precipitated as hydrated oxides. Leidié and Quennessen[10] treated the *aqua regia* extract of a concentrate with sodium carbonate and nitrite to remove base metals, volatilised osmium and ruthenium by chlorinating the filtrate, acidified the residual liquid, removed rhodium and iridium with potassium chloride and sodium nitrite, and finally precipitated platinum and palladium with formaldehyde in an alkaline medium. These authors[11] also developed a method for the determination of constituents of iridosmine, and a procedure for the dissolution of resistant residues by chlorination followed by the application of a series of separations, many of which remain acceptable. Final precipitations on the separated metals were usually accomplished by reagents which are now outmoded.

EXTRACTION FROM ORES

In general the extraction from a fused mixture is accomplished by providing for the production *in situ* of an alloying metal, of which the most frequently used is lead. This practice has grown out of an irrational ascription to the platinum metals of the nobility of gold. With the exception of platinum, all of these metals will form oxides when heated in air by a Bunsen flame; and even platinum at higher temperatures suffers an unexplained loss of weight. There is also the fact that in aqueous media at least, the reduction of gold salts to form metal is accomplished with relative ease. It is indeed a surprising fact that the fire assay for the more common platinum metals has been acceptably successful. Deville and Debray[8] fused the ore with borax in the presence of wood charcoal and silver to produce an alloy said to contain all of the platinum metals. Perry[12] fused alloys of the metals with lead and silver, cupelled to remove the base metals and then re-alloyed with silver. Deville *et al.*[13] applied fusion methods to larger samples of ores and alloys, previously treated with *aqua regia.* The residues were fused with litharge, silica and carbon to produce a button to be parted with nitric acid to give a residue from which a zinc alloy was prepared. This alloy, treated with acid, produced finely divided iridium, osmium etc., which could then be satisfactorily corroded with fused nitrates. It is interesting to note that the authors used the recently described[14] Gilchrist fusion with lead, followed by acid treatments to produce fairly pure iridium crystals.

It is significant that in 1885 Wilm[15] criticised all contemporary methods of analysis for the platinum metals, and submitted that no satisfactory procedure had been recorded. Duparc[16] in 1919 stated that before his proposed procedures, it was difficult or impossible to obtain concordant results upon the same sample.

Hampton[17] drew attention to the ease with which vanadium, as NH_4VO_3, could be mistaken for $(NH_4)_2PtCl_6$ and suggested that some presumably dishonest assays may have been due to this error. The author charged the U.S. Bureau of Standards with failure to draw attention to the sources of error in the determination of platinum. Davis[18] reported that the results from various assayers for a concentrate containing 40–50% of copper varied so much that the U.S. Bureau of Mines was requested to devise an analytical scheme.

As late as 1940 Lathe[19] stated that so far as he was aware "no simple and at the same time reliable methods for the determination of metals of the platinum group in ores and concentrates have yet been published . . . There is in the literature much that is uncertain, contradictory, or inapplicable to any particular case". Perry[12] also criticised these "established" methods and recommended an initial selective parting with sulphuric acid to remove silver, followed by re-alloying with silver, parting with nitric acid to remove platinum, and treating the residue with *aqua regia* to remove gold. The insoluble residue was called iridosmine.

The United States Bureau of Mines, in 1921, published an extensive pamphlet dealing with various aspects of platinum metals assaying. A significant part of the publication deals with the claim that platinum metals may occur in natural deposits in forms which resist determination by the classical lead collection. An array of evidence is marshalled by Davis to refute this claim and while the present author agrees with the conclusions in general, one does well to remember that negative evidence is not conclusive evidence.

One of the questionable aspects of the fire assay concerns the influence of the character of the platinum metals minerals. Since one cannot with assurance write the mechanically mixed composition, the claim is sometimes made that with certain ores the collection by molten lead is ineffective. To avoid this possibility, wet treatments of the ore with various mixed acids were sometimes applied before fire assay in order to convert platinum metals to forms which are known to be amenable to fire-assay procedures. The fact that all of the platinum metals except palladium resisted attack by single mineral acids suggested to the early analyst the use of selective dissolution to separate associated base metals. Wilm[20] and others recorded methods which involved collective precipitations by zinc or iron and subsequent removal of base metals by nitric or hydrochloric acid. Seliverstov[21] decomposed the ores with concentrated sulphuric acid and treated the mixture with sulphur to form sulphides which were filtered and roasted, and then fire assayed to form a bisilicate slag. For high valued ores an alternative procedure was provided by which the roasted residue was treated with formic acid, then with *aqua regia* to extract the black residue selectively; after filtration the platinum and palladium were precipitated by formic acid in an ammoniacal medium. The residues were treated to determine platinum, palladium, gold, rhodium and iridium. Karpov *et al.*[22] used an *aqua regia* extract of the ore and digested the residue with ammonium acetate to extract lead sulphate and silver chloride. The residue was fused with silver and borax and, curiously and incorrectly, the increase in weight was taken to indicate the content of iridosmine. The silver bead was then treated with sulphuric acid, the insoluble was fused with sodium peroxide and sodium hydroxide, and the osmium and ruthenium were distilled from a chlorinated solution. The procedure involved the separation of platinum and iridium by ammonium chloride, roasting, and subsequent cupellation with silver, parting with nitric acid and re-precipitation of platinum with ammonium chloride . The iridium residue was fused with bismuth, and treated with nitric acid and *aqua ergia* to purify the iridium. Rhodium was separated from the acid by zinc, and this process was followed by fusion with silver and parting with acids. Zhemchuzhny *et al.*[23] described a somewhat similar modification for the treatment of the *aqua regia* residue and included a procedure for the treatment of the *aqua regia* extract. The method involved oxidation by chlorine and precipitation of platinum and iridium by ammonium chloride, removal of palladium and gold by dimethylglyoxime from a portion of the filtrate, followed by treatment of the palladium-gold filtrate by zinc to precipitate rhodium and the remaining iridium. Gold was also produced by a reduction with sodium nitrite of a second portion of the platinum-iridium precipitation, and subsequently palladium was precipitated by mercuric cyanide. The iridium precipitates were collected and fused with soda to dissolve ruthenium selectively. Lovely[24] recommended a combination assay method which involved the conversion of ores or concentrates by fusion in a plumbago crucible with iron, sulphur and carbon to form a matte; this was subsequently ground and treated with *aqua regia* from which mixture osmium and ruthenium were said to be evolved. Methods of separating platinum, thorium, iridium, polonium, actinium, palladium, gold and rhodium were included. A similar method of concentrating was described by Griffith[25] who fused nickel-copper ores of the Sudbury district containing not less than 15% and not more than 50% of sulphides; beyond these limits, blank sulphates were added or the sulphide ore was partially roasted and silica was added to the charge. The fused matte was removed from the broken pot and treated with dilute sulphuric acid to produce a final residue of 20–30 g, which was assayed in the usual manner. Griffith did not prove that the matte is a sufficiently effective collector, and the low palladium recovery was ascribed, without sufficient evidence, to the failure of sulphuric acid to extract all of this metal. A somewhat comparable method for the analysis of platinum concentrate was described by Schwitter[26]. A series of *aqua regia* extractions resulted in a residue which was alloyed with lead; the latter was parted with nitric acid and the ignited residue was erroneously termed osmium. From the *aqua regia* extract the author removed platinum by ammonium chloride, gold by ferrous sulphate, and palladium by potassium iodide; and in the final filtrate zinc was used to collect rhodium and iridium. In the present author's opinion none of the above combination assays can be considered efficient; none has been proved accurate or precise. In many instances the methods of individual metal determination are outdated. In practically all instances large samples of ore or concentrate are required since each determination involves a precipitation reaction. Adams[27] stated that preliminary acid treatment applied to South African flotation concentrates provided no advantage and proved extremely tedious. The single recorded research which deals quantitatively with the merits of leaching was recorded by Hoffman *et al.*[28] The authors used a technique involving preliminary treatment of the oxidised ore or concentrate with hydrochloric acid, followed by precipitation with hydrogen sulphide from the acid extract or by a zinc precipitation. These authors' results indicated that "leaching processes do not, in general, provide values higher than those obtained by normal fire assay." An extraction of platinum from ores by an amalgamation process was described by Plaksin and Schtamova.[29] The 65-mesh ore was treated with dilute sulphuric acid and then by grinding with zinc amalgam, mercury, copper sulphate and sulphuric acid. The ore was then washed with a caustic solution which, the authors claimed, resulted in removal of 90–97% of the platinum. Unfortunately no further publications of this interesting extraction are known to the present author.

Fire assay

Aside from the classical lead collection, various procedures have been considered for the analytical concentration of the platinum metals. The separation of noble metals in copper-nickel slimes was accomplished by Pshenitsyn and Lazareva[30] through a fusion with borax. The platinum groups were selectively removed from copper, nickel, iron and lead by a fusion at 1200° for 2 hours. The fused mixture was boiled with hydrochloric acid solution and the residue weighed as noble metals. Obviously this method could not produce good analytical accuracy. A method based on the fact that arsenic and antimony speisses are good collectors of osmium, iridium, and ruthenium, but less effective for platinum and palladium, has been reported by Rusden and Henderson[31]. The fluxing mixture included arsenic as well as the conventional mixture and the fusion was carried out in the presence of an iron rod. The same authors found[32] that the fused mixture solidified in distinct layers, lead on the bottom, then speiss, then matte and finally slag. The addition of iron filings to an assay charge and subsequent melting in a clay or graphite crucible was recommended by Savelsberg and Fischer[33] to avoid slag losses of the platinum metals. Nickel was removed from the lead regulus by fluxing with soda and borax. The addition of silver to the charge encouraged quantitative collection. These approaches, examined with accuracy by modern methods, could produce potentially useful extractive methods.

In general the modern fire assay involves a preliminary fusion with fluxes containing an excess of litharge together with a reducing reagent such as flour in amounts sufficient to provide approximately 30 g of lead alloy. The lead alloy may be treated by acids directly; or, if the silver content is sufficient, the button may be oxidised to produce a silver bead or prill which subsequently may be dissolved by sulphuric or nitric acid to permit the application of two, more or less distinct, wet procedures for the separation and determination of platinum metals. If the cupellation process is used the osmium content may be reduced or even entirely eliminated. A fourth analytical procedure involves the cupellation of the button in the absence of silver to produce a total-platinum-metals residue; in general this approach is used to obtain only the total platinum metals content although the residue may also be treated by a variety of wet methods.

Fluxes: Assay fluxes practically always contain sodium carbonate, borax or borax glass, silica and litharge, the proportions of each varying considerably with the composition of the ore or concentrate. Whether or not there is an optimum slag composition for each ore is not known and Bugbee[34] states "that no two assayers working on the same ore will agree exactly on the flux proportions to use, so it is safe to say that, for any given ore, there is a comparatively wide range within which the four common flux constituents may be varied and still, in the hands of an able assayer, yield practically identical results." The present author agrees with this opinion. The problem of slag losses, either of mechanical or chemical origin has received surprisingly little attention. Beamish and coworkers have examined the problem from the point of view of efficiency of lead collection from samples of slag prepared by preliminary fusion with the platinum metals. Significant slag losses were thus found for iridium,[35] palladium[36] and osmium.[37] It is not improbable, however, that at least a part of these losses resulted from the technique of pre-fusion, which in the case of platinum[38] arose from a tendency toward pot-wall adsorption caused by creeping beyond the meniscus of melted flux. There is now little dispute about the adverse effect on platinum metals recovery of the presence of nickel in the slag. Seath and Beamish[39] reported that "with ores or concentrates containing high proportions of nickel oxide, one or two fusions of the slag are necessary for complete collection of platinum metals in a lead regulus". Hoffman and Beamish[38] confirmed these findings and reported that there appears to be no outstandingly successful type of flux for the over-all recovery of platinum. A high silica content, because of the high viscosity, produced the lowest recovery of the fluxes tried, and three re-assays of the slag were required for acceptable results. The nitre assay for sulphide ores was found particularly satisfactory and only one re-assay of the slag was required. In the case of iridium, Barefoot and Beamish[35] found that with neutral or acid slags two re-assays were sufficient to recover most of the iridium. With basic slags the loss of iridium was high and may be the result of chemical reaction with slag constituents and/or mechanical effects since iridium does not alloy with lead. There were no significant differences in the losses of iridium in nitre assays and assays of the pre-roasted ore, and the period of fusion appeared to play no part in the completeness of the collection of iridium. The authors concluded that the fire assay for iridium was not suitable for copper or nickel ores, which require slags rich in litharge. Palladium[36] was shown to be "one of the best behaved of all the platinum metals". With viscous fluxes containing high silica, considerable palladium was carried through to the fourth button. The best flux was a monoborate but in normal assaying this could rarely find application since most platinum ores contain appreciable silica. In conformity with the findings for all the platinum metals, high nickel content resulted in serious losses. The sulphide ores assayed by the nitre method yielded almost complete recovery with only one re-assay. Osmium[37] also responded adversely to a viscous slag with high silica content. Even with a very fluid flux, however, a basic slag resulted in high osmium losses; with a high osmium content, gas losses were also appreciable with the basic flux. The best collection was achieved with a neutral flux in the absence of silica. Nitre fluxes were acceptable but the iron-nail method was unsatisfactory. Pot-wall losses were in general insignificant, but basic fluxes gave evidence of appreciable reaction with osmium, with much of the latter unrecoverable by lead collection.

In the case of ruthenium[40] significant losses occurred with acidic, basic and other standard types of slags produced under optimum conditions. The results obtained indicated that the slag losses were the smallest when the assay required a long heating period and a high temperature. Furthermore, the slag losses for the nitre assay were not unduly high and again the iron-nail assay was not applicable. The examination of the fire assay for rhodium[41] indicated that slag losses were not related to slag composition and the conclusion was reached that the slag losses were of mechanical origin, *e.g.* losses to the pot wall. Unfortunately these suspicions were not verified and this investigation must be considered less vigorously pursued than those for the remaining five metals. In an informative article Adams[27] dealt with the claim that platinum metals may be dissolved in the slags, and that once in this condition, they are not recovered by a subsequent assay of the slag. Among various methods synthetic samples containing platinum and palladium were assayed, presumably with no slag losses. Adams reached the conclusion that "when good fusions are obtained no serious errors are caused by losses in slags." However, this claim is to a degree vitiated by the subsequent statement that "when the greatest accuracy is aimed at, slags and cupels are again fused with a suitable flux." In any case, only palladium and platinum were investigated, and furthermore no results were provided. Thus one cannot accept these conclusions without considerable reservations.

The effect of roasting before fire assay was found by Gray and Toombs[42] to give a more complete recovery for iridium, an effect due to the presence of nickel and arsenic. The iron-nail method resulted in the retention by the iron of 70–80% of the iridium present in the ore. The solvent action of iron for the platinum metals, and the resulting failure to collect completely by the lead alloy, was discussed by Savelsberg and Fisher.[33]

The lead-button collection: In general, the collection of platinum metals through the formation of a lead alloy is a step intermediate to cupellation, resulting finally in a silver alloy. In some instances, however, direct analysis of the lead button has been preferred. Lead alloys for the separation of binary platinum metal systems found early application in the separation of rhodium from iridium, one of the most difficult techniques. Zhemchuzhnij[43] fused the sample with lead at about 1300° in a graphite crucible. The button was parted with nitric acid, lead was removed as the sulphate, and the excess of sulphuric acid was precipitated by barium chloride. The residue of impure iridium was treated by *aqua regia* and weighed. Stanley[44] believed that the lead alloy failed to remove all of the iridium quantitatively.

For the determination of osmium and ruthenium the fire-assay collection in a silver bead is not acceptable. In the case of osmium, cupellation results in almost complete loss of the metal. With ruthenium the alloy formed is often a mechanical mixture, with the metal appearing as an excrescence on the silver bead surface, particularly if the proportions are high. This effect, of course, results in the probability of mechanical loss. Both osmium and ruthenium, however, may be quantitatively removed from an ore or concentrate by the lead collection, and subsequent analysis of the lead button is not a difficult procedure. The obvious parting acid for osmium-lead buttons is nitric acid, since the button not only dissolves in this medium but osmium may be quantitatively distilled. However, when osmium occurs with ruthenium, subsequent distillation of the latter requires the removal of nitric acid, which is usually accomplished by evaporations in the presence of sulphuric or hydrochloric acid; but since large amounts of lead are present this process is inapplicable. Indeed, one seldom encounters an artificial mineral concentrate of the platinum metals which includes osmium, whereas ruthenium is quite frequently present. The cause of this has not been recorded; in some instances the manufacturing processes involve the loss of osmium. The present author has examined the various parting solutions, and the most suitable thus far recorded is perchloric acid, which not only dissolves the button but may be used to distil quantitatively the osmium and ruthenium which has not been incorporated in the assay-insoluble. Thiers, Graydon and Beamish[40] used 72% perchloric acid for ruthenium and collected the octavalent oxide in solutions of hydrogen peroxide and hydrobromic acid. The parting-insoluble was filtered and dissolved by a caustic solution in a silver crucible, or by sodium hypochlorite solution and was subsequently distilled in chlorine from the caustic solution. Allan and Beamish[37] used essentially the same procedure for the determination of osmium. The lead button was parted by perchloric acid and the tetroxide was collected in hydrochloric acid solution saturated with sulphur dioxide. These authors concluded that in general, gas losses during the fire assay were negligible.

The lead-button analysis applied to rhodium was discussed by Allen and Beamish.[41] With nitric acid some difficulty was encountered in removing rhodium from the nitric acid parting solution and the maximum recovery was obtained by reduction with zinc. The rhodium-insoluble in the parting acid was dissolved by sulphuric acid and hydrogen peroxide, with appropriate precautions to eliminate lead and to convert the rhodium to the chloride complex. The results indicated a small loss of rhodium.

Better recovery was experienced with 72 % perchloric acid, *e.g.* 99 % to 101 % recovery as compared to 97 % to 98 % for nitric acid. The interference by copper, however, was greater in the case of perchloric parting. With the latter acid the rhodium in the button was dissolved completely.

The collection of iridium by lead and subsequent parting by nitric acid results in the quantitative deposition of iridium as a residue. Barefoot and Beamish[35] used this method of assay together with a dissolution of iridium by chlorine and sodium chloride, with a subsequent separation of base metals and other impurities by hydrolysis from a nitrite medium. The perchloric acid parting was also applied to lead buttons, but the average recovery was lower than for the nitric acid parting; and furthermore, the treatment of the parting acid to recover iridium was unsatisfactory. Alternative and more rapid procedures were discussed for both parting acids.

For the recovery of palladium, Fraser and Beamish[36] parted the lead button with nitric acid, evaporated, diluted, and precipitated and re-precipitated the palladium directly with salicylaldoxime. For small amounts, the palladium in the parting acid was treated to form the dimethylglyoximate, which was then extracted with chloroform. This procedure allowed the quantitative recovery of as much as 1000 μg of palladium from solutions containing 15 g of lead. As would be expected, parting with nitric acid resulted in complete dissolution of palladium.

Hoffman and Beamish[38] used nitric acid to part platinum-lead buttons. It was found that appreciable platinum dissolved in the parting acid, particularly when copper and nickel were present in the button, a situation not infrequently encountered. The removal of this dissolved platinum in the presence of the large amount of lead salts is difficult, and a procedure for this recovery was included. The platinum insoluble in the parting acid was treated with *aqua regia* following standard methods. Unfortunately the authors did not examine the perchloric acid parting method for either palladium or platinum. Indeed the work with perchloric acid was abandoned, at least temporarily, since a method of collection of the platinum metals superior to that with lead was being developed; and furthermore, perchloric acid introduced the danger of explosions since carbon was frequently present, and it became evident that a general method of recovery of platinum metals from the parting acid would be required.

It is a surprising fact that no proved wet procedure has been recorded for the determination of all of the platinum metals in lead buttons, despite the advantage that osmium is thus collected, and that a greater accuracy can be attained for at least the more insoluble platinum metals which do not alloy with the silver bead.

The silver bead: Some effort has been made to use the more or less specific effects of the platinum metals on the surface of the silver bead to arrive at both the detection and the approximate determination of the metals present. Davis[45] presumably accepted at least some of the quantitative aspects of surface effects of the silver-platinum metals beads. There is no doubt that to the experienced eye some success can be achieved at identification when the platinum metal content is high, but even an approximate estimation of the quantity of metal is a hazardous undertaking. Bannister and DuVergier[46] and Brzeziner[47] were perhaps the first to discuss this aspect of assaying. They found that rhodium increased the tendency of the silver bead to "spit". The fact that iridium and platinum produce similar surface phenomena made necessary a preliminary separation of these two metals. Warren[48] alloyed the platinum metals with silver, parted with nitric acid, precipitated platinum and silver with copper, and selectively extracted silver and copper by nitric acid. A somewhat similar procedure[49] required the parting of the silver alloy with sulphuric acid, followed by the removal of silver with copper; and the platinum in the filtrate was eventually removed by ammonium chloride. From this filtrate gold was precipitated by iron^{II} sulphate. Van Riemsdlik[50] discussed the errors incident to selective parting with both nitric and sulphuric acid and this author was one of the earliest to note that sulphuric, the most selective of all parting acids would under certain conditions dissolve appreciable amounts of platinum. Steinmann[51] also recorded that platinum was far from totally insoluble in sulphuric acid, although there was some compensation by the retention of some lead and silver. The magnitude of this error will vary with the time of parting, the proportion of silver or gold, and the concentration of the acid. Below certain minimum proportions of silver the assay bead parts with difficulty, if at all. Spiller[52] disagreed with the accepted efficiency of the nitric acid parting of a silver bead. Carmichael[53] discussed the optimum proportion of gold and platinum which permitted effective parting by nitric acid. He treated a silver-gold-platinum bead with sulphuric acid to remove silver, and then with nitric acid to remove platinum. For these alloys Richards[54] used sulphuric acid to remove silver, then dissolved gold and platinum with *aqua regia*, and separated the metals by conventional methods which, of course, is the better procedure. Selective parting has long been used with relative efficiency to isolate the more insoluble platinum salts. From beads containing gold, silver and iridium, Mietzschke[55] isolated iridium from silver and gold by treatment with sulphuric and nitric acids and *aqua regia*. Surprisingly, some loss through dissolution of iridium was reported. Perhaps the most indefensible procedure employing selective dissolution was recorded by Dart,[56] who disclaimed responsibility for its efficiency and ascribed the procedure to accepted texts. The method involved a series of successive selective dissolutions; sulphuric acid to remove silver and palladium; nitric acid to remove platinum subsequent to a second cupellation with 15:1 ratio of silver; dilute *aqua regia* to remove gold; concentrated *aqua regia* to remove iridium: and the final insoluble residue was recognised as rhodium and iridosmine. Commendably, the author later recognised the gross inaccuracy of the method and substituted an improved procedure,[57] which, however, failed to correct such completely erroneous conclusions as that cupelled iridium could be selectively isolated by strong *aqua regia*, in which it is practically always completely insoluble. Unfortunately this error is retained by at least one of the existing text books on fire assaying.[58]

An unique separation of gold and silver from a platinum alloy was recorded by Arsem,[59] who heated the alloy under a pressure of 1 mm of mercury at 1300° to remove silver, then at 1500° to distil the gold. Presumably no further attention has been paid to this procedure. Selective dissolution methods were used by Lathe[19] to isolate various platinum metals in silver beads. Of particular interest is this author's method of separating rhodium from iridium in the "parting-insoluble" by fusion with alkali bisulphate to corrode rhodium selectively. No results were provided to prove the effectiveness of the separation, and the present author cannot recommend the procedure as one that would consistently remove all of the rhodium.

Adams[27] reported on the relative merits of the sulphuric acid parting, the modified parting method and the non-parting procedure. With appreciable proportions of palladium, the low-temperature sulphuric acid parting, which involved removal from the heat source immediately following the dissolution of silver, was subject to a personal interpretation of the "end-point;" the latter to a degree determined the proportions of retained lead and silver, and consequently "no constant correction factor can be applied". For platinum-palladium ratios of 1:1, Adams was reasonably satisfied with the weight of the cupelled bead obtained by final heating at 1300°. By this process palladium tends to retain lead, and the presence of silver would, of course, introduce an error.

To improve the selective parting of the silver bead, various techniques have been employed. One method[60] involved the addition of the bead to a solution prepared by fusing potassium cyanide and cadmium metal. Water was then used to remove the cyanide, and the silver and cadmium were parted with diluted nitric acid. The remaining residue was fused with potassium hydrogen sulphate to remove the palladium and rhodium selectively; gold and platinum were then dissolved by *aqua regia*, leaving a residue of iridosmine. The addition of cadmium, and sometimes of zinc, was designed to prevent the dissolution of platinum in nitric acid. The claim for clean separations by these procedures, of course, is unacceptable. Davis[61] pointed out that small quantities of platinum are precipitated quantitatively by hydrogen sulphide only when all silver has been removed from solution. He[18] outlined a simple but effective bead-analysis for palladium, gold and silver, which involved a scorification of the combined buttons, parting of the cupelled bead with nitric acid, annealing the gold, removing silver by hydrochloric acid, and precipitating palladium by dimethylglyoxime. Smoot[62] described a procedure which avoided the errors incident to selective dissolution; the silver bead was parted with nitric acid and the residue was treated with *aqua regia;* silver was removed as chloride, and ample recognition is given to the fact that chloride specifically adsorbs palladium. The resulting solution contained all of the platinum, palladium and gold together with traces of silver and lead. Gold was removed with oxalic acid. Platinum and palladium were precipitated together by hydrogen sulphide and subsequently dissolved in *aqua regia;* and platinum was precipitated by ammonium chloride, then by hydrogen sulphide, and finally was assayed to produce a silver bead which was parted with sulphuric acid; palladium was determined by dimethylglyoxime. This method involves the application of techniques which are unnecessarily cumbersome and the method is not recommended. The effectiveness of the selective dissolution of the silver bead by the various standard acids has been the subject of some dispute. Davis's opinion[45] to the contrary, one of the most useful parting acids has been concentrated sulphuric acid, which in general has been used to remove palladium alone. Trenkner[63] outlined a procedure used at the Royal Mint, Berlin, which applied the modified sulphuric acid parting procedure, avoiding boiling temperatures. The residue of gold and platinum was dissolved in *aqua regia*, gold was precipitated by $N_2H_4.HCl$, and was subsequently separated from platinum by cupellation and parting with nitric acid. In a paper dealing with the variation of platinum-metal values experienced by the Rand mines of South Africa, Graham[64] recorded an important contribution which provided an explanation for as much as 50% variation in values obtained by referee assayers. The partial solubility of palladium and platinum in overheated sulphuric acid accounted for the errors and the author stressed the necessity of removing the acid immediately visible reaction ceased. He recognised that better methods of parting could be made available, but the speed of the modified parting method and the moderate accuracy required justified its application. Fröhlich[65] found that the duration of the boiling period and the temperature of the acid had an appreciable effect on the dissolution of the platinum. Errors between +8% and −9% were experienced. The difficulty was appreciably reduced by the addition of charcoal, crystallised sulphur and electrolytic iron. The addition of arsenic up to 0.5% was effective for certain ratios of platinum to gold.

One of the most common methods of selective dissolution applied to the silver bead, provided that the ratio of silver to platinum is sufficiently high, and provided that several alloying and parting treatments are used, is a nitric acid parting to dissolve platinum. Gavrilov[66] stated that with more than 20% platinum the results were erratic and the cupellation method was inapplicable. Dewey[67] agreed with this conclusion. Efforts have been made to remove silver selectively without attacking the platinum. Bell[68] and Dewey[67] disagreed with Crosse,[60] who claimed that the addition of cadmium to the silver bead prevented the dissolution of platinum by nitric acid.

Downie[69] suggested a method of removing iridium from a silver bead which involved the addition of arsenic to the melted lead and skimming off the speiss which presumably selectively extracted iridium. The method cannot be reliable, since neither iridium nor the remaining platinum metals can thus be separated. One of the first procedures for the analysis of the bead which incorporated contemporary improvements in methods of precipitation was described by Beamish and Russell.[70] The method involved a relatively strenuous parting with boiling sulphuric acid, which removed most of the palladium and traces of platinum, rhodium, ruthenium and osmium; most of the osmium is lost during cupellation. The palladium was separated from the silver as the hydrated oxide and later determined by dimethylglyoxime. If high accuracy was required, recognition was made of the fact that rhodium and ruthenium co-precipitated with the palladium dioxide. Platinum remained with the silver. The parting-insoluble containing gold, palladium and platinum, ruthenium, osmium, rhodium and iridium, was treated with *aqua regia* to remove gold, palladium and platinum. Gold was precipitated by oxalic acid, palladium was isolated as the hydrated oxide, and platinum was determined by formic acid. Ruthenium, together with iridium, were fused with sodium peroxide in a silver crucible and subsequently isolated as the hydrated oxides. To the degree that the fire assay extracted the platinum metals, the method provided good accuracy in the hands of a careful analyst. The method, however, is tedious and time-consuming. A procedure for bead analysis by the modified sulphuric acid parting was described by Seath and Beamish[71]. As would be expected, the distribution of the platinum metals differs as compared with the parting at boiling temperatures. The parting-insoluble contains a greater proportion of palladium, and the parting acid contains insignificant amounts of platinum metals other than palladium. The methods used for the separations and precipitations were similar to those employed by Beamish and Russell.[70] It was found that strong *aqua regia* did not attack cupelled rhodium and iridium, but did dissolve all but traces of platinum and palladium. Of selective dissolution methods the present author prefers this "modified parting method" to all others which have thus far been proposed. Davis[45] recorded a nitric acid parting method developed in the United States Bureau of Mines, which, while incorporating no new principles, provided for contemporary assayers a very acceptable, and much needed, procedure for routine determinations. The method was designed for the determination of silver, gold, platinum, palladium and *aqua regia*-insolubles. In the parting acid, palladium and platinum were simultaneously precipitated by formic acid, and palladium was selectively removed by nitric acid. The parting residues were treated with *aqua regia*, gold being removed by oxalic acid and platinum by formic acid. The insoluble residue was weighed. For high accuracy one cannot recommend the selective dissolution of palladium by nitric acid and most assuredly one cannot recommend weighing the final residue as platinum-metal insolubles. This opinion is supported by the findings of Griffith[25] who reported that "this separation is by no means perfect" and included results showing appreciable losses of palladium. This presentation included the erroneous statement that some ruthenium is lost by volatilisation during cupellation. He described briefly the methods of bead analysis used by nine prominent assayers, each of which, in the present author's opinion, will produce comparable results and none of which will provide the accurate results which can be obtained by more modern methods. Seath and Beamish[71] examined the characteristics of nitric acid parting of the silver assay bead, and concluded that with ratios of 15% silver to 1% platinum at least three successive parting treatments were required to remove platinum, while only one parting was required for palladium. The presence of gold in the bead seemed to assist the dissolution of both platinum and palladium. Not unexpectedly, the presence of iridium, rhodium and ruthenium interfered appreciably with the parting of both platinum and palladium; and the presence of platinum reduced the efficiency of the first parting of palladium. A method of analysing the silver bead which incorporated several new procedures, and which is capable of providing very acceptable accuracy, was described by Barefoot and Beamish.[72] The beads weighing 100 mg and containing milligram-amounts of gold, palladium and platinum and microgram-amounts of rhodium and iridium, were heated in sulphuric acid to the rapid evolution of bubbles and the appearance of the initial orange colour of palladium. The filtered parting acid, containing only silver and palladium, was treated directly at about 10° with aqueous sodium dimethylglyoximate. The parting-insoluble, containing gold, platinum, palladium, rhodium, iridium, silver and small amounts of other insolubles, was heated, reduced, and weighed. By suitable arrangement of the stages of weighing one could obtain platinum by difference with good accuracy. The insoluble, dissolved in *aqua regia*, was treated successively to remove silver, palladium as dimethylglyoximate, gold by hydroquinone and platinum by reduction with zinc, this procedure avoiding the necessity of destroying organic matter. The final insoluble, containing rhodium and iridium, could not be determined by direct weighing with any acceptable accuracy. While dissolution presented no problem, no method of separation and subsequent determination of iridium in the proportions usually present in a bead had been made available at that time. Methods for this process have now been developed, and there remains only their proved application. In one of the very acceptable publications dealing with the selective parting of silver beads, Lathe[19] described two methods of parting silver beads and subsequently of separating gold, platinum, palladium, rhodium and iridium. He recognised the inapplicability of the methods for osmium, but incorrectly predicted large losses of ruthenium tetroxide. Here it is well to stress again that ruthenium does not oxidise extensively (or perhaps does not oxidise at all) to the volatile oxide by heating the insoluble of a parted silver bead. Lathe included in his discussion a reasonably satisfactory parting procedure of the bead by a nitric-sulphuric acid treatment. Unfortunately there is no description of the fluxes used in the fire extraction, and one would expect that the processes of concentration used would often involve appreciable losses of most of the platinum metals. Allan and Beamish[41] and Truthe[73] rejected cupellation of lead-rhodium alloys, since lead cannot be completely removed because of the high melting points of rhodium-rich alloys; also rhodium may be lost during cupellation because of oxidation and subsequent mechanical loss of oxide particles. For similar reasons, cupellation to a silver bead was unacceptable to Barefoot and Beamish[72] in the case of iridium and to Thiers, Graydon and Beamish[40] in the case of ruthenium. With the latter metal, cupellation losses were shown to be high, even on partial cupellation to 6.5 g; and the losses were to the cupel, not to the air by volatilisation, which fact invalidated the inferences made by Lathe[19] and other researchers. In the case of osmium,[37] cupellation to a silver bead resulted in a practically complete loss of the metal both as the volatile oxide and by adsorption within the cupel. Partially cupelled buttons indicated that serious losses occurred when the weight was reduced to 7 g or less, although in some cases losses occurred after removal of as little as 4 g of lead. The cupellation and subsequent parting, in the case of palladium-silver beads, offers relatively little difficulty. Either nitric or sulphuric acid will dissolve palladium completely. Furthermore, Fraser and Beamish[36] recorded that the cupellation losses of palladium were not significant. Palladium, however, does not occur alone in natural sources, and the presence of other platinum metals materially alters its behaviour during parting. On the assumption that the acid-insoluble of the bead contains no palladium, the latter may be extracted quantitatively, although not selectively, after several cupellations and acid partings.

Cupellation losses of platinum were also significant when the silver-platinum ratio was sufficiently high. In the case of a 10:1 ratio, appreciable losses occur. Hoffman and Beamish[38] recorded that parting the bead with sulphuric until the rapid evolution of bubbles had ceased resulted in negligible losses of platinum to the parting acid. In the case of beads containing platinum, together with some of the insoluble platinum metals, selective parting with nitric acid with several cupellations is frequently recommended. The resulting solution generally contains the platinum colloidally dispersed, and too often the platinum is not quantitatively extracted. For accurate analysis the method is not recommended. The sulphuric acid parting of such complex beads is a preferable procedure, but it also does not extract selectively. At low temperature, palladium is generally incompletely removed, and at high temperature there may be loss of both rhodium and platinum to the parting acid. Traces of base metals would probably increase this dissolution. Potentially one of the most sensitive and accurate procedures for the analysis of the silver-platinum metals assay bead involves an application of the chromatographic method devised by Kember and Wells.[74] The bead was parted, the silver was removed, and the residue was converted to soluble salts by *aqua regia* and, if necessary, was chlorinated either by chlorine and salt[75] or by a modification[75] of the bomb dissolution procedure.[76] Plummer *et al.*[77] used a modification of this chromatographic method for a 10-mg silver bead, which involved parting with nitric acid, removal of silver chloride and its purification, dissolution of the residue of platinum, palladium, rhodium, iridium and gold by the nitric acid-bomb method, and subsequent subjection of an aliquot of the platinum metal solution to the chromatographic procedure. It was noted that in this the rhodium and iridium appear as a single band and thus require a separation. The paper sections containing the gold, platinum and palladium were treated to determine each metal by standard colorimetric methods. While the proposed chromatographic application will require further investigation, it can be stated with conviction that from the point of view of accuracy, for small amounts of the metals, the chromatographic method is superior to all other published methods. It remains true, however, that where speed is required, and a limited variation in composition is involved, the established selective dissolution methods may remain the preferred procedure.

Dry assay: The all-dry assay involves production of a lead button by the usual fire treatment, without the addition of silver, and subsequent cupellation of a platinum metals residue containing gold and silver if these two metals are present in the ore or concentrate. The method is particularly suitable for routine determinations where the variation in proportions of platinum metals can be reasonably well predicted, and particularly where the palladium to platinum ratio is low and the proportions of rhodium, iridium and ruthenium are low. The method is, of course, unacceptable for osmium determinations. Seath and Beamish[39] found that "over a wide range of compositions and extended cupellation treatment at 850° to 900° the lead was never quantitatively removed. As much as 40–50 mg of lead may remain with an 80-mg bead". Adams[27] and Adams and Westwood[78] preferred this preparation of a bead without the addition of silver for ores of the Transvaal, which contained chiefly platinum, palladium and gold and only minor amounts of the other platinum metals. For ores the usual button was cupelled and in the case of concentrates containing 10–60% of platinum metals, the buttons were scorified. The lead beads were heated for 2 hours at 1300° to produce a residue of at least 10 mg and preferably of 50 mg. The bead was treated with *aqua regia* to produce a solution containing platinum, palladium and gold and a residue of "other metals of the platinum group". The platinum was removed by ammonium chloride, and the palladium plus gold by α-nitroso-β-naphthol. The gold and palladium were inquarted with silver and subsequently the gold was weighed and palladium determined by difference. The *aqua regia*-insoluble was treated with lead acetate, zinc, and silver nitrate and the sponge was cupelled. The insoluble residue from the nitric acid parting constituted the remaining metals. The method is typical of routine procedures, but incorporates most of the objections of selective dissolution and is not acceptable as an accurate procedure. Contrary to the findings of Adams,[27] Seath observed that continued treatment of the bead at about 1300° often resulted in increasing losses of the platinum metals. Even with low proportions of insolubles, cupellation at 1300° failed to remove all of the lead. With proportions of insolubles usually found in lode deposits, however, the retention of lead was not significant. A further difficulty was encountered, particularly with large beads in that the lack of coherence of the bead increased the possibility of mechanical losses. Adams found that high proportions of palladium encouraged the retention of lead; platinum discouraged this effect.

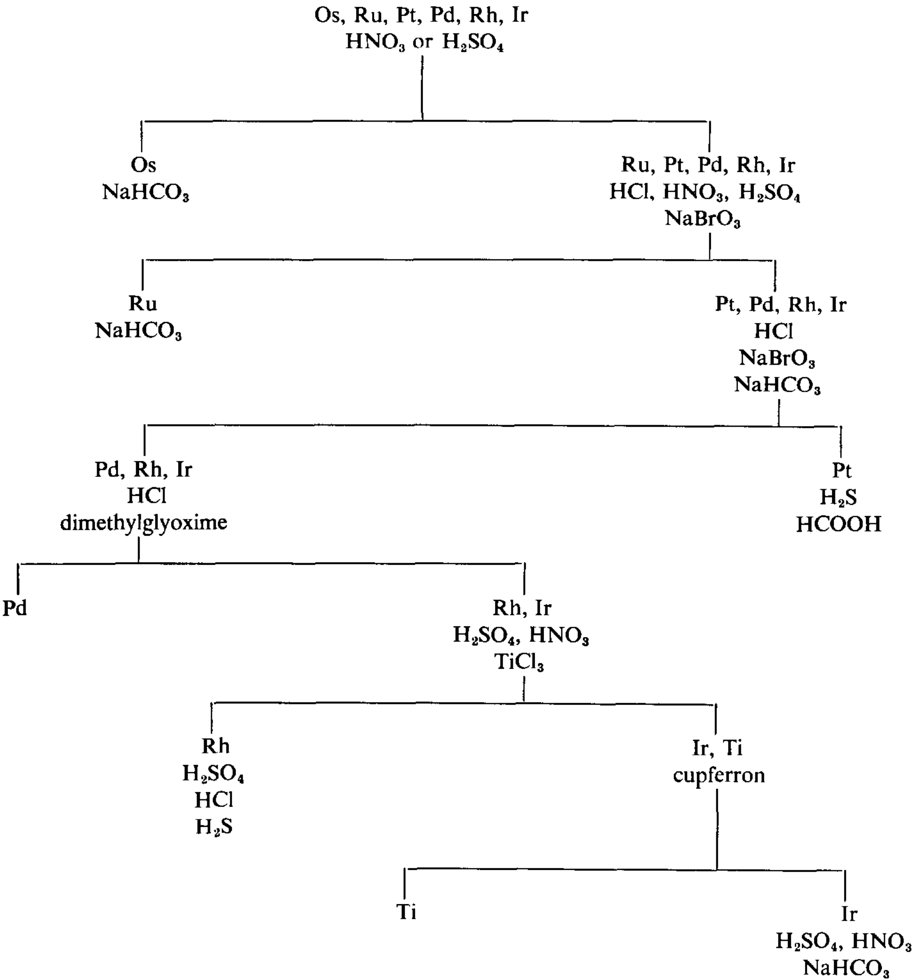
SEPARATIONS FROM AQUEOUS MEDIA

1. *Direct wet separation of the six platinum metals*

En masse separations from base metals: While this review is not concerned with the methods of analysis of artificial alloys, other than those produced as a result of fire assay, nor indeed with the analytical methods for native platinum or other isolated platinum minerals, the assayer who requires the highest accuracy obtainable must inevitably become acquainted with the most suitable wet separational procedures. Required reading by all analysts who are especially interested in the chemistry of platinum metals should be the review published by Gilchrist[79] which is undoubtedly the most effective condensation of acceptable wet methods of separations on a macro scale published before 1943. Gilchrist rejected the application of hydrogen sulphide and various reducing reagents as general methods of separation. However, it is a surprising fact that no one has recorded an attempt to use the solubility of platinum metals' sulphides in alkaline medium as a means of separation. Taimini and Salaria[80] have used this medium for specific precipitations of each platinum metal, and have indicated an accuracy which will require further confirmation, but unfortunately a general separational method of this type has not been attempted. Bismuth amalgam in dilute hydrochloric acid was used by Tananaev and Levina[81] for a limited separation of noble metals from iron and copper, the latter two metals being reduced only to lower valencies. In 1901 Leidié[82] introduced a method which involved the formation of stable nitrite complexes of the platinum metals in an alkaline medium from which base metals were readily precipitated as oxides or hydrated oxides. As would be expected, gold precipitates with the base metals. In 1926 the Institute Platine[83] used the procedure for the separation of gold and base metals in alkaline sodium nitrite medium from rhodium, iridium, ruthenium, platinum and palladium. Platinum and iridium were isolated with ammonium chloride, palladium with mercurous cyanide, and the remaining platinum metals with various zinc treatments. Gilchrist and Wichers[84] developed this approach to the isolation of the six platinum metals and produced a procedure which, in the present author's opinion, is the most generally effective separation thus far recorded. Unfortunately the method is not applicable to ores or to small amounts of platinum metals in the presence of large proportions of base metals. The tendency toward occlusion or adsorption inherent in a metal hydroxide precipitate would make a large number of re-precipitations necessary, thus encouraging losses of platinum metals. While the basic nitrite separation has without a doubt a very wide use, its application to silver beads or lead buttons is sometimes vitiated by the presence of traces of lead in the solution of these alloys or their extracted platinum metals. In contradiction of Gilchrist's claim,[85] Barefoot *et al.*[86] experienced failure to separate iridium from lead by the nitrite method used at either pH 8 or pH 12. In the presence of iridium, but not in its absence, no precipitate of lead appeared, although the addition of phosphate resulted in the removal of lead at pH 6. This peculiar phenomenon has not been explained.

Separation of ruthenium and osmium: Very little is known about the mineral sources of osmium. In a series of informative papers Gibbs[4,7] recorded the results of examinations of iridosmines from various sources, and confirmed earlier findings that osmium could be partially removed by roasting the minerals in air, although certain samples required fusion. Gibbs could offer no better method for the separation of osmium "than that which is universally employed, namely the volatilisation of the osmium in the form of osmic acid". Tennant,[87] who discovered osmium in 1803, was the first to use oxidising fusion and distillation processes. With solutions containing the six platinum metals it is practically always advisable first to remove both osmium and ruthenium, by oxidation to provide the volatile octavalent oxides. The problem of removing osmium^{VIII} oxide quantitatively is a relatively simple one, but one cannot use any of the described methods indiscriminately when the remaining platinum metals are to be determined, since serious interference may be developed in the preparation of the residual liquid for subsequent separations. Gilchrist[88] discussed various peculiarities of the osmium distillation with nitric acid. From solutions of the hexabromosmate or solutions made by caustic fusions osmium is quickly distilled in the presence of a 10 % (volume) nitric acid solution. With the hexachlorosmate distillations with nitric acid are very much prolonged, and sulphuric acid solutions of osmium are recommended for the chlorosmate but not for the bromosmate. The complete procedure, as derived from Gilchrist's separation of the platinum metals, is given schematically in Table I. The method is recommended for amounts of the platinum metals of the order of about 100 mg or more. With aqueous solutions of the platinum

TABLE 1.—SEPARATION OF MACRO AMOUNTS OF PLATINUM METALS*

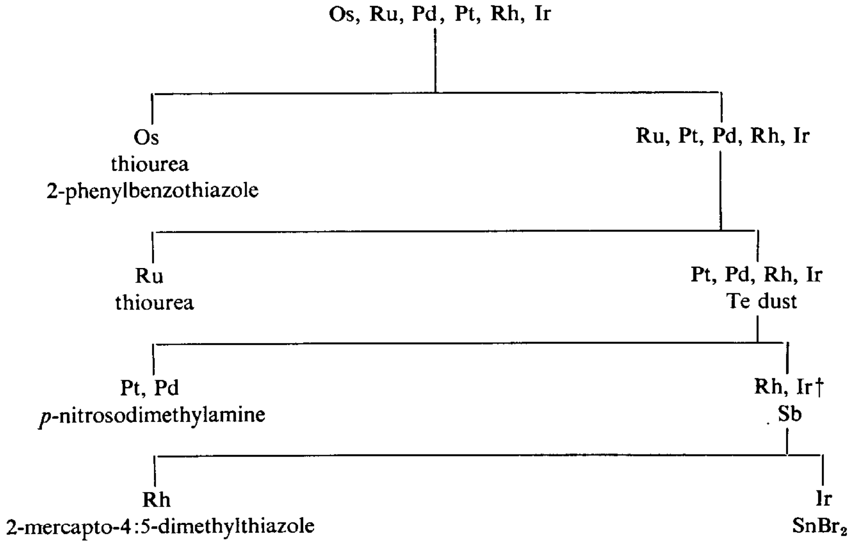


* Reference (84)

metals the optimum conditions become more or less a matter of free choice, a situation which does not exist when one must determine osmium in ores. As stated above, the only proved method for the latter involves a preliminary collection in a fire-assay lead button and a subsequent parting by either nitric acid or perchloric acid. While quantitative distillation of the volatile oxide from a nitric acid solution containing approximately 30 g of lead nitrate is not a difficult procedure, there is the subsequent necessity of removing ruthenium from the nitric acid-lead nitrate solution, and both osmium and ruthenium from the platinum metals residue insoluble in the parting acid. The elimination of nitric and hydrochloric acids, in preparation for removal of ruthenium, by fuming with sulphuric acid[89] is obviously not applicable to the lead nitrate parting acid. Allan and Beamish[90,37] parted the lead buttons with 72% perchloric acid, and the volatile oxide was, in general, collected in the hydrochloric acid-sulphur dioxide solution recommended by Gilchrist.[88] Allan and Beamish[90] and Sandell[91] found that when small amounts of osmium were to be collected, the required evaporation of the HCl—SO_2 distillate resulted in losses of osmium. This was avoided[90] by allowing the distillate to stand for 12–16 hours during which period the dissolved octovalent oxide was presumably reduced to a non-volatile form, a procedure supported by the fact that fresh distillate gave the familiar rose-coloured complex, whereas distillates aged 24 hours yielded no colour. For various purposes hydrobromic acid was preferred to the hydrochloric-sulphur dioxide receiving liquid, since no ageing or evaporations to dryness to destroy sulphur dioxide were necessary; however, inexplicably, with hydrobromic acid the silica derived from impurities and from partial evaporations was contaminated by osmium, whereas there was little or no contamination in the case of HCl—SO_2 distillates. For amounts of osmium which required colorimetric determination Allan and Beamish[90] eliminated the objectionable sulphur deposit by substituting the HCl—SO_2 receiving liquid for one comprising 6*N* hydrochloric acid containing thiourea, in which the coloured complex was developed immediately. In a later paper[92] Westland and Beamish used cold 30% hydrogen peroxide to collect both osmium and ruthenium from a perchloric acid distillation of the chlorosalts. The distillate was then treated with sulphuric acid and boiled to remove osmium selectively. Ruthenium was subsequently distilled from a bromate mixture. Procedures for both gravimetric and colorimetric determinations were included. The method was devised primarily for the analysis of lead buttons, but this application has not yet been developed. A complete procedure for the separation and determination of the platinum metals on a microscale was recorded by Westland and Beamish,[93] and a schematic description is presented in Table II. The method involved chloride solutions and therefore will be applicable to the lead button only with some modification. With this method the perchloric acid distillation is avoided and osmium is removed selectively by distillation at 115° of a hydrogen peroxide-sulphuric acid solution, which may be carried out without loss of ruthenium. The tetroxide was absorbed by either 5% thiourea in 1:1 ethanol-hydrochloric acid, or in a 40% hydrobromic acid solution, in either case preceded by an intermediate trapping by perchloric acid. The procedure permitted either gravimetric or colorimetric determination. Sandell[91] determined osmium in meteoric iron by dissolution of the latter by nitric acid. Direct distillation was incomplete, presumably as a result of nitric oxide evolution. The difficulty was avoided by dissolving the iron in sulphuric acid, oxidising the ferrous salt with permanganate, destroying excess of the latter with ferrous salt and then treating with nitric acid. In the presence of permanganate or manganese dioxide some ruthenium was co-distilled.

Immiscible solvent extraction methods for the isolation of osmium have also been recorded. After collective distillations of both osmium and ruthenium,[94] diphenylthiourea formed an additive product extractable with $CHCl_3$ from 5–7N hydrochloric acid. Tetraphenylarsonium hexachlorosmate in 0·1–0·3N hydrochloric acid could also be selectively extracted by $CHCl_3$. The error for 60 μg of osmium in the presence of 5 mg of ruthenium amounted only to 1 μg. The separation of ruthenium from the remaining platinum metals, particularly from iridium, was in Claus's period one of the most difficult operations. The volatilisation of the octovalent oxide had not been applied and a variety of methods was proposed. Claus prepared ruthenium by the usual fusion of osmiridium, followed by precipitation of the oxides from the alkaline medium, distillation of osmium by *aqua regia* and then precipitation of ammonium chlororuthenate. The most effective of the older procedures involves a distillation with chlorine from a basic solution.[95,96] This method was used by Thiers *et al.*[40] to make standard solutions by the addition of caustic soda and chlorine to weighed ruthenium metal. These authors also used the method to isolate the ruthenium from the platinum metals residue resulting from a perchloric acid parting of the lead assay button. Gilchrist[89] rejected the procedure as a means of separating ruthenium from other platinum metals since the hydrolysis in the distillation liquid of the remaining metals, *e.g.* iridium, resulted in adsorption of some ruthenium. While nitric acid is the most commonly used reagent for the preliminary removal of osmium, it effectively interferes in the removal of ruthenium. Thiers[40] failed to produce the octovalent ruthenium oxide quantitatively from a nitric acid solution of the parted lead button by oxidising with perchloric acid, sodium bromate-sulphuric acid, sodium

TABLE 2.—SEPARATION OF MICRO AMOUNTS OF PLATINUM METALS*



* Reference (93)

† Alternative separation, reference (123)

hypochlorite-ammonium peroxysulphate or ammonium hexanitrocerate. Gilchrist[89] in his general scheme removed nitric acid by preliminary evaporation with sulphuric acid, a process which may result in loss of ruthenium.[40] To avoid this loss Gilchrist[89] evaporated the nitric solution in the presence of hydrochloric acid to the complete evolution of nitrous fumes, and following this by fuming with sulphuric acid to remove the hydrochloric acid. The oxidising reagent was sodium bromate and the receiving liquid was, as with osmium, sulphur dioxide-hydrochloric acid. Thiers[40] used perchloric acid to part the lead assay button and to distil the ruthenium in the parted liquid. The residue insoluble in the parting acid was dissolved, and the ruthenium was distilled as described above. By this procedure both osmium and ruthenium are quantitatively removed. Westland and Beamish[92] used this distillation but collected the combined octovalent oxides in cooled 30% hydrogen peroxide. From the latter, with the addition of sulphuric acid, the osmium was selectively distilled, and this process was followed by removal of ruthenium by sodium bromate. Contradicting the findings of Gilchrist, these authors were able to distil both osmium and ruthenium from solutions containing palladium, rhodium, iridium and platinum. However, the difference in results may be due to the microgram amounts of platinum metals as compared to the macro samples used by Gilchrist. In a later paper,[93] again dealing with micro amounts of metal, the distillation with perchloric acid was omitted and osmium was distilled directly from the peroxide-sulphuric acid solution, following which the ruthenium was distilled after addition of bromic acid, to avoid the objectionable presence of salt during the subsequent separations of the remaining platinum metals. It was of particular interest that the peroxide-sulphuric solution converted the ruthenium to a form which resisted the formation of any octovalent oxide. Here again, there was no interference with either the osmium or ruthenium volatilisation from the presence of the remaining four platinum metals.

Separation of palladium and platinum: In practically all of the acceptable analytical schemes for the separation of the platinum metals, platinum and palladium are isolated following the removal of osmium and ruthenium and before the determination of rhodium and iridium. The sequence of separation of platinum from palladium varies with the method. With the older schemes platinum was almost always separated by precipitation with ammonium chloride; and for separation of large quantities or where the highest accuracy is not required this method is undoubtedly effective. In a few instances palladium and platinum have been removed simultaneously as the hexachloride[97] but this procedure cannot be recommended for quantitative determinations. Pshenitsyn and co-workers have recorded various procedures for the separation of platinum and palladium. When dealing with copper-nickel slimes Pshenitsyn and Yakovleva[98] used calomel at 90–95°. A second procedure [99]required reduction by acetylene following a period of boiling with tartaric acid. Repeated treatments with acetylene were necessary. Neither of these two methods is recommended for analytical applications. Pshenitsyn and Ginsburg[100] also used a hydrolytic separation of platinum from rhodium, iridium and palladium by the addition of zinc oxide. One of the earliest applications of hydrolytic separation of platinum from the remaining platinum metals was described in 1835 by Dobereiner,[101] who used lime water to isolate platinum in an analytical scheme involving osmium, rhodium, iridium, palladium and copper. Moser and Hackhofer[102] used a hydrolytic method for the separation of platinum from iridium. The method involved hydrolysis from a nearly neutral solution to which was added successively sodium bromate and sodium bromide. Gilchrist recorded a procedure some fifteen years earlier[103,85] for the analysis of alloys, minerals and solutions in which platinum metals constituted the major proportion of the composition. After the removal of osmium and ruthenium, the four platinum metals, oxidised to their higher valence states, are hydrolysed by sodium hydrogen carbonate to pH 6–8, resulting in the precipitation of palladium, rhodium and iridium.[103,84] Ryan[104] used the hydrolytic separation of platinum to remove successfully as little as 5-μg amounts of platinum from solutions of gold, palladium, rhodium and iridium. Concerning the oxidising procedure, it may be noted that Gilchrist and Wichers[84] encountered no difficulty with the oxidation of platinum from a solution which had been subjected to fuming with sulphuric acid in preparation for the removal of ruthenium. Beamish and Scott[105] attempted to apply this hydrolytic separation to platinum metals solutions which had been fumed with sulphuric and nitric acids, the nitric acid having subsequently been removed. Solutions such as these had been heated with bromate for more than 10 hours and invariably a heavy brown platinum oxide settled out when the solution was neutralised to pH 6 and boiled. Dissolution of this brown precipitate and re-oxidation did not eliminate re-precipitation of platinum upon neutralising. While the explanation of the different findings may lie in the strongly oxidising conditions required for the preliminary removal of ruthenium, the application of this hydrolytic separation to the small amounts of platinum metals extracted by fire assay, which process frequently required preliminary fuming with sulphuric acid, was, in general, found tedious and unreliable. However, Beamish and Russell[70] applied the method to remove palladium from sulphuric acid parting solutions of silver beads, and from the *aqua regia* extract of platinum and palladium. For the platinum metal ores and concentrates whose major proportions consisted of base metals, and which frequently contained gold, the most advantageous procedure involved the removal of gold by hydroquinone or sulphur dioxide etc., followed by the removal of palladium by dimethylglyoxime or other suitable oximes. None of the methods of isolating palladium used before the discovery of the dimethylglyoxime method by Wunder and Thuringer[106] and by Duparc[107] are now acceptable for accurate analytical work. Recently a number of oximes have been used for the determination of palladium and these have been evaluated in a previous review.[108] In so far as separatory action is concerned all of the oximes behave very much alike. In addition to precipitating palladium, dimethylglyoxime will precipitate gold quantitatively[109] and under certain conditions will precipitate platinum almost quantitatively.[109,110] With the last metal, precipitation is encouraged in solutions which have been fumed with sulphuric acid, and along with palladium the co-precipitation is made evident by the green precipitate, which is a mixture of the yellow palladium and the blue-bronze anisotropic platinum compound. However, from chloride solutions, properly treated, the dimethylglyoxime separation from platinum, rhodium and iridium is eminently satisfactory and may be applied directly to the hydroquinone filtrate from the gold separation[105] provided that the proportion of palladium is greater than 1 mg to 25 mg of gold. Gilchrist[103] used dimethylglyoxime to separate palladium from rhodium and iridium; and Beamish and Scott[105] used the reagent for a variety of methods applied to the silver bead. For the extraction of as much as 1000 μg of palladium from the nitric acid parting solution of lead buttons Fraser *et al.*[111] used dimethylglyoxime and subsequently extracted the palladium complex with chloroform. The gravimetric separation was accomplished with salicylaldoxime, in which case lead was eliminated by a second precipitation. Of the base metals which normally are present in the nitric acid parting solution, only iron interfered, and this difficulty was eliminated by using Versene. Pollard[112] rejected dimethylglyoxime and recommended α-nitroso-β-naphthol for microgram amounts of palladium. This reagent precipitates gold, but only palladium of the platinum group. An improved separation of palladium from the sulphuric acid parting solution of a silver bead was recorded by Barefoot and Beamish.[72] The acid solution, cooled to 10°, was treated directly with sodium dimethylglyoximate and the palladium was determined gravimetrically. No loss of the metal was experienced and only insignificant traces of silver accompanied the palladium complex. Proper care in parting permits only palladium and silver in the solution and thus the method is a rapid one. Westland and Beamish,[93] working with microgram amounts of platinum and palladium, isolated these metals, after distillation of osmium and ruthenium, by precipitation with tellurium powder. To avoid the simultaneous precipitation of rhodium, the solution was fumed slightly and then treated with hydrochloric acid, from which both metals precipitate quantitatively; with fuming only, platinum resists reduction by tellurium. Unexpectedly, iridium precipitated in the presence of excess palladium; when more than 20 μg of the latter are present a preliminary separation of palladium is necessary. This is a serious restriction to the application of the method since the details of this separation were not included. The precipitated platinum and palladium were burned in air and then reduced in hydrogen to remove occluded tellurium.

Separation of rhodium and iridium: In practically all analytical schemes rhodium and iridium appear together after separation of osmium, ruthenium, gold, palladium and platinum. In fire-assay extractions they constitute most of the insolubles, usually contaminated by some of the remaining platinum metals. Rhodium and iridium are resistant to the usual acid dissolution, but dissolution may be accomplished by chlorination in the presence of sodium chloride[75] or by a bomb technique[76] or by fusion with sodium peroxide preferably in a silver crucible.[70]

The separation of these two metals presents the most difficult aspect of platinum metals analysis. Until recently no acceptable method was available. The long-used selective extraction with fused sodium bisulphate is by no means an acceptable analytical method.[113] Karpov and associates recommended the use of mercury and its salts for this separation. In one method[114] the mixed hexachloro salts were reduced under water by mercury, which also reduced platinum. In a second method[22] the selective reduction was accomplished by mercurous chloride mixed with a solution of the two chlorides and heated to 90–95°. A method of some interest was recorded by Zhemchuzhnij[43] who fused with lead at about 1300° in a graphite crucible and then treated the button with nitric acid. The insoluble residue contained all of the iridium and most of the rhodium. The latter was selectively isolated by *aqua regia* and combined with the rhodium in the parting acid, which was separated from the lead by a sulphate precipitation. None of these methods can be recommended when high accuracy is required. The first acceptable analytical separation was recorded by Gilchrist[115] who converted to sulphate salts and then reduced rhodium selectively by titanium^{III} chloride. Two precipitations offered a quantitative separation from iridium. The most serious criticism of the method concerns the necessity of removing excess titanium from the filtrates before determination of iridium. This was done by producing a titanium cupferron precipitate, which is bulky and encourages adsorption of iridium. Re-precipitation is difficult and time-consuming, although with care very acceptable results can be obtained if the amounts of iridium are of the order of about 100 μg or more. The present author does not recommend the method for very small amounts of iridium. Pollard,[116] however, introduced a separation of very small amounts of rhodium and iridium which involved a reduction of rhodium by titanium^{III} chloride in the presence of mercaptobenzothiazole to produce a reddish-brown complex of rhodium. Titrimetric methods of determination were then applied.

Pshenitsyn and co-workers recorded a method for the separation of rhodium from iridium. One procedure[117] was a modification of an early method and involved the precipitation of rhodium from its hexanitrite solution by sodium sulphide; iridium in the filtrate could be hydrolysed to the hydrated oxide. A second procedure[118] required the selective reduction of rhodium by chromous chloride. Neither method is recommended where high accuracy is required or small amounts of metal are involved. In the latter condition Westland and Beamish[119,93] reduced rhodium by boiling a sulphuric acid solution with antimony dust. The antimony in the iridium filtrate was removed by distillation as the trichloride; with large amounts of iridium the antimony produced little or no interference. Copper metal has been used by various authors for general precipitations of platinum metals; Mukhachev[120] thus determined the sum of these metals, and Gol'braikh[121] used copper to determine platinum and palladium in precious metal sludges. Aoyama and Watanabe[122] precipitated palladium and ruthenium, and separated platinum from iridium by copper powder; and Tertipis and Beamish[123] used copper powder to separate both milligram and microgram amounts of rhodium and iridium. The procedure required precipitation of rhodium in 1·0N hydrochloric acid by an excess of copper powder. Rhodium was separated from admixed copper by cationic-exchange after dissolution by *aqua regia* and then by dry chlorination. Gravimetric and colorimetric methods could be applied for rhodium. Iridium in the filtrate was separated from copper by cationic-exchange, and was determined either gravimetrically or colorimetrically. The authors point out that the recorded reduction potentials indicate that such reducing reagents as titanium^{III} chloride, antimony, copper, vanadium^{II} or chromium^{II} ion which have been used successfully for the separation of rhodium from iridium should also reduce iridium. The fact that separations can be made suggested that "the resistance to reduction of iridium is the result of unusually stable dissolved complexes". Recently, Jackson[124] recorded a method for the precipitation of an organic rhodium complex in the presence of iridium. The procedure required evaporation to fumes in a sulphuric acid-lithium sulphate solution and additional heating with perchloric acid. Rhodium was selectively precipitated by thioacetanilide after reduction by fresh chromium^{II} chloride solution. The organic complex was ignited, reduced in hydrogen, then treated with hydrofluoric acid and evaporated to remove silica. Hydrochloric acid was added, the mixture was filtered, again ignited and reduced, and heated to 650° to 700° in a current of chlorine, and this treatment was followed by addition of *aqua regia*, filtration, ignition, reduction by hydrogen and weighing. The filtrate from the rhodium thioacetanilide precipitation was evaporated with nitric-sulphuric acids and heated to 250°, and the residue was oxidised by nitric and perchloric acids. Iridium was then precipitated as the sulphide in the presence of chromium by the addition of thiourea. The iridium sulphide was ignited and treated with hydrofluoric acid, and the dried residue was finally purified by selective dissolution with concentrated hydrochloric acid, and was ignited, reduced and weighed. Directions were included for the treatment of amounts of iridium of the order of 500 μg, in which case iridium was finally determined titrimetrically. Acceptable results were obtained for amounts of metal over the range of 500 μg to about 100 μg. While the author's claim of providing a method which is "relatively simple" is unacceptable, the procedure may well be improved and the principle involved is an important one.

2. *Electrolytic separations*

The author has made no exhaustive examination of literature dealing with analytical electrolytic separations. However it seems evident that no separational method has been recorded which deals with the six metals. A few procedures are concerned with separations of two metals and the determination of single metals. Most of these were the work of E. F. Smith in the early present century. Recently MacNevin and Tuthill[125] proposed a separation of rhodium and iridium in which, after prescribed pre-treatment of a solution of the chlorides of the two metals, rhodium was electrolytically deposited, contaminated with oxide, on to a platinum cathode. The potential of the cathode (w.r.t. a saturated calomel electrode) was gradually lowered from −0.25 V in four stages to −0.40 V over a period of 90 min. The cathode had then to be reduced by heating in a small chamber in an atmosphere of hydrogen for 30 min. Although iridium is not deposited from its chloride solutions at the cathode potentials mentioned above, deposition of iridium is induced by that of rhodium, so that there is a likelihood of some co-deposition of the former when a separation of the two metals is attempted. MacNevin and Tuthill claimed that chlorination of the solutions and addition of ammonium chloride to a molarity of 3·5 before electrolysis resulted in a deposition of rhodium free from iridium. Experiments by McBryde[126] and his associates have failed to confirm the reliability of this separation, or to explain in any way the mechanism of the co-deposition of iridium, or to suggest any better means of avoiding it. Thus it was found that the evolution of hydrogen at the cathode, which occurred in many of the experiments and which resulted from a lowering of pH arising from the consumption of hydroxylamine at both electrodes, brought on a co-deposition of iridium. Where cathodic gassing was observed and the electrolysis was stopped to avoid the induced deposition of iridium, the recovery of rhodium on the cathode was incomplete.

NEW TECHNIQUES FOR ISOLATION AND SEPARATION OF THE PLATINUM METALS

1. *Ion-exchange*

In the author's opinion the major contribution of ion-exchange techniques in the field of platinum metal separations will lie in the area of *en masse* isolation of associated base metals present in ores, concentrates, natural and artificial alloys. The applications to separations within the platinum group can be expected to supply new procedures but in general these will not, in the foreseeable future, displace the existing chemical and chromatographic procedures. On the other hand it is not impossible, and perhaps not improbable, that certain aspects of fire-assay extraction may find serious competition, particularly in the case of ores where the amounts of platinum metals occurring are sufficiently small to require some method of mechanical concentration.

One of the first attempts to use ion-exchange methods for the separation of platinum metals was recorded by Stevenson *et al.*[127] The solution of platinum, palladium, rhodium and iridium was converted to perchlorates to remove the chloride ion, and was passed through a Dowex-50 cation-exchange column. Palladium, rhodium and iridium were retained, while platinum passed through. Palladium was stripped with 0·05 to 0·5*M* hydrochloric acid, then rhodium was eluted slowly with 2*M* hydrochloric acid, and finally iridium with 4–6*M* hydrochloric acid. No detailed results were provided and the authors expressed their intention of continuing the research. The method does not appear promising.

McNevin and Crummett[128] used the anion-exchanger Dowex-2 to adsorb the complex chlorides of palladium, platinum, rhodium and iridium, followed by selective elution with a solution of ammonium hydroxide-ammonium chloride. While the elution of palladium was satisfactory the remaining separations were unsatisfactory. Better results were obtained with an ammoniacal solution of the four metals and a column of the cation-exchanger Amberlite IR-100. The authors proposed to adopt the scheme of first hydrolysing the solution to isolate platinum and then of adsorbing palladium selectively by cation-exchange, followed by separation of rhodium from iridium by an electrolytic process. The authors claim that the separation of palladium constitutes "a valuable simplification", as compared to the dimethylglyoxime separation, is not a valid one. In any case the discussion includes no experimental results. In a second publication,[129] however, dealing with much the same material, the authors provide values which indicate a satisfactory separation of palladium as the ammonia complex from the iridium anion by Amberlite IR-100. By an analogous method Berman and McBryde[130] succeeded in separating rhodium from iridium. The aged solution was treated with ammonium hydroxide to produce a yellow precipitate of rhodium, which was just redissolved. Passage of this solution through the anion-exchanger IRA-400 resulted in adsorption of iridium and weakly attached rhodium which could be eluted with water. The iridium was stripped with 6*M* hydrochloric acid. When fresh rhodium and iridium solutions were thus treated the recovery of the two metals was a time-consuming process and the authors rejected the method. MacNevin and McKay[131] discussed the ion-exchange separation of rhodium from platinum, palladium and iridium. The authors prepared the yellow cationic rhodium by precipitation of the hydrated oxide and dissolution in hydrochloric acid; in the same way palladium also assumes the cationic form but, upon ageing, the anionic condition is developed. The author's attempts to isolate rhodium quantitatively were unsuccessful due presumably to failure to eliminate the pink anionic form.

Berg and Senn[132] used Dowex 50-W exchanger to retain rhodium selectively in the presence of iridium. The solution of the metal chlorides was fumed to a moist residue with *aqua regia;* hydrochloric acid was added followed by solid thiourea. The bivalent rhodium^{III} complex was retained at the top of the column as a sharp reddish-orange zone and was subsequently eluted by 6*M* hydrochloric acid at 74°. The first colourless fraction of the effluent contained the iridium^{IV}-thiourea complex which was eluted with 3*M* hydrochloric acid. Both rhodium and iridium were determined spectrophotometrically, and the results indicate very acceptable accuracy. The method suffers, however, from the necessity of destroying the thiourea before the analysis of rhodium and iridium. Blasius and Wachtel[133] recorded ion-exchange applications which are potentially useful and which one may hope will be extended. These authors used the hydroxide form of the basic exchanger Permutite E. S. Palladium and platinum were adsorbed by the resin, the former being eluted by sodium hydroxide, the latter by nitric acid. With platinum and iridium, the latter was reduced to the tervalent state by sodium oxalate and after adsorption, iridium was first eluted with sodium hydroxide followed by platinum with nitric acid. Rhodium and platinum were similarly separated. The separation of rhodium from iridium was unsuccessful. The authors were able to apply their method to the quantitative removal of iron, copper and nickel but they failed to elute platinum and iridium from the anion-exchanger and recommended ignition of the latter to recover these metals. In any case these are significant experiments and they may provide wet methods for the determination of platinum metals in natural occurrences. An interesting application of ion-exchange was reported by Kimura *et al.*[134] who separated radioactive forms of rhodium and ruthenium found in ashes collected from fall-out. The cation-exchange resin Dowex-50 was used, but with this resin one would not expect a quantitative isolation of ruthenium. Cluett, Berman and McBryde[135] recorded an ion-exchange separation of rhodium from iridium which is comparable in effectiveness to that of Berg and Senn.[132] Amberlite IRA-400 was used to adsorb the chloride solutions of rhodium in the tervalent state and iridium in the quadrivalent state; the latter was maintained by the addition of bromine water to the metal solution of 2% sodium chloride in $0.1M$ hydrochloric acid. Rhodium was eluted by the above solution, followed by iridium, with a solution of $5M$ ammonium hydroxide and $1M$ in ammonium chloride, then with either $6M$ hydrochloric acid or $8M$ nitric acid. The method was applied to weights of the order of 10 mg, and very acceptable accuracy was obtained. In a later paper[130] the authors rejected the former method of removing iridium since the exchange "required the use of large quantities of salts and acids which must be destroyed prior to the determination of iridium". Also, losses of iridium in the feed solution indicated that attempts to use the procedure for smaller quantities of the metals would lead to relatively appreciable quantities of iridium remaining with the rhodium. The authors also recommended against their former use of the bromine oxidant, since for small amounts of the metals any procedure which would recover the rhodium quantitatively resulted in a loss of about 1% of the iridium present; and since the loss was more or less an absolute one it thus became significant when microgram amounts of metals were to be separated. The proposed new procedure[130] involved the use of Amberlite IRA-100 freshly converted to the chloride form, and was applied with accuracy to samples of microgram amounts. The samples in hydrochloric acid and sodium chloride were passed through the resin previously treated with cerium^{IV} solution to counteract its reducing effect. The rhodium^{III} was eluted with $2M$ hydrochloric acid and the iridium^{IV} was subsequently eluted by a Soxhlet extraction with $6M$ hydrochloric acid, which process could be accomplished in about 1½ hours. Berman and McBryde[136] also used Amberlite IRA-400 for exchange separations of rhodium, iridium, palladium and platinum, and simultaneously they recorded distribution coefficients for the chlorides of these metals, together with ruthenium. The recovery of platinum from the remaining three metals was incomplete, presumably because of the reduction to bivalency during the necessary reduction of iridium by hydroxylamine. The authors preferred to remove platinum by hydrolytic precipitation of rhodium, iridium and palladium. With this method the oxides of the three metals were dissolved in hydrochloric acid and evaporated to dryness with sodium chloride; hydroxylamine was added to reduce the iridium, and the solution was fed into the exchanger. Rhodium and iridium were eluted with $2M$ hydrochloric acid, then with $9M$ acid to recover the palladium. The separation of rhodium and iridium was made as previously described.[130] Kraus *et al.*[137] provided potentially useful data on the adsorbability of palladium^{II}, iridium^{III} and iridium^{IV}, and platinum^{IV}, and suggested the feasibility of using the relatively easy elution of iridium^{III} as a means of separating iridium from platinum and palladium.

Pshenitsyn and coworkers[138] used the cationite Espatite-KV-1 in either the H^+ or Na^+ form to remove copper, nickel, iron and lead from the chloride complexes of platinum, palladium, rhodium and iridium. This report contains much useful information, although the analytical applications to the various industrial products is a peculiar admixture of new and effective, and antiquated and relatively ineffective procedures. The amounts of both platinum metals and base metals are of the order of milligrams and the accuracy of recovery is not of a high order. The information concerning the tendency for fresh rhodium solutions to assume the cationic condition and for aged solutions to assume the anionic form is in agreement with results from other researchers, as is their observation of the relative difficulty of retaining nickel in the cationic condition. The tendency for bivalent palladium to hydrolyse was prevented by the addition of zinc oxide. In general the chloride solution of base and precious metals was evaporated in the presence of sodium chloride and the pH adjusted to between 1 and 2. Of the various procedures proposed for the analysis of commercial products, one dealt with the integration of the cation-exchange method for rhodium and iridium after chemical removal of arsenic, antimony, tin, selenium and tellurium by volatilising methods. For materials containing gold, platinum, palladium, ruthenium, copper, iron, nickel, lead, rhodium and iridium the authors recommend first the removal of gold, platinum and palladium by calomel, followed by distillation of ruthenium by bromate oxidation, then the removal of base metals by their cationic procedure. The report is a good one and it can be hoped that the work will continue. Coburn *et al.*[139] used the cation-exchanger Dowex-50 × 8 (acid form) to separate iron, copper and nickel from the platinum and palladium contained in a base metal button obtained by the new fire-assay procedure described below. The button, weighing about 25 g, was dissolved in *aqua regia*, and the nitric acid was removed by evaporations with hydrochloric acid. The filtered residue, mainly silica, was extracted with *aqua regia*, and the combined chloride solution was adjusted to pH 1·5 and passed through the column. The eluate was evaporated and treated with sodium nitrite at pH 8 to remove traces of copper, iron and nickel. The platinum and palladium in the filtrate were converted to diethyldithiocarbamates and extracted with chloroform. Palladium was then selectively extracted by *p*-nitrosodimethylaniline and determined by dimethylglyoxime; platinum was determined by thiophenol. Completeness of recovery was checked by standard solutions. Marks and Beamish[140] applied a modified procedure to determine rhodium and iridium in iron-copper-nickel buttons. The removal of traces of base metals from the effluent was accomplished by passage through a second small cation-exchange column. Organic matter from the resin was removed by nitric acid and hydrogen peroxide. The chlorides of rhodium and iridium were separated by an IRA-400 anion-exchanger in the presence of cerium^{IV} to produce iridium^{IV} as described by Berman and McBryde.[130] Both milligram and microgram amounts of rhodium and iridium were used.

No successful application of either cation- or anion-exchange separation of osmium and ruthenium has been reported. One would guess that the ease of reduction of osmium salts by organic reagents would preclude such separations. The few reports which include ruthenium etc. indicate that reduction or partial hydrolysis or both have prevented quantitative separation. The authors own experience with cation-exchangers for ruthenium has not been encouraging analytically.

2. *Chromatographic separations*

A second major advance in the analytical chemistry of the platinum metals has been the development of chromatographic methods of separation. The integration of this technique with cation- and anion-exchange and fire-assay separations will produce a whole new series of relatively simple and accurate methods of analysis for the six metals. By far the most difficult aspect of analysis with these metals lies in determining the amounts present in ore occurrences and it is precisely in this area that chromatographic methods serve their most useful purpose.

One of the first chromatographic methods for the platinum metals involved the use of a column of carbon. The application of this adsorbing medium has, during the past decade, received only desultory attention, but in the present author's opinion, carbon has considerable separatory potentialities. One must expect difficulties in achieving selectivity when direct adsorption of platinum metals on carbon sites is expected. However, chromatographic adsorption through intermediate action of platinum metal reagents may yet prove profitable both on an analytical scale and perhaps with large samples. Dubrisay[142] stated that when a dilute solution of a noble metal was passed through a column of finely divided carbon, the metals collected in the upper part of the tube and could subsequently be extracted with suitable solvents. The method was proposed only for approximate evaluation of precious metals in dilute solutions. The single result given was applied to silver and indicated a moderately good recovery. To a lesser extent the use of carbon as a selective adsorbent for group separations has received little attention. Bauer and Nagel[143] acquired a patent for thus removing gold, silver and platinum from ocean water. The ash of the resulting mixture was treated by conventional methods of isolation. Venturello and Saini[144] used alumina for adsorption and subsequently applied various reagents to reveal the presence of platinum, rhodium and iridium. The procedure was applied with good results to dilute solutions and alloys of the metals. Alumina was also used by Schwab and Ghosh[145] for the separation of the complex chlorides of iridium, platinum, palladium and rhodium, in this order. Both X-ray measurements and colours of the various fractions confirmed the separation. Ashizawa[146] used a paper chromatographic method for the separation of palladium, nickel, cobalt and copper. The bluish-green adsorption band for palladium developed by dithizone occurred between nickel and cobalt, and one could detect 0·005 μg. Interfering elements were eliminated by preliminary chemical treatments. The most significant of the early researches with the platinum metals was introduced in a note by Lederer[147] who used paper chromatography for the separation of silver, copper, palladium, platinum and gold. The author correctly predicted the successful application of the method to the analysis of a silver assay bead, making the claim that chromatographic methods would supersede other methods of separation for this purpose. The author used a paper cylinder which, after addition of the solution of the precious metals, was placed in a dish of butanol saturated with normal hydrochloric acid, and the whole was placed for 20–24 hours in a crock in which the atmosphere was saturated with hydrochloric acid and butanol. In a later paper Anderson and Lederer[148] recorded their use of an electro-chromatographic method for the separation of as much as 20 mg of copper from gold, platinum and palladium. The method required the use of paper-pulp strips, the ends of which were immersed in hydrochloric acid and potassium chloride; a potential of 12 volts was maintained between the carbon electrodes and a current of 200 milliamperes was used. The sample was added to the paper and the spot was placed in the anode compartment. The paper was moistened with normal hydrochloric acid and the whole was set aside overnight. The copper moved to the cathode as a blue band. The method will find restricted applications to the separation of associated base metals from the platinum metals. In a third paper Lederer[149] reported a study of tervalent rhodium complexes by paper electrophoresis and ion-exchange chromatography. Rhodium hydroxide, with hydrochloric or hydrobromic or nitric acid, produced unstable intermediate cations of low mobility. Irrespective of these complexes rhodium could be separated chromatographically from platinum^{IV} and palladium^{II}. Majumdar and Chakrabartty[150] have indicated the possibility of limited group separations of the platinum metals by electro-chromatography. With a potential of 150 volts, and over a period of 5 hours, at least four ions in microgram amounts could be isolated. The sequence of separation for different electrolytes is included but unfortunately no analytical results are provided. An interesting and potentially useful continuous separation of platinum metals by paper electrochromatography was described by MacNevin and Dunton.[151] The success of the method depended upon the fact that the rate of diffusion of the four metals in descending chromatography and in horizontal electro-chromatography varied appreciably with each metal. Amounts up to 100 mg of mixtures of two or three metals could thus be separated, but the fact that conditions for rhodium required a slightly acid medium, under which conditions platinum was diffusely distributed, prevented the application to mixtures containing platinum, palladium and iridium. The procedure involved the use of ethylenedinitrilotetra-acetic acid in a medium of pH 9 to complex iridium and palladium, under which conditions precipitation usually occurs. The equipment included suitable paper, 11 × 13 inch, held vertically, notched at top and bottom, with platinum electrodes interwoven at the two sides. One must regret the lack of quantitative results, only a few of which are included to prove the separation by horizontal electro-chromatography of rhodium^{III}, palladium^{II}, platinum^{IV} and iridium^{IV}. The medium was $0{\cdot}1M$ in Versene and was adjusted to pH 9, at which acidity rhodium remained stationary. Burstall *et al.*[152] recorded the results of an extensive application of inorganic chromatography on cellulose to a variety of metals which included the six platinum metals. This work formed the basis for the later advances described below, but no quantitative results were included. Fournier[153] separated platinum, palladium and rhodium chromatographically by applying butyl alcohol as solvent with nitric and hydrochloric acids.

Kember, Wells and associates have contributed the most useful advances to the paper chromatographic separation of platinum metals so far reported. In an informative article they[74] described separations of platinum, palladium, rhodium and iridium in microgram amounts, and to a limited degree discussed separations from associated base metals present in milligram amounts. Three solvents were used to accomplish specific separations; hexone-pentanol-hydrochloric acid gave three well-defined and equally spaced bands of rhodium, palladium and platinum, in that order. With iridium, reduction occurred, and this metal remained with rhodium. The solvent was satisfactory with mixtures of iridium, palladium and platinum. With certain base metals which introduced interferences on the strips, *n*-butanol saturated with $3N$ hydrochloric acid was used. Former researches which suggested the use of $1N$ acid[147] or $2N$ acid[152] with butanol showed a tendency to form double bands. For the conversion of iridium to the more mobile higher valency the butanol solvent was treated with hydrogen peroxide, and this enabled the separation from and determination of rhodium. The use of nitric acid as recommended by Lederer and Lederer[154] was rejected, since it resulted in rhodium trailing forward. To avoid the double bands resulting from platinum^{II} and platinum^{IV}, sodium chlorate was added to the metal solution. The procedure involved the use of a control strip to indicate the positions of the metals as developed by a tin^{II} chloride spray; the temperature was maintained between 22° and 26° and the time of standing was 14–18 hours. Detailed directions were included for the extracting procedure. Spectrophotometric methods were used for determining platinum, palladium and rhodium and a titrimetric method was used for iridium. Rees-Evans, Ryan and Wells[155] have recently described a cellulose column chromatographic separation of the four non-volatile platinum metals each in 100-mg amounts and in the presence of limited amounts of associated base metals. The procedure involved 15–30-cm columns of cellulose pre-treated with solvents; one of the latter consisting of hexone with 3% of concentrated hydrochloric acid and the other, to be used for the collection of iridium, an oxidising solvent similar to the first but containing chlorine dioxide. The preparation of the metal sample involved evaporations in the presence of zinc chloride to prevent the formation of insoluble compounds; sodium chloride proved to have a deleterious influence during the chromatographic separations. The authors' results indicated that the addition of 20 mg each of copper, nickel and iron, 100 mg of zinc and small amounts of mercuric chloride offered no interference in subsequent determinations. Notes were provided for the separation of various two-component systems, the most useful of which were rhodium-iridium. The separation of platinum, palladium, rhodium and iridium required the removal of nitric acid by evaporation with hydrochloric acid, with an intermediate addition of chlorine, and addition of hexone solvent. Platinum and iridium were collected as a single fraction, and were later separated by column extraction under reducing conditions to decrease the mobility of iridium. The palladium fraction follows the platinum-iridium, moving away from the immobile rhodium and nickel, which are subsequently removed by hydrochloric acid solution. Iron^{III}, copper and zinc were found with the platinum fraction and mercury^{II} chloride with the iridium when the metal was separated from the rhodium.

The authors leave the inference that their method is superior to that of the wet separations of base metals from platinum metals by hydrolysing in the presence of nitrite. They stated that "the nitrite procedure for the separation of base metals has been found to be satisfactory when the total weight of platinum metals exceeds that of the base metals, but the accuracy of the separation is lowered when the reverse circumstances apply". Apart from the fact that the accuracy of the nitrite separation is by no means necessarily lowered with higher proportions of base metals, the proposed column procedure, as described, involved equally low proportions of base metals, excluding the zinc which is added as part of the procedure. While the question of general relative value must await continued application in the laboratory, the present author does not anticipate the abandonment of the existing methods of separation; rather it is believed that the essential improvements provided by chromatographic techniques will ultimately become integrated with classical wet methods of fire-assay and ion-exchange methods to provide simple and accurate methods of isolating and separating the platinum metals.

3. *A new fire assay method*

Because of the deficiencies of quantitative collection of the more insoluble platinum metals in the classical fire assay, and because, in a field which involves extensive financial implications, a second proved method of isolation of precious metals from ores is required, the author has in recent years attempted the development of a fire extraction which makes use of the naturally occurring base metal associates. In the earlier experiments[77] the iron, copper and nickel in the roasted natural ore were reduced to form a button containing the platinum metals. The reduction was accomplished by the walls of the carbon pot placed in a high-frequency furnace to produce a reaction temperature of 1450°. With ores containing insufficient base metals, or with synthetic ores, the base metals were added in the form of oxides. Since the reaction time was short and difficult to control, thus producing excessively large buttons, and since the equipment was expensive and not readily available, efforts were made to devise an assay method which would allow control of button size and which require furnaces and pots of standard quality. This aim was accomplished and a procedure was developed[156] which was comparable in every way with the classical lead collection. The base metal alloy button was prepared by reduction with mechanically mixed carbon, sodium carbonate, borax, and ore, with base metal oxides added if required. The standard clay crucibles were heated in a gas-air furnace to a temperature of 1450° as determined from the top of the melt by an optical pyrometer. Button size was controlled by the amount of carbon with an efficiency equal to that obtained with the lead button. The 25-g base metal button was dissolved in conc. hydrochloric acid, and nitric acid was added at intervals followed by hydrochloric acid to remove the nitrous fumes. The solution was diluted and filtered, and if necessary the residue was ignited, and the platinum metals were extracted. The combined filtrates were evaporated to adjust the solution to a pH of 1·5 and passed through a cation-exchanger Dowex-50 × 8 (20–50 mesh). The eluate was evaporated and treated to remove successively sulphuric acid, organic matter, selenium and boron, and was then passed through a small column of cation-exchanger to remove traces of base metals. It was finally treated by a modification of the chromatographic procedure described by Kember and Wells[74] for microgram amounts of platinum metals or by standard methods of separation and precipitation for milligram amounts. The new fire-assay method has been proved for ores salted with platinum and palladium in the presence of rhodium and iridium[156] although the efficiency of recovery of the latter two metals remains to be demonstrated. In a third paper[157] the base metal collection has been proved for ores salted with milligram amounts of osmium and ruthenium. The button, of approximately 25 g, was placed in a standard distilling apparatus with 72%

perchloric acid and heated to dissolve the button. The volatile oxides were collected in concentrated hydrochloric acid and subsequently precipitated with thionilide.

Further reports on this project will be issued as they are completed.

Zusammenfassung—Die Zusammenstellung umfasst Publikationen bis zum Jänuar 1960. Wenu auch die frühe Literatur nur wenig behandelt wird sind doch einige Methoden eingeschlossen, die möglichen Nutzen haben. Die mitgeteilten Daten bezüglich der Genauigkeit von Kuppelationsanalysen werden in Hinblick auf die Zusammensetzung von Flussmittel, Gewinnung des Regulus sowie Aufarbeitung des letzeren behandelt. Charakter und Nutzen von Solventextraktion vor der Kupperlierung wird kritisch untersucht. Nasse Methoden zur Trennung der sechs Platinmetalle werden zusammenfassend beschrieben; die Anwendung von Ionenaustauschharzen sowie chromatographische Trennungen werden diskutiert.

Résumé—Cette revue englobe les publications appropriées jusqu'a janvier 1960. Tandis qu'on discute relativement peu de la littérature ancienne, certains procédés qui restent virtuellement utilisables ont été inclus.

Toute information publiée relative à l'efficacité de la reprise de "l'essai au feu" est discutée du point de vue de la composition du flux, des rassemblements de "boutons et de perles" et des méthodes de partage de ces derniers. Le caractére et l'utilité d'une extraction sélective par voie humide avant la fusion par "l'essai au feu" sont examinés d'un point de vue critique. Les méthodes de séparation des six métaux de la mine de platine par voie humide sont passées en revue, et les applications des séparations par résines échangeuses d'ions et par chromatographie sont discutées.

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DETERMINATION OF ^{131}I, ^{137}Cs, AND ^{140}Ba IN FLUID MILK BY GAMMA SPECTROSCOPY*

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Summary—The radionuclides ^{131}I, ^{137}Cs, and ^{140}Ba are determined in fluid milk by multi-channel gamma spectroscopy, using a heavily shielded 4″ × 4″ sodium iodide (thallium-activated) crystal as a detector. The contribution of each of the above nuclides, and also of the naturally-occurring ^{40}K and background, to the composite gamma spectrum is determined by means of simultaneous equations describing their mutual interferences. No sample preparation is required for the analysis.

The sensitivity of the method is about 10 $\mu\mu$c/litre, with an accuracy of about 5–10 $\mu\mu$c/litre when the nuclides are present at levels up to about 50–100 $\mu\mu$c/litre. At higher levels, the precision and accuracy are about 5–10%.

GAMMA scintillation spectroscopy is a particularly valuable technique in radionuclide analysis because it requires no sample preparation or chemical separations. This represents a considerable saving of labour, and eliminates the possibility of error in processing. In quantitative applications, spectrometer stability with respect to high voltage, amplifier gain, and channel widths is critical. If a number of gamma emitting nuclides are present, the complex spectrum must be resolved for quantitative measurement of each individual component.

Measurement of nuclides at the very low levels found in environmental samples imposes particularly stringent requirements in both instrumentation and spectrum interpretation. Since the nuclides of interest are present in such small quantities as to be barely recognisable above the background response of the detector, the measurement must be made for a considerable length of time to realise even fair counting statistics. For this, very good instrument stability is essential.

Since May, 1957, analyses of the radionuclide content of milk at the Robert A. Taft Sanitary Engineering Center[5] have shown that the principal radionuclides found in milk are ^{89}Sr, ^{90}Sr, ^{137}Cs, ^{131}I, ^{140}Ba, ^{40}K, and their daughters. Other radioisotopes ingested by the cow are eliminated by metabolic processes and do not reach the milk in significant quantities.

Anderson[1] and Booker[2] have utilised gamma scintillation techniques in analysing for ^{137}Cs and ^{40}K in dried milk. Because gamma emitters of short half-life were not present in this material, stringent spectral interference corrections were not necessary.

The method described below, similar to techniques used by others,[3] was developed to permit the determination of ^{131}I, ^{137}Cs, and ^{140}Ba in fluid milk entirely by gamma spectroscopy. The individual nuclide contributions to the gamma spectrum were

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separated by solution of simultaneous equations, describing the spectral interference. This technique does not concentrate the error in the nuclide of the lowest energy, as does the more common procedure of successive spectrum subtractions.[6] Although the sensitivity is not quite as good as by chemical methods, it nevertheless permits measurements far below maximum permissible values of each nuclide. Furthermore, the possibility of error during sample processing is eliminated.

DEVELOPMENT OF THE METHOD

The gamma spectrum obtained from a milk sample is a composite of individual spectra from ^{137}Cs, ^{131}I, ^{140}Ba, ^{40}K, and instrument background. By measuring the spectrum of each of these separately, it was possible to determine the effect of each nuclide on the others.

The spectrum of a monoenergetic source as obtained with a scintillation detector consists of a Gaussian-shaped photopeak, at the full energy of the gamma ray, plus a Compton continuum from somewhat below the full energy to zero energy. In a mixture, consequently, a photopeak will be superimposed on the Compton region from all higher energy emitters. The extent to which a spectrum is masked by the Compton continua depends upon the number of higher-energy gamma emitters present and the quantity of each. The contributions of all higher-energy emitters must be subtracted from the gross spectrum in order to obtain the net spectrum of the emitter of lower energy. Direct spectral subtraction is reasonably satisfactory although, as in all cases of successive subtractions, errors are cumulative.

In addition to this Compton interference, there is sometimes direct interference between photopeaks of two gamma emitters. In this case, straightforward subtraction is not possible since neither spectrum has a characteristic region free of interference from the other. For example, ^{131}I has a minor photopeak at 0.64 MeV which interferes with the ^{137}Cs photopeak at 0.66 MeV, while the ^{137}Cs Compton continuum interferes with the main (0.364-MeV) photopeak of ^{131}I. Similarly, the 1.60-MeV photopeak of ^{140}La is often obscured in actual samples by the 1.46-MeV peak of ^{40}K, present in the sample and in background.

The gross activity of each of the pertinent nuclides considered can be expressed analytically as:

$$G_I = I + C_IC + L_IL + K_IK + B_I \qquad (^{131}\mathrm{I}) \tag{1}$$

$$G_C = I_CI + C + L_CL + K_CK + B_C \qquad (^{137}\mathrm{Cs}) \tag{2}$$

$$G_L = I_LI + C_LC + L + K_LK + B_L \qquad (^{140}\mathrm{Ba}\,^{140}\mathrm{La}) \tag{3}$$

$$G_K = L_KI + C_KC + L_KL + K + B_K \qquad (^{40}\mathrm{K}) \tag{4}$$

The nomenclature for these equations is given in Table I.

The fractional coefficients, C_I, etc., are determined from the individual nuclide spectra as the ratio between the activity in the region of interest and that in the principal photopeak region. For example, in a pure ^{137}Cs spectrum, 32.4 counts in the iodine spectral region (0.32–0.40 MeV) are obtained for each 100 counts in the cesium spectral region (0.60–0.72 MeV). C_I, which accounts for the interference of ^{137}Cs in the ^{131}I region is therefore equal to 0.324. Since the G's and B's are experimentally determined, the four equations (1)–(4) can be solved for the unknowns I, C, L and K, the net counting rates. Once these net counting rates are known, the absolute quantity of each nuclide in the sample is readily determined from calibration data.

The necessity for extremely good stability throughout a spectrometer system is apparent, since drifts in amplifier gain, high voltage, and the like change appreciably the spectral regions covered by certain channels. The resulting variations in the fractional coefficients introduce error into the calculations of the net count of each nuclide. While the influence of drift is not fully known, a one-channel (20 KeV) shift in the location of the ^{40}K peak changes fractional coefficients for this nuclide about 8%.

TABLE I. NOMENCLATURE—EQUATIONS (1)–(4)

	Spectral region for			
	^{40}K	^{131}I	^{137}Cs	^{140}Ba^{140}La
Gross activity (cpm) in:	G_K	G_I	G_C	G_L
Background (cpm) in:	B_K	B_I	B_C	B_L
Fractional coefficient of ^{40}K in:	I	K_I	K_C	K_L
Fractional coefficient of ^{131}I in:	I_K	I	I_C	I_L
Fractional coefficient of ^{137}Cs in:	C_K	C_I	I	C_L
Fractional coefficient of ^{140}Ba^{140}La in:	L_K	L_I	L_C	I
Net activity (cpm) of each nuclide in its spectral region.	K	I	C	L

It should be observed that the fractional coefficients are determined only once for the particular counter system employed. Day to day measurements of a ^{137}Cs standard have shown the constancy of coefficients over many months of operation. In addition, analytical results obtained on mixtures of nuclides measured over several months (See Tables III and IV) further verify coefficient stability.

MATERIALS

The basic instrument used in this method is the low level gamma spectrometer.[4] It consists of a heavily shielded scintillation detector in association with a 100-channel pulse height analyser. The detector is a 4″ × 4″ solid NaI(Tl) crystal, optically coupled to a 5″-photomultiplier tube and housed inside 6″ of steel shielding.

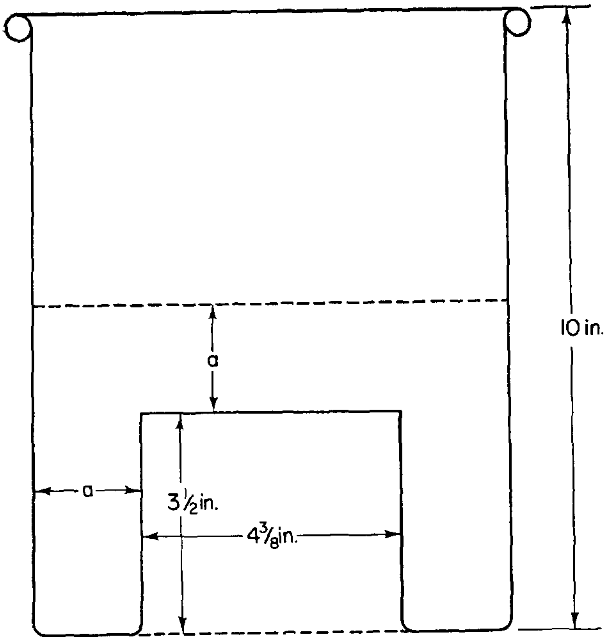
Since the geometry of the sample grossly affects the spectral shape obtained it was important to keep it constant in all work. Specially designed aluminium sample beakers (Fig. 1) surround the crystal for optimum and rigidly fixed geometry. A steel shelf supports the crystal and the sample.

The ^{137}Cs, ^{131}I, and ^{140}Ba^{140}La used for calibration were purchased as certified standards or were standardised by conventional 4-π beta-counting at our laboratory, before dilution for use.

EXPERIMENTAL

To determine the effect of each nuclide on the others and to calibrate the spectrometer, the spectra of the pure individual isotopes were determined. To simulate a milk solution a known quantity of the emitter was diluted to 3.5 litres with distilled water, suitable carrier was added, and precautions were taken to insure homogeneous distribution. After adding sodium chloride to approximate the density of milk, this solution was then placed in one of the specially designed beakers and the nuclide spectrum was determined. Figs. 2 and 3 are the spectral curves for ^{131}I, ^{137}Cs, ^{140}Ba^{140}La, ^{40}K, and background.

Suitable spectral regions (peak areas) were selected for each nuclide, and are listed in Table II. Calculations of ^{140}Ba^{140}La are based on the 0.49-MeV gamma ray which occurs in a portion of the spectrum relatively free from other nuclides. Once these regions have been chosen, the fractional



Volume	a
1L	¾ in
2L	1⅓ in.
3·5L	1$\frac{17}{20}$ in.

FIG. 1—Specially designed sample beaker

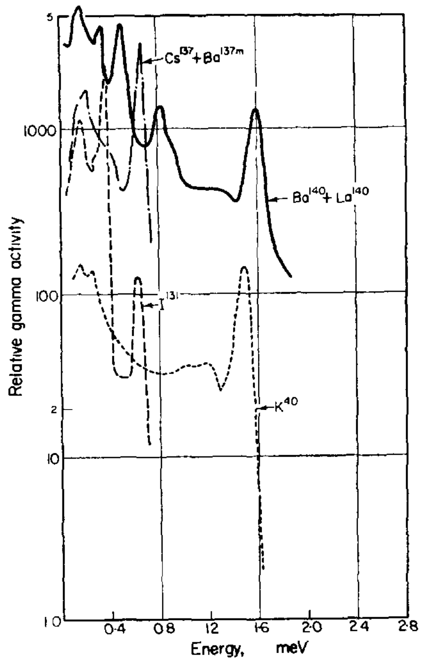


FIG. 2—Spectra of ^{131}I, Cs + ^{137m}Ba ^{140}Ba + ^{140}La and ^{40}K on low level gamma spectrometer

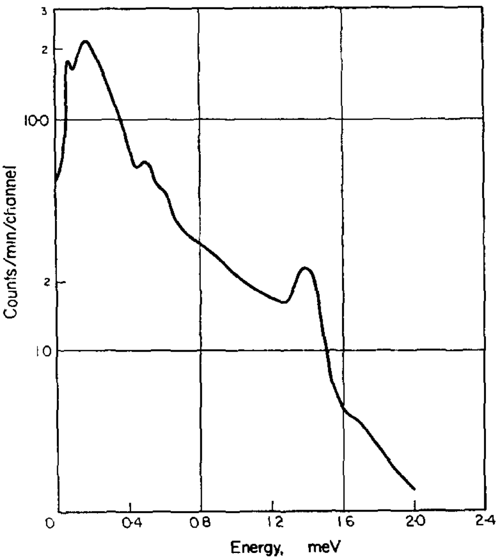


FIG. 3—Background spectrum on low level gamma spectrometer

coefficients for the interference of one nuclide with another were obtained from the spectra of the pure isotopes, and are also listed in Table II.

ANALYTICAL PROCEDURE

A 3.5-litre sample in the aluminium beaker is placed on the detector and the spectrometer is adjusted to cover the energy range 0–1.9 MeV, in 95 20-KeV channels. The spectrum is usually measured for 100 min which gives the required sensitivity and precision, and still permits measurements of an adequate number of samples. From the results, printed on standard adding machine tape, the values of the various G's of equations (1)–(4) are obtained. Background spectra are obtained in a similar manner, using distilled water, usually over 1000 min. The B's of equations (1)–(4) are obtained from an average of the background spectra of an entire week.

TABLE II. SPECTRAL REGIONS AND FRACTIONAL COEFFICIENTS

Nuclide	E_γ, *MeV*	Spectral region energy, *MeV*	Coefficient	Value
^{131}I	0.364	0.32–0.40	I_C	0.075
			I_L	0.025
			I_K	0
^{137}Cs	0.66	0.60–0.72	C_I	0.324
			C_L	0.186
			C_K	0
^{140}Ba^{140}La	0.49	0.46–0.54	L_I	0.866
			L_C	0.313
			L_K	0.185
^{40}K	1.46	1.40–1.52	K_I	0.389
			K_C	0.300
			K_L	0.256

For ease of calculation, equations (1)–(4) are solved explicitly for I, C, and L, yielding the new equations (5), (6) and (7).

$$I = 1.034(G_I - B_I) - 0.812(G_L - B_L) - 0.183(G_C - B_C) - 0.139(G_K - B_K) \qquad (5)$$

$$C = -0.074(G_I - B_I) - 0.226(G_L - B_L) + 1.066(G_C - B_C) - 0.233(G_K - B_K) \qquad (6)$$

$$L = -0.013(G_I - B_I) + 1.115(G_L - B_L) - 0.203(G_C - B_C) - 0.219(G_K - B_K) \qquad (7)$$

As a further convenience, equations (5), (6) and (7) have been programmed on an IBM 650 computer, since manual solution for a large number of samples is excessively tedious.

EVALUATION

Solutions containing known amounts of ^{137}Cs, ^{131}I, ^{140}Ba^{140}La, and ^{40}K were analysed as described above. The first mixture studied contained amounts of ^{137}Cs and ^{40}K comparable to those found in routinely analysed milk samples, with initial ^{131}I and ^{140}Ba^{140}La levels comparable to the highest values found during two years of operation. Analyses were repeated at various time intervals. Because of the decay of ^{131}I and ^{140}Ba^{140}La components, the sample represented a different nuclide mixture for each measurement.

The results of these analyses are shown in Table III. The observed and known values for ^{131}I are in excellent agreement throughout, the difference being within 5% down to 40$\mu\mu$c/l. The observed values for ^{137}Cs are, on the average, 10% higher than the actual levels. In the first two or three measurements, the ^{137}Cs photopeak was almost completely masked by the large quantity of ^{131}I present. Nevertheless, the mathematical solution eliminated this interference quite well. Results on ^{140}Ba in this sample were disappointing. The standardisation of the ^{140}Ba^{140}La solution was later found to be in error because of contamination from longer half-life activity, predominantly strontium isotopes.

Table IV shows the results obtained on a sample containing ^{137}Cs, ^{40}K and uncontaminated ^{140}Ba^{140}La. Again the ^{137}Cs results are, on the average, about 4% higher than the actual activity added. Those for ^{131}I and ^{140}Ba are slightly lower, but are sufficiently accurate at these concentrations for all but the most exacting work. The ^{131}I errors become insignificant as the ^{140}Ba^{140}La concentration decreases, indicating that the coefficient L_I may require adjustment.

TABLE III. OBSERVED VS. KNOWN VALUES OF ^{131}I, ^{137}CS, ^{140}BA (MIXTURE OF ^{131}I, ^{137}CS, ^{140}BA AND ^{40}K)

Date	^{131}I, $\mu\mu c/l$			^{137}Cs, $\mu\mu c/l$			^{140}Ba, $\mu\mu c/l$		
	Observed (A)	Known (B)	(A − B)	Observed (C)	Known (D)	(C − D)	Observed (E)	Known (F)	(E − F)
1/26	998	†987 ± 5%	20	57	†61 ± 5%	−4	154	†181 ± 5%	−27
1/28	862	824	38	63	61	2	140	162	−27
2/2	541	538	3	64	61	3	115	124	−9
2/6	400	384	16	72	61	11	84	100	−16
2/10	270	274	−4	62	61	1	75	81	−6
2/13	214	211	3	66	61	5	66	69	−3
2/20	114	118	−4	72	61	11	43	48	−5
2/26	74	70	4	72	61	11	33	34	−1
3/4	39	42	−3	66	61	5	24	25	−1
3/13	26	20	6	66	61	5	18	14	4
3/23	7	8	−1	69	61	8	12	8	4
4/1	7	4	3	74	61	13	5	5	0
Average	—	—		67	61	6	—	—	
S.D.*	—	—		5	—		—	—	

* Single observation.

† Initial values are the result of standardisation to ±5% accuracy whereas subsequent "Known" values are derived from decay properties of each nuclide.

TABLE IV. OBSERVED VS. KNOWN VALUES OF ^{131}I, ^{137}CS, ^{140}BA (MIXTURE OF ^{137}CS, ^{140}BA, ^{40}K)

Date	^{131}I, $\mu\mu c/l$			^{137}Cs, $\mu\mu c/l$			^{140}Ba, $\mu\mu c/l$		
	Observed (A)	Known (B)	(A − B)	Observed (C)	Known (D)	(C − D)	Observed (E)	Known (F)	(E − F)
5/29	−12	0	−12	180	†171 ± 5%	9	776	†823 ± 5%	−47
6/5	−21	0	−21	188	171	17	526	564	−38
6/9	−37	0	−37	184	171	13	407	456	−51
6/15	−16	0	−16	169	171	−2	317	329	−12
6/18	−16	0	−16	175	171	4	266	282	−16
6/22	−4	0	−4	180	171	9	211	226	−15
6/29	−2	0	−2	179	171	8	164	156	8
7/1	−4	0	−4	174	171	3	125	132	−7
7/6	−5	0	−5	179	171	8	98	100	−2
7/10	−6	0	−6	176	171	5	70	81	−11
7/16	−1	0	−1	182	171	11	49	59	−10
7/27	−4	0	−4	177	171	6	22	33	−11
8/6	−3	0	−3	184	171	13	5	19	−14
8/13	−4	0	−4	172	171	1	9	13	−4
Average	−10	0	−10	178	171		—	—	
SD *	10	—	10	5	—		—	—	

* Single observation.

† Initial values are the result of standardisation to ±5% accuracy whereas subsequent "Known" values are derived from decay properties of each nuclide.

It should be noted in Tables III and IV that the deviations of "known" from "observed" values may in part be due to the ±5% accuracy of the "known" value as a result of standardisation. This would make possible the deviations of predominantly one sign for a given nuclide.

Counting statistics alone cannot account for deviations of "observed" from "known" results in the above analyses. Slight instabilities in the equipment affect results, as already mentioned. In addition, the fractional coefficients are not known sufficiently well in all cases to ensure a uniform spread of results about an average close to the true value. Thus, ^{131}I values of Table IV are not distributed uniformly about the true mean value of zero.

Another possible source of error is correction for background. Day-to-day variation in background measurements is about 4% of the average value, about twice as much as can be attributed to statistical fluctuations. Although this variation is small, it nevertheless contributes its part to the overall errors.

Considering all these sources of error and the results obtained in Tables III and IV the accuracy of the method is estimated to be ±5–10 $\mu\mu$c/l at $<50\mu\mu$c/l. At higher concentrations the tabular results show the accuracy to be approximately 5–10%. As more experience is gained, it may be possible to adjust the constants of equations (5)–(7) to obtain more accurate results.

DISCUSSION

Although this paper describes specifically the gamma spectroscopic analysis of radionuclides in milk through simultaneous equations accounting for mutual interferences, this technique can obviously be applied directly to any material containing any or all of the four nuclides that have been considered, but no other gamma emitters. Furthermore, such a technique can be used in principle for the quantitative analysis of any combination of radionuclides by gamma spectroscopy when the identity of all the gamma emitters is known.

Use of gamma spectroscopy to determine some of the nuclides of milk permits simplification of the radiochemical techniques when pure beta-emitters, such as ^{89}Sr and ^{90}Sr, are to be determined in the same sample. These simplified radiochemical techniques can involve the use of reagents which would interfere with subsequent steps of a completely chemical sequential analysis. For example, oxalate ion employed in determining strontium interferes with the subsequent precipitation of caesium. When the ^{137}Cs is determined by gamma spectroscopy, this interference becomes unimportant. In addition, ashing of the milk,[8] as a preliminary step to radiochemical analysis becomes unnecessary.

CONCLUSIONS

Gamma spectroscopy offers a convenient technique for the simultaneous measurement of ^{137}Cs, ^{131}I, and ^{140}Ba in milk. Many difficulties associated with radiochemical techniques such as reagent-interference in completely sequential chemical analysis, or loss of material in concentration or procedural steps, are eliminated since no sample preparation is required. Thus the ashing of fluid milk, the initial step in radiochemical analysis, becomes unnecessary, and hence, potential losses of ^{131}I and ^{137}Cs are avoided.

The gamma-emitting nuclides can be determined if present at concentrations of 10$\mu\mu$c/l or greater. The accuracy is about 5–10 $\mu\mu$c/l for levels up to 50–100 $\mu\mu$c/l and about ±5–10% at higher levels. Possibly this accuracy can be improved by the use of specialised equipment to provide more stable long-term operation.

Acknowledgment—We wish to express our thanks to Mr. Donald Licking of our Statistics Staff for his help in programming this information on the computer.

Zusammenfassung—Die Radionucleide ^{131}J, ^{137}Cs und ^{140}Ba werden in flussiger Milch bestimmt unter Verwednung von Gamma-Spectroscopie. Als Detector dient ein 4 × 4 Inch Natriumjodidkristall (thalliumaktiviert), der stark abgeschirmt ist. Der Beitrag jedes einzelnen der obigen Nucleide sowie des vorhandenen natürlichen ^{40}K, zur Zusammensetzung des Gammaspectrums wird durch Lösung einer Reihe von Simultangleichungen erhalten, die auch die gegenseitigen Beeinflussungen berücksichtigen. Keine besondere Zubereitung der Probe ist nötig um die Analyse durchzufuhren. Die Empfindlichkeit der Methode ist etwa 10 $\mu\mu$c/Liter mit einer Reproduzierbarkeit von 5–10 $\mu\mu$c/L, wenn die Nucleide eine Konzentration von etwa 50–100 $\mu\mu$c/L aufweisen. Bei höheren Gehalten sind Prezision und Genauigkeit etwa 5–10%.

Résumé—Les radioéléments ^{131}I, ^{137}Cs, ^{140}Ba sont dosés dans le lait fluide par spectroscopie gamma multi-canaux en utilisant comme détecteur un cristal d'iodure de sodium (activé par le thallium) de 4 × 4 inch fortement protégé. La contribution de chacun des éléments ci-dessus, et aussi de ^{40}K naturel, au spectre gamma composé, est évaluée en résolvant une série d'équations simultanées décrivant leurs interférences mutuelles. L'analyse n'exige pas de préparation d'échantillon.

La sensibilité de la méthode est environ de 10 $\mu\mu$c/litre, avec une précision d'environ 5–10 $\mu\mu$c/litre quant les éléments sont présents en quantités supérieures à 50–100 $\mu\mu$c/litre. Pour des quantités plus importantes, la précision est d'environ 5 à 10 pour cent.

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NEW REDOX SYSTEMS—II

OXIDATION OF COBALT^{II} WITH IRON^{III} CHLORIDE IN 1:10-PHENANTHROLINE SOLUTIONS

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Summary—The oxidation of cobalt^{II} with iron^{III}, in the presence of 1:10-phenanthroline, has been studied both potentiometrically and colorimetrically. From these studies it can be deduced that the course of the reaction is

$$[Fe_2(Phen)_4(OH)_2]^{4+} + 2Co(Phen)_3{}^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_3{}^{2+} + 2Co(Phen)_3{}^{3+} + 2H_2O \quad (1)$$

Conditions have been found in which the reaction proceeds quantitatively. Its utilisation in both macro and micro determination of cobalt is discussed.

IN a preliminary communication,[1] it was reported that cobalt^{II} can be oxidised quantitatively with iron^{III} chloride, in weakly alkaline solution, in the presence of 1:10-phenanthroline. Ferroïn, the intensely red complex of iron^{II} with 1:10-phenanthroline, $Fe(Phen)_3{}^{2+}$, is produced. The redox character of the reaction was verified by potentiometric titration. Since this reaction can be utilised in various ways analytically, apart from the quantitative determination of cobalt, its stoichiometry has been studied both potentiometrically and colorimetrically. The results obtained are presented in this paper.

EXPERIMENTAL

Reagents

Standard solutions of 0·05*M* cobalt^{II} nitrate and of 0·01*M* iron^{III} chloride were prepared from reagent grade chemicals. 0·01*M* and 0·001*M* cobalt^{II} nitrate solutions were prepared from the 0·05*M* solution by suitable dilution. The titre of all of the solutions was controlled gravimetrically.

A solution of 0·01*M* 1:10-phenanthroline was prepared by dissolution of 1·802 g of the analytically pure substance in 1 litre of water, weakly acidified by hydrochloric acid (resulting in a pH of 3). Buffer solutions were prepared by neutralisation of the calculated quantity of chloracetic acid or formic acid with aqueous ammonia to the necessary pH while a potentiometric control was maintained with a glass electrode. The resulting molarity of the solutions was 1.

The other solutions employed in the tests were prepared from reagent grade chemicals.

Apparatus

The potentiometric measurements were carried out with a Trüb and Täuber (Switzerland) compensation potentiometer. The indicator electrode was a platinum wire and the reference electrode was a saturated calomel electrode.

The colorimetric measurements were carried out with a colorimeter produced by Laboratorní potřeby, National Corporation, Prague.

POTENTIOMETRIC RESULTS

In the potentiometric titrations optimum conditions were sought for the above-mentioned reaction to proceed quantitatively. The influence of the concentration of 1:10-phenanthroline, of pH, of temperature and of dilution was studied. Unless otherwise stated, the titrations were carried out as follows:

To a measured solution of 0·01*M* cobalt^{II} nitrate (in most cases 2 ml) was added 0·01*M* 1:10-phenanthroline solution and 10 ml of a suitable buffer solution. The pH was eventually adjusted with sodium hydroxide during potentiometric control. The solution was diluted to 50 ml and titrated potentiometrically with 0·01*M* iron^{III} chloride solution from a microburette.

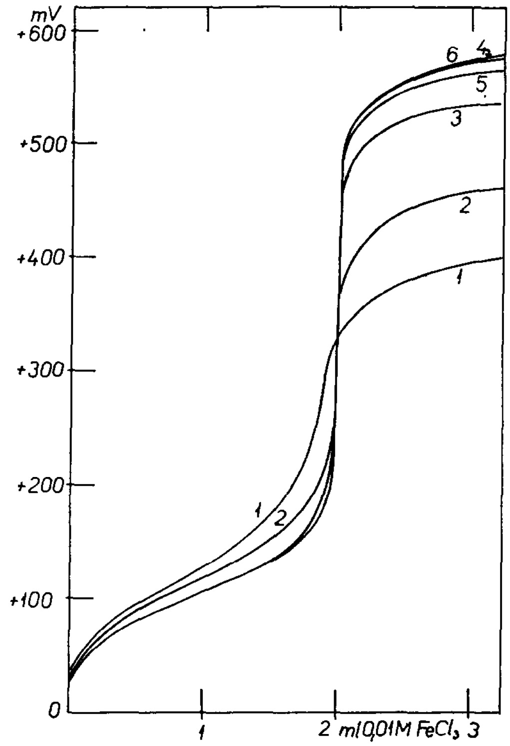


FIG. 1. Oxidation of Co^{II} with FeCl$_3$ solution. Effect of concentration of 1:10-phenanthroline. 2 ml of 0·01*M* Co(NO$_3$)$_2$, 25 ml of 1*M* buffer solution of pH 2·1 (monochloracetic acid–ammonia)—total volume of 50 ml—titrated with 0·01*M* FeCl$_3$. Pt-electrode vs. SCE. The curves were obtained with the following ratios of Co : Phen:—
1. 1 : 5, 2. 1 : 7·5, 3. 1 : 2·5, 4. 1 : 25, 5. 1 : 37·5, 6. 1 : 75.

Influence of 1:10*-phenanthroline concentration*

A number of potentiometric determinations of a constant quantity of cobalt were carried out with 0·01*M* iron^{III} chloride solution at pH 2 in the presence of various amounts of 1:10-phenanthroline. Fig. 1 shows certain potentiometric curves. It is evident that, for example, with the ratio Co:Phen = 1:5, the course of the reaction is not entirely quantitative and that the potential jump at the equivalence point is very small. The stabilisation of the potential in close proximity of the equivalence point is also slow (2 to 3 min). With the ratio Co:Phen = 1:7·5, the course of the reaction is quantitative. The potential jump at the equivalence point is disproportionately higher and, also, the stabilisation of the potential is considerably quicker. Higher concentrations of 1:10-phenanthroline, as was to be expected, favourably influence the size of the potential jump. Concentrations of 1:10-phenanthroline greater than the ratio Co:Phen = 1:25, however, have no influence. From these results it is evident that the minimum concentration of 1:10-phenanthroline, expressed in molarity, must be 6 to 7·5 times higher than the concentration of cobalt. This in no way contradicts the expected equation (1), the right-hand side of which requires the ratios Co:Phen = 1:3 and Co + Fe:Phen = 1:6, respectively. More precise results can be obtained only by colorimetric measurements as will be shown later.

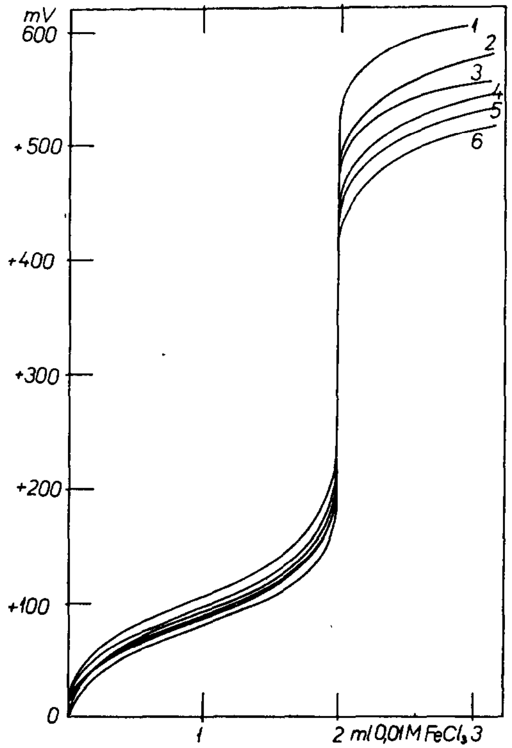


FIG. 2. Oxidation of Co^{II} with $FeCl_3$ solution. Effect of pH. 2 ml of 0·01*M* $Co(NO_3)_2$, 25 ml of 1*M* buffer solution (monochloracetic acid–ammonia) and 5 ml of 0·1*M* 1:10-phenanthroline—total volume of 50 ml—titrated with 0·01*M* $FeCl_3$. Pt-electrode vs. SCE.
1. pH 2·1, 2. pH 2·6, 3. pH 3·1, 4. pH 3·5, 5. pH 4·1, 6. pH 4·5

Influence of pH

Similar measurements were carried out in the study of the influence of pH on the course of the titration. Fig. 2 shows curves of the titration of $cobalt^{II}$ in the presence of a constant excess of 1:10-phenanthroline (Co:Phen = 1:25). The buffering was each time carried out with monochloracetic acid and aqueous ammonia. It is evident that, with a decrease of pH, the potential jump increases (curve 2 at pH 2·1, curve 6 at pH 4·1). In solutions of pH below 2 and above 4 the course of oxidation of $cobalt^{II}$, and consequently also the stabilisation of the potential, is slow. Curve 1, Fig. 2, was obtained in an unbuffered medium, the same ion concentration being maintained by the addition of sodium nitrate. In this titration the potential jump at the equivalence point is the highest. The explanation of this fact is simply that the reaction in an unbuffered medium is not influenced by the formation of competitive complexes with components of the buffer. Fig. 3 is, therefore, very illustrative as it shows the curves of the titration of cobalt^{II} at pH 2·6 in buffered and unbuffered media. It is principally the buffer solution of formic acid and formate which unfavourably affects the potential jump.

Influence of temperature and dilution

The increase of temperature of the titrated solution favourably effects the rate of the reaction. At 50° the stabilisation of the potential is practically instantaneous.

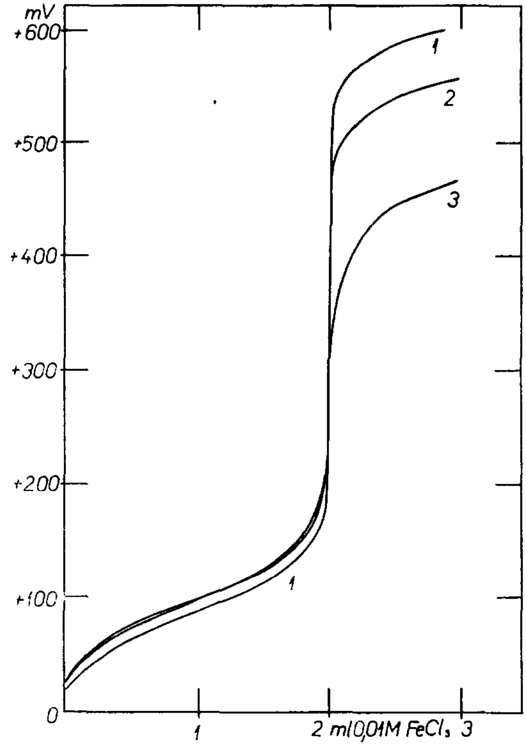
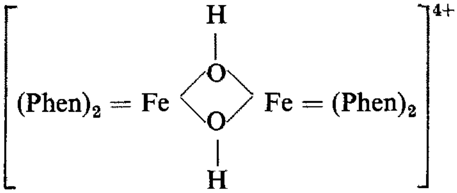


FIG. 3. Oxidation of Co^{II} with FeCl$_3$ solution. Effect of quality of pH-buffer. 2 ml of 0·01*M* Co(NO$_3$)$_2$, 5 ml of 0·1*M* 1:10-phenanthroline, pH adjusted with 25 ml of buffer solution with respect to a glass electrode—total volume of 50 ml—titrated with 0·01*M* FeCl$_3$. Pt-electrode vs. SCE. 1. Non-buffered medium of pH 2·5. 2. Buffer solution of pH 2·5 based on monochloracetic acid–ammonia. 3. Buffer solution of pH 2·5 based on formic acid–ammonia.

With too strongly diluted solutions, for example, diluted to 500 ml, when the concentration of cobalt was only 8 × $10^{-5}M$, the potential jump decreased at the equivalence point by about 80 mV.

Formal redox potentials

The change of the potential of the platinum electrode in the titration of cobalt^{II} with iron^{III} chloride, with sufficient 1:10-phenanthroline present, is given by the changes of the potentials of two redox systems. Before the equivalence point the potential of the electrode is given by the system Co(Phen)$_3^{2+}$/Co(Phen)$_3^{3+}$, and after the equivalence point by the system $Fe(Phen)_3^{2+}/[Fe_2(Phen)_4(OH)_2]^{4+}$. Cobalt^{II} and cobalt^{III} form complexes with 1:10-phenanthroline which can be expressed as $Me(Phen)_3^{n+}$, as in the case of iron. According to certain authors,[2,3] the yellow complex with iron^{III} is of a somewhat different composition. It is a binuclear complex to which the following structure is ascribed



This complex behaves as a dibasic acid ($pK_1 = 4{\cdot}3$ and $pK_2 = 6{\cdot}4$). By simple analysis of a number of potentiometric curves, obtained by titration of a constant amount of cobalt^{II} with iron^{III} chloride in the presence of an excess of 1:10-phenanthroline at different pH values, the values were obtained for the formal potentials of the two systems

$$Co(Phen)_3^{2+} \rightleftharpoons Co(Phen)_3^{3+} + e \tag{2}$$

$$2Fe(Phen)_3^{2+} + 2H_2O \rightleftharpoons [Fe_2(Phen)_4(OH)_2]^{4+} + 2e + 2HPhen^{+} \tag{3}$$

The dependence of the redox potential of system (2) on pH is shown in Fig. 4.

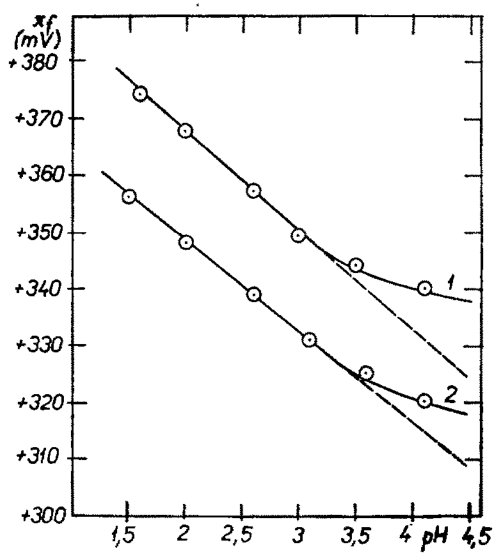


FIG. 4. Dependence on pH of formal redox-potential (π_f) of the system: $Co(Phen)_3^{2+} \rightleftarrows Co(Phen)_3^{3+} + e$.
Values were plotted from the potentiometric titration curves under the different pH for the following ratios of Co : Phen:— 1. 1 : 3, 2. 1 : 25.

Curve 1 was obtained by potentiometric measurements in solutions with the ratio Co:Phen = 1:3, and curve 2 in solutions with the ratio Co:Phen = 1:25. A larger excess of phenanthroline does not influence the system $Co(Phen)_3^{2+}/Co(Phen)_3^{3+}$.

For the same system of phenanthroline complexes, Paglia and Sironi[4] have found a value of 0·37 V for the redox potential.* The same value was found in our case at pH 2 (curve 1, Fig. 4) in a buffered solution (chloroacetic acid–ammonia).

Fig. 5 shows the influence of pH on the formal redox potential of system (3). The two curves were obtained under the same conditions as in the previous case (Co:Phen = 1:3 and 1:25). The influence of 1:10-phenanthroline on the redox potential of the system Fe^{2+}/Fe^{3+} is greater than on the system Co^{2+}/Co^{3+}. Since the complexity constant of the complex $Fe(Phen)_3^{2+}$ is very high, $pK_k = 21·3$,[5] it is principally the formation of the considerably weaker binuclear complex of iron^{III} which is influenced by the concentration of 1:10-phenanthroline.

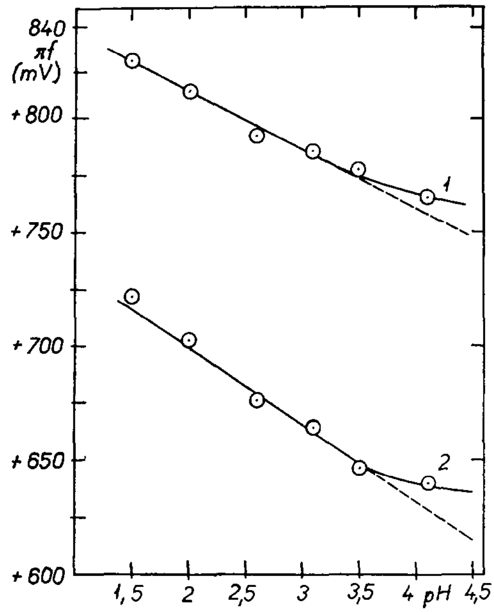


Fig. 5. Dependence on pH of the formal redox potential (π_f) of the system:

$$[Fe_2(Phen)_4(OH)_2]^{4+} + 2HPhen^+ + 2e \rightleftharpoons 2Fe(Phen)_3{}^{2+} + 2H_2O.$$

Values were plotted from the same potentiometric curves as in Fig. 4, for the following ratios of Co : Phen:—1. 1 : 25, 2. 1 : 3.

COLORIMETRIC RESULTS

In the colorimetric study of reaction (1), use was made of the intense red ferroïn colour developed; it has a maximum absorption at 510 mμ. The colorimetric measurements were carried out as follows:

To 2 ml of a 0·001*M* solution of cobalt^{II} nitrate was added 10 ml of 1*M* buffer solution of the required pH, then 0·001*M* iron^{III} chloride solution and 0·005*M* 1:10-phenanthroline solution. The volume was adjusted to 25 ml and after a certain time, usually 20 min, the intensity of the developed colour was measured in 20-cm diameter cells, using a filter of maximum permeability at 510 mμ. A solution free from cobalt, prepared by the same method, was used as the comparison solution.

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* The authors realised the above-mentioned system by mixing synthetically prepared complexes. The measurements were carried out in an unbuffered medium.

Determination of the ratio of reacting components

The ratio of the reacting components was ascertained by the titration curve method.

Fig. 6 proves that, in conformity with the potentiometric results, cobalt^{II} reacts quantitatively, in the presence of 1:10-phenanthroline, with iron^{III} in the ratio of 1:1 (the measurements were carried out at pH 3). The ratio of cobalt and iron to 1:10-phenanthroline is evident from Fig. 7. It represents the titration curve obtained in the case when the ratio of cobalt to iron was 1:1. The measurements were carried out also at pH 3. The break in the curve shows that the stoichiometric ratio Co + Fe:Phen is 1 to 6. Since the composition of ferroïn is accurately known (ratio Fe:Phen = 1:3), the given measurements indirectly also prove the composition of the two cobalt complexes $Co(Phen)^{+2}{}_3$ and $Co(Phen)_3{}^{3+}$.

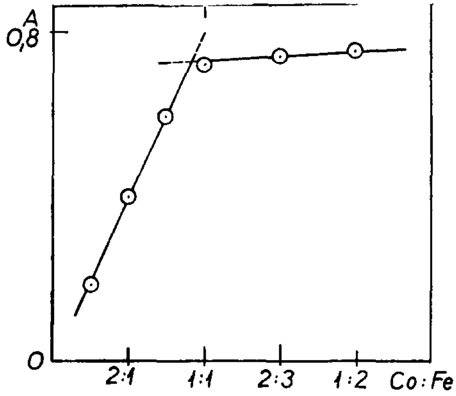

FIG. 6. Dependence of extinction of $Fe(Phen)_3{}^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of the ratio Co : Fe. 2 ml of 0·001*M* $Co(NO_3)_2$, 0·5–4 ml of 0·001*M* $FeCl_3$, 1 ml of 0·05*M* 1:10-phenanthroline, pH 3·5; total volume of 25 ml. The extinction was measured 15 min after mixing (1-cm cell, filter λ_{max} 500 m).

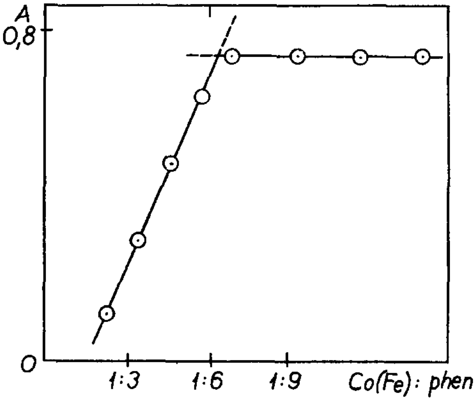

FIG. 7. Dependence of extinction of $Fe(Phen)_3{}^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of ratio (Co + Fe) : Phen. 2 ml of 0·001*M* $Co(NO_3)_2$, 0·5 ml of 0·05*M* $FeCl_3$, 1–5 ml of 0·005*M* 1:10-phenanthroline, pH 3·5, total volume of 25 ml. The extinction was measured 15 min after mixing (1-cm cell, filter λ_{max} 500 mμ).

Influence of pH on the rate of reaction

The influence of pH on the rate of the studied reaction was followed in the same manner. Since it had been ascertained that the course of the reaction is very slow in solutions showing a pH below 1·5 and above 5, all of the measurements were carried out 3 h after mixing all the solutions (Fig. 8). At optimum conditions of acidity, namely pH 2 to 5, the course of reaction is quantitative for 10 to 15 min. This deduction is very important for the utilisation of this reaction in the indirect colorimetric determination of cobalt.

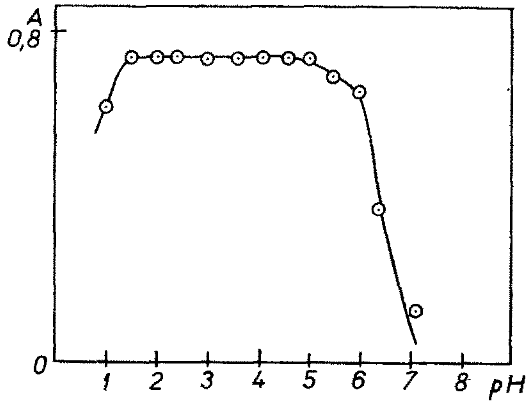

FIG. 8. Dependence of extinction of $Fe(Phen)_3^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of pH-effect on reaction (1) 2 ml of 0·001*M* $Co(NO_3)_2$, 3 ml of 0·001*M* $FeCl_3$, pH adjusted with 0·1*M* HCl or 0·1*M* NaOH (glass electrode) and 5 ml of 0·05*M* 1:10-phenanthroline of the same pH; total volume of 25 ml. The extinction was measured after 3 hr (1-cm cell, filter λ_{max} 50mμ).

CONCLUSIONS

The studied redox reaction (1) has a number of possible analytical applications. Of more theoretical importance is, for example, the oxidimetric determination (in the presence of iron) of cobalt^{II}, using iron^{III} chloride in the presence of 1:10-phenanthroline, followed by cerium^{IV} sulphate. The quantitative formation of ferroïn during this reaction can be utilised, for example, in the colorimetric determination of cobalt in the presence of a large number of elements, including iron. The high redox potential of the system $[Fe(Phen)_4(OH)_2]^{4+}/Fe(Phen)_3^{2+}$ can be utilised also for the determination of other reducing substances. All of these possibilities are under systematic study.

Zusammenfassung—Die Oxydation des o-Phenanthrolincomplexes von Cobalt (II) durch den des Eisen (III) wurde photometrisch und potentiometrisch studiert. Man kommt zum Schluss dass folgender Reaktionsablauf stattfindet:

$$[Fe_2(Phen)_4(OH)_2]^{4+} + 2Co(Phen)_3^{2+} + 2H(Phen)^+ \rightleftharpoons 2Fe(Phen)_3^{2+} + 2Co(Phen)_3^{3+} + 2H_2O$$

Bedingungen unter denen diese Reaktion quantitativ verläuft wurden ausgearbeitet. Die Anwendung der Reaktion zu Makro- und Mikrobestimmungen wird diskutiert.

Résumé—L'oxydation de la complexe de cobalt (II) par cette du fer (III) a été étudiée par potentiométrie et par colorimétrie. On peut déduire de cette étude que le mécanisme de la réaction est le suivant:

$$[Fe_2(Phen)_4(OH)_2]^{4+} + 2Co(Phen)_3{}^{2+} + 2H(Phen)^+ \rightleftharpoons 2Fe(Phen)_3{}^{2+} + 2Co(Phen)_3{}^{3+} + 2H_2O$$

Les auteurs ont trouvé les conditions pour lesquelles la réaction est quantitative. Son utilisation dans les dosages de grandes et petites quantités de cobalt est discutée.

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A DERIVATOGRAPHIC STUDY OF POTASSIUM HYDROGEN PHTHALATE

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Summary—Derivatographic measurements have shown that the decomposition of potassium hydrogen phthalate, which is often used as a primary standard, begins at 190–200°. The non-hygroscopic preparation can be dried between 100° and 150°. Decomposition proceeds in three steps, the rate depending on the rate of increase of temperature. Dipotassium phthalate is formed first, phthalic anhydride and water being removed. Enthalpy changes can also be obtained from the derivatograms; this yields information on the further mechanism of thermal decomposition and changes of state of the sample.

Potassium hydrogen phthalate is often used in titrimetric analysis as a primary standard for aqueous alkaline solutions[1] and for solutions of perchloric acid in glacial acetic acid.[2] It is important to know the temperature at which the preparation can be dried without any danger of decomposition. Willard[6] recommended a drying temperature of 110°, Hillebrand[5] 120°, Kolthoff[4] 125° and Hendrixson[1] 150°. Caley and Brundin[7] state that potassium hydrogen phthalate begins to decompose at 145°, but Dupuis and Duval[3] found that decomposition started only at 172° in their thermogravimetric measurements. Duval[8] later repeated his measurements and found 240° as the decomposition temperature. Borchardt,[9] using a differential thermoanalytical method, found that the preparation is stable to heat up to 290°.

We have investigated the thermal stability of potassium hydrogen phthalate by our derivatographic method[10]. Our results are summarised in this paper.

EXPERIMENTAL

The construction and operation of the derivatograph have already been described.[10] The instrument measures simultaneously the temperature, the enthalpy change (DTA), and the change in weight (DTG). In Figs. 1 and 2 the original derivatograms which show the curves as functions of time, have been re-drawn as functions of the temperature of the sample (T) in order to make the results more readily understood. The samples weighed for the determinations were about 0.5 g. The potassium hydrogen phthalate was heated in a nitrogen atmosphere; above 750° air was introduced so that the elementary carbon contamination of potassium carbonate, which is the final product of the heating, could be burned off. The influence of the heating rate on the decomposition temperature was investigated by the use of three different furnace heating programmes. The continuous lines of the derivatograms correspond to a heating rate of 5°/min, while broken lines correspond to 0.5°/min. The dotted TG curves were obtained by an isothermal heating method, *i.e.* the temperature of the furnace was raised stepwise by 2°–5°, and was maintained at each level until no further weight changes occurred. Apart from potassium hydrogen phthalate, the pyrolysis of dipotassium phthalate was also studied (Fig. 2) in a nitrogen atmosphere with a heating rate of 5°/min.

The pyrolysis of dipotassium phthalate was transitionally retarded at about 580° (see Figs. 1 and 2). The composition of the sample at this temperature was determined as follows. One sample was heated only up to this critical temperature, and was then removed rapidly from the furnace (so that the decomposition reaction was stopped); the sample was then analysed. Carbon dioxide was liberated with hydrochloric acid and weight loss of the sample was determined. The K_2CO_3 content of

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this transitional product was 62%; the other 38% consisted of elementary carbon and a highly polymerised, tar product which was insoluble in organic solvents.

DISCUSSION

Thermal decomposition of potassium hydrogen phthalate began at 200° when the temperature of the furnace was raised continuously (at a rate of 5° or 0·5°/min). In the case of gradual isothermal heating the decomposition temperature was somewhat lower (about 190°). It should be mentioned that the derivatograph measures the temperature inside the sample, hence the decomposition temperature (and conversion temperatures generally) may be measured more precisely than by classical thermoanalytical methods. Thermal balances measure the temperature of the heating furnace, which naturally differs from the temperature of the sample.

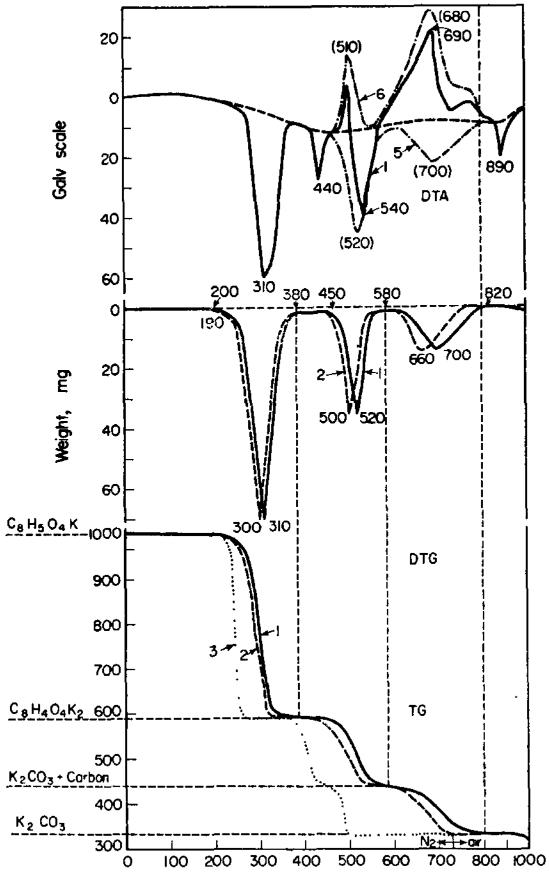

FIG. 1.

Thermal decomposition of potassium hydrogen phthalate proceeded stepwise in three stages (see Fig 1). First, dipotassium phthalate was formed between 200° and 380° (DTG) from 2 molecules of potassium hydrogen phthalate, by removal of phthalic anhydride and water; the same conclusion was reached by Caley and

Brundin.[7] The decomposition was stoichiometric, no other products being formed. This is shown by the TG curves and by the results in Table I. In the table the measured and stoichiometrically calculated weights are shown. The decomposition mechanism

TABLE I.

	5°/min	0.5°/min	isothermal	$C_6H_4(COOK)_2$	theoretical
$C_6H_4COOHCOOK$	*1000*	*1000*	*1000*		*1000*
$C_6H_4(COOK)_2$	592	594	592	*593*	593
Transitional product	437	466	455	424	(—)
K_2CO_3	339	337	338	341	338

was also proved by derivatographic studies of dipotassium phthalate (Fig. 2); derivatograms of the latter correspond to those of potassium hydrogen phthalate between 400° and 900°.

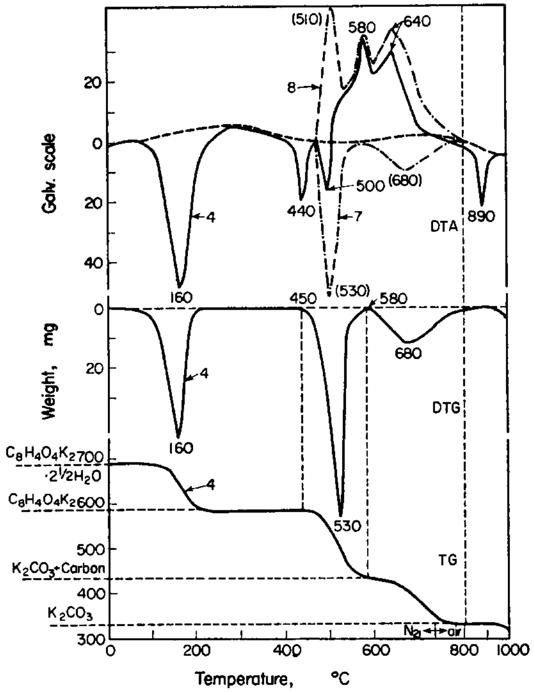

FIG. 2.

Dipotassium phthalate seemed to be quite thermally stable between 380° and 450° (TG, DTG); it melted at 440°, hence there are exothermal peaks at 440°. The change of state was checked by melting-point determinations.

Just after melting the sample began to decompose. It was clear, however, that further decomposition proceeded in two stages. The TG and DTG curves show that the change in weight of the sample was retarded at 450°, 550° or 580° in relation to the heating rate. It should be noted that the slowing of the decomposition occurred in all four cases at the same weight ratio (see Table I). From these facts it is clear that the decomposition yielded either one homogeneous product or other products having the same weight ratio. The analysis of the transition product (prepared by freezing the reaction) showed that the potassium content of the sample was quantitatively present as potassium carbonate which was contaminated with elementary carbon, or more probably with highly polymerised tar products of high molecular weight. The composition of the latter was not homogeneous, of course, but the quantity was almost the same in all cases. Analogous results have been found in derivatographic studies of other organic compounds.[11] Experience has shown that in the thermal decomposition of an organic material the same amount of elementary carbon is always retained; however, the amount is highly dependent on the oxygen content of the compound.

The shapes of the curves between 450° and 800° are interesting. Analysis of the curves shows that the conversion of potassium hydrogen phthalate to dipotassium phthalate between 190° and 380° is a completely endothermic reaction but that two different types of reaction take place in the decomposition of dipotassium phthalate, the first being endothermic and the second exothermic. DTA curves show the resultant of these different heat effects. Similar reactions with double heat effects have been found on several occasions in derivatographic investigations of other organic compounds.[10–12] This was explained by the fact that bond splitting in organic compounds is endothermic, while the formation of new, thermally stable compounds is exothermic. The DTA and DTG curves are nearly parallel. This means that the rate of bond splitting and the rate of formation of gaseous molecule fragments (H_2, CO, CO_2, CH_4, etc) vary in very similar ways. Therefore the supposed curve of the endothermic heat effects was drawn on the figure by broken and dotted lines (curves 5, 7). Regarding the two DTA curves, the curves of the exothermic heat effect can easily be constructed (curves 6, 8). Although this method of extrapolation does not seem to have been substantiated, its correctness may be proved by the fact that when these determinations were repeated, the shapes of the DTA curves could alter considerably while the shapes of the extrapolated curves (5–7 and 6–8) remained almost the same; only phase differences occurred which caused the changes in shape of the DTA curves.

Other conclusions can be made from these derivatograms. It can be established that dipotassium phthalate contains 2·5 moles of hydrate water, which is lost between 60° and 220°. The end-product of the heat decomposition is potassium carbonate. At 890° the product melts. The change of state is indicated by an endothermic peak on the DTA curve. The TG and DTG curves show that the weight of potassium carbonate then begins to decrease slowly. A similar decrease of weight is also found in the case of sodium carbonate.

Zusammenfassung—Derivatographische (Kurven durch differentielle Thermogravimetrie erhalten) Messungen haben gezeigt, dass die Zersetzung von Kaliumhydrogenphthalat, welches häufig als Urtitersubstanz verwendet wird, bei 190–200° beginnt. Die nichthygroskopische Substanz kann zwischen 100 und 150° getrocknet werden. Der Zersetzungsprozess geht in drei Stufen vor sich. Die Zersetzungsgeschwindigkeit hängt von der Geschwindigkeit der Temperatursteigerung ab. Erst wird Dikaliumphthalat gebildet unter Entfernung von Phthalsäureanhydrid und Wasser. Enthalpieänderungen können ebenfalls aus den Derivatogrammen erhalten werden; dies ergibt weitere Informationen über den Mechanismus der thermischen Zersetzungen sowie über Änderungen im Zustand der Probe.

Résumé—Des mesures à partir des courbes d'analyse thermique différentielle ont montré que la décomposition du biphtalate de potassium, qui est souvent utilisé comme étalon primaire commence à 190–200°. La préparation non hygroscopique peut être séchée entre 100 et 150°. La décomposition a lieu en trois stades. la vitesse dépendant de la vitesse d'accroissement de la température. Le phtalate de potassium est formé le premier, l'anhydride phtalique et l'eau étant éliminés. Les variations d'enthalpie peuvent aussi être obtenues à partir des courbes d'analyse thermique différentielle; cela donne des renseignements sur le mécanisme ultérieur de la décomposition thermique et les changements d'état de l'échantillon.

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SHORT COMMUNICATIONS

A new colour reaction for alkali metal ions

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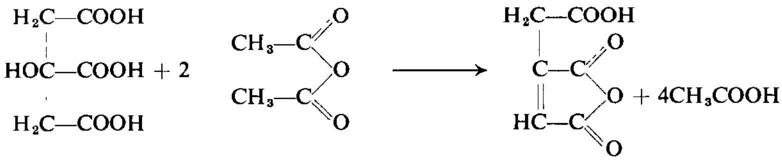
INTRODUCTION

WHEN citric acid is heated in an acetic anhydride medium with a tertiary amine, an intense violet-red colour is formed.[1] A similar colour reaction is obtained when *cis*-aconitic anhydride is used instead of citric acid.[2] The latter reagent was recently utilised as a quantitative reagent for tertiary amines.[3] Presumably, the two reactions are related in that citric acid probably loses two moles of water in hot acetic anhydride to form *cis*-aconitic anhydride as follows:



The latter compound is probably the reacting species in both colour reactions.

During an investigation of the above colour reaction as a means of determining tertiary amines, alkali metal ions were observed to undergo the same reaction to form a compound with an absorption maximum at 560 mμ. Alkali metal ions undergo very few colour reactions because of their inability to form chelates and complexes. For this reason the above colour reaction has been further investigated as a possible method of determining alkali metal ions.

EXPERIMENTAL

Reagents and apparatus

Acetic anhydride: Union Carbide Chemicals Company, commercial grade or equivalent. The iron content of the solvent should be less than 0.5 ppm.

2:4-*Pentanedione:* Union Carbide Chemicals Company, commercial grade or equivalent.

Toluene: redistilled.

Citric acid reagent: dissolve, by heating, 2.5 g of citric acid, Mallinckrodt reagent grade, in 100 ml of 2:4-pentanedione.

Beckman model B spectrophotometer, or equivalent, equipped with 1-cm cells.

Procedure

Add 0.3 ml of the citric acid reagent, by means of a graduated 1.0-ml pipette, to each of three 25-ml glass-stoppered graduated cylinders. Reserve one of the cylinders as a blank. To each of the other cylinders transfer an aliquot of an acetic anhydride dilution of the sample containing not more than 0.5 micromoles of alkali metal ion. Dilute the contents of each cylinder to 5 ml with acetic anhydride. Pipette 5 ml of toluene into each cylinder. Stopper the cylinders and mix. Loosen the stoppers so that pressure will not build up in the cylinders, then place the latter in a steam bath at 98° for 25 min. Cool the cylinders to room temperature and measure the absorbance of their contents, using 1-cm cells, at 560 mμ by means of a suitable spectrophotometer. Read the concentration of alkali metal ion from a previously prepared calibration curve.

Calibration curve

Prepare a dilution of the alkali metal salt in acetic anhydride so that a 5-ml aliquot contains approximately 0.5 micromoles of alkali metal ion. Dissolve the salt initially in a minimum amount of water to effect solution in the anhydride. The water content of the final dilution should be less than 0.5%. To each of five 25-ml glass-stoppered graduated cylinders add 0.3 ml of the citric acid reagent by means of a graduated pipette. Transfer 1.0, 2.0, and 3.0-ml aliquots of the standard dilution to respective cylinders, reserving an additional one as a blank. Measure the absorbance of each standard at 560 mμ using the procedure described previously. Plot a calibration curve of absorbance versus μg of alkali metal ion.

DISCUSSION

The calibration curves in Fig. 1 for sodium, potassium, and lithium salts are plotted in terms of micromoles of the alkali metal salt. When the results are plotted in this manner, sodium and potassium salts give the same calibration curve (Curve 1, Fig. 1). This indicates that, using the procedure specified, the colour reaction is quantitative for sodium and potassium ions and that the colour is independent of the anion. The colour development for lithium salts is not as intense, on an equimolar basis, as for sodium and potassium ions and does not follow Beer's law (Curve 2, Fig. 1). Evidently the reaction is not quantitative for this ion under the conditions used.

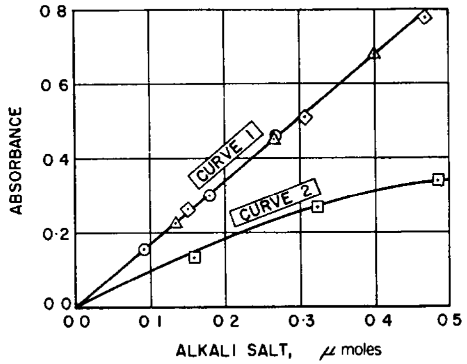


FIG. 1.—Calibration curves for the determination of alkali metal ions by reaction with citric acid.

○—Potassium acetate
△—Sodium acetate
◇—Potassium chloride
□—Lithium acetate.

Interference of other metal ions

The alkali metal ions were the only ions found that give a colour reaction with citric acid in acetic anhydride medium. The reaction is not obtained with Ca, Hg^{II}, Cu^{II}, Fe^{II} or Fe^{III}. However, as shown in Fig. 2, traces of Fe^{III} inhibit the colour reaction, and therefore interfere in the method.

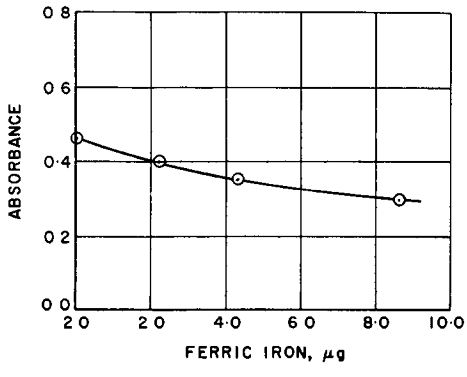


FIG. 2.—Effect of iron on the reaction of 35·2 μg of potassium chloride with citric acid.

Fe^{I} does not affect the colour development. Most organic solvents contain traces of iron, and therefore inhibit the colour formation. This is also true of acetic anhydride which is essential for the colour reaction. In fact, when the citric acid reagent was prepared in acetic anhydride medium, reproducible calibration curves could not be obtained when different batches of acetic anhydride were used. This difficulty was overcome by preparing the reagent in 2:4-pentanedione (acetylacetone), a chelating agent. However, even using this reagent all solvents must contain less than 0.5 ppm of Fe^{III} or the colour will be inhibited.

Attempts were made to incorporate into the citric acid reagent a reducing reagent that would convert Fe^{III} to Fe^{II}, thus eliminating this serious interference. Among the reducing reagents tried unsuccessfully were formic acid, ascorbic acid, phenylhydrazine, hydroxylamine and oxalic acid. Of these compounds only oxalic acid tended to inhibit the bleaching effect of Fe^{III}. Under the conditions of the study 0.03 g of oxalic acid were capable of inhibiting only 2μg of Fe^{III}. This indicates that the reduction of Fe^{III} to Fe^{II} does not take place readily in the non-aqueous media essential for the colour reaction.

An unsuccessful attempt was made to de-activate Fe^{III} by reacting it with a chelating agent. Among the compounds investigated were mercaptoacetic acid, dimethylglyoxime, N:N′-bis(salicylidene)propylenediamine and mercaptobenzoic acid. None of these affect the inhibition of the colour by Fe^{III}.

Other interferences

Of the substances investigated, only tertiary amines and the alkali metal ions were observed to give the colour reaction with citric acid. The usual type of interference is an inhibition of the colour development. In general, alcohols, most acids, and water interfere in this manner. Substances that have been investigated for interference are listed in Table I.

TABLE I.—INTERFERENCES IN THE COLOUR REACTION OF CITRIC ACID WITH ALKALI METAL IONS

Substance	Amount[a]	Type of interference
Ca	32.6 μg	none
Cu^{II}	313.0 μg	none
Fe^{III}	0.5 μg	inhibits
Fe^{II}	13.0 μg	none
Hg^{II}	68.6 μg	none
acetic acid	0.1 g	inhibits
methanol	0.05 g	inhibits
oxalic acid	0.03 g	none
phosphorous acid	40.0 μg[b]	inhibits
tertiary amines	1.0 μg	colour
water	0.03 g	inhibits

[a] Unless otherwise noted, the indicated amount can be tolerated without interference.
[b] Completely inhibits colour development.

CONCLUSION

The nature of this colour reaction with alkali metal ions is not known. When citric acid is used as the reagent, *cis*-aconitic anhydride is probably the reacting species.

Although the colour reaction is apparently very specific for alkali metal ions, many inhibitive interferences are encountered. The most serious is obtained with Fe^{III}. Unsuccessful attempts were made to eliminate this interference by an *in situ* reaction. Presumably the interference could be eliminated by preliminary treatment of the sample with an ion-exchange resin. If the reaction is used for quantitative purposes, the sample should be evaporated to dryness to remove water and other organic interferences.

Summary—When citric acid is heated in an acetic anhydride medium with an alkali metal ion, an intense violet-red colour develops. The colour reaction is almost specific, except for the similar, well-known reaction of tertiary amines. The reaction with sodium and potassium is quantitative and can be used for such purposes if several inhibitive interferences are eliminated from the sample. Fe^{III} is the most serious interference of this type.

Zusammenfassung—Wenn Citronensäure in einem Medium von Essigsäureanhydrid mit einem Alklimetallion erhitzt wird entsteht eine intensiv violettrote Färbung. Die Farbreaktion ist nahezu spezifisch und wird sonst nur in bekannter Weise mit tertiären Aminen erzielt. Die Reaktion verläuft mit Natrium und Kalium quantitativ und kann analytisch verwendet werden, wenn verschiedene störende Faktoren ausgeschaltet sind. Ferriion ist die ägregste Störung.

Résumé—Quand l'acide citrique est chauffé en milieu anhydride acétique avec un ion métallique alcalin, une coloration violet-rouge intense apparaît. Cette réaction colorée est presque spécifique, sauf pour la réaction semblable, bien connue des amines tertiaires. La réaction avec le sodium et le potassium est quantitative et peut être utilisée dans ce but si plusieurs ions gênants inhibiteurs sont éliminés de l'échantillon. L'ion ferrique est l'ion le plus serieusement gênant de ce genre.

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A polarographic method for fluoride

(*Received* 16 *February* 1960)

SEVERAL methods for the polarographic determination of fluoride have been proposed; many of these require relatively large amounts of fluoride. For microgram amounts Langer[1] described the first amperometric method, and Shoemaker[2] was able to measure 1–200 μg fluoride with a rotating platinum electrode. McNulty *et al.*[3] described the determination of 0.1–40 μg of fluoride. None of these methods makes use of the full potentialities of the polarographs now available.

The basic reaction in all the most widely-used fluoride analyses is the complexing of a metal by fluoride, and the amount of uncomplexed metal is measured, in equilibrium methods (which are more sensitive than titrations), either directly or by adding an indicator. The effect of fluoride is thus to decrease the reading, and the estimated value is the difference between two large values, which reduces the accuracy of the measurement. The components of the system which increase on addition of fluoride are the fluoride complex and the free indicator. Since there are no known fluoride complexes which give a polarographic wave distinct from that of the metal, a survey has been made of polarographically reducible compounds capable of binding thorium, which forms one of the strongest fluoride-metal complexes.

Two substances have so far been found which, under appropriate conditions, give a polarographic wave increasing in height with added fluoride (Table I).

TABLE I.—OPTIMUM CHANGE IN POLAROGRAPHIC WAVE HEIGHT DUE TO FLUORINE

System	Change, *μamp/μg* F
Al + Solochrome Violet RS[3]	−0·15
Th + Chrome Azurol S	+0·012
Th + *o*-nitrobenzenearsonic acid	+0·56

well-known reaction of tertiary amines. The reaction with sodium and potassium is quantitative and can be used for such purposes if several inhibitive interferences are eliminated from the sample. Fe^{III} is the most serious interference of this type.

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It is apparent that Chrome Azurol S is unsatisfactory, but it has been possible to develop a simple method for the determination of microgram amounts of fluoride with *o*-nitrobenzenearsonic acid.

The reagent is made up to contain:

0·006% *o*-nitrobenzenearsonic acid
0·00025M thorium nitrate
8 mg/litre fluoride as sodium fluoride
0·3N chloracetic acid
0·15N sodium hydroxide
0·05N ammonium chloride (for Ag/AgCl anode)

The solution is stable for two weeks in polythene. Two ml of the sample is neutralised, if necessary, with perchloric acid using 1 drop of 0·002% paramethyl red as indicator, and 1 ml of reagent is added. The total volume should not exceed 3·4 ml. The peak heights are measured with a cathode-ray polarograph after de-oxygenation.

The polarogram of *o*-nitrobenzenearsonic acid has three peaks: the second is small and the third is double. The calibration curve for fluoride is derived from the ratio of the height of the second part of the third peak to the height of the first peak, and is essentially linear for 2–10 μg of fluoride.

One reagent solution was used for 5 determinations on pure fluoride solutions over a period of a fortnight: the results are shown in Table II.

TABLE II.—MEANS AND STANDARD DEVIATIONS OF THE RATIO OF PEAK HEIGHTS OF THE REAGENT AFTER ADDITION OF FLUORIDE

F added, μg	Peak ratio	Corrected for blank
Nil	0·161 ± 0·002	—
1	0·192 ± 0·005	0·031 ± 0·003
10	0·578 ± 0·006	0·417 ± 0·006

It is apparent that the method is simple and accurate, although it has not been possible to take advantage of the full sensitivity of the polarograph. The procedure has been developed for use in conjunction with the diffusion separation of fluoride,[4] which eliminates the relatively high blank values of the standard distillation separation.

The addition of fluoride to the reagent is necessary to avoid a flat portion of the calibration curve; without this addition the reagent could be used for 10–18 μg of fluoride.

Summary—A polarographic method is proposed for the determination of fluoride, based on the action of fluoride on a complex formed between thorium and *o*-nitrobenzenearsonic acid. Increasing amounts of fluoride liberate increasing amounts of the organic compound, of which the polarographic wave is utilised. The wave-height therefore increases with increasing amounts of fluoride, in contrast to existing polarographic methods for the ion.

Zusammenfassung—Eine polarographische Methode für Bestimmung von Fluorid wird vorgeschlagen. Das Verfahren beruht auf der Reaktion von Fluorid mit dem Thoriumkomplex von *o*-Nitrobenzolarsinsäure. Steigende Mengen Fluorid setzen steigende Mengen der organischen Verbindung in Freiheit. Die durch die organische Komponente verursachte polarographische Welle ist in ihrer Höhe proportional der Fluorid-Menge; dies ist gegenteilig zu allen bisherigen polarographischen Fluoridbestimmungen.

Resumé—Une méthode polarographique est proposée pour le dosage des fluorures; cette méthode est basée sur l'action du fluorure sur un complexe thorium-acide *o*-nitrobenzène arsonique. Des quantités croissantes de fluorure libèrent des quantités croissantes du composé organique dont on suit la vague polarographique. La hauteur de la vague augmente donc avec des quantités croissantes de fluorure, à l'opposé des méthodes polarographiques existant déjà pour cet ion.

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New methods of detection of glyoxal

(*Received* 11 *January* 1960)

INTRODUCTION

GLYOXAL is a product of the oxidation of such compounds as ethylene[1] and acetylene[2] by nitrogen dioxide under laboratory conditions. Since all these reactants are present in polluted atmospheres, it seems plausible that glyoxal may also be formed in city air. For this reason and because of the intense bioanalytical interest in glyoxal, it seems worthwhile to examine methods for its detection.

Glyoxal, heated with naphthoresorcinol or resorcinol in strong hydrochloric acid solution, is reported to give red and blue colours, respectively.[3] However, the sensitivity of the test is not great, and formaldehyde also gives a red colour with these reagents.

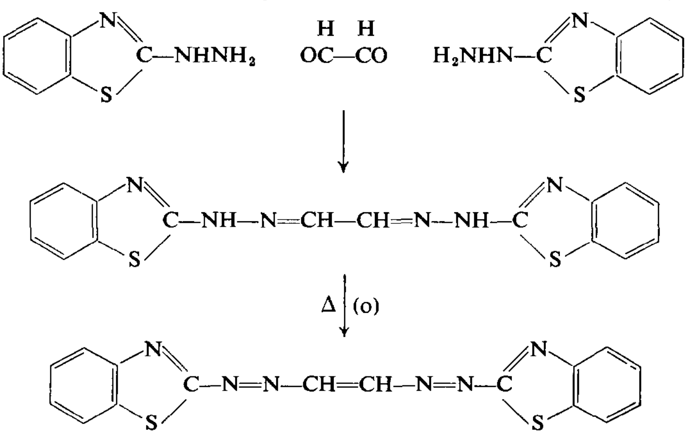
2:3-Diaminophenazine has been used to determine glyoxal.[4] However, this method requires several subsequent reactions to eliminate the interfering effect of excess reagent. Another disadvantage is that pyruvaldehyde also reacts with the reagent.

Wanzlick and Löchel[5] have introduced the reagent, 1:2-dianilinoethane, for the analysis of glyoxal. A modified method has been applied to the determination of glyoxal in periodate-oxidised starch.[6] This approach shows promise of further development and of possible application to air pollution.

Glyoxal and 1:2-dianilinoethane react to give 1:1′:3:3′-tetraphenyl-2:2′-bi-imidazolidine. A solution of this latter compound in dilute hydrochloric acid solution turns blue after a short period of heat and agitation. In a nitrogen atmosphere the blue colour does not form readily. Both oxygen and acid appear necessary for the formation of the blue compound. It is possible that the blue dye is the dicationic tetraphenylbi-imidazoline, but the evidence for this is not yet unequivocal.

On the basis of this type of mechanism, reagents containing the skeletal chain X—C—(C)$_n$—X, where $n = 1$ or 2 and $X = NH_2$ or SH, were investigated. Of the few thus examined, 2-aminothiophenol and 2:3-diaminonaphthalene showed the most promise.

A second type of mechanism that was investigated was the reaction between an aryl or heteroaryl hydrazine and glyoxal to form a fluorescent compound containing an extended chain of conjugation. With 2-hydrazinobenzothiazole as the reagent, the mechanism of reaction is probably as follows:



Yellow Fluorescence

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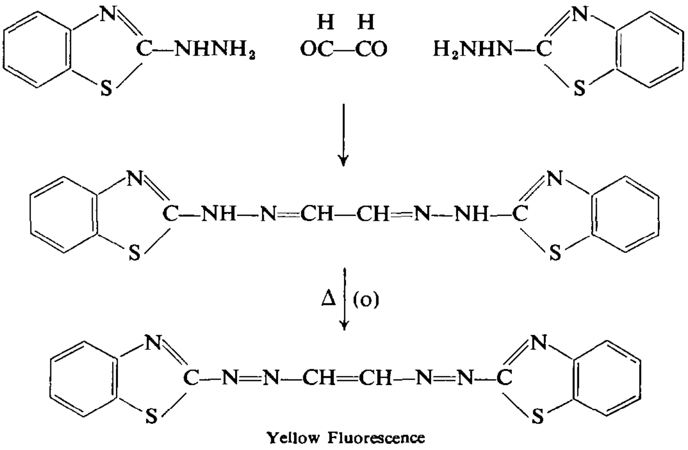

Yellow Fluorescence

EXPERIMENTAL

Reagents

1:2-Dianilinoethane and 2:3-diaminonaphthalene (Aldrich Chemical Co.), 2-hydrazinobenzothiazole (Distillation Products, Inc.), and 2-aminothiophenol (American Cyanamide Co.) were used.

Reagent solutions

Gently warm 0.5 g of reagent in 4 ml of concentrated hydrochloric acid and 10 ml of water until the crystals have gone into solution. Dilute to 50 ml with water. The solution is stable for at least 1 day.

Equipment

The ultraviolet light source used to detect fluorescence was a Model B-50 Blak-Ray Long Wave Ultraviolet Lamp (Ultra-Violet Products, Inc., S. Pasadena, California).

Spot test procedure

One drop (0.03 ml) of the reagent solution is placed on the filter paper. In the centre of this spot 1 μl or 1 drop (0.03 ml) of the aqueous test solution is deposited. After a 1–2 min wait the spot is heated with a jet of steam for 10–60 sec. When using the reagent solution containing 2-aminothiophenol, 1 drop of concentrated hydrochloric acid is added just before the spot is steamed.

The coloured stains and the identification limits obtained in testing for glyoxal with the different reagents are shown in Table 1.

TABLE I—SPOT TESTS FOR GLYOXAL

Reagent	Colour	Identification Limit[a], μg	
		A	B
1:2-Dianilinoethane	Blue[b]	0.1	5
2:3-Diaminonaphthalene	Green	0.2	5
2-Aminothiophenol	Blue	0.05	2
2-Hydrazinobenzothiazole	Yellow fluor.	0.008	0.3

[a] A = 1 μl of test solution.
B = 1 drop (0·03 ml) of test solution.

[b] If the paper is steam-heated for several minutes, the blue stain will change to red.

DISCUSSION OF RESULTS

A method is introduced for the detection of glyoxal on paper. As some heat is necessary for the reaction to take place, the area of the paper containing the reagent and test solutions is exposed to steam for 10–60 sec. In this manner heat is applied to the reaction area without evaporating the solvent. If dry heat were applied, the solvent would evaporate and a poor or negative reaction would be obtained. The concentration of hydrochloric acid on the paper is high enough, in spite of the steam heat, for the blue dye to be formed in the 2-aminothiophenol reaction.

The advantages of a microlitre pipette in applying the test solution lie in the ease of handling and in the ability to concentrate a minute volume of test solution in a small area. As seen in Table I a 20- to 50-fold decrease in the identification limit can thus be obtained.

The following compounds gave negative results with all reagent solutions—formaldehyde, acetaldehyde, benzaldehyde, phthalaldehyde, terephthalaldehyde, cinnamaldehyde, acrolein, acetone, benzalacetone, dibenzalacetone, anisalacetophenone, 2:4-pentanedione, anthraquinone, ethyleneglycol, nitromethane, 1-octene and 2:4-pentadiene. Especially noteworthy were the negative results with α-dicarbonyl compounds, such as pyruvaldehyde, biacetyl, benzil, phenanthraquinone and acenaphthenequinone.

The interference of formaldehyde with the detection of glyoxal was investigated more fully. Using the 1:2-dianilinoethane reagent and 1 μl of test solution, 0.2 μg of glyoxal could be detected in the presence of 1900 μg of formaldehyde. With the 2-aminothiophenol reagent 0.03 μg of glyoxal could be detected in the presence of 190 μg of formaldehyde. With the 2-hydrazinobenzothiazole reagent 0.03 μg of glyoxal could be detected in the presence of 76 μg of formaldehyde.

Using 1% aqueous glyoxal solution as the reagent it was possible to detect 0.1 μg of 2-aminothiophenol, 1 μg of 1:2-dianilinoethane and 1 μg of 2:3-diaminonaphthalene. The procedure in this case would be 1 drop (0.03 ml) of the glyoxal solution, 1 μl of the 3% aqueous hydrochloric acid test solution, and then treatment of the paper with steam for several seconds. When testing for the 2-aminothiophenol 1 drop of concentrated hydrochloric acid is added just before the steam treatment. A green fleck is obtained for the diaminonaphthalene while a blue stain is obtained with the other two amines.

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Summary—In the new colour and fluorescent tests for glyoxal introduced in this paper it was found that a solution of the reactants on filter paper could be heated with a one-inch wide jet of steam without any serious loss of solvent or acid. By this technique the reagents 1:2-dianilinoethane, 2:3-diaminonaphthalene and 2-aminothiophenol gave blue, green and blue stains respectively, with corresponding identification limits of 0.1, 0.2 and 0.05 μg of glyoxal. With 2-hydrazinobenzothiazole a golden-yellow fluorescence and an identification limit of 0.008 μg of glyoxal was obtained. On the other hand, 0.1 μg 2-aminothiophenol, 1 μg 2:3-diaminonaphthalene, and 1 μg 1:2-dianilinoethane could be detected with glyoxal as the reagent.

Zusammenfassung—Bei Untersuchungen über den neuen, hier beschriebenen Farb- und Fluorescenztest auf Glyoxal wurde gefunden, dass man die Lösungen der Reaktanten auf dem Filterpapier mit einem ca 2–3 cm weiten Dampfstrahl erhitzen kann, ohne erhebliche Verlust an Lösungsemittel oder Säure zu erleiden. Mit dieser Technik ergaben 1,2-Dianiloäthan, 2,3-Diaminonaphthalin und 2-Aminothiophenol blaue, grüne bzw. blaue Flecken. Die entsprechenden Nachweisgrenzen waren 0.1, 0.2 und 0.05 μg Glyoxal. Mit 2-Hydrazinobenzthiazol erhält man einen gold-gelb fluoreszierenden Flack bei einer Nachweisgrenze von 0.008 μg Glyoxal. Andrerseits kann 0.1 μg 2-Aminothiophenol, 1 μg 2,3-Diaminonaphthalin und 1 μg 1,2-Dianiloäthan mit Glyoxal als Tüpfelreagens nachgewiesen werden.

Résumé—Dans les nouveaux tests colorimétriques et fluorimétriques du glyoxal présentés dans ce mémoire, les auteurs ont rtouvé qu'une solution des corps réagissant sur papier filtre pouvait être chauffée avec un jet de vapeur large de 1 inch sans perte sérieuse de solvant ou d'acide. Par cette technique les réactifs suivants: 1–2 dianiloéthane, 2–3 diaminonaphtalène et 2 aminothiophénol donnaient respectivement des taches bleue, verte et bleue, avec les limites d'identification correspondantes de 0,1; 0,2; 0,05 μg de glyoxal. Avec la 2 hydrazinobenzothiazole une fluorescence jaune d'or et une limite d'identification de 0,008 μg de glyoxal étaient obtenues. D'autre part, 0,1 μg de 2 aminothiophénol, 1 μg de 2–3 diaminonaphtalène et 1 μg de 1–2 dianiloéthane pouvaient être decelés avec le glyoxal comme réactif.

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NOTICES

Dr. Rudolph Přibil

Dr. Rudolph Přibil, who is one of the regional editors of Talanta, attained his fiftieth birthday this year. Because of the many contributions Dr. Přibil has made to analytical chemistry, particularly in the field of compleximetry, it is perhaps fitting that an account be given of his career.

Dr. Přibil was born on July 23rd, 1910, in Prague. He studied chemistry at the Charles University, Prague, from 1928 to 1933. During this time he studied analytical chemistry under Professor Tomlcek and physical chemistry under Professor Heyrovský. He received the degree of Doctor of Natural Sciences, in 1933.

He continued to work in the University as an assistant in the Institute of Analytical Chemistry, where he studied in the field of electrometric titrations. During the second world war, when the University was closed, Dr. Přibil worked in a chemical factory at Rybitví as a research analyst. After the war, Dr. Přibil returned to the University as Dozent (Assistant Professor) in analytical chemistry; later he became the representative of the Institute of Inorganic and Forensic Chemistry at the University.

From 1950 to 1955 Dr. Přibil was head of the Division of Analytical Chemistry in the Institute for Biochemistry and Pharmacy. From 1955 to the present date, he has been head of the Laboratory of Analytical Chemistry at the Czechoslovak Academy of Science in Prague, and he has recently been given responsibility for the Institute of Geochemistry in the same organisation.

Immediately after the war, Dr. Přibil began his work on the use of EDTA and other complex-forming compounds in analytical chemistry. His achievements in this field are well known and it was fitting that in the year of 1953 he was awarded the State Prize for analytical chemistry. In 1958 he obtained the highest degree in Czechoslovakia (Doctor of Science).

Dr. Přibil has published about 200 papers in Czech and foreign Journals and also several monographs on the use of EDTA in analytical chemistry.

It is indicative of Přibil's energy and strength of character that he has not allowed consistent ill-health to affect his tremendous activity. As all those who have met him know well, he is excellent company, a humanist and completely international in his outlook on life.

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6.45 for 7.15 p.m.—Dinner.

8.45 p.m.—Discussion Meeting.

Monday–Wednesday 24–26 *October* 1960: **Association of Analytical Chemists**: *Eighth Detroit Anachem Conference.* McGregor Memorial Conference Centre, Wayne State University, Detroit, Michigan.

The lectures are grouped into the following sessions:

Monday 24 *October*
- *General Analytical Chemistry.*
- *Clinical and General Analytical Chemistry.*
- *Symposium on Applied Neutron Activation Analysis using Sealed Sources, Machine Sources, and Reactors.*

Tuesday 25 *October*
- *Emission Spectrography, Flame Photometry, and General Analytical Chemistry.*
- *Symposium on Absorption Spectroscopy.*

Wednesday 26 *October*
- *Symposium on Gas Chromatography.*
- *Analytical Chemistry—Corrosion Metals and Polarography.*
- *Symposium on X-Ray Fluorescence.*
- *Solvent Extraction and General Analytical Chemistry.*

The programme also includes the Anachem Award session, the Conference Dinner and the Conference Address.

Enquiries should be addressed to THOMAS O. MORGAN, Publicity Chairman, Eighth Detroit Anachem Conference, General Motors Research Laboratories, 12 Mile and Mound Roads, Warren, Mich.

Wednesday–Saturday 26–29 *October* 1960: Analytical Chemistry Section, **German Chemical Society**: Symposium on *Modern Methods of Analysis of Organic Compounds.* Organic Chemistry Institute, Technical University, München.

The lectures will be grouped under the following headings:

1. Elementary Analysis.
2. Chemical Group Analysis.
3. Analytical Methods such as Chromatography, Electrophoresis, etc.
4. Determination of Structure of Organic Compounds by Chemical and Physical Methods.
5. Application of Isotope-labelled Compounds in Organic Analysis.

The arrangements for the symposium are being made by Herr Prof. Dr. F. WEYGAND, Organisch-chemisches Institut der Technischen Hochschule, München 2, Arcisstraße 21, and Herr Dr. H. KIENITZ, Ludwigshafen/Rhein.

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Determination of chloride ion in glycol by pCl measurements. R. B. Leblanc and R. T. McFadden. (20 *May* 1960).

Un réactif défini de diazocopulation, le 3-phényl-5-nitrosamino-1:2:4-thiodiazole ou phénitrazole. Maurice Pesez, Jaroslav Bartos et Jean-Francois Burtin. (23 *May* 1960).

Sur un principe de colorimétrie en milieu non aqueux: Son application à l'analyse organique functionelle. Maurice Pesez et Jaroslav Bartos. (23 *May* 1960).

The formation of interhalogens. E. Schulek and K. Burger. (23 *May* 1960).

The use of bromine chloride in analytical chemistry: Determination of unsaturated aldehydes. K. Burger and E. Schulek. (23 *May* 1960).

Verfahren zur Bestimmung geringer Mengen, das Jod in verschiedenen Oxydationszuständen enthaltender Jodberbindungen nebeneinander. E. Schulek und L. Barcza. (23 *May* 1960).

Radiometric trace analysis, V: Determination of cobalt with zinc-diethyldithiocarbamate-^{35}S. P. C. Van Erkelens. (30 *May* 1960).

Radiometric trace analysis, VI: Determination of cobalt with zinc-diethyldithiocarbamate and ^{203}Hg^{2+} ions. P. C. Van Erkelens. (30 *May* 1960).

Titrimetric analysis with chloramine-T, II: The chloramine-T-arsenic^{III} reaction. (a) A potentiometric study. E. Bishop and V. J. Jennings. (30 *May* 1960).

A new selective metallochromic reagent for the detection and chelatometric determination of calcium. R. A. Close and T. S. West. (30 *May* 1960).

Titrimetric analysis with chloramine-T: The chloramine-T-arsenic^{III} reaction. (b) A study of visual indicators. E. Bishop and V. J. Jennings. (1 *June* 1960).

2:5-Dihydroxy-*p*-benzoquinone as an analytical reagent for the gravimetric determination of cerium^{III}, cerium^{IV}, lanthanum, yttrium, uranium and titanium. B. D. Jain and S. P. Singhal. (3 *June* 1960).

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Precipitation of metal 8-hydroxyquinolates from homogeneous solution, II: Thorium. Kazuyoshi Takiyama, Eugene D. Salesin and Louis Gordon. (10 *June* 1960).

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THIOUREA COMPLEXES OF SOME NOBLE METALS

A POLAROGRAPHIC DETERMINATION OF RHODIUM

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(*Received* 21 *January* 1960)

Summary—Rhodium^{III}, stabilised by heating in thiourea solution, gives a polarographic irreversible wave, suitable for its determination. The influence of supporting electrolyte, rhodium and thiourea concentrations, as well as of pH and gelatin are fully investigated. Platinum interferes, iridium does not, and palladium can be determined at the same time as rhodium. Evidence is given for the presence of a bi-coordinated platinum complex, and mono- and tetra-coordinated palladium complexes.

SOME thiourea complexes with platinum metals have already been investigated in the solid state; but the ionic species existing in solution are very poorly defined. Thiourea appears to be a suitable colorimetric reagent for osmium and ruthenium;[1] however, where other metals of the family are concerned, a survey of the literature shows that only one investigation has been carried out in respect of the colorimetric determination of palladium;[2] the yellow colour of the thiourea-palladium complex was first noted by Yoe and Overholser[3].

In the course of an extensive investigation carried out in this Institute[4,5,6] on the chemistry of noble metals, a well-defined polarographic wave, previously quite unknown, was observed in thiourea solutions of rhodium. The behaviour of this element, together with metals of the same group, was therefore investigated thoroughly. Rhodium was investigated primarily for analytical purposes, as polarographic determinations of this element are seldom found in the literature.[7,8,9,10]

EXPERIMENTAL

A Leybold polarograph and a Beckman DU spectrophotometer were used. A forward-and-backward recording of current-potential curves was carried out, and the mean value taken, in order to minimise the hysteresis effect. The temperature was held at 25° and the reference electrode was a saturated calomel electrode; purified nitrogen was used for deoxygenation; the capillary characteristics were: $m^{2/3}t^{1/6} = 2{\cdot}125$.

Standard solutions: Na_3RhCl_6, $2{\cdot}5 \,.\, 10^{-2}M$; $PdCl_2$, $5 \,.\, 10^{-2}M$, HCl, $0{\cdot}1M$; H_2PtCl_6, $5 \,.\, 10^{-2}M$; K_2PtCl_4, $5 \,.\, 10^{-2}M$; $IrCl_4$, $1 \,.\, 10^{-2}M$, HCl, $2 \,.\, 10^{-2}M$. Suitable volumes of these solutions were mixed with the determined amount of thiourea and supporting electrolyte and were held on a boiling water-bath for at least 10 min. Such heating is necessary in order to stabilise rhodium complexes, whereas reaction takes place at room temperature where platinum, iridium and palladium are concerned.

RESULTS

Rhodium solutions, after heating with an excess amount of thiourea, show a yellow-brown colour. Polarographic examination gives a well-shaped step at about —0·4 volt v. S.C.E. The characteristics of the wave are affected by several factors and extensive investigation was necessary in order to establish the best conditions for analytical determination.

Influence of the supporting electrolyte: When sulphates or nitrates are present, the waves are ill-developed and half-wave potentials cannot be measured, though the limiting current may still be well enough defined. On the other hand, reliable and reproducible results are obtained when potassium chloride is used, although its concentration is not without effect on the rhodium wave; in fact, the higher the chloride concentration, the more is the wave shifted to negative potentials, this variation being accompanied by a decrease of the diffusion current. Such phenomena are strictly correlated with variation of ionic strength, and therefore a fixed KCl concentration, such as 0·5*M*, must be used.

TABLE I. HALF-WAVE POTENTIALS OF $5 \,.\, 10^{-4}M$ Rh IN 0·5*M* KCl AT SEVERAL CONCENTRATIONS OF THIOUREA
(neutral solutions, without gelatin)

Thiourea, *moles/litre*	$E_{\frac{1}{2}}$, *V*(vs S.C.E., 25°)
0·01	−0·27
0·02	−0·28
0·04	−0·291
0·06	−0·306
0·08	−0·319
0·1	−0·330
0·2	−0·372
0·3	−0·398
0·4	−0·415
0·5	−0·430
0·6	−0·441

pH: Reproducibility is secured in neutral or slightly acidic medium. At a pH higher than 7 a turbid solution is obtained; at a pH lower than 2, the H^+ wave is shifted to more positive potentials by the electrodeposition of rhodium, and therefore the limiting current is stable only over a very small range, after which discharge of H^+ occurs.

Maximum suppression: Sometimes a maximum is present; occasionally, however, a surface-active substance such as gelatin, in concentration not less than 0·002%, may be used. When such a maximum suppressor is used, the half-wave potentials are shifted to more negative values. For instance the values $E_{\frac{1}{2}} = -0{\cdot}330$, −0·346, −0·358, −0·367, −0·370, −0·372 V corresponded respectively to gelatin concentrations of 0, 0·005, 0·01, 0·02, 0·035, 0·05%, with a $5 \,.\, 10^{-4}M$ solution of Rh, 0·1*M* in thiourea, and 0·5 *M* in KCl. In Fig. 1 two waves, obtained with and without gelatin, are shown.

The half-wave potentials obtained at various thiourea concentrations are given in Table I. Because a rhodium complex is involved, the more thiourea present, the more $E_{\frac{1}{2}}$ is shifted to negative values. If the thiourea is less than 0·02*M*, a red-brown precipitate is formed on heating; the molecular ratio of this compound is not well defined and depends on the heating time: in fact, it was possible to observe, in the anodic step of thiourea, a decrease in agreement with any rhodium-thiourea ratio between 1:2 and 1:3.

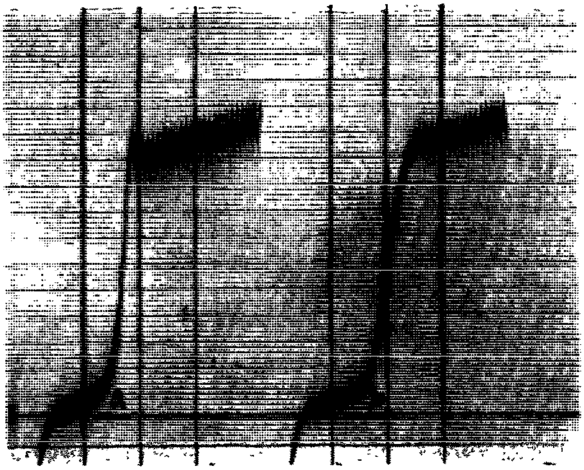

FIG. 1.—Polarograms of 5 . $10^{-4}M$ Rh^{III} in $0{\cdot}2M$ thiourea + $0{\cdot}5M$ KCl: (*a*) without gelatin; (*b*) 0·01% gelatin. —0·3, —0·4 and —0·5 V vs S.C.E. are indicated on each polarogram.

The limiting current proportional to the rhodium concentration is really a diffusion-controlled one: it is directly proportional to the square root of the height of the mercury column, corrected for the back-pressure at the Hg-solution interface. Experiments at various temperatures showed that the wave height increases by 1·2% for a 1° rise, as would be expected for a diffusion current. At the same time, $E_{\frac{1}{2}}$ is shifted about 5 mV per degree to more positive values, so that above 60° a composite anodic-cathodic wave is obtained, rhodium reduction taking place at the same potential at which the anodic step of thiourea is apparent. A large temperature coefficient constitutes fair evidence of the irreversibility of the reaction. In addition, the slope of E against $\log i/(i_d - i)$ along the wave is never lower than 35 mV per logarithmic unit, which also supports the irreversibility. Hence no attempt was made to draw any quantitative conclusion about the stability of complexes from the shift of $E_{\frac{1}{2}}$ at increasing thiourea concentration.

The diffusion current constant was found to be 5·10 in 0·2*M* thiourea solution. No significant difference was observed over the range of thiourea concentration shown in Table I. This value indicates that a three electron reduction is concerned, but millicoulometry was used to confirm the value for "n" of three.

On spectrophotometric examination, no maxima are noted in the absorption curves of rhodium-thiourea solutions, apart from the absorption of thiourea itself. The sensitivity around 400 mμ being small (rhodium must not be less than 10 μg/ml), colorimetric determination is not very reliable, although Beer's law is followed. The behaviour of the other metals of the group is summarised below.

Platinum

A chloroplatinic acid solution turns nearly colourless on addition of an excess of thiourea. After several hours standing at room temperature, or a few minutes heating on a boiling water-bath, a turbidity is noted. Polarographic waves are never well-defined: immediately after thiourea is added, however, the limiting current, though ill-developed, is nearly as large as without thiourea, there being no reduction, but only complexing. After long standing, the solution becomes more and more turbid, and the diffusion current decreases, but is never reduced to zero.

$\text{Platinum}^{\text{II}}$ is also complexed by thiourea, and no precipitation occurs. The resulting solution has a pale yellow colour. A cathodic diffusion current may be recorded at the end of the anodic wave of thiourea. Platinum therefore constitutes a serious interference when determining rhodium.

It is possible to identify the complex of $\text{platinum}^{\text{IV}}$ present in solution, by determining free Pt^{IV} colorimetrically with potassium iodide while thiourea is added. A discontinuity is noted in Fig. 2, in the plot of optical densities against the thiourea-platinum ratio, at a value of the latter of nearly 2. The complex present is therefore probably bi-coordinated.

Palladium

A palladium solution, with an excess of thiourea, turns yellow, no maxima in the spectrum being noted apart from those arising from the absorbance of thiourea itself. A composite anodic-cathodic wave is recorded polarographically, the yellow complex not being sufficiently stable to give a true step. This behaviour allows simultaneous determination of rhodium and palladium when they are present together. In such a case, as is shown in Fig. 3, there are two steps in the polarographic wave, the former being proportional to the palladium concentration, the latter to that of rhodium. Results of the determination of these two elements in the presence of one another are reported in Table II, showing the reliability of the method.

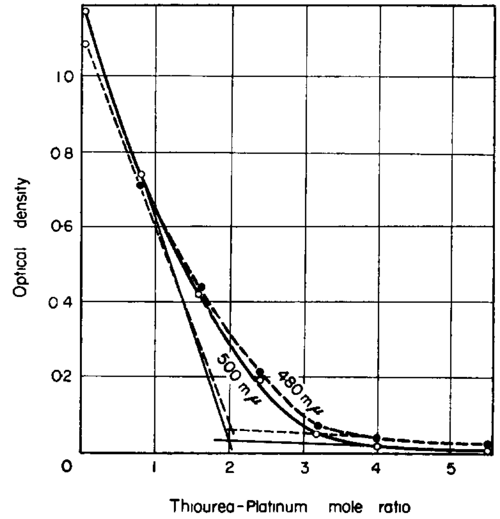

FIG. 2.—1 . $10^{-4}M$ Pt^{IV} in excess of KI: decrease of absorbance by adding thiourea.

With a very small amount of thiourea an orange-brown colour is developed, quite different from the yellow one obtained with an excess of complexing agent. A few minutes later a brown precipitate can be observed; the addition of gelatin (0·05%), however, holds the compound in solution sufficiently long to permit of spectrophotometric measurement. This change of colour according to the amount of thiourea present produces an unusual optical density curve when studying the molecular ratios (Fig. 4) and when applying Job's method (Fig. 5). The most reliable interpretation appears to be the following: when thiourea is present at nearly the

TABLE II. SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF RHODIUM AND PALLADIUM, IN SOLUTIONS OF:
0·3*M* thiourea, 0·5*M* KCl, H^+ about 1 . $10^{-3}M$, gelatin 0·002%

Taken		Found	
Rh, *mg*	Pd, *mg*	Rh, *mg*	Pd, *mg*
0·64	0·67	0·65	0·67
0·64	1·33	0·64	1·32
0·64	2·67	0·63	2·64
1·29	0·67	1·30	0·66
1·29	1·33	1·29	1·35
1·29	2·67	1·30	2·68
2·57	0·67	2·52	0·68
2·57	1·33	2·51	1·36
2·57	2·67	2·58	2·67

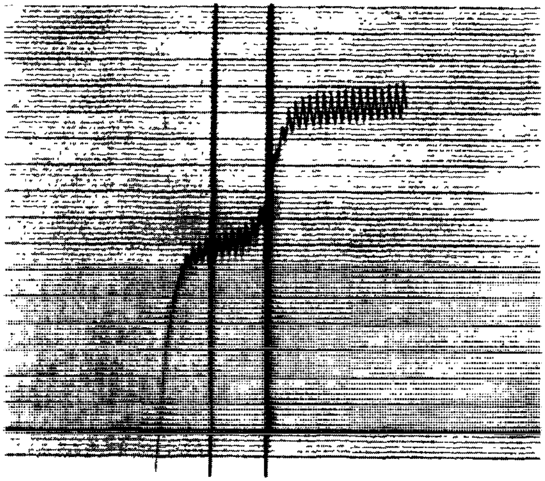

FIG. 3—Polarogram of 5 . $10^{-4}M$ Rh^{III} and 1 . $10^{-3}M$ Pd^{II} in 0·2M thiourea + 0·5M KCl, with 0·002% gelatin. −0·3 and −0·4 V vs S C.E. are indicated.

same concentration as palladium, the red-brown, slightly-soluble 1:1 complex is formed. With an excess of thiourea, more molecules of the latter are coordinated and the yellow complex appears. From the position of the discontinuity in the curves of Figs. 4 and 5, this complex seems to be tetra-coordinated.

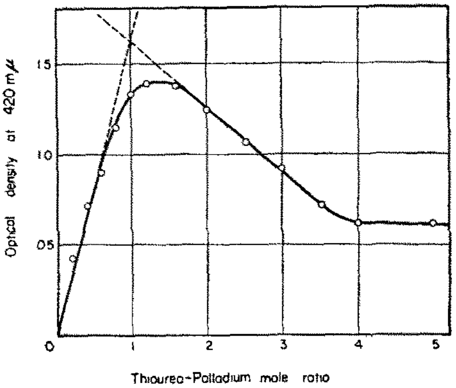

FIG. 4.—Variation of absorbance by adding thiourea to solutions of 5 . $10^{-4}M$ Pd^{II}.

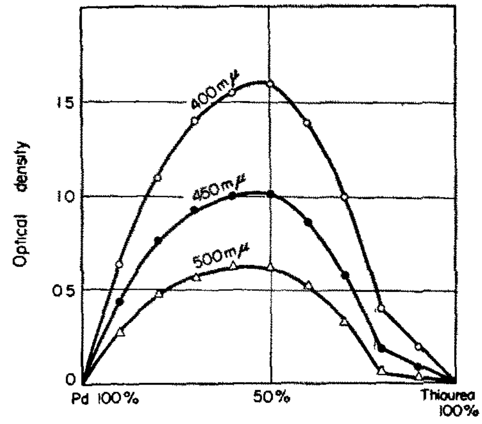

FIG. 5.—Variation of absorbance with molar fraction of palladium-thiourea: total concentration = 1 . $10^{-3}M$.

Iridium

An iridium^{IV} solution turns colourless a few minutes after adding thiourea in a concentration at least as great as that of iridium. On standing, a white precipitate is observed. The colourless solutions give a polarogram exactly the same as the supporting electrolyte alone. Therefore determination of rhodium with sufficient accuracy is possible, even when an excess of iridium is present. From several polarograms of mixtures of rhodium and iridium, the latter being present up to 8 times the amount of the former, it was found possible to determine rhodium with a 2–3 % error.

Zusammenfassung—Rhodium(III), durch Erhitzen in Thioharnstofflosung stabilisiert, gibt eine irreversible polarographische Stufe, die zur Bestimmung des Rhodiums verwertet werden kann. Der Einfluss von Grundlösung, Rhodium- und Thioharnstoffkonzentration, sowie pH und Gelatin wurde eingehend studiert. Platin stört, während Iridium ohne Einfluss ist. Palladium kann zugleich mit Rhodium bestimmt werden. Evidenz ist vorhanden für die Existenz eines bikoordinierten Platin- und eines mono- und tetrakoordinierten Palladiumkomplexes.

Résumé—Le rhodium III, stabilisé par chauffage dans une solution de thiourée, donne une vague polarographique irréversible, convenable pour son dosage. L'influence de l'électrolyte support, des concentrations de rhodium et de thiourée, ainsi que du pH et de la gélatine a été complètement étudiée. Le platine gêne, mais non l'iridium, le palladium peut être dosé en même temps que le rhodium.

La présence d'un complexe bicoordoné du platine et de complexes mono et tétracoordonnés du palladium est prouvée.

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SCINTILLATION RADIOAUTOGRAPHY OF TRITIUM-LABELLED COMPOUNDS ON PAPER CHROMATOGRAMS*

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(*Received* 21 *April* 1960)

Summary—A simple scintillation radioautographic method using ordinary fast photographic film has been developed for tritium-labelled compounds on paper chromatograms impregnated with anthracene. Tritium analysis can now be undertaken by any laboratory without the need for special equipment or controlled conditions.

INTRODUCTION

A SIMPLE, reliable and inexpensive analytical method to detect and determine tritium-labelled compounds was developed and proved useful in an investigation of nicotine metabolism in tobacco plants. The details for the paper chromatographic separation of tobacco alkaloids from tobacco extracts have been recorded,[1] but it was necessary to develop a method which would extend this for application of tritium autoradiography. A major obstacle in detection of the very soft tritium β-particle ($E_{max} = 18$ keV) by radioautography is its absorption by the paper before it can enter the film. Wilson[4] described a "scintillation autographic" technique to overcome this by using a liquid scintillator to convert weak β-particles into light quanta which produced an image on X-ray film. Because toluene is the primary solvent used for the scintillator, Wilson's method could not be applied in a study of nicotine, which is soluble in toluene.

In his study of steroid hormones, which are also soluble in toluene, Rogers[2] coated the paper chromatogram directly with melted photographic emulsion (Ilford K2). The strips were dried and placed in a desiccated light-proof box and exposed in a cold room at 5°. Although this technique avoids the use of toluene, it requires a nuclear emulsion, which is not generally available. In addition, considerable preparation is involved before exposure, and the chromatogram can be exposed only once.

Seliger and Agranoff[3] incorporated anthracene as microcrystals to overcome the high degree of absorption by the paper. In their solid scintillation technique the photons produced are reflected from the paper and counted at 12° on the face of a phototube in a light-tight enclosure. The stability of the strips in this technique permits reproducible recounting, but considerable equipment involving special electronic circuits is needed.

Our simple procedure makes feasible the detection and determination of tritium-labelled compounds on paper chromatograms in any laboratory, and overcomes the drawbacks mentioned above. A paper chromatogram is dipped momentarily into a scintillation compound dissolved in a highly volatile solvent. The dry impregnated

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* Contribution Nos. 67 and 10 of the Plant Research Institute and Analytical Chemistry Research Service respectively.

paper is placed in close contact with ordinary fast film and exposed for the desired time at room temperature. The developed spots can be compared with known amounts of activity either visually or by densitometer readings.

EXPERIMENTAL

Tritiated nicotine, prepared by the Wilzbach technique, was used as the best material. Various amounts of it, with activities of 6·20, 3·10, 1·55, 0·77, 0·38, 0·19 and 0·085 microcuries, were spotted on 1-cm^2 discs cut from Whatman No. 1 filter paper. The discs, after being allowed to dry, were dipped in the scintillation agent (a saturated solution of anthracene in benzene). The benzene evaporated almost instantly, leaving the discs impregnated with fine crystals of anthracene. Each disc was then given a second dip in the scintillator. Comparisons were made with discs spotted with the same activities of tritiated nicotine, but without added scintillator. Blank discs, dipped either in benzene or in benzene with anthracene, were also prepared. The discs were attached with wire staples to a suitable thick paper backing, and were placed in contact with Kodak Royal-X Pan sheet film. Glass plates were placed on the outside, and pressure was applied to ensure close contact during the exposure time of 1–2 weeks. Five replicates were run for each exposure time. The film was developed in Kodak D-19 for 6 min at 20°. Although this developer is not usually recommended for this film, it was found to give extra contrast and a short development time. In some cases spots were formed even by the controls which had no scintillator added, showing the extreme sensitivity of the film to tritium emissions. Visual comparisons are satisfactory for many experiments, but a quantitative approach would be helpful for others. A Photovolt 525 densitometer was used to determine the darkening intensity of the exposed film.

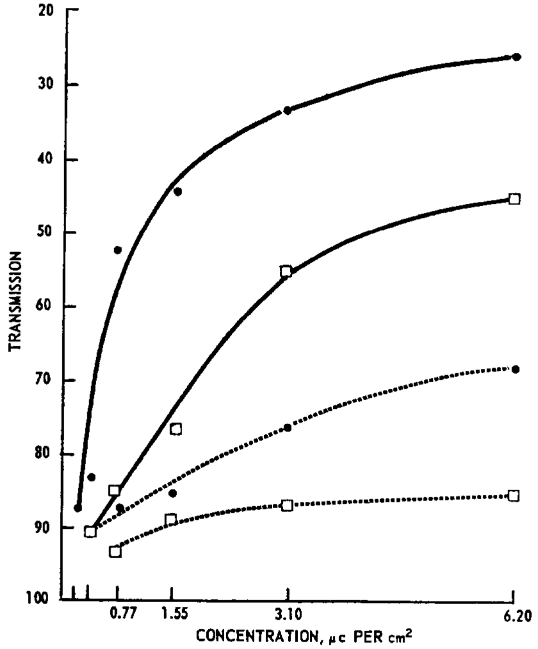

Fig. 1.—Variation of average densitometer readings with concentration of tritium. Solid lines represent 2-week exposures; dotted lines 1-week. ● with anthracene; ☐ without anthracene.

RESULTS

No less than four readings were made on different portions of each spot. Fig. 1 is a plot of the average values, expressed as percentage transmission against concentration in microcuries. This figure shows that the presence of anthracene increases the

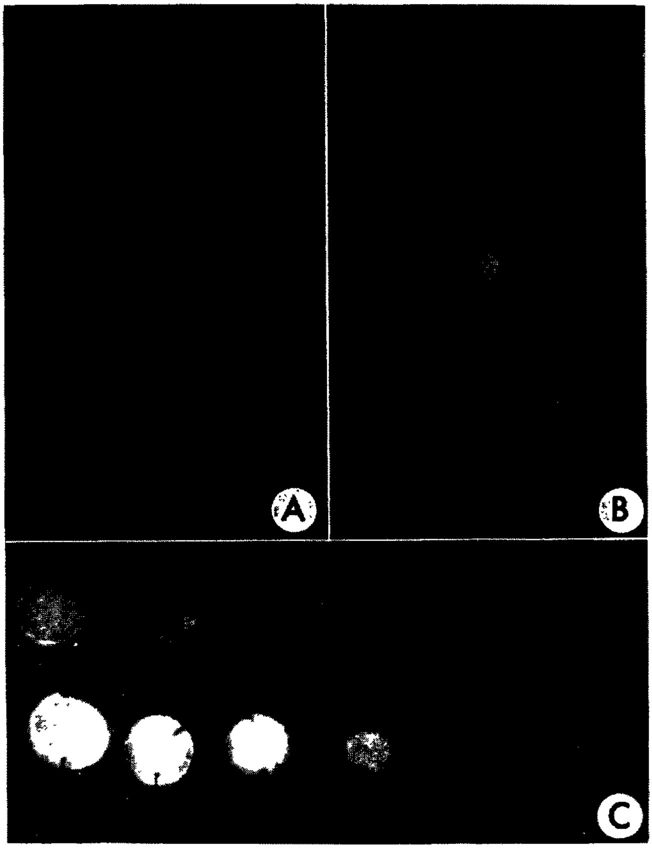

FIG. 2.—Autoradiograms of tritium-labelled nicotine. A—without scintillator; B—with scintillator. C—top row—without scintillator, bottom row—with scintillator.

darkening on the film to a marked degree during both the 1- and 2-week exposure times. Darkening of the film could be distinguished with 0·38 and 0·19 microcuries per cm^2 after exposures of 1 and 2 weeks, respectively. Exposure times beyond 2 weeks would tend to increase the sensitivity of the method. For the 2-week exposure period a near-linear relationship exists for levels of activity ranging from 0·19 to 1·51 microcuries per cm^2. Similarly, 0·38 to 3·10 microcuries per cm^2 is the range for the 1-week exposure period.

In Fig. 2, photographs are shown displaying varying amounts of activity both with and without anthracene; and also the intensifying effect of anthracene added to actual chromatograms of nicotine made from extracts of a tobacco plant treated with tritiated nicotine.

Zusammenfassung—Eine einfache Scintillationsmethode zur radioautographischen Bestimmung von mit Tritium markierten organischen Verbindungen wurde entwickelt. Gewöhnlicher, hochempfindlicher Film wird in Verbindung mit Chromatogrammen auf, mit Anthrazen imprägniertem, Papier verwendet. Tritiumanalysen können nun in jedem Laboratorium durchgefuhrt werden, ohne dass spezielle Einrichtungen oder Kontrollbedingungen nötig sind.

Résumé—Une méthode simple de "radioautographie" par scintillation utilisant un film photographique ordinaire rapide a été élaborée pour des composés marqués par du tritium sur des chromatogrammes de papier imprégnés d'anthracène. L'analyse du tritium peut être entreprise maintenant par tout laboratoire sans nécessiter un équipement spécial ou des conditions contrôlées.

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DETERMINATION OF CHLORIDE ION IN GLYCOL BY pCl MEASUREMENT*

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(*Received* 20 *May* 1960)

Summary—Measurement of pCl with a silver-silver chloride electrode affords a rapid means of detecting chloride in solution above the solubility limit of silver chloride in the solvent. The behaviour of the silver-silver chloride electrode in ethylene glycol was studied. A method was developed for rapidly analysing as little as 0.1 ppm of inorganic chloride in ethylene glycol.

INTRODUCTION

SEVERAL workers have investigated the measurement of chloride ion in aqueous solution using silver-silver chloride electrodes in concentration cells.[1,3,6] Chanin[2] used a silver-silver chloride electrode and a mercury-mercury^{I} sulphate electrode to determine chloride in aqueous solution. Helmkamp *et al.*[4] and Stern *et al.*[8] used a silver-silver chloride electrode and a calomel electrode with a pH meter to determine the pCl of solutions.

This work was undertaken to develop an empirical method for determining small amounts of chloride ion in ethylene glycol using a silver-silver chloride electrode and a calomel electrode. The limit of detection of chloride ion should be lower in ethylene glycol than in water since silver chloride is less soluble in glycol than in water.

The cell used for chloride determination is:

$$\text{Ag, AgCl; Cl}^- \text{(glycol)} \;\|\; \text{Saturated Calomel Electrode}$$

The salt bridge in the above cell is of potassium nitrate to eliminate any chloride contamination. No theory is offered for the EMF of the above cell since no data on appropriate oxidation potentials in glycol are available. In addition, no estimate of the liquid junction potentials in the cell can be made.

The EMF of the above cell is given by the empirical equation:

$$\log C_{Cl^-} = k_1 + \frac{E}{k_2}$$

The constant k_1 would be a function of the activity coefficient of the chloride ion. At constant ionic strength the activity coefficient would be essentially constant. The Cl^- concentration of glycol solutions may be determined without first determining the constants k_1 and k_2. Calibrations can be made on solutions of known Cl^- concentration over the range of interest.

APPARATUS AND REAGENTS

The Ag-AgCl electrodes were prepared by a modification of the fusion method of Owen[7] and Keston[5] followed by electrolysis in dilute hydrochloric acid. A paste was made of 7 parts of silver

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* Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

oxide, 1 part of silver chlorate and a little water. Platinum spirals (embedded in glass) were coated with the paste and placed in a furnace at 650° for 7 or 8 min. The electrodes were cooled and made anodes in a 0.2*M* hydrochloric acid solution for 1 hour with about 2 milliamps of current flowing. After the electrolysis, the Ag-AgCl electrodes were shorted to each other and soaked in a 0.01*M* potassium chloride solution for 1–2 days to eliminate any potential difference between them and to condition them for use.

The saturated calomel electrode used was a Beckman double-junction type calomel electrode (No. 4970-6). The outer chamber of this electrode, which is a salt bridge, was filled with saturated potassium nitrate solution. By this means possible chloride contamination from the calomel electrode was eliminated.

A Beckman Model G pH meter was used for the potential measurements. The silver-silver chloride electrode was plugged into the glass electrode jack on the meter.

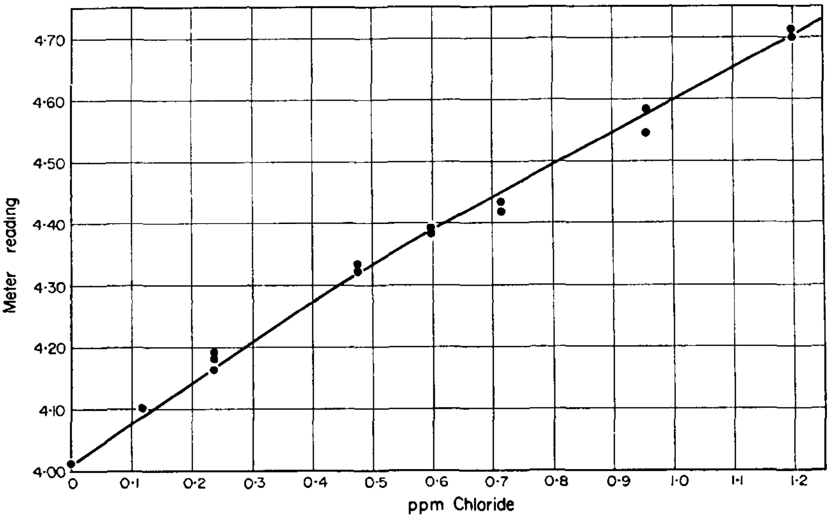

FIG. 1.

The 3.0*M* potassium nitrate solution was prepared from A.R. grade material.

The ethylene glycol used for preparation of the chloride solutions was a carefully distilled material which was chloride-free.

A glycol solution containing 1000 ppm chloride was prepared and this stock solution was used to prepare other standard chloride solutions by successive dilutions with the pure glycol.

EXPERIMENTAL

The pH meter was calibrated before each series of measurements. The electrodes were immersed in a glycol solution containing 1 ppm chloride and 5 drops of 3.0*M* potassium nitrate in 100 ml. The potassium nitrate was added to raise the conductivity of the solution so that the electrode system would not be sluggish. The meter was set at a reading (on the pH scale) of 4.60. This is an arbitrary number, which has no theoretical significance. The solution on the electrodes was stirred with a magnetic stirrer to attain equilibrium between the electrodes and the solution which required about 3–5 min. The zero adjustor was used to zero the meter.

A calibration curve was constructed for chloride in glycol. A series of solutions of different chloride concentrations (0–1.0 ppm) were prepared. Five drops of 3.0*M* potassium nitrate were added to 100 ml of each, and the EMF reading was determined on them in the same manner that the pH would be determined. A plot of this meter reading vs. ppm chloride is shown in Fig. 1.

Glycol samples with unknown chloride concentrations were analysed by this same technique. Five drops of 3.0*M* potassium nitrate are added to 100 ml of the sample. The EMF is read and the chloride concentration taken from the calibration curve (Fig. 1).

DISCUSSION

From repeated runs of standard samples of chloride in glycol the accuracy of the analysis is better than ±0.1 ppm. As little as 0.1 ppm of chloride in glycol can be detected by this method.

The analysis was extended up to the 100-ppm range. These results are not given, because glycol usually does not contain such a high content of chloride.

The silver-silver chloride electrodes are stable in glycol for more than 6 months.

The usual impurities in commercial ethylene glycol are: aldehyde, 15 ppm; acid, 1-2 ppm; and iron, 0.02 ppm. No effect on the EMF was detectable when 30 ppm propionaldehyde, 10 ppm acetic acid, and 0.5 ppm iron were added to some samples of glycol. This is twice the aldehyde, 10 times the acid and 25 times the iron content of glycol.

Iron was added as an aqueous solution of iron^{III} sulphate. This produced an effect at higher concentrations of iron. The effect of 1 ppm of iron was equivalent to that of —0.1 ppm chloride. This concentration of iron is well above that found in glycol. Also, it is not known in what form iron occurs in glycol. In any case these common impurities do not interfere with the analysis.

Interference would be caused by materials which formed silver salts more insoluble than silver chloride or ligands which formed stable complexes with silver.

This technique should be applicable to the analysis of ionic chloride in any polar solvent, such as polyglycols, glycerine, etc.

Zusammenfassung—Die messung von pCl mit einer Silber-Silberchloridelektrode erlaubt rasches Nachweiss von Chlorid in Lösungen, die mehr Chlorid enthalten, als dem Löslichkeitsprodukt von Silberchlorid entspricht. Das Verhalten einer Silber-Silberchloridelektrode in Äthylenglycol wurde studiert. Eine Methode wurde entwickelt um bis hinab zu 0.1 ppm an anorganischem Chlorid in Äthylenglycol zu analysieren.

Résumé—La mesure de pCl avec une électrode argent-chlorure d'argent apporte un moyen rapide de détection du chlorure en solution au-dessus de la limite de solubilité du chlorure d'argent dans le solvant. Le comportement de l'électrode argent-chlorure d'argent dans l'éthylène glycol a été étudié Une méthode a été élaborée pour l'analyse rapide de quantité aussi faible que 0,1 p.p.m. de chlorure minéral dans l'éthyléne glycol.

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PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

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Summary—By reacting biacetyl and hydroxylamine in the presence of nickel^{II}, large, well-developed and readily filterable crystals of nickel dimethylglyoximate were precipitated from homogeneous solution. The needle-like crystals were frequently up to several mm in length. Large amounts of nickel—of the order of 200 mg—were easily handled. The usefulness of this method of precipitation from homogeneous solution is shown with results obtained for nickel in the presence of a few selected diverse substances, namely, cobalt, copper, iron, and in National Bureau of Standards steel samples.

INTRODUCTION

SINCE 1905, the reaction[1] of dimethylglyoxime with nickel^{II} has been used extensively for the quantitative determination of nickel. Many other dioximes were subsequently suggested, in some cases to increase the molecular weight of the dioxime and in other cases to overcome certain deficiencies, *e.g.* the slight solubility of dimethylglyoxime in water. One difficulty, namely, the voluminous and somewhat gelatinous character of nickel dimethylglyoximate, which has generally limited the quantity of nickel precipitated to less than 40 mg, was overcome by Bickerdike and Willard[2] who used urea to precipitate the chelate from homogeneous solution.

In the present paper, a method is described for the precipitation of large, well-developed, and readily filterable crystals of nickel dimethylglyoximate from homogeneous solution; dimethylglyoxime is generated in the presence of nickel^{II} by reacting biacetyl and hydroxylamine.[3] The utility of the method is shown with results obtained for nickel in the presence of a few selected diverse substances, namely cobalt, copper, iron, and also in National Bureau of Standards steel samples.

REAGENTS AND APPARATUS

Unless otherwise specified, all chemicals were reagent grade.

Nickel, copper, cobalt and iron solutions: Appropriate amounts of reagent grade $NiSO_4 \cdot 6H_2O$, $CuCl_2 (NH_4Cl)_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $FeNH_4(SO_4)_2 \cdot 12H_2O$ were each dissolved in distilled water, filtered, and diluted so that each solution contained about 40 mg of metal per 25 ml of solution. The exact concentration of nickel was determined by precipitation as nickel dimethylglyoximate by the conventional method[4] and checked by electrolytic deposition of nickel.[5] The metal salts were obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J.

Biacetyl solution: Approximately 25 ml of biacetyl (Distillation Products Co., Rochester, N.Y.) was distilled through a small fractionating column packed with 0.25 in. glass helices. About 6 ml of the fraction which distilled between 87.5° and 90.2° (750 mm of Hg) was weighed, dissolved in distilled water, and diluted to 500 ml; the solution contained about 12 mg of biacetyl per ml.

Hydroxylamine hydrochloride: The reagent grade hydroxylamine hydrochloride used in the experimental work was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J.

All measurements were made with a Beckman Model 9600 pH meter calibrated with a Beckman pH 7 buffer solution (No. 3581).

PRECIPITATION OF NICKEL ALONE

Experimental

Preliminary investigations were conducted to determine the appropriate concentration of reagents, the temperature of reaction, and the pH which would result in quantitative precipitation of the nickel chelate in a readily filterable form but would not produce enough dimethylglyoxime to precipitate along with the nickel chelate.

The photomicrographs of Fig. 1 show the difference in the precipitates obtained by the conventional method of precipitation and by PFHS (precipitation from homogeneous solution). The needle-like crystals of nickel dimethylglyoximate precipitated from homogeneous solution are often up to several mm in length. They do not settle to the bottom of a solution as precipitates formed by the PFHS method ordinarily do because of their fine needle-like character. They can be filtered and washed quite easily, and are not characterised by the somewhat gelatinous nature of the conventionally prepared precipitate. The crystals exhibit a somewhat different reddish hue from that of the crystals obtained by conventional precipitation.

Procedure

Adjust the pH of the solution, containing no more than 200 mg of nickel, to 7.5 ± 0.1 with ammonium hydroxide. Add a quantity of biacetyl equal to 6 times the approximate weight of nickel to be precipitated, but never less than 0.12 g in any case. Next add, with stirring, 50 ml of a solution, adjusted to pH 7.5 ± 0.1 with ammonium hydroxide, containing a quantity of hydroxylamine hydrochloride equal to 4 times the weight of biacetyl added, but in no case less than 0.5 g. Adjust the final volume of the solution to 100 ml if 0.5–5 mg of nickel are present, to 200 ml for 5–50 mg, to 300 ml for 50–100 mg, or to 400 ml for 100-200 mg. Allow the solution to stand at room temperature for at least 1 hr (or longer) after precipitation begins, then heat to 80–90° for 2 hr. Cool the solution, filter, wash the precipitate with water, and dry to constant weight at 140°.

Nickel content of filtrate and wash solution

In several instances, the filtrates and washings were evaporated to dryness, 10 ml of concentrated sulphuric acid added, and this solution evaporated to dense fumes and subsequently to dryness. Ten ml of concentrated nitric acid were then added twice to the residue and evaporated to dryness. The organic-free residues were dissolved in distilled water, and the nickel determined colorimetrically with 2:3-quinoxalinedithiol.[6]

Results

The above procedure was used to precipitate from 0·5 to 200 mg of nickel as shown in Table I. The results indicate quantitative precipitation of nickel. The amounts of nickel in the filtrates and washings from several determinations were found to coincide closely to those found in the filtrates from conventional determinations (*cf.* Table II).

PRECIPITATION OF NICKEL IN PRESENCE OF DIVERSE IONS

Experimental

Nickel dimethylglyoximate was precipitated from homogeneous solution in synthetic mixtures containing (*a*) copper, (*b*) cobalt, and (*c*) cobalt and iron. The procedure used was essentially that previously described with modifications as indicated.

After the precipitates were weighed, they were dissolved in concentrated hydrochloric acid, the solutions evaporated to dryness and the organic matter destroyed by treatment with nitric and sulphuric acids. The organic-free residues were dissolved in distilled water and the co-precipitated elements colorimetrically determined as follows:
(*a*) copper was separated from nickel by extraction with dithizone and determined with dithizone;[7] (*b*) cobalt was separated from iron and nickel by extraction with ammonium thiocyanate solution and determined with nitroso-R-salt;[7] (*c*) iron was separated from cobalt and nickel by chloroform extraction of the iron cupferrate and determined with *o*-phenanthroline.[7]

The general procedure was also used to precipitate nickel in National Bureau of Standards steel samples. The samples were dissolved in hydrochloric acid, the iron oxidised with nitric acid, then

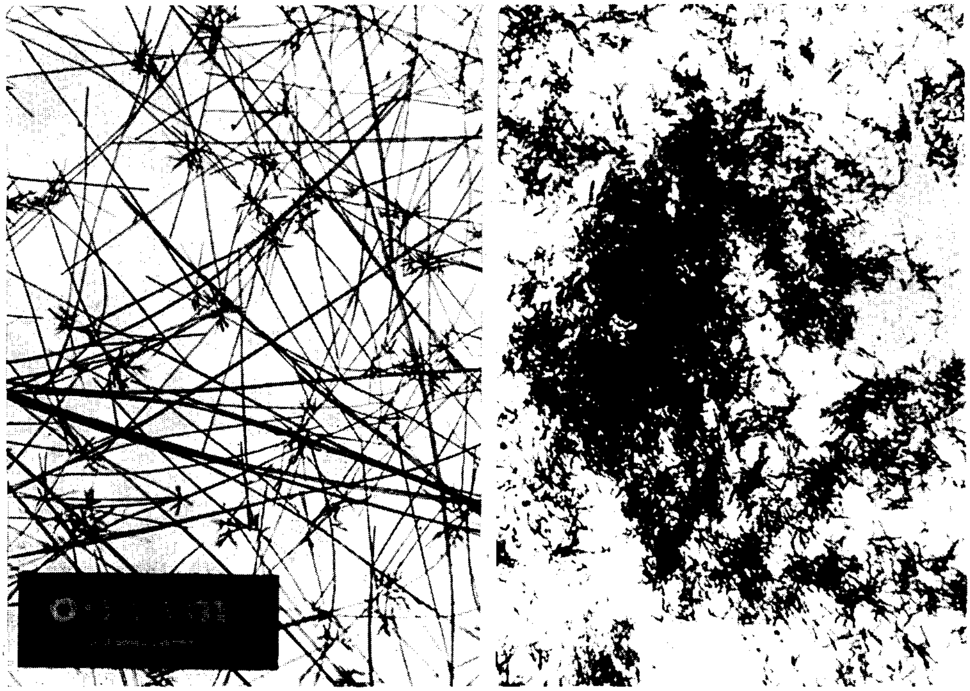

FIG. 1.—Photomicrographs of nickel dimethylglyoxime (both photomicrographs are at same magnification). a. left panel: method of PFHS. b. right panel: conventional method of precipitation.

tartaric acid was added. The pH was adjusted to 7.5 ± 0.1 with ammonia and the solutions were filtered. Biacetyl and hydroxylamine were added as described in the general procedure. The solutions were allowed to react for 24 hr and were then heated to 80–90° for 2 hr.

Results

The results obtained in the presence of copper are shown in experiments No. 1–11 of Table III. The superior separation of nickel obtained with the method of precipitation from homogeneous solution is clearly indicated by the comparatively negligible quantity of co-precipitated copper.

TABLE 1. SEPARATION OF NICKEL BY PFHS

Nickel taken, *mg*	Nickel found (difference), *mg*
0.49	−0.04, −0.04, −0.04
4.92	0.00, +0.01, +0.01
9.83	+0.05, +0.03, +0.01
39.3	0.0, 0.0, 0.0
98.3	−0.1, −0.2, −0.1
196.6	+0.4, +0.5

TABLE II. NICKEL IN FILTRATE AND WASHINGS[a]

Nickel found (PFHS method), *mg*	Nickel found (conventional method), *mg*
0.050	0.040
0.050	0.043
0.063	0.050

[a] 39·3 mg of nickel precipitated in all cases

In the case of cobalt (No. 12–17) low results for nickel are obtained by conventional precipitation[4] although the cobalt content of the precipitates was negligible. The reagent is apparently consumed by cobalt although this can be rectified by adding additional dimethylglyoxime. The gravimetric results obtained with the method of precipitation from homogeneous solution were excellent.

With both cobalt and iron present (No. 18–23) the method of PFHS gave satisfactory results only when the solution was allowed to stand at room temperature for a long period before being heated. Experiments No. 18 and 19 strikingly show the effect of a short standing period. It is likely that a shorter period of standing (less than 24 hr) will suffice but this was not investigated. The conventional method of precipitation gave excellent results, the only advantage of the PFHS method being that of easier handling of the precipitate along with the potential for handling larger quantities of nickel.

The results obtained for the National Bureau of Standards steel samples are shown in Table IV. The results clearly show the need here of a 24 hr standing period at room temperature before heating. The total time required to effect complete precipitation could possibly be reduced through the use of a shorter standing period followed by a period of heating of longer than 2 hr.

TABLE III. SEPARATION OF NICKEL FROM DIVERSE IONS BY PFHS AND

Number	1	2	3	4	5	6	7	8	9	10
Method of precipitation	PFHS[a,h]	PFHS[a,h]	PFHS[b,h]	PFHS[b,h]	PFHS[b,h]	PFHS[b,h]	PFHS[b,h]	Conv.[d,f,i]	Conv.[d,f,i]	Conv.[c,g,i]
Diverse element(s) taken, *mg*	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40
Nickel taken, *mg*	39.3	39.3	9.83	9.83	9.85	9.85	9.85	9.83	9.83	9.83
Nickel found, *mg*	39.5	39.4	9.90	9.88	9.90	9.88	9.90	11.81	11.81	10.02
Difference, *mg*	+0.2	+0.1	+0.07	+0.05	+0.05	+0.03	+0.05	+1.98	+1.98	+0.19
Diverse element(s) in precipitate, *mg*				Cu, 0.057	Cu, 0.13	Cu, 0.12	Cu, 0.11	Cu, 2.03	Cu, 1.83	Cu, 0.18

[a] Time before heating about 1 hr.
[b] Time before heating about 24 hr.
[c] Temperature about 70° when dimethylglyoxime was added.
[d] Temperature about 25° when dimethylglyoxime was added.
[e] One g each of anhydrous sodium sulphite and tartaric acid dissolved in the solution before precipitation.

No attempt was made to determine nickel in the presence either of the many other diverse ions or the various combinations of diverse ions with which it might conceivably be associated in practice. The present investigation was undertaken primarily to demonstrate the feasibility of precipitating nickel from homogeneous solution by synthesis *in situ* of the chelate and to test the method with a limited number of diverse ions. It is hoped that the basic information presented herein will enable other investigators to apply the method to their particular problem of analysis.

TABLE IV. DETERMINATION OF NICKEL IN NICKEL STEELS

NBS sample number	Sample taken, *g*	Nickel found, *g*	% Nickel	
			Reported	Found
33b	1.3076	0.0454	3.48	3.47
	1.1652	0.0404		3.47
	1.4072	0.0488		3.47
101c	0.5667	0.0527	9.27	9.29
	0.5692	0.0529		9.29
	0.7063	0.0656		9.29
	1.1437	0.0986		8.62[a]
	1.1693	0.1036		8.86[a]
	1.0091	0.0922		9.14[a]

[a] Solutions allowed to stand for only 18 hr before heating for 2 hr at 80–90°.

Other oximes were also considered; nickel was precipitated from homogeneous solution with *cyclo*hexanedionedioxime generated in a similar manner from *cyclo*-hexanedione and hydroxylamine. However, work with the other oximes was discontinued because it became quickly apparent that these offered no great advantage over the dimethylgloxime method for nickel utilising PFHS. It has also been found that palladium^{II} can be precipitated by the present method. This work will be subsequently reported in *Talanta*.

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under contract AT(11-1)-582.

BY CONVENTIONAL PRECIPITATION AS NICKEL DIMETHYLGLYOXIMATE

11	12	13	14	15	16	17	18	19	20	21	22	23
Conv.^{c,g,i}	PFHS^{b,h}	PFHS^{b,h}	PFHS^{a,h}	PFHS^{a,h}	Conv.^{c,f,i}	Conv.^{c,f,i}	PFHS^{a,e,h}	PFHS^{a,e,h}	PFHS^{b,e,h}	PFHS^{b,e,h}	Conv.^{c,e,f,j}	Conv.^{c,e,f,j}
Cu, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40
9.83	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3
10.89	39.4	39.4	39.2	39.3	38.7	38.6	20.2	19.4	39.4	39.4	39.5	39.5
+1.06	+0.1	+0.1	−0.1	0.0	−0.6	−0.7	−19 1	−19.9	+0.1	+0.1	+0.2	+0.2
Cu, 0.83					Co, 0 066	Co, 0.072			Co, 0.013; Fe, 0.10	Co, 0.005; Fe, 0.04	Co, 0.044; Fe, 0.05	Co, 0.061; Fe, 0.02

[f] Solution acidified with 1 ml of 0.6*N* hydrochloric acid solution before addition of dimethylglyoxime. The solution was then made alkaline by the addition of ammonium hydroxide solution.

[g] Like *f* except the solution was acidified with 3 ml of 6*N* hydrochloric acid solution before addition of dimethylglyoxime.

[h] Approximately 0.3 g of biacetyl and 1.0 g of hydroxylamine hydrochloride used in the determination.

[i] Approximately 0.23 g of dimethylglyoxime used in the determination.

[j] Approximately 0.33 g of dimethylglyoxime used in the determination.

Zusammenfasung—Wenn Diacetyl mit Hydroxylamin in Gegenwart von Nickel reagiert, werden. wohlausgebildede und leicht filtrierbare Kristalle von Nickeldimethylglyoxim erhalten. Die nadelförmigen Kristalle sind des öfteren mehrere Millimeter lang. Grosse Mengen von Nickel (bis hinauf zu 200 mg) können leicht gehandhabt werden. Die Nützlichkeit der Methode zur Bestimmung von Nickel neben anderen Elementen wird gezeigt indem Nickel in Gegenwart von Kupfer, Kobalt und Eisen, und in Standardstählen vom National Bureau of Standards gefällt wird.

Résumé—En faisant réagir du biacétyl et de l'hydroxylamine en présence de nickel (II), de grands cristaux de diméthylglyoxinate de nickel bien développés et facilement filtrables sont précipités à partir d'une solution homogène. Les cristaux aciculaires ont fréquemment jusqu'à plusieurs millimètres de long. De grandes quantités de nickel—de l'ordre de 20 mg—sont facilement manipulées. L'utilité de cette méthode de précipitation à partir d'une solution homogène est montrée par les résultats obtenus pour le nickel en présence de quelques substances sélectionnées, telles que le cobalt, le cuivre, le fer et des échantillons d'acier du Bureau National des Standards.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—I*

DAS VERHALTEN VON MANGAN UND ERDALKALIEN

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(*Eingegenagen am* 29 *Februar* 1960)

Zusammenfassung—Es wurde das Verhalten der Mangan- und Erdalkalikomplexe mit Äthylendiamitetraessigsäure (AeDTA) und mit 1.2-Diaminocyclohexan-N.N.N.'N'-tetraessigsäure (DCTA) an stark sauren Kationenaustauschern in Abhängigkeit von pH untersucht. Die durch entsprechende Sorptionskurven gegebenen Existenzbereiche der einzelnen Komplexe wurden mit dem Verlauf der pH-Abhängigkeit der scheinbaren Komplexbildungskonstante der einzelnen Komplexe verglichen. Es wurde eine selektive Trennung der Erdalkalien von grossen mittels DCTA komplex gebundenen Mengen Mangan ausgearbeitet.

Metallkomplexe mit Reagenzien des Komplexantyps sind zur Verwendung in der Ionextechnik besonders geeignet. Wie bekannt, gehen die meisten Kationen solche Komplexe im eifachen stöchiometrischen Verhältnis (meist 1:1) ein; die Komplexe sind sehr stabil und untereinander durch ihre Komplexbildungskonstanten verschieden, was bereits bei komplexometrischen Titrationen und auf anderen Gebieten der analytischen Chemie bereits ausgenutzt wurde.[1]

Eine der ersten Arbeiten, in der die Anwendung von AeDTA in der Ionexchromatographie behandelt wird, ist die Studie bon Bovy und Duyckaerts[2] über die Trennung von Strontium und Barium an Katexen. Honda[3] eluierte mit 0,01-m AeDTA das sorbierte Calcium bei pH 6,6 und Strontium bei pH 10. Fouarge und Fregar[4] trennen Calcium und Strontium von Barium und Radium durch Auswaschen mittels AeDTA bei pH 7,4. Schwarzenbach[5] bediente sich zur Trennung des Calciums von Magnesium der geringen Stabilität des AeDTA-Magnesiumkomplexes gegnüber Natronlauge. In stark alkalicher Lösung wird durch Titration gegen Murexid nur das Calcium komplex gebunden. Nach Herabsetzen der Alkalität bilden sich Magnesiumionen, die an Katex sorbiert werden, während der stabile Calciumkomplex durch die Katexsäule unveränder durchgeht. Die beiden sorbierten Elemente lassen sich auch durch selektives Auswaschen mittels AeDTA-Lösung bei pH 6,1 trennen;[6] mit der gleichen Lösung wurde Mangan von Calcium bei pH 4,7 chromatographisch abgetrennt.[7]

In der vorliegenden Arbeit untersuchten wir systematisch das Verhalten von Mangan und den Erdalkalien nicht nur gegenüber AeDTA sondern auch gegenüber DCTA. Insbesondere widmeten wir unsere Aufmerksamkeit der Abhängigkeit der Kationensorption von pH. Wir knüpften hierbei an die Ergebnisse unserer früheren

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* Auf der 20. IUPAC-Tagung in München in September 1959 wurde empfohlen, für Polyaminopolycarbonsäuren, die mit Metallen komplexe Ahionen bilden, statt Komplexone, die Bezeichnung Komplexane zu verwenden.

Arbeit an[7] und bedienten uns auch z.T. der von Fritz und Umbreit[8] beschriebenen Methodik, mittels der die letzgemannten das Verhalten einiger Kationen an Ionenaustauschern in Gegenwart von AeDTA untersucht hatten. Das Verhalten der DCTA-Metallkomplexe an Ionenaustauschern wurde bisher nicht beschrieben.

VERSUCHSTEIL

Apparatur:

Es wurde mit stark saurem, Sulfongruppen enthaltendem Katex, Amberlite IR-120 (Röhm und Haas) der Korngrösse 0,1–0,3 mm gearbeitet. Der Ionenaustauscher wurde durch wiederholtes Dekantieren mit 3 m-Salzsäure und 3 m-Natronlauge gereinigt, dann mit Wasser bis zur neutralen Reaktion gewaschen und mittels 5% iger Kochsalzlösung in den Na-Cyclus übergeführt. Es wurde eine für die kinetische Methode[9] übliche Säule verwendet. Zur Untersuchung der Sorption eine Säule von 15 × 1 cm², zur Untersuchung der Trennung und zur praktischen Anwendung eine Säule von 25 × 1 cm².

Das pH wurde potentiometrisch (Apparatur Typ K, Kovodružstvo, Prag) mit Hilfe der Glaselektrode gegen Normal-Kalomelelektrode gemessen.

Reagenzien:

Die 0,05 m-AeDTA-Lösung wurde durch Lösen von 37,22 g des AeDTA-Dinatriumsalzes (Chelaton 3 der Firma Lachema, Brünn) in 2 Liter deionisiertem Wasser hergestellt.

Die 0,05 m-DCTA-Lösung wurde durch Neutralisieren von 19,4 g 1.2-Diaminocyclohexan-N.N.N.'N'-tetraessigsäure (J. R. Geigy, Basel, Schweiz) mit 10% iger Natronlauge zu pH 8 und durch Auffüllen mit deionisiertem Wasser zu 1 Liter hergestellt.

Die 0,05 m-Lösungen der untersuchten Metallsalze wurde aus Präparaten der Fa. Lachema, Brünn, ČSR, bereitet. Auch die entsprechenden Pufferlösungen (s. Tab. 1) wurden aus analytisch reinen Substanzen hergestellt.

Verwendete Arbeitstechnik:

Zu 10 ml der 0,05 m-Lösung des untersuchten Metalls wurden 25 ml der 0,05 m-AeDTA oder DCTA-Lösung und 20 ml der entsprechenden Pufferlösung (Tab. 1) zugesetzt.

TAB. 1. ZUSAMMENSETZUNG DER VERWENDETEN PUFFERLÖSUNGEN. pH-BEREICH.

Zusammensetzung der verwendeten Pufferlösungen.	pH–Bereich
0,5 m Ameisensäure/Natronlauge	2–3,5
0,5 m Essigsäure/Natronlauge	3–6,2
0,2 m Borsäure/0,05 m Borax	7,1–8,5
0,2 m Borsäure/Natronlauge	8,0–10
0,2 m Borax/Natronlauge	9,5–12

(1) Unter potentiometrischen Kontrolle wurde das pH der Lösung mit Hilfe einer 10% igen Lösung der entsprechenden schwachen Säure oder mittels 10% iger Natronlauge auf den gewünschten Wert eingestellt. Nach Abspülen der Elektroden wurde die Lösung auf 70 ml verdünnt.

(2) Die mit dem Ionenaustauscher beschickte Säule wurde zunächst mit 20 ml des entsprechenden verdünnten Puffers (1:3) in der Weise ausgewaschen, dass die Katexsäule nach beendetem Auswaschen noch mit 5 ml der überstehenden Pufferlösung bedeckt war. Alsdann wurde die untersuchte Lösung durch die Säule mit einer Geschwindigkeit von 5 ml/min cm² durchgelassen und die ausfliessende Lösung wurde in einen Titrierkolben gefangen. Das Becherglas wurde zweimal mit 5 ml der verdünnten Pufferlösung ausgespült und die Katexsäule mit 50 ml deionisiertem Wasser nachgewaschen. In den vereinigten Eluaten wurde die freie AeDTA bzw. DCTA durch Rücktitration mit Masslösung des jeweils untersuchten Kations bestimmt. Bei der Bestimmung von Calcium, Strontium und Barium wurde als Indikator das Fluorescein Komplexon, bei der Bestimmung von Magnesium und Mangan

das Eriochromschwarz T verwendet. Das sorbierte Kation wurde aus der Säule mit 0,05 m-AeDTA-Lösung von pH-Wert 12 ausgewaschen. Nach dem Auswaschen mit 5% iger Natriumchloridlösung und mit Wasser war die Säule zur weiteren Verwendung bereit.

ERGEBNISSE UND DISKUSSION

Die Menge der durch Sorption zurückgehaltenen Kationen wurde titrimetrisch bestimmt und in Prozenten der Sorption ausgedrückt. Die Ergebnisse dieser sowohl mittels AeDTA als auch mittels DCTA durchgeführten Versuche in Abhängigkeit vom pH-Wert der Lösung sind in Abb. 1 wiedergegeben.

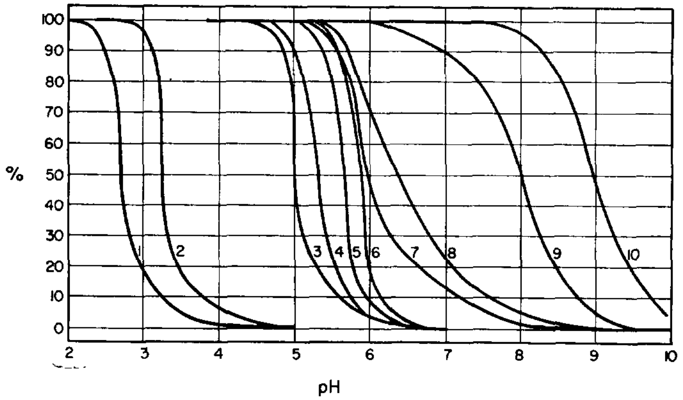

ABB. 1.–Sorption von Mangan und Erdalkalien an Amberlite IR–120 aus Komplexanlösung in Abhängigkeit von pH. Konzentration Me^{II}: $7{,}2 \cdot 10^{-3}$ m; Konzentration des Komplexans: $1{,}8 \cdot 10^{-2}$ m. Ordinate: % der Sorption, 1 MnDCTA, 2 MnAe DTA, 3 MgDCTA, 4 CaDCTA, 5 CaAeDTA, 6 MgAeDTA, 7 SrAeDTA, 8 SrDCTA, 9 BaAeDTA, 10 BaDCTA.

Aus den erhaltenen Ergebnissen tritt der wesentliche Unterschied im Verhalten beider Komplexbildner bei der Einstellung des Gleichgewichtes zwischen dem Komplex und dem Ionenaustauscher klar hervor. Dieser Unterschied ist in erster Linie durch die Werte der thermodynamischen Komplexbildungskonstanten und ferner durch verschiedene Affinität der betreffenden Ionenart zum Austauscher gegeben. Die Konzentration des freien Kations in der Lösung seines Komplexes ist nicht nur durch die entsprechende thermodynamische Konstante K gegeben, sondern sie wird auch durch die in die scheinbare Komplexbildungskonstante in Form der H-Funktion einbezogene Wasserstoffionenkonzentration beeinflusst. Um die Bedingungen der Verteilung zwischen dem Komplex und dem Ionenaustauscher vergleichen zu können, berechneten wir die scheinbare Komplexbildungskonstante bei einem solchen pH-Wert, bei dem der Verteilungskoeffizient zwischen dem Kation und dem Ionenaustauscher gleich 1 ist. Bei der graphischen Darstellung der Funktion $\log K' = f(pH)$ für AeDTA wurden die von Körbl und Přibil[11] berechneten α_H-Werte verwendet. Die analogen Werte für DCTA wurden nach dem gleichen Verfahren[10] berechnet. Alle Werte der Dissoziations- und Komplexbildungskonstanten wurden den Bjerrumschen Tabellen[12] entnommen. Die Abhängigkeit des K'-Wertes einiger Kationen vom pH veranschaulicht Abb. 2. In Tab. 2 sind die Werte von thermodynamischen Konstanten, scheinbaren Komplexbildungskonstanten und diejenigen pH-Werte verglichen, bei denen die Verteilung des Kations gleich 1 ist. Die Reihenfolge einzelner Spalten in der Tabelle ist durch die Reihenfolge der Sorptionskurven aus der Abb. 1 bestimmt. Aus diesen Abhängigkeiten geht hervor, dass die Lage jeder Sorptionskurve im pH-Abhängigkeitsbereich durch die Differenz derscheinbaren Komplexbildungskonstanten bestimmt ist. Ausserdem macht sich hier auch der Einfluss der Komplexstärke und der Sorbierbarkeit einzelner Ionenarten bemerkbar. Die Sorptionskurven von Mangan aus AeDTA- bzw. CDTA-Lösungen nehmen bezüglich der Sorptionskurven anderer Metallionen eine Sonderstellung ein (Abb. 1, Kurve 1, 2). Ihre Stellung zueinander stimmt mit dem Verlauf der pH-Abhängigkeit ihrer Konstanten K'(Abb. 2, Kurven 1, 2) gut überein. Die beiden in Abhängigkeit von pH veranschaulichten Kurven des Bariums (Abb. 1, Kurven 9, 10) unterscheiden sich von den Kurven anderer Erdalkalien durch Verschiebung des pH zu höheren Werten. Diese Verschiebung ist nicht nur durch die Differenz der Komplexbildungskonstanten verursacht, sondern ist auch auf die durch Bildung von schwerlöslichen Bariumverbindungen mit der Funktionsgruppe des Ionenaustauschers bedingte

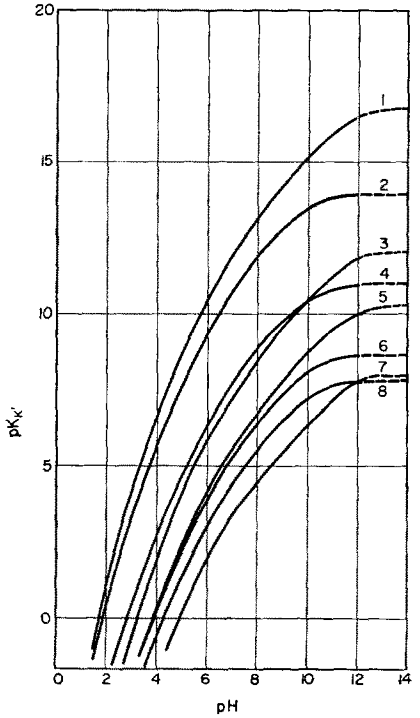

ABB. 2.–Abhängigkeit einiger scheinbaren Konstanten K' von Komplexen einiger Metalle mit Komplexanen von pH. 1. MnDCTA, 2 MnAeDTA, 3 CaDTA, 4 CaAeDTA, 5 MgDCTA, 6 MgAeDTA, 7 BaDCTA, 8 BaAeDTA.

TAB. 2. WERTE VON SCHEINBAREN KOMPLEXBILDUNGSKONSTANTEN K' UND VON pH, BEI DEM DIE VERTEILUNG DES METALLS ZWISCHEN DEM AUSTAUSCHER UND DEM KOMPLEX GLEICH 1 IST.
C=DCTA: Y=AeDTA

Komplex	MnC	MnY	MgC	CaC	CaY	MgY	BaY	BaC
pH	2,90	3,35	5,15	5,35	5,55	5,85	8,00	8,90
K	16,8	14,0	10,3	12,1	11,0	8,7	7,8	8,0
K'	4,2	3,7	2,7	4,6	5,5	3,8	5,5	5,2

betrachtliche Sorbierbarkeit der Bariumionen zurückzuführen. Die scheinbar anomale Sorption des Bariums aus dem thermodynamisch stabileren Komplex mit DCTA ist im guten Einklang mit dem Verlauf der scheinbaren Komplexbildungskonstanten K′ (Abb. 2, Kurven 7, 8).

Die unterschiedliche Lage der einzelnen Sorptionskurven ermöglicht einige analytische Trennungen. In dieser Arbeit wird die Bestimmung von Calcium und Magnesium bei Gegenwart grosser Mengen Mangan beschrieben.

Arbeitsanleitung: Eine schwach saure, Mangan, Calcium und Magnesium enthaltende Lösung versetzt nan im einem 250 ml Becherglas mit einem auf den Mangangehalt bezogenen, etwa 10% igen Überschuss von 0,05 m-DCTA-Lösung.

TAB. 3. TRENNUNG DER ERDALKALIEN VON MANGAN IM DCTA-MEDIUM BEI pH 4,0–4,4. IN ALLEN FÄLLEN WURDE MIT 140 MG Mn GEARBEITET.

Gegeben, *mg*		Gefunden, *mg* Mg(Ca)	Differenz, *mg*	Abweichung, rel %	Mn:Mg(Ca)
Mg	Ca				
2,49		2,63	0,14	105,6	56:1
6,23		6,24	0,01	100,2	22:1
12,45		12,39	−0,06	99,5	11:1
24,90		24,98	0,08	100,3	5,6:1
	4,01	4,40	0,39	111	35:1
	10,00	10,00	—	100,0	14:1
	20,04	20,34	0,30	101,5	7:1
	40,08	40,10	0,02	100,1	3,5:1

(Die Trennung kann ohne Verluste an Erdalkalien auch bei einem 200% igen DCTA-Überschuss durchgeführt werden.) Man fügt 25 ml 0,5 m-Acetatpuffer hinzu, stellt das pH unter potentiometrischer Kontrolle auf den Wert von 4,0–4,4 ein und verdünnt auf 150 ml. Die Lösung lässt man nun mit einer Geschwindigkeit von 5 ml/min cm^2 durch die Säule durchfliessen und wäscht alsdann mit Prufferlösung und deionisiertem Wasser wie in der Anleitung unter 2 angegeben ist, nach. Nach der Abtrennung von Mangan wäscht man die sorbierten Ionen mit abgemessenen mengen 0,05 m-AeDTA-Lösung bei pH 11,5 aus und bestimmt den AeDTA-Überschuss durch Rücktitration mit 0,05 m-Zink- oder Mangesiumsalz. Wie aus Tab. III ersichtlich ist, stimmen die Ergebnisse dieser Trennung mit den kannten Werten gut überein.

Die Trennung an Ionenaustauschern ist unvergleichbar schneller als die bisherigen klassischen Trennverfahren. Die obige Arbeitsvorschrift ermöglicht eine schnelle Bestimmung von Calcium und Magnesium im Material mit hohem Mangangehalt wie z.B. in Manganschlacken, in Flüssen für Schweissautomate und in zahlreichen Mineralen.

Auf einem ähnlichen Prinzip beruht auch die Trennung des Calciums von Barium, bzw. die Trennung der Erdalkalien. Einzelheiten darüber werden demnächst veröffentlicht. Die weitere Anwendung von DCTA in der Ionen-Technik bildet den Gegenstand der nächsten Mitteilungen.

Summary—The behaviour of manganese and of alkaline earth complexes with ethylenediaminetetra-acetic acid and with 1:2-diamino*cyclo*hexane-N:N:N′:N′-tetra-acetic acid (DCTA) has been studied on strongly acid cation-exchangers in respect of pH-dependence. The actual range of existence of individual complexes indicated by sorption curves has been correlated with the pH dependence of the apparent stability constants of the complexes. A procedure has been developed for the separation of alkaline earths from large amounts of manganese complexed by DCTA.

Résumé—Le comportement des complexes du manganèse et des alcalinoterreux avec l'acide éthylène diamine tétracétique et l'acide 1–2 diamino cyclohexane N-N-N′-N′ tétracétique (DCTA) a été étudié sur des échangeurs de cations fortement acides au point de vue de sa variation avec le pH. Le domaine réel d'existence des complexes particuliers indiqué par les courbes de sorption a été reliée à la manière dont les constantes de stabilité apparente des complexes dépendent du pH. Un procédé a été développé pour séparer sélectivement les alcalino-terreux de grandes quantités de manganèse complexé par le DCTA.

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NEW REDOX SYSTEMS—III

INDIRECT CERIMETRIC DETERMINATION OF COBALT

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Summary—The previously studied redox reaction:

$$[Fe_2(Phen)_4(OH)_2]^{4+} + 2Co(Phen)_3^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_3^{2+} + 2Co(Phen)_3^{3+} + 2H_2O \quad (1)$$

is utilised for the indirect cerimetric determination of cobalt. The determination is based on the titration of the resulting ferroïn with potentiometric or visual control.

RECENTLY we studied the oxidation of cobalt^{II} salts with a solution of iron^{III} chloride in the presence of 1:10-phenanthroline.[1,2] It was proved that the reaction takes place according to equation (1). The equilibrium of this reaction in solutions of pH 2-4 is shifted in practice to the right. It was found further that highly diluted solutions of cobalt^{II} salts can, under optimal pH, be titrated directly with 0·01M iron^{III} chloride, The potential jump at the equivalent point is 250 mV per 0·05 ml of iron^{III} chloride solution. The direct titration is limited to solutions in which iron is not present or is suitably removed or is reduced to its bivalent form. Experiments towards solving this problem are still being carried out, and these will be published in a future paper.

The reaction described above for the determination of cobalt could be utilised in another way. The intensely coloured ferroïn resulting from this reaction could be determined colorimetrically. This fact enables the indirect determination of cobalt to be made.[3] At higher concentrations of cobalt, the ferroïn coloration is too intense to be suitable for colorimetry. Therefore, oxidimetric titration of ferroïn to ferriïn was studied. Cerium^{IV} sulphate was found to be most suitable for this purpose. This titration is easily followed potentiometrically, or, after sufficient dilution, even visually (intensely red ferroïn turns to weakly blue ferriin).

EXPERIMENTAL

Reagents and solutions

0·1M 1:10-phenanthroline solution was prepared by dissolving 18·022 g of reagent grade substance in redistilled water acidified with hydrochloric acid. After adjusting the pH to 3, the solution was diluted to 1 litre with water. Other solutions—0·01M and 0·05M $Co(NO_3)_2$, 0·01M and 0·05M $FeCl_3$ and 0·075M $Ce(SO_4)_2$—were prepared from the reagents of highest purity.

Apparatus

Potentiometric measurements were carried out with a Trüb and Täuber potentiometer (Switzerland). A platinum electrode and a saturated calomel electrode were used. The control of pH was carried out potentiometrically using a glass electrode and pH-meter (Kovodružstvo, Praha).

RESULTS AND DISCUSSION

Cerimetric determination of ferroïn

Oxidation of red ferroïn to blue ferriïn was applied for the visual indication of some cerimetric titrations. In all cases only small amounts of ferroïn indicator were used. In this particular case, when ferroïn functions as a reducing agent, it was important to study the conditions of its quantitative oxidation, particularly at higher concentration. Due to the instability of ferroïn in a strongly acidic medium, especially at higher temperatures, the effect of acidity at room temperature was particularly studied. Experiments were carried out as follows:

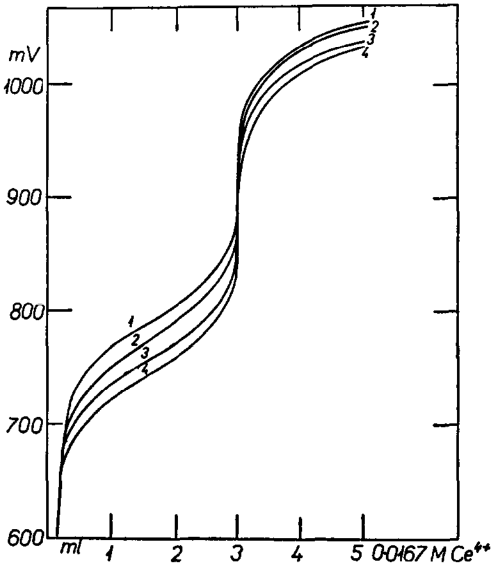

Fig. 1.—Cerimetric determination of ferroïn at various molarities of H_2SO_4. Curves: (1) 0·5*M*, (2) 1*M*, (3) 2*M*, (4) 4*M*.

5 ml of 0·01*M* cobalt$^{\text{II}}$ nitrate solution were mixed with 2 ml of 0·05*M* iron$^{\text{III}}$ chloride solution and 5 ml of 0·1*M* 1:10-phenanthroline solution. The pH of the solution was adjusted to 2–4 by appropriate addition of sodium hydroxide or hydrochloric acid. After 15 min a suitable volume of 9*N* sulphuric acid was added, and the solution diluted to 100 ml and titrated potentiometrically with 0·0167*M* cerium$^{\text{IV}}$ sulphate using a 5-ml microburette.

From the shape of the curves in Fig. 1, representing the titrations in 0·5-4*M* sulphuric acid medium, it is evident that during the 30 min in which the titrations took place, the determination was not effected by acidity. A similar condition of acidity had to be kept also for the proper determination of cobalt. It is necessary to emphasise that the basic reaction (1) has its optimum at pH 2–4. The subsequent cerimetric oxidation of the resulting ferroïn takes place in a strongly acidic medium. That is why reaction (1) was carried out in a non-buffered solution at pH 2–4.

Visual titration

Cerimetric determination of ferroïn, as well as the indirect titration of cobalt, can be observed very exactly visually when the titration is carried out sufficiently slowly. The colour change at the end-point is from orange-red to distinct blue. Thus relatively low concentrations of cobalt may be determined. At higher concentrations it is necessary to dilute the solution to render the colour change more distinct. In Table I some results of visual and potentiometric determinations of cobalt are given.

TABLE I. INDIRECT CERIMETRIC DETERMINATION OF COBALT.

Co taken, *mg*	Co found, *mg*	
	potentiometrically	visually
1·45	1·48	1·47
2·90	2·90	2·92
5·80	5·77	5·78
14·50	14·56	14·60
29·00	28·95	29·13

Selective determination

The effect of other cations on reaction (1) and on the subsequent cerimetric determination of the resulting ferroïn was studied in some detail. The procedure was the same as described above.

1. *Effect of iron.* From the colorimetric measurements[3] it was obvious that an excess of iron^{III} in comparison with 1:10-phenanthroline has such an effect on reaction (1) that either the reaction does not proceed quantitatively or it does not proceed at all. The explanation is that, under the given conditions, the complex $[Fe_2(Phen)_4(OH)_2]^{4+}$ is not formed. The resulting complex of different constitution is not readily reduced by cobalt. The effect of iron was studied potentiometrically in detail. It was found that, for example, in the presence of 5 ml of 0·1*M* 1:10-phenanthroline, 3 mg of cobalt could be reliably determined in the presence of 90 mg of iron (Co:Fe = 1:30). This ratio could be higher if the iron was masked with a suitable complex-forming compound. This problem will be discussed in a subsequent paper dealing with the colorimetric determination of cobalt.[3]

2. *Effect of other metals.* From a series of experiments it was obvious that none of the common cations is capable of reducing iron^{III} in the presence of 1:10-phenanthroline, but cobalt^{II}, under the same conditions, is able to reduce copper to its univalent form which combines with 1:10-phenanthroline to form a very stable complex. This reaction proceeds more slowly than reaction (1) and, from this point of view, it may be considered as a specific reaction for cobalt. Strong reductants (hydroxylamine, ascorbic acid) and strong oxidants have a comprehensibly interfering effect. Some bivalent cations in higher concentrations interfere because they form stable complexes (soluble or insoluble) with 1:10-phenanthroline. This effect could be suppressed by the addition of 1:10-phenanthroline in excess. But at present the use of 1:10-phenanthroline is somewhat limited because of its high cost. Some interfering cations could be screened by the addition of EDTA.[3] Unfortunately, EDTA is not suitable for potentiometric titrations because it is oxidised by cerium^{IV} sulphate. Metals which do not form complexes with 1:10-phenanthroline, *e.g.* alkaline earths and rare earths,

thorium, beryllium, titanium, uranium, chromium, aluminium, lead and zirconium, do not interfere in this reaction.

The maximum permitted concentration of interfering elements was determined as follows:

The definite amount of cobalt solution was mixed with 5 ml of 0·05*M* 1:10-phenanthroline solution and 5 ml of 0·05*M* iron^{III} chloride solution, then the cerimetric titration was carried out as described above.

The experiments showed that, for example, it is possible to determine 2·9 mg of cobalt with an error of up to 1 % in the presence of 110 mg of Ni, 25 mg of Cd, 65 mg of Zn, 20 mg of Cu, 30 mg of Mo, 45 mg of V (as VO_3) and 50 mg of W. Silver, mercury and thallium^{I} made this determination impossible, even when present in low concentration, because of the formation of insoluble precipitates, and they must, therefore, be removed.

Analytical application

The proposed method was used for the determination of cobalt in steels, ferrous and non-ferrous alloys containing moderate amounts of cobalt (about 2-40 %). As an example, this method was applied to the cerimetric determination of cobalt in an alloy used for the manufacture of permanent magnets (procedure 1), and for a special cobalt-chromium alloy (procedure 2).

Procedure 1. About 0·5 g of sample is treated with *aqua regia*, partly evaporated, then diluted. Any insoluble residue is filtered off and washed with hot dilute hydrochloric acid. The filtrate is accurately diluted to 250 ml. Twenty-five ml of this solution are neutralised with 5 % sodium hydroxide to the formation of a precipitate, which is then dissolved in the minimum amount of hydrochloric acid. The pH is adjusted to a value of 2–4 (glass electrode, universal indicator paper), and 10 ml of 0·1*M* 1:10-phenanthroline of pH 3 are added. After 15 min the solution is acidified with 50 ml of 9*N* sulphuric acid, diluted to 200 ml with water and titrated with 0·05–0·1*M* cerium^{IV} sulphate solution from a suitable microburette, with potentiometric control.

With this procedure cobalt was determined in permanent magnet alloy BCS No. 233 (11·22 % Ni, 6·98 % Al, 0·78 % Ti, 0·23 % Mn and 23·7 % Co). The average of 3 determinations was 23·78 % of cobalt. (0·35 % error).

Procedure 2. This was the same as for procedure 1. With regard to the fact that the sample contained a small amount of iron, after dissolving the alloy, a sufficient amount of iron^{III} chloride was added to make its concentration in the solution higher than that of the cobalt.

The special cobalt-chromium alloy has the following composition: 0·58 % C, 0·23 % Si, 1·67 %Fe, 57 % Cr and 39·21 % Co. With the modified method the average of 3 determinations was 39·10 % of cobalt (0·25 % error).

Zusammenfassung—Das früher studierte Redoxsystem:

$$Fe_2(Phen)_4(OH)_2^{4+} + 2Co(Phen)_3^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_3^{2+} + 2Co(Phen)_3^{3+} + 2H_2O$$

wurde zur indirekten cerimetrischen Bestimmung von Cobalt herangezogen. Die Bestimmung beruht auf der potentiometrischen oder visuellen Titration des enstehenden Ferroins.

Résumé—Le système rédox préalablement étudié

$$Fe_2(Phen)_4(OH)_2^{4+} + 2Co(Phen)_2^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_2^{2+} + 2Co(Phen)_3^{3+} + 2H_2O$$

a été utilisé pour le dosage indirect du cobalt par cérimétrie. Le dosage est basé sur le titrage de la ferroine formée avec contrôle potentiométrique ou visuel.

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ANALYTICAL USES OF BROMINE MONOCHLORIDE

DETERMINATION OF HYDROXYLAMINE. CONTRIBUTIONS TO THE BROMIC ACID-HYDROCHLORIC ACID REACTION

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Summary—The oxidation of hydroxylamine by bromine monochloride, by elementary chlorine in hydrochloric acid medium, and by bromate and bromic acid has been investigated. Oxidation by bromine monochloride is utilised for the analytical determination of hydroxylamine.

Detailed examination of the reaction of bromate with hydrochloric acid proves that, in the presence of excess of hydrochloric acid, these compounds quickly react forming bromine monochloride and elementary chlorine. The proportions of the reaction products have been determined. On the basis of the results of these investigations, it is possible to present an interpretation of the analytical method suggested by Kurtenacker for the determination of hydroxylamine.

The conventional analytical determination of hydroxylamine is based on determination of the acid component of its sulphate or hydrochloride. Rupp and Mäder[1] were the first to use oxidation by bromine for the determination of hydroxylamine, and they found that hydroxylamine is oxidised by bromine to nitric acid. Kurtenacker and co-workers,[2,3] however, pointed out that this method is only suitable for minute amounts of hydroxylamine. With greater quantities of hydroxylamine, nitrogen oxides are also formed. In the opinion of Kurtenacker and Wagner[2] the best method for the determination is to oxidise hydroxylamine with bromate in strong hydrochloric acid medium. According to these authors, hydroxylamine is then oxidised to nitric acid by nascent chlorine which is formed by the reaction of bromate with hydrochloric acid.

During our investigations into the analytical uses of bromine monochloride, we studied the oxidation of hydroxylamine by bromine monochloride. It was found that hydroxylamine is quantitatively oxidised to nitric acid by an excess of bromine monochloride:

$$NH_2OH + 3BrCl + 2H_2O = HNO_3 + 3HBr + 3HCl \qquad (1)$$

In our attempts to utilise this reaction for the analytical determination of hydroxylamine, we used a $0{\cdot}1N$ standard solution of bromate which contained an equivalent amount of bromide according to the equation:

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ = 3BrCl + 3H_2O \qquad (2)$$

This standard solution was added in excess to a weighed amount of hydroxylamine in a bromination flask. On acidification with hydrochloric acid, reaction (2) takes place and hydroxylamine is oxidised according to (1). The excess of bromine monochloride is determined iodometrically. In this reaction, the equivalent weight of hydroxylamine is $M/6$.

On examining the reaction between bromine monochloride and hydroxylamine in detail under the conditions mentioned later it was found that:

1. When bromine monochloride is present in an excess greater than 100%, hydroxylamine is quantitatively oxidised to nitric acid in 3 min.
2. The results are not affected by using longer reaction periods.
3. It is practical to use 5–10 ml of 20% hydrochloric acid.
4. On varying the excess of bromine monochloride (greater than 100%), no change was observed in the results. The use of excesses of bromine monochloride greater than 100% is necessary because, during the oxidation, bromine monochloride is reduced to bromide which latter itself reduces bromine monochloride to elementary bromine. Because of this fact the reaction is slowed down, since the elementary bromine oxidises the hydroxylamine more slowly.

TABLE I

$NH_2OH{\cdot}HCl$ taken, *mg*	0·1*N* BrCl added, *ml*	0·1*N* $Na_2S_2O_3$ consumed, *ml*	0·1*N* BrCl consumed, *ml*	Reaction time, *min*	20% HCl used, *ml*	$NH_2OH{\cdot}HCl$ found, *mg*	Δ mg	Δ %
2·971	9·96	7·40	2·56	5	5	2·965	−0·006	−0·2
5·010	9·96	5·63	4·33	5	5	5·015	+0·005	+0·1
9·862	20·00	11·48	8·52	5	5	9·869	+0·007	+0·1
9·862	20·00	11·50	8·50	5	10	9·846	−0·016	−0·2
9·862	20·00	11·50	8·50	10	10	9·846	−0·016	−0·2
9·862	20·00	11·46	8·54	10	5	9·892	+0·030	+0·3

By utilising the afore-mentioned observations, 3–12 mg of hydroxylamine hydrochloride could be determined with an error of ±0·5% (*cf.* Table I).

The bromatometric method suggested by Kurtenacker[2] for the determination of hydroxylamine was also examined.

First, in the reaction between bromate and hydrochloric acid it was found that, on pouring only 5 ml of 20% hydrochloric acid* into 10 ml of 0·1*N* bromate solution in a volume of 20 ml, no bromate is present in the solution after 5 min. To disclose this fact we used the method suggested by us[4] for the eventual bromate content of a bromine monochloride standard solution. By raising the concentration of hydrochloric acid, the rate of reaction was increased. The proportions of reaction products were established as well. Thus, bromine monochloride and elementary chlorine formed in the reaction were converted into halogen cyanides, and the amount of cyanogen bromide measured by iodometry in the presence of the iodometrically inactive cyanogen chloride. According to our investigations, the following reaction takes place quantitatively between bromate and an excess of hydrochloric acid:

$$HBrO_3 + 5HCl = BrCl + 2Cl_2 + 3H_2O \qquad (3)$$

By raising the concentration of hydrochloric acid the rate of reaction increases. The kinetics of the reaction will be discussed in another communication.

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* In his determination Kurtenacker used 40 ml of 20% hydrochloric acid.

The oxidation of hydroxylamine by chlorine and bromic acid, respectively, were studied too. It was found that hydroxylamine is oxidised to nitric acid by elementary chlorine at approximately the same rate as by bromine monochloride. In our studies of the oxidation by bromic acid, it was necessary to maintain conditions which exclude the possibility of formation of bromine monochloride, elementary bromine or elementary chlorine. Therefore, oxidation was carried out in a medium containing sulphuric acid, in the presence of mercury^{II} ions, which are capable of preventing interference from halide ions binding them as poorly dissociating mercury halides. Under these conditions the reaction is extremely slow and ambiguous. No equation can be given for this process.[5]

Accordingly, as proved by our investigations, in the oxidations by bromate carried out in a medium of hydrochloric acid, bromine monochloride and elementary chlorine are always the oxidising reagents. The situation is the same in the method suggested by Kurtenacker.[2]

EXPERIMENTAL

Determination of hydroxylamine by oxidation with bromine monochloride

Reagents

0·1*N* *bromate solution*: 2·7835 g of potassium bromate and 3·9670 g of potassium bromide dissolved in water and diluted to 1000 ml in a standard flask.

Hydrochloric acid: 20%.

Potassium iodide.

0·1*N* *solution of sodium thiosulphate.*

Potato starch solution: 1%, decomposed and preserved by 0·1% of salicylic acid.

All the reagents were of analytical grade. The hydroxylamine hydrochloride was Merck analytical grade.

Procedure

An aliquot of solution, containing 3–12 mg of hydroxylamine hydrochloride was, transferred to a Schulek bromination flask and treated with sufficient 0·1*N* standard solution to maintain, on acidification with hydrochloric acid, an excess of bromine monochloride greater than 100%. Subsequently, the volume of the reaction mixture was diluted with distilled water to 30–40 ml. Then 5–10 ml of 20% hydrochloric acid were poured into the cup-shaped, broadened neck of the bromination flask. On loosening the stopper, the liquid flowed into the flask. After 5 min, 10 ml of a freshly prepared 5% solution of potassium iodide were added to the reaction mixture in a similar way. The amount of iodine liberated was determined, without allowing the mixture to stand, with 0·1*N* standard sodium thiosulphate solution using potato starch solution as indicator.

1 ml of 0·1*N* solution corresponds to 1·1583 mg of hydroxylamine hydrochloride (equivalent weight is $M/6$ in this reaction).

The error of the results is ±0·5%.

Investigation of the reaction between bromate and hydrochloric acid

Reagents

0·1*N* *bromate solution.*

Hydrochloric acid: 20%, distilled, free from bromide.

Potassium cyanide.

Potassium iodide.

Sodium hydroxide: 20%.

Potato starch solution: 1%, decomposed and preserved by 0·1% of salicylic acid.

All the reagents were of analytical grade.

Procedure

10·00 ml of 0·1*N* standard bromate solution were diluted with distilled water to 20 ml, and acidified with 5 (10 and 20) ml of 20% hydrochloric acid. On allowing the mixture to stand for 5 min, 0·5 g of potassium cyanide was dissolved in the mixture and then 20% sodium hydroxide was added to attain an alkali excess of about 2 ml. Bromine monochloride and elementary chlorine reacted with cyanide forming cyanogen bromide and cyanogen chloride and, in the alkaline medium, both hydrolysed to cyanate and bromide or chloride ions, indifferent to iodometry. Accordingly, the bromate content of the solution could be measured iodometrically after 5 min.

Results

Our results showed that, after a reaction period of 5 min, no bromate could be detected.

In order to determine the proportion of the reaction products, about 0·20 g of potassium cyanide was dissolved in the acidic solution when the reaction between bromate and hydrochloric acid was already completed. In a period of about 10 min, bromine monochloride was quantitatively converted into cyanogen bromide and chloride ions even in an acidic solution, while cyanogen chloride and chloride ions developed from elementary chlorine. In the solution containing an excess of cyanide, cyanogen chloride is present as a complex, $[Cl(CN)_2]^-$, which is iodometrically inactive due to its high stability. Thus, it is possible to measure cyanogen bromide iodometrically in the presence of cyanogen chloride.

According to our results, one third (33·35 %) of the products formed in the reaction of bromate and hydrochloric acid consists of bromine monochloride, while two thirds (66·65 %) consist of elementary chlorine (*cf.* equation (3)).

Oxidation of hydroxylamine by elementary chlorine

In these experiments, aliquots of chlorine water containing exactly known amounts of chlorine were added to the solution of hydroxylamine hydrochloride with the aid of the bromine monochloride apparatus suggested by Schulek.[6] Excess chlorine was determined iodometrically.

With oxidation by elementary chlorine for 5 min, 98·7% of the weighed amount is recovered. On considering that, under the applied experimental conditions, a deviation of 1–2% in the results is hardly avoidable, oxidation by chlorine can be accepted as quantitative.

Oxidation of hydroxylamine by bromic acid

The aqueous solution of hydroxylamine hydrochloride was allowed to flow into a mercury^{II} sulphate solution (0·2 g of mercury^{II} oxide dissolved in a few ml of 50% sulphuric acid) and the necessary amount of 0·1*N* standard bromate solution was added. Excess bromate was determined by iodometric titration after 5 (in another experiment after 30) min.

The results obtained showed a marked deviation, and it was impossible to evaluate them from an analytical point of view. On calculating with the equivalent weight of the oxidation by bromine monochloride, only about 25% of the weighed substance could be recovered after 30 min oxidation.

Zusammenfassung—Die Oxydation von Hydroxylamin durch Bromchlorid, elementarem Chlor sowie in salzsaurem Medium durch Bromat und Bromsäure wurde untersucht. Die Oxydation durch Bromchlorid wurde zur Bestimmung von Hydroxylamin gebraucht.

In Gegenwart von Säureeüberschuss reagiert Bromate rasch mit Salzsäure unter Bildung von Bromchlorid und elementarem Chlor. Das Verhältnis der entstehenden Produkte wurde bestimmt. Auf Grund der erhaltenen Resultate war es möglich die von Kurtenacker ausgearbeitete Metlische zur Bestimmung von Hydroxylamin zu interpretieren.

Résumé—L'oxydation de l'hydroxylamine par le chlorure de brome, le chlore élémentaire et, en milieu acide chlorhydrique par le bromate et l'acide bromique, a été étudiée. L'oxydation par le chlorure de brome a été utiliseé pour le dosage de l'hydroxylamine.

En présence d'un excès d'acide, le bromate réagit rapidement avec l'acide chlorhydrique formant du chlorure de brome et du chlore élémentaire. Les proportions des produits ont été déterminées. En se basant sur ces résultats, il a été possible de donner une interprétation de la méthode analytique suggérée par Kurtenacker pour le dosage de l'hydroxylamine.

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POTENTIOMETRISCHE UNTERSUCHUNG EINIGER FÄLLUNGS-UND KOMPLEXIERUNGSREAKTIONEN DES SILBERS IN STARK ALKALISCHEM MEDIUM

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Zusammenfassung—Es wurde die potentiometrische Titration des Silbers in stark alkalischer Lösung der 4-Sulfonamidobenzoesäure untersucht. Als Titriermittel wurden Kaliumchlorid, Kaliumbromid, Kaliumjodid und Kaliumcyanid verwendet. Weiterhin wurden die Fehlerquellen geprüft und einfache Mittel zu ihrer Ausschaltung gezeigt.

Die Abtrennung des Silbers mit Hilfe der 4-Sulfonamidobenzoesäure in alkalischem und karbonathaltigem Medium, gefolgt von einer potentiometrischen Titration mit Kaliumcyanid oder Kaliumjodid bildet eine schnelle und genaue Bestimmungsmethode des Silbers.

DIE 4-Sulfonamidobenzoesäure ist eine seit langem synthetisierte Substanz, aber eine analytische Bedeutung fand sie erst in neuester Zeit. Die Löslichkeit des Silbersalzes der 4-Sulfonamidobenzoesäure in alkalischem Medium, wie auch seine leichte Reduzierbarkeit aus dieser Lösung, wurde erstmals von Gh. Ciuhandu zum Nachweis und zur Bestimmung des Kohlenoxyds in der Luft[1,2] und anderen Gasen[3] verwendet. Dieses spezifische Verhalten des Silbers wurde auch zum Erkennen und Bestimmen des Silbers ausgenützt.[4]

Da sich das Silber mit Hilfe einer alkalischen Lösung der 4-Sulfonamidobenzoesäure, mit oder ohne Zugabe eines Alkalikarbonats, von den anderen Metallen leicht trennen lässt, haben wir die Möglichkeit einer direkten potentiometrischen Titration des Silbers in dieser Lösung geprüft. Zu diesem Zweck wurden einige der bekanntesten Fällungs bzw. Komplexierungsagenten des Silbers verwendet: Cl^-, Br^-, J^- und CN^-. Diese Reagentien ergeben beim Titrieren in neutraler Lösung eine hohe Genauigkeit[5] so dass sie zur Überprüfung der in alkalischem Medium erhaltenen Ergebnisse verwendet werden konnten.

Bei unseren Untersuchungen in alkalischem Medium wurde folgenderweise vorgegangen: zu 5 cm^3 $AgNO_3$ 0,1*N* wurde ein gleiches Volumen einer 0,1*N* Lösung des Natriumsalzes der 4-Sulfonamidobenzoesäure hinzugefügt, der erhaltene Niederschlag in einem Überschuss an 0,1*N* NaOH aufgelöst und schiesslich mit Wasser bis zu einem Gesamtvolumen von 70–80 cm^3 verdünnt.

Als Indikatorelektrode wurde ein Silberdraht verwendet, während als Bezugselektrode eine gesättigte Kalomelelektrode. Ein mit gesättigter Kaliumnitratlösung gefüllter Heber diente als Stromschlüssel.

Um das an der Kontaktstelle des Hebers mit der zu titrierenden alkalischen Lösung auftretende Diffusionspotential auszuschalten, wurde in einer Versuchsserie an Stelle der Kalomelelektrode eine Bezugselektrode mit Quecksilberoxyd(II) und 0,1*N* Natriumhydroxyd als Elektrolyt, verwendet. Wie zu erwarten war, konnten keine Unterschiede gegenüber den anderen Titrationen festgestellt werden.

EXPERIMENTELLE ERGEBNISSE

Wenn das Potential einer Silberelektrode in alkalischer Lösung der Silberverbindung der 4-Sulfonamidobenzoesäure als Funktion der Alkalinität verfolgt wird, ergibt sich die in Abb. 1 dargestellte Kurve. Aus ihrem Verlauf geht hervor dass die

Konzentration der freien Silberionen mit steigender Alkalinität stark zurückgeht, was die Existenz folgenden, schon früher vorausgesetzten, Gleichgewichts[4] bestätigt:

$$H_2N{\cdot}SO_2{\cdot}C_6H_4{\cdot}COO^- + Ag^+ + OH^- \rightleftharpoons AgHN{\cdot}SO_2{\cdot}C_6H_4{\cdot}COO^- + H_2O \quad (1)$$

Aus diesem Verhalten lässt sich der Einfluss der Alkalinität auf die Grösse des Potentialsprunges im Äquivalenzpunkt abschätzen: der Potentialsprung wird um so kleiner, je grösser die Alkalinität der zu titrierenden Lösung ist.

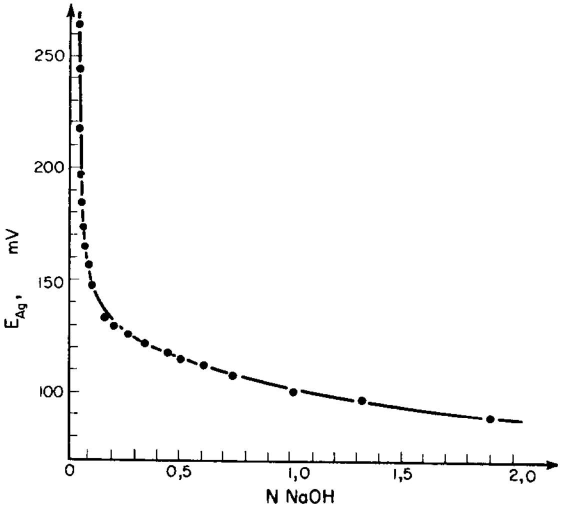

Abb. 1.—Potential der Silberelektrode (bezogen auf die gesättigte Kalomelektrode) als Funktion der Alkalinität.

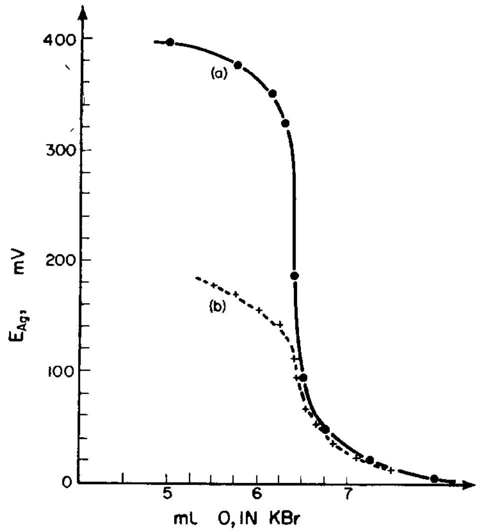

Abb. 2.—Titrationskurven mit KBr 0,1*N*; (*a*) in neutralem Medium; (*b*) in alkal. Medium.

Beim Titrieren mit Kaliumchlorid (sämtliche Titriermittel wurden in 0,1*N* Lösung verwendet), war der Potentialsprung selbst bei kleinster Hydroxydkonzentration die ein Auflösen des Silberniederschlages eben noch ermöglicht, äusserst flach, so dass der Äquivalenzpunkt nicht mit genügender Genauigkeit zu bestimmen war.

Mit Kaliumbromid ist der Sprung ausgeprägter, so dass der Abschnitt grösster Neigung leicht zu finden ist (Abb. 2). Trotzdem, waren die Ergebnisse im Vergleich mit jenen aus neutraler Lösung, systhematisch um 1 % bis 1,5 % zu hoch.

Benützt man Kaliumjodid als Titriermittel, erhält man einen noch grösseren Potentialsprung (Abb. 3). Aber auch in diesem Fall wurden immer zu hohe Werte gefunden, die bis zu 1,8 % über dem aus neutraler Lösung ermittelten Gehalt lagen.

Beim Arbeiten mit Kaliumjodid konnte überraschenderweise festgestellt werden dass erst nach dem Äquivalenzpunkt ein Ausfallen des Silberjodids beginnt, aber auch dann nur als schwache Opaleszenz. Dieses Verhalten könnte auf eine hohe Stabilität des Silberjodid-Sols im benützten Medium hinweisen.

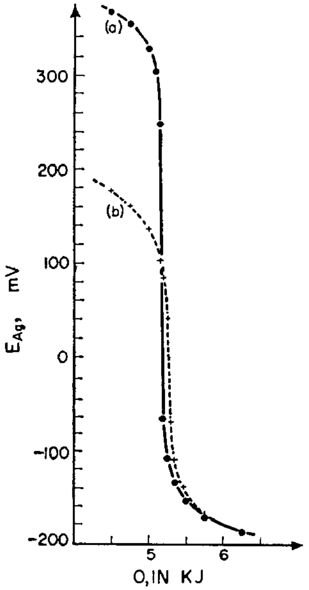

ABB. 3.—Titrationskurven mit KJ 0,1*N*; (*a*) in neutralem Medium; (*b*) in alkalischem Medium.

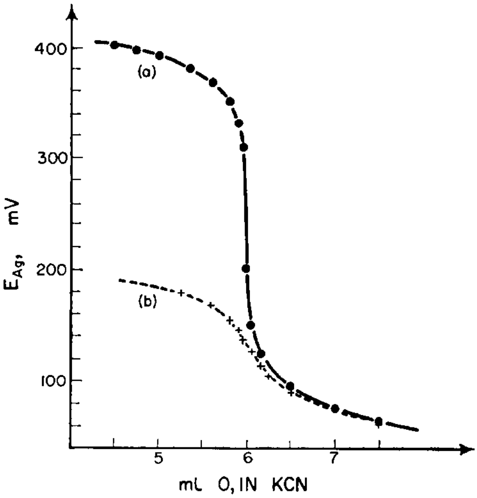

ABB. 4.—Titrationskurven mit KCN 0,1*N*; gemäss Reaktion (*a*) in neutralem Medium; (b) in alkalischem Medium.

Die besten Ergebnisse konnten mit Kaliumcyanid erhalten werden. In diesem Fall benützt man, je nach Alkalinität der Lösung, den ersten Potentialsprung entsprechend der Reaktion:

$$Ag^+ + CN^- \rightleftharpoons AgCN \tag{2}$$

oder den zweiten Potentialsprung, der im Äquivalenzpunkt folgender Reaktion auftritt:

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^- \tag{3}$$

Der erste Sprung ist relativ klein (Abb. 4). Trotzdem sind die Ergebnisse besser als beim Titrieren mit Kaliumjodid, obzwar auch hier immer um 0,4-0,6 % zu viel gefunden wurde.

Um entsprechend der Reaktion (3) zu titrieren, muss die zu titrierende Lösung stark alkalisch sein, damit die Konzentration der freien Silberionen soweit zurückgedrängt wird, dass ein Ausfällen von Silbercyanid nicht mehr eintritt. Das erreicht man sobald die Alkalinität höher als 1*N* ist, was einem Anfangspotential der Silberelektrode von annähernd +100 mV gegenüber der Kalomelelektrode entspricht (Abb. 1).

Wenn man in diesen Bedingungen titriert, erhält man die besten Resultate, die praktisch gleich sind mit jenen die sich beim umgekehrten Titrieren (Cyanid mit Silber) in neutraler Lösung ergeben (Abb. 5).

Bekanntlich ist beim Titrieren einer neutralen Silbersalzlösung mit Kaliumcyanid, der zweite Potentialsprung, entsprechend der Reaktion:

$$AgCN + CN^- \rightleftharpoons Ag(CN)_2^-$$

unsicher, da sich das Gleichgewicht sehr langsam nach rechts verschiebt. Beim Titrieren in alkalischem Medium hingegen wird ein Ausfällen von Silbercyanid verhindert und daher ist auch der Potentialsprung, bei kürzester Einstellzeit, am richtigen Platz.

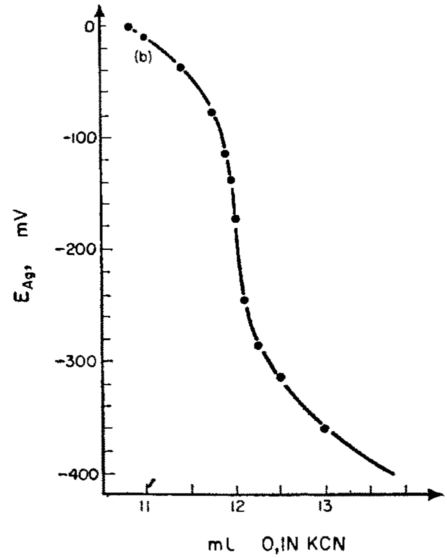

Abb. 5.—Titrationskurve mit KCN 0,1*N* in alkalischem Medium, gemäss Reaktion (3).

BESPRECHUNG DER ERGEBNISSE

Aus den Titrationskurven ist zu ersehen dass die geprüften Titriermittel zu hohe Werte ergeben, wobei die Abweichungen beim Kaliumbromid und Kaliumjodid besonders gross sind.

Es könnten folgende Quellen systhematischer Fehler in Betracht kommen: Beim Titrieren sinkt die Alkalinität der zu titrierenden Lösung, was zu einem Ansteigen des Potentials der Indikatorelektrode (Abb. 1) und damit zu einer Verspätung des Potentialsprunges führt.

Es gibt zwei Möglichkeiten diesen Effekt auszuschalten:

(a). Alkalinisierung des Titriermittels, damit die Alkalinität der zu titrierenden Lösung konstant bleibt;

(b). Alkalinisierung der zu titrierenden Lösung bis zu einem Wert für den der Verdünnungseffekt vernachlässigbar ist (Abb. 1).

Beide Methoden haben beim Titrieren mit Kaliumcyanid zu richtigen Werten geführt. Für Kaliumbromid und Kaliumjodid konnten die Fehler zwar vermindert aber nicht ganz ausgeschaltet werden (Abb. 6).

Daraus kann man auf das Bestehen einer weiteren Fehlerquelle schliessen.

Eine solche könnte die Oxydation der Halogenide in alkalischem Medium auf Kosten gelösten Sauerstoffs sein. Zu dieser Vermutung leitet die Feststellung dass die ersten Tropfen beim Titrieren mit Kaliumjodid eine starke Gelbfärbung der Lösung hervorrufen (freies Jod in alkalischem Medium). Die Farbe verschwindet aber nach einiger Zeit, wahrscheinlich gemäss einer Gesamtreaktion folgender Form:

$$^{-}OOC\cdot C_6H_4\cdot SO_2\cdot NH_2 + J^- + 1/2\ O_2 = {}^{-}OOC\cdot C_6H_4\cdot SO_2\cdot NHJ + OH^-$$

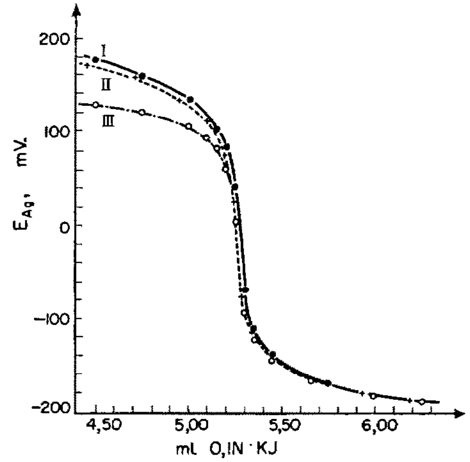

ABB. 6.—Titrationskurven mit KJ 0,1*N* bei verschiedenen Alkalinitäten der zu titrierenden Lösung. I- 0,05*N* NaOH; II- 0,05*N* NaOH mit alkalinisiertem Titriermittel. III- 0,1*N* NaOH.

Um diese Voraussetzung zu prüfen wurden Titrationen mit Kaliumjodid in Gegenwart von Natriumsulfit durchgeführt. Tatsächlich konnten in diesem Fall die gleichen Werte wie beim Titrieren in neutraler Lösung erhalten werden.

Beim Titrieren mit Kaliumcyanid finden die Oxydationsreaktionen durch gelösten Sauerstoff nicht statt und daher sind die Fehler wesentlich kleiner und können durch Verhindern des Verdünnungseffektes ausgeschaltet werden.

Abschliessend kann man sagen, dass beim Titrieren des Silbers in alkalischem Medium, von den untersuchten Titriermittel die besten Ergebnisse mit Kaliumcyanid zu erhalten sind, wenn bis zum zweiten Potentialsprung, entsprechend Reaktion (3) titriert wird.

Mit Kaliumjodid sind ebenfalls gute Werte zu erhalten, aber nur in Gegenwart von Natriumsulfit.

Auch auf diesem Weg danken wir Herrn Dr. Gh. Ciuhandu für das freundliche Überlassen von 4-Sulfonamidobenzoesäure sowie auch für einige Hinweise über noch unveröffentlichte Eigenschaften dieses Reagens.

Summary—The potentiometric titration of silver in strongly alkaline solutions of 4-sulphoamidobenzoic acid has been investigated. Potassium chloride, bromide, iodide and cyanide were used as titrants. Sources of error were investigated and means indicated for their elimination. The separation of silver by means of 4-sulphoamidobenzoic acid in alkaline or carbonate-containing media, followed by a potentiometric titration with potassium cyanide or iodide promises a rapid and accurate method for the determination of silver.

Résumé—Les auteurs ont étudié le titrage potentiométrique de l'argent dans des solutions fortement alcalines d'acide 4-sulfoamidobenzoïque. Les chlorure, bromure, iodure et cyanure de potassium ont été utilisés comme agents titrants. Les causes d'erreurs ont été étudiées et les moyens de les éliminer indiqués. La séparation de l'argent au moyen de l'acide 4-sulfoamidobenzoïque en milieu alcalin ou carbonate, suivie d'un titrage potentiométrique par le cyanure ou l'iodure de potassium est une méthode rapide et précise de dosage de l'argent.

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ÜBER DIE ANFÄNGE DER KOLORIMETRISCHEN ANALYSE

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Zusammenfassung—Es wird ein historischer Überblick der ersten kolorimetrischen und photometrischen Bestimmungen gegeben.

DIE Fachbücher, die über einen Zweig der analytischen Chemie verhandeln, geben in den ersten Seiten meistens einen kurzen, mehr oder weniger richtigen historischen Rückblick der betreffenden Methode. Es ist mir jedoch kein Buch über die Kolorimetrie bekannt, in dem man einen derartigen, wenn auch noch so kurzen Rückblick auffinden könnte.

Die kolorimetrische Methode ist ein der verbreitesten Verfahren der analytischen Chemie. Es schien mir deshalb der Mühe wert die Pioniere dieses Verfahrens aus der Vergessenheit herauszugraben.

Schon bevor irgend einer in Form eines exakten Gesetzes es proklamiert hätte, nahm man an, dass zwischen der Farbenstärke von färbigen Lösungen und der Konzentration der die Farbe liefernden Substanz eine direkte Proportionalität besteht. Diese Annahme entstand offensichtlich aus der alltäglichen Beobachtung des praktischen Lebens.

Ich fand aus dem Jahre 1845 die erste Beschreibung einer auf Farbenvergleich beruhenden Bestimmung. Sie stammt von Heine[1] und verhandelt über die Bromidbestimmung in Mineralwassern. Er benützte hiezu die braungelbe Färbung die Brom mit Äther gibt.

Im folgenden Jahr (1846) veröffentlichte Jacquelain[2] ein Verfahren zur Kupferbestimmung auf Grunde einer Titration bis Farbengleicheit mit Hilfe einer ammonalkalischen Kupferlösung von bekanntem Kupfergehalt.

Herapath bestimmte mit Hilfe von Vergleichslösungen 1852 Eisen auf Grunde der mit Rhodanid gebildeten Färbung[3]. Der Vergleich erfolgte ebenfalls in Epruvetten vor einem weissen Papier. Er wendete bald das Verfahren zu verschiedenen praktischen Bestimmungen an, z.B. zur Bestimmung des Rhodanids in Speichel.[4]

Man findet aus dem Jahre 1853 das erste turbidimetrische Verfahren, das ebenfalls von Herapath entworfen war. Mit Hilfe von Vergleichslösungen bestimmte er Jodid auf Grunde der dunklen Färbung die der suspendierte Niederschlag des Palladiumjodids in den Lösungen erzeugt[5].

1853 konstruierte Müller ein Gerät, mit dessen Hilfe die Auswertung von kolorimetrischen Bestimmungen seiner Meinung nach genauer erfolgen kann. Er nannte das Gerät Komplementer-Kolorimeter[6].

In einer folgenden Veröffentlichung[7] berichtete Müller über gewisse Modifikationen des Gerätes. Er empfahl zur Auswertung statt farbigen Glasplatten, die auf ein für allemal einen Standardvergleich ermöglichen, die Anwendung von Vergleichslösungen, die dieselbe Substanz in bekannter Konzentration enthalten. Er untersuchte derart das Verhalten von Eisenrhodanid, Kupferammoniak und Chromatlösungen und stellte z.B. fest, dass die Eisenrhodanidfärbung zwischen den Konzentrationsgrenzen von 0,00075–0,003 g Fe/100 ml zur Bestimmung geeignet ist und dass die Färbung von der Säure- und Rhodanidkonzentration abhängig ist.

Dehm[8] konstruierte 1864 einen neuartigen Kolorimeter, bei welchem schon zwei Zylinder nebeneinander standen in welchen ebenfalls Röhre beweglich und die Flüssigkeitsschichten biplan begrenzt waren. Man konnte von oben durch eine Linse beide Röhre auf einmal betrachten. In dem einen Zylinder befand sich Wasser auf einer blauen Glasplatte, in dem anderen die zu bestimmende Kupferammoniaklösung. Die Höhe der wässrigen Lösung regelte man solange bis die Farbe in beiden Zylindern gleich wurde. Die Ermittelung der Konzentration ergolgte ebenfalls durch Vergleichslösungen.

Auf diesem Weg schritt Duboscq[9] weiter, der 1870 direkt mit der Vergleichslösung die Färbung der unbekannten Lösung verglich und das Licht durch Glasprismen führte, so dass die eine Hälfte des Sehkreises von dem durch den einen Zylinder, die andere von dem durch den zweiten Zylinder kommenden Licht beleuchtet wurde.

Soviel über die Anfänge der Kolorimetrie. Jetzt folge noch einiges über die Anfänge der Photometrie. Bei der sogenannten Photometrie erfolgt die Bestimmung nicht durch Konzentrations- oder Schichthöheänderung der farbigen Lösungen, sondern man schwächt oder erhöht die Intensität eines monochromatischen Lichtes im notwendigen Masse.

Theoretisch beruht die Photometrie auf dem Lambert-Beer-schen Gesetz. Lambert veröffentlichte 1760 ein Werk mit dem Titel *Photometria.* Das Buch ist von reinem optischem Inhalt. In diesem Werk berichtete er über seine Untersuchungen bezüglich des Verhältnisses zwischen der Lichtabsorption und der Schichtbreite von festen Stoffen, in erster Linie von Glas. Er fand, dass wenn ein Licht von Intensität I eine Glasschicht von einer gewissen Längeneinheit durchschreitet, seine Intensität auf $I \cdot \frac{1}{\mathrm{n}}$, im Falle des Fortpflanzens durch eine zweite Schicht von gleicher Länge auf $I \cdot \frac{1}{n} \cdot \frac{1}{n}$ sinkt. Beträgt die Breite in Längeneinheiten m, so ist die Intensität des austretenden Lichtes

$$I = \frac{I}{n^m}$$

Es soll jedoch erwähnt werden, dass schon vor Lambert, im Jahre 1729 Bougouer[10] dasselbe Gesetz feststellte.

Beer untersuchte dann 1852 die Lichtabsorption in färbigen Lösungen, stellte das Verhältnis zwischen der Dicke der durchstrahlten Lösung und deren Konzentration fest und führte den Begriff des Absorptionskoefficienten ein: "Unter dem Absorptionscoefficienten wollen wir den Coefficienten der Schwächung verstehen, welche die Amplitude eines Lichtstrahls erleidet, wenn dieser durch die Längeneinheit eines absorbierenden Stoffes sich fortpflanzt."[11] Er berechnete den Absorptionskoefficienten von verschiedenen färbigen Lösungen wie von Kupfer- und Chromsalzen. Der Ausdruck des Extinktionskoefficienten stammt von Bunsen und Roscoe. Sie nannten in ihren photochemischen Versuchen den Reciproken derjenigen Schichtdicke so, bei deren Durchschreiten die Lichtintensität auf $\frac{1}{10}$ des ursprünglichen Wertes sinkt. Es lag jedoch bei dieser Gelegenheit kein analytisches Problem vor.[12] Den Bunsen-schen Koefficienten zog zur Konzentrationsbestimmungen zuerst Vierordt heran.

Absorptionsspektroskopie benützten zuerst Bahr und Bunsen[13] zu quantitativen Bestimmungen.

Der Vergleich erfolgte nicht auf Grunde von Lichtintensitätsregelung, sondern mit Hilfe von Konzentrationsänderung. Lichtintensitätsänderung benützten zuerst Govi und Vierordt. Bei dem Spektralapparat von Govi befanden sich vor dem Spalt zwei Prismen übereinander, die das aus zwei Quellen kommende Licht auf eine halbdurchsichtige Platte projizierten. Ein schmaler Spalt diente dazu um das zur Untersuchung geeignete Gebiet vom übrigen Spektrum zu separieren. Die gleiche Lichtintensität wurde durch geeignete Regelung der Entfernungen der Lichtquellen gesichert. Govi benützte seine Apparatur jedoch nur zu physikalischen Messungen.[14] Später trat er gegenüber Vierordt mit Prioritätsansprüchen auf.[15] Diese waren jedoch ganz unberechtigt, da es zweifellos ist, dass zu analytischen Zwecken eine derartige Apparatur zuerst Vierordt konstruierte und benützte.

Bei Vierordts erstem Apparat bestand der Spalt aus einem unteren und oberen Teil. Die Breite beider konnte durch eine Mikrometerschraube geregelt werden. Vor dem Spalt setzte er einen planparallelen Glastrog, den er bis zur Hälfte mit der zu untersuchenden Lösung füllte. Ein Teil des aus einer Petroleumlampe kommenden Lichtes durchschritt die Lösung und den unteren Spalt, der andere Teil pflanzte sich über die Lösung und durch den oberen Spalt durch. Das durch das Fernrohr betrachtete spektrale Sehfeld gab somit im oberen Teil das reine Spektrum, im unteren Teil das durch das vorgelegte Medium veränderte Spektrum der Lichtquelle. Bei gleicher Spaltbreite war das Spektrum des Lichtes, das durch die Lösung kam, natürlich dunkler. Durch Regelung der entsprechenden Spaltbreite machte er die beiden Spektren gleich. Die Regelung der Spaltbreite erfolgte durch eine Trommel, die gemäss der Durchlassung in 100 Teilen eingeteilt war. Die zu den einzelnen Durchlassungswerten gehörenden Extinktionswerte gab er tabellarisch an, mit Hilfe dieser konnte man leicht die Konzentrationen ermitteln. Um das Spektrum auf das gewünschte Gebiet zu verengen wandte er in dem Okularrohr verschiebbare Blendungen an, welche ausser den zu untersuchenden, sämtliche Teile des Spektrums abblendeten. Vierordt bestimmte derart Permanganat, Chromat, Kupferammoniak, Fuchsin, Blutfarbstoff und weitere Substanzen[16] (1870).

Um den durch einseitige Regelung der Spalte hervorgerufenen Fehler, nämlich dass dadurch nicht nur die Lichtintensität, sondern auch im gewissen Masse die Qualität des Lichtes geändert wird, zu beseitigen, konstruierten Glan,[17], weiterhin zu gleicher Zeit Hüfner[18] Photometer bei denen nicht durch Spaltregelung, sondern durch Polarisation die Lichtintensitäten geregelt wurden.

Bis zu 1880 verfügte also die analytische Chemie über beide Typen der Photometer (Spaltregelung und Polarisation) aus denen dann alle weitere Apparattypen abstammten.

Zur lichtelektrischen Auswertung soll Berg das erste Patent im Jahre 1911 erhalten haben.[19]

BIOGRAPHISCHE DATEN

Bahr, Jöns Fridrik (1815–1875): Adjunkt an der Universität Upsala.
Beer, August (1825–1863): Professor der Mathematik an der Universität Bonn.
Bougouer, Pierre (1698–1758): französischer Astronom und Mathematiker.
Bunsen, Robert Wilhelm (1811–1899): Professor der Chemie an der Universität Heidelberg.
Duboscq, Jules (1817–1886): Inhaber einer optischen Werkstätte zu Paris.
Glan, Paul (1846–1898): Professor an der Universität Berlin.
Govi, Gilberto (1826–1889): Physiker, Professor der Physik an den Universitäten in Florenz, Turin und Neapel.
Heine, Carl (1808–?): Direktor von Berg- und Hüttenwerken in Böhmen.
Herapath, Thornton John (1830–1858): Chemiker in der Industrie in England u. Südamerika.
Hüfner, Carl Gustav (1840–1908): Professor der organischen und physiologischen Chemie an der Universität Tübingen.
Jacquelain, Augustin (1804–1885): Chemiker in der Industrie in Frankreich.
Lambert, Johann Heinrich (1728–1777): Zuerst Buchhalter, dann Hauslehrer, endlich Oberbaurat zu Berlin.
Müller, Alexander (1828–1906): Professor an der höheren Gewerbeschule zu Chemnitz, nachher Professor der Agrikulturchemie an der Universität Stockhlom.
Vierordt, Carl (1818–1884): Arzt, Professor der Physiologie an der Universität Tübingen.

Summary—A historical account of the earliest colorimetric and photometric determinations is presented.

Résumé—L'auteur présente un compte-rendu historique des dosages colorimétriques et photométriques les plus récents.

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UV SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF SELENIUM WITH *o*-PHENYLENEDIAMINE*

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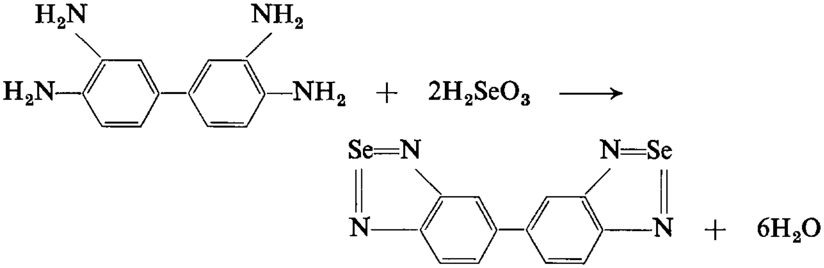
(*Received* 14 *March* 1960)

Summary—3:3′-Diaminobenzidine is an excellent reagent for selenium and the semi-molecule of the reagent, *o*-phenylenediamine, is found to be even better. This forms piaselenol with selenous acid over the pH range of 1·5 to 2·5, which may be extracted with toluene. From the absorbance at 335 mμ of the toluene extract, selenium is determined. Of many different ions tested only iron^{III}, tin^{IV} and iodide ions interfere. But iron^{III} can be masked with EDTA.

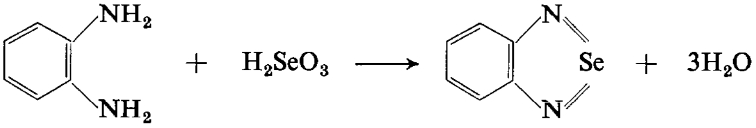
INTRODUCTION

A SELECTIVE colorimetric reagent for selenium^{IV}, 3:3′-diaminobenzidine, was first introduced by Hoste and Gillis.[1,2] The reagent forms an intense yellow product, piaselenol, with selenium in an acidic medium. Cheng[3] recently reported that the piaselenol could be extracted with toluene between pH 6 and 7, and the quantity of selenium could be determined from the absorbance at 420 mμ. The following reaction scheme was presented:



The functional group of 3:3′-diaminobenzidine reacting with selenium is the diamine at the ortho position. The semi-molecule of the reagent, *o*-phenylenediamine, could also react with selenium.

Hinsberg[4] described in 1889 the reaction of *o*-phenylenediamine with selenium^{IV} as follows:



piaselenol

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[*] Read at the 8th annual meeting of Japan Analytical Chemistry Society held in Okayama, September 1959.

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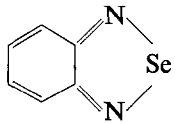
Piaselenol was easily prepared by mixing the aqueous solutions of *o*-phenylenediamine hydrochloride and selenous acid. It was recrystallised from the alcoholic solution as white needles which melt at 76°. He also stated that aromatic orthodiamine derivatives could react with selenium but that the aromatic meta- or para-diamines and the aliphatic diamines could not.

According to Luzzati[5] the structural formula was found by X-ray analysis to be as follows:



In this paper, the determination of selenium was studied with *o*-phenylenediamine as in the procedure described by Cheng[3] for 3:3′-diaminobenzidine.

REAGENTS AND APPARATUS

o-Phenylenediamine hydrochloride solution: 0·2% aqueous solution, freshly prepared, although the solution could be stored for a few days in a refrigerator.

Standard selenium solution: 1·4053 g SeO_2 dissolved in 1 litre of water (1·001 mg of Se in 1 ml). A Se solution 1·001 μg per ml was prepared by diluting the stock solution.

Standard piaselenol solution: 43·5 g piaselenol dissolved in 250 ml toluene. A piaselenol solution, 3·48 μg per ml (as selenium, 1·5 μg) was prepared by diluting the stock solution with toluene.

Formic acid: 80% and 2·5*M*.

EDTA solution: 0·1*M*.

Other reagents were of analytical reagent grade.

Shimadzu Model QB-50 spectrophotometer with 1-cm quartz cell.

Horiba Model M-3 Glass-electrode pH meter.

EXPERIMENTAL AND DISCUSSION

Spectral properties

An aliquot containing 25 μg of selenium was placed in a 100-ml beaker. The solution was diluted to approximately 50 ml with water after adding 2 ml of 2·5*M* formic acid. The pH was adjusted to between 2 and 3. Two ml of 0·2% *o*-phenylenediamine was added to the solution, and it was then allowed to stand for 2 hours. The absorbance curves of this solution and of a blank without selenium were measured. After the solutions were neutralised with 7*M* ammonium hydroxide to a pH between 6 and 7, the absorbance curves were measured again (Fig. 1).

The same maximum at 335 mμ was found in the absorbance curves of those different pH solutions containing 25 μg of selenium. The above-mentioned solutions were transferred into 125-ml separatory funnels and exactly 10 ml of toluene were added to each. The funnels were shaken vigorously for 30 sec, and the toluene portions were centrifuged for a few min. Their absorbance curves were measured over the range of 300-400 mμ (curves 1, 2, 3 and 4 in Fig. 2). The absorbance curve of the standard piaselenol solution was also measured (curve 5 in Fig. 2).

The curves containing selenium have the same absorption maximum at 335 mμ. This result indicates the formation of piaselenol.

Time required for the formation of piaselenol

On the toluene extract, curve 1 in Fig. 3 shows that at pH 1·8 a constant absorbance value was obtained after standing for 30 min at room temperature. Curve 2 shows

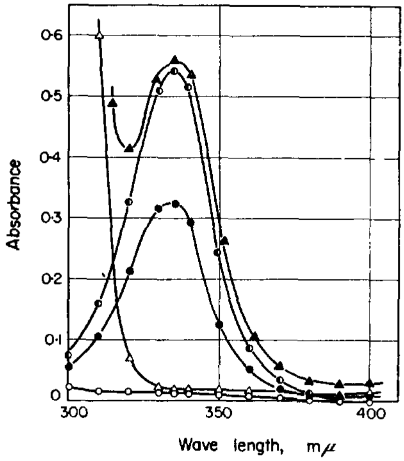


Fig. 1.—Absorbance curves of aqueous solution.
○ *o*-phenylenediamine in water at pH 2–3. (Curve 1)
● 25 μg of Se in 50 ml of water at pH 2–3. (Curve 2)
△ *o*-phenylenediamine in water at pH 6–7. (Curve 3)
△ 25 μg of Se in 50 ml of water at pH 6–7. (Curve 4).
Water as blank.

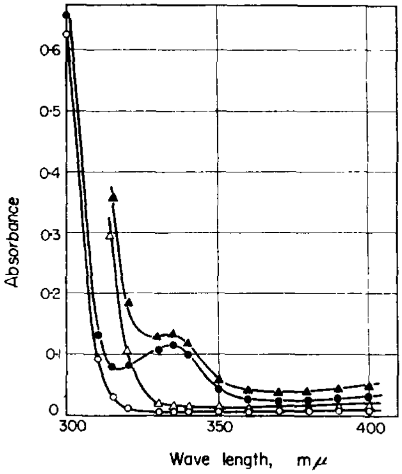


Fig. 2.—Absorbance curves of toluene solution.
○ *o*-phenylenediamine in toluene at pH 2–3. (Curve 1)
○ 25 μg of Se in 10 ml of toluene at pH 2–3. (Curve 2)
△ *o*-phenylenediamine in toluene at pH 6–7. (Curve 3)
△ 25 μg of Se in 10 ml of toluene at pH 6–7. (Curve 4)
● piaselenol (15 μg of Se) in toluene. (Curve 5).
Toluene as blank.

that at pH 0·05 (adjusted by 2*N* hydrochloric acid instead of formic acid) a better value was not obtainable even after standing for 4 hours.

On standing for 24 hours the aqueous solution turned deep brown, because the reagent was decomposed by air.

Though heating hastens the formation of piaselenol, it is not recommended under ordinary conditions, because the reagent decomposes at the same time.

Effect of pH

Piaselenol was formed only in acid medium. After 2 hours to allow the formation of piaselenol at various pH values, 10 ml of toluene were added. The absorbances of toluene extracts were measured at 335 mμ (Fig. 4). Between pH 1·5 and 2·5, a constant value was obtained.

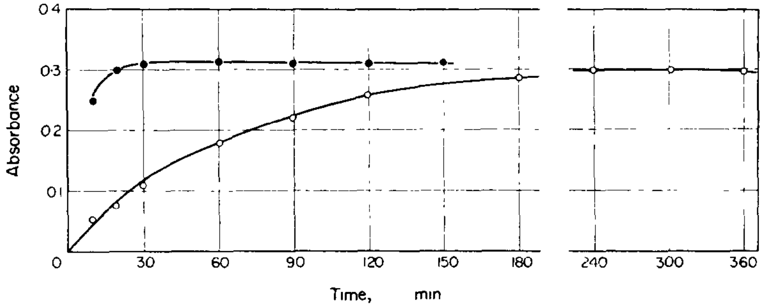
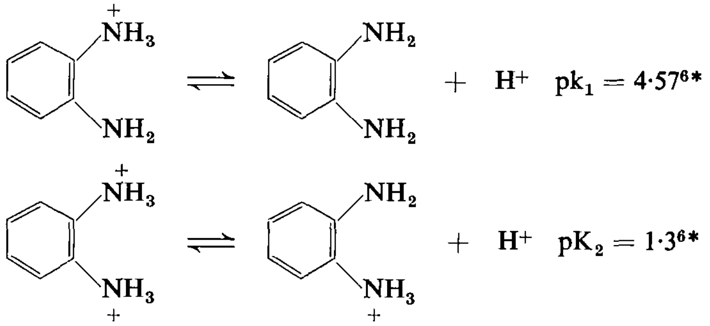


FIG. 3.—Effect of time of standing on maximum formation of piaselenol.
● 15 μg of Se in 10 ml of toluene pH 1·8. (Curve 1)
○ 15 μg of Se in 10 ml of toluene pH 0·05. (Curve 2)

The following explanation may be proposed for this phenomenon. In the acid medium, selenous acid and *o*-phenylenediamine behave as follows:

$$H_2SeO_3 \rightleftharpoons H^+ + HSeO_3^-, \quad pK_1 = 2\cdot6$$



At pH below 2·6, selenous acid will be predominantly in the undissociated form, whereas *o*-phenylenediamine will be in the singly protonated form. Below pH 1·3, *o*-phenylenediamine exists in the doubly protonated form. Since the optimum reactivity observed is in the range of pH 1·5 ~ 2·5, we can conclude that the reactive species are the undissociated selenous acid and the singly protonated *o*-phenylenediamine.

Solvent extraction

In each extraction, 10 ml of toluene was used for approximately 50 ml of the solution containing selenium. The toluene extract from the acid medium was colourless, but that from the medium neutralised with ammonium hydroxide was coloured pale pink. When the absorbance curve of the neutralised solution was measured, a new absorption

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* In 50% alcoholic solution.

maximum appeared at 420 mμ, which influenced the absorbance at 335 mμ. The absorbances at 335 mμ and 420 mμ of the reagent alone were measured over various pH ranges. Though the absorbance at 420 mμ was not directly connected with pH, it was related closely to the absorbance at 335 mμ (Fig. 5). After the formation of piaselenol, the aqueous solution was adjusted to various pH values and extracted with toluene. The absorbance at 335 mμ was measured and corrected by the value at 420 mμ according to Fig. 5. The results are shown in Fig. 6.

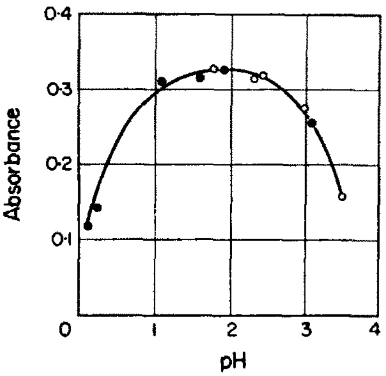

FIG. 4.—Effect of pH on colour development of piaselenol.
○ formic acid. ● hydrochloric acid.

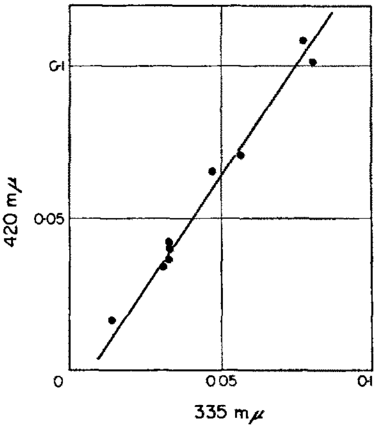

FIG. 5.—Correction curve for colour development in an alkaline medium.

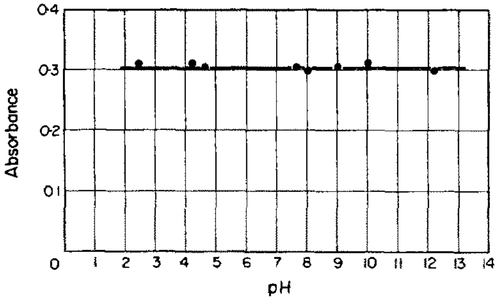

FIG. 6.—Effect of pH on extraction of piaselenol with toluene. 15 μg of Se in 10 ml of toluene.

From Fig. 6, a constant value was obtained whether or not the aqueous solution was neutralised before the extraction. This implies that the neutralisation is not essential and that the extraction can be carried out without it after standing for 2 hours.

Back extraction of standard piaselenol with solution of varying pH

Ten ml of standard piaselenol solution were added to 50 ml of each of the aqueous solutions, adjusted to various pH values. The back extraction was carried out by the same procedure as the extraction. The absorbances at 335 mμ were plotted against pH (Fig. 7). The absorbances are constant from pH 0 to 13 and this indicates that the neutralisation before the extraction is not necessary. The recoveries are about 97%

and the absorbance values are somewhat higher than those of Fig. 6. The extractability from the solution in which piaselenol is formed is about 95%.

Procedure

Place an aliquot containing not more than 30 μg of selenium in a 100-ml beaker. Dilute to approximately 50 ml with water after adding a few ml of 80% formic acid. Adjust the pH to between 1·5 and 2·5. Add 2 ml of 0·2% *o*-phenylenediamine solution and set aside for 2 hr at room temperature. Transfer to a 125-ml separatory funnel, add exactly 10 ml of toluene, and shake vigorously for 30 sec. Centrifuge the toluene portion for a few min. Separate, and determine the absorbance at 335 mμ, using a reagent as blank.

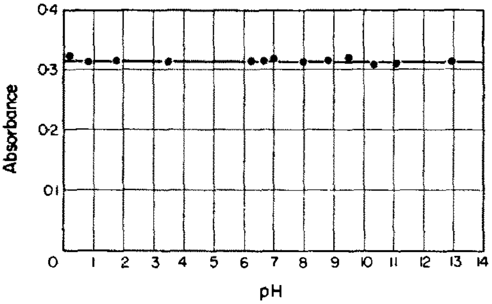

FIG. 7.—Back extraction of standard piaselenol with solutions of varying pH.

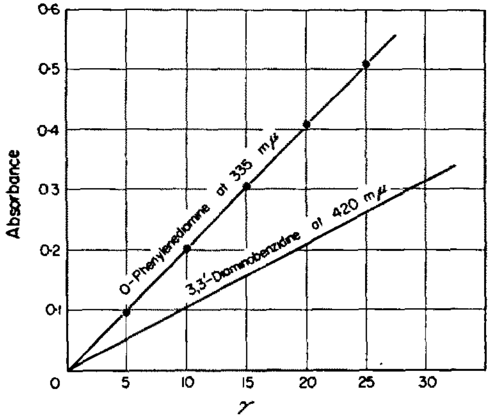

FIG. 8.—Calibration curves for selenium.

The calibration curve follows Beer's law up to 25 μg of selenium per 10 ml of toluene. For comparison with 3:3'-diaminobenzidine, the calibration curve at 420 mμ is also shown in Fig. 8.

Interference studies

The effects of the presence of many different ions are summarised in Table I. 15 μg of selenium were added to aqueous solutions containing different salts. The determination was made by the above-mentioned procedure.

Aluminium, ammonium, antimony, arsenic, barium, cadmium, calcium, chromium cobalt, copper, lead, magnesium, manganese^{II}, nickel, potassium, sodium and zinc ions do not interfere. An aqueous solution containing bismuth should be adjusted to pH 0, because the ion precipitates as bismuthyl hydroxide even at pH 1. Thus in the presence of bismuth, the pH must be very low to obtain the correct value for selenium. Iron^{III} and tin^{IV} also interfere.

Chloride, nitrate, sulphate, phosphate and tartrate ions do not interfere, but iodide ion disturbs the formation of piaselenol.

The interference of iron^{III} may be effectively eliminated by the addition of EDTA to the sample solution[3]. The excess of EDTA may deposit in acid solution, but the determination can be carried out by extraction and centrifugation without any difficulty.

TABLE I. ABSORBANCES OF 15 μg OF SELENIUM IN PRESENCE OF VARIOUS SALTS

Salt, 0·1*M*	*ml*	Absorbance	Salt, 0·1*M*	*ml*	Absorbance
$CuSO_4$	1	0·310	$(NH_4)_2SO_4$*	2g	0·315
	5	0·310		5g	0·314
	30	0·312	$Ni(NO_3)_2$	5	0·307
$ZnSO_4$	1	0·312	$MnSO_4$	30	0·306
	5	0·308	$KAl(SO_4)_2$	30	0·304
	30	0·305	$KCr(SO_4)_2$	30	0·298
$MgCl_2$	1	0·311	$SbOC_6H_4O_6$	30	0·306
	5	0·299	$CaCl_2$	30	0·303
	30	0·302	$Ba(NO_3)_2$	30	0·305
$Pb(NO_3)_2$	5	0·305	$CdCl_2$	5	0·302
	30	0·305		30	0·310
$Co(NO_3)_2$	5	0·313	$CdSO_4$	30	0·308
$BiCl_3$	30	0·162	$KNaC_4H_4O_6$	30	0·306
	10	0·283	$(NH_4)_2HPO_4$	30	0·301
			$AsCl_3$	30	0·297
$SnCl_4$	30	0·004	$FeNH_4(SO_4)_2$	5	0·043
KI	30	0·044			

* Added as solid.

Acknowledgement—The authors wish to express their sincere thanks to Professor Koichi Emi for his encouragement.

Zusammenfassung—3,3′-Diaminobenzidin ist ein ausgezeichnetes Reagens auf Selen; das Semimolekul, o-Phenylendiamin, wurde als noch besser gefunden. Es bildet Piaselenol mit seleniger Säure im pH-Bereich 1·5–2·5. Dieses kann mit Toluol extrahiert werden. Durch Messung der Absorption des Extraktes bei 335 mμ kann das Selen bestimmt werden. Von vielen untersuchten Ionen stören nur Fe(III), Zinn(IV) und Jodid. Eisen kann mit EDTA maskiert werden.

Résumé—La 3-3′ diaminobenzidine est un excellent réactif du sélénium, et la semi-molécule du réactif, l'o-phénylènediamine se trouve même être meilleure. Celle-ci forme avec l'acide sélénieux le piasélénol dans le domaine de pH 1,5–2,5, et celui-ci est extrait par le toluène. L'absorption du corps extrait par le toluène à 335 mμ, permet de doser le sélénium. Parmi les nombreux ions essayés, seuls le fer(III), l'étain(IV) et l'iodure gênent. Le fer(III) peut être dissimulé par l'EDTA.

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PRELIMINARY COMMUNICATION

Precipitation of metal cupferrates from homogeneous solution

(*Received* 23 *June* 1960)

THE ammonium salt of nitrosophenylhydroxylamine, known as cupferron, is one of the most important and versatile reagents used in analytical separations. Although more than fifty years have passed since its introduction by Baudisch[1], considerable interest still centres around its use, as shown by recent publications. The method of precipitation from homogeneous solution has not yet been applied to cupferron precipitates.

Heyn and Brauner[2] devised a method for the generation of α-nitroso-β-naphthol from β-naphthol and sodium nitrite in acetic acid medium. This method of generating the precipitant from an organic parent compound by nitrous acid appeared to be appropriate for the synthesis of cupferron also. Copper, iron and titanium have been determined by this method.

When acidic solutions of appropriate cations are mixed with solutions of β-phenylhydroxylamine and sodium nitrite, the cupferrate of the metal is generated and precipitated. Cupferron itself, however, is not precipitated in the reaction mixture and the reagents produce the cupferrate directly. This is an advantage because cupferron is not very soluble in water, and in the conventional procedure it precipitates along with the cupferrate. Moreover, cupferron decomposes in acidic medium, in which the precipitation is almost universally carried out. The decomposition products tend to contaminate the precipitate. In the present method the precipitate is obtained from water-soluble substances which are not precipitated under the conditions of precipitation. It is only necessary to filter off the precipitate after digestion, if desired. The precipitates thus obtained are not curdy, and are more easily filtered than those obtained by direct precipitation.

The β-phenylhydroxylamine required for precipitation can be prepared easily[3] and then recrystallised from benzene. This substance is not very stable at room temperature, but can be stored in a refrigerator for more than a month.

For carrying out the precipitation, the cation solution is diluted to about 100 ml and cooled well in an ice-bath. Phenylhydroxylamine and sodium nitrite are also dissolved separately and cooled. When the solutions are cold (0–5°), phenylhydroxylamine is filtered, and the clear solution is added to the cation solution. The mixture is stirred and sodium nitrite solution is added quickly. Precipitation begins after a few sec and stirring is continued for about 5 min. The precipitate is filtered off after 15 min, washed with 1:20 HCl, followed by 1:3 NH_4OH, and finally with water. It is then dried, ignited and weighed as oxide.

In order to establish the composition of the precipitate and to prove its identity with the precipitate obtained with cupferron, C, H and N analyses were run, which showed good agreement with the theoretical values.

Further proof of the identity of the precipitates was obtained by X-ray diffraction patterns, which proved to be identical with those obtained from the corresponding cupferrates prepared by the conventional procedures.

Work is in progress with a number of cations.

Summary—A method has been devised to synthesise metallic cupferrates in homogenous solutions. Sodium nitrite and β-phenylhydroxylamine solution are added to a cold acidic solution of the cations and generate and precipitate the metallic cupferrate. Good results have been obtained for iron, titanium and other metals. This method produces more easily filtered precipitates than are obtained by direct precipitation.

Zusammenfassung—Eine Methode zur Fällung von Metallkupferonaten aus homogener Lösung wurde beschrieben. Natriumnitrit und 2-Phenylhydroxylaminlösung werden zur sauren, kalten Lösung des Metallions zugegeben und erzeugen so den Niederschlag. Gute Ergebnisse wurden bei Eisen, Titan und anderen Metallen erzielt. Die Methode führt zu Niederschlägen die leichter filtrierbar sind, als die durch direkte Fällung erhaltenen.

Résumé—Les auteurs ont établi une méthode de synthèse des cupferrates métalliques en solution homogène. Du nitrite de sodium et une solution de β phénylhydroxylamine sont ajoutés à une solution acide froide des cations, produisent et précipitent le cupferrate métallique. De bons résultats ont été obtenus pour le fer, le titane et d'autres métaux. Cette méthode produit des précipités plus facilement filtrables que ceux obtenus par précipitation directe.

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SHORT COMMUNICATIONS

The ultraviolet spectra of some inorganic solids*

(*Received* 15 *February* 1960)

Summary—The ultraviolet spectra of nine sulphates, three chromates, and two nitrates have been investigated in the solid state using the KBr disc technique. The sulphate samples show absorption in the 260 mμ and 300 mμ regions; the chromates at both 270 mμ and 370 mμ; and the nitrates absorb slightly in the 290 mμ region. Qualitative identification of these ions in artificial samples has been demonstrated.

INTRODUCTION

THE measurement of ultraviolet spectra of solutions has long been a recognised analytical tool, especially for the characterisation and analysis of organic samples. Similar investigations involving inorganic materials have not been as abundant and many of the inorganic systems examined have involved co-ordination complexes in which the ligands are organic in nature. In attempting to identify or assign observed absorption bands, it is frequently of value to study the role of the solvent. In such studies it is convenient, even necessary, to have the corresponding spectrum of the "anhydrous" material.

The ultraviolet spectra of solids can be obtained by studying single crystals, by examining the powder sublimed or otherwise deposited onto a quartz plate, or by measuring the optical properties of a compacted sample in which the absorbing substance has been diluted with another material which is transparent in the particular spectral region being investigated. This latter method is the basis of the widely used potassium bromide disc technique of Stimson and O'Donnell[1] which, although originally proposed for both I.R. and U.V. work, has been most extensively employed in the infrared range with organic samples.

This investigation was undertaken, therefore, to determine the applicability of the KBr disc technique to the study of simple inorganic compounds in the 220–400 mμ region.

EXPERIMENTAL

Apparatus

Spectrophotometer: A line-operated Beckman spectrophotometer, Model DU, was used for all absorbance measurements.

Sample die: A standard Perkin–Elmer KBr evacuable die, part number 021–106, was used for all disc preparations. Sample discs thus prepared were approximately 0·5 inch in diameter.

Sample holders: Matched 1-cm silica cells were used for all solution measurements. For the solid samples a special holder was constructed. This holder accommodates four discs at one time and replaces the usual cuvette holder in the DU without modification of the cell compartment. Construction details for this holder have been described by Waggoner[2].

Reagents

Potassium bromide: Reagent-grade potassium bromide was ground to approximately 100-mesh in an agate mortar and then dried in a vacuum oven at 100° for 24 hr before disc preparation. Blanks of equal weight were made from this same material to be used with the disc samples.

Other reagents: All other reagents were analytical grade and were used without further purification. Distilled water was used in the preparation of all solutions and as a blank for all solution measurements.

Sample preparation

Solutions: Aqueous solutions were prepared by standard volumetric techniques using the same reagents as were employed in making the solid samples. The concentrations finally employed varied considerably from solute to solute but were generally chosen after examination of several different concentrations.

Solid samples: Both the potassium bromide and the sample compounds were separately ground in an agate mortar to approximately 200-mesh particle size before being pressed. For the preparation of a disc, the appropriate weight of potassium bromide was taken and the desired weight of sample added directly, its weight being determined by difference from the weight of the mixture. The mixture was then thoroughly blended by further grinding together, placed in the die, and pressed under approximately 25,000 psi for 3 min. Discs thus prepared were quite transparent and faintly coloured if the sample material was coloured. For all sulphate samples, the final composition of the discs was 0.1 mg of metal sulphate in 500 mg of KBr; for the chromate samples, 0.2 mg of metal chromate in 400 mg of KBr. The nitrate samples were more concentrated, containing 2.1 mg of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.7 mg $Co(NO_3)_2 \cdot 6H_2O$, respectively, each in 400 mg of potassium bromide.

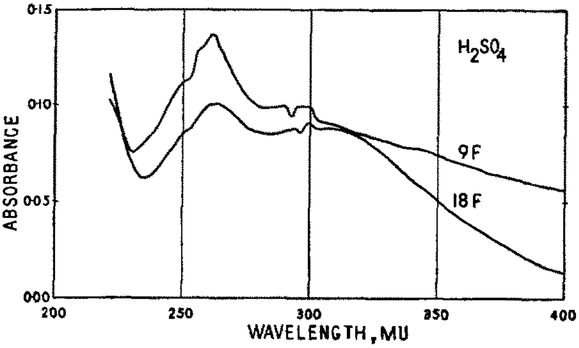

FIG. 1.—Absorbance curves for sulphuric acid solutions.

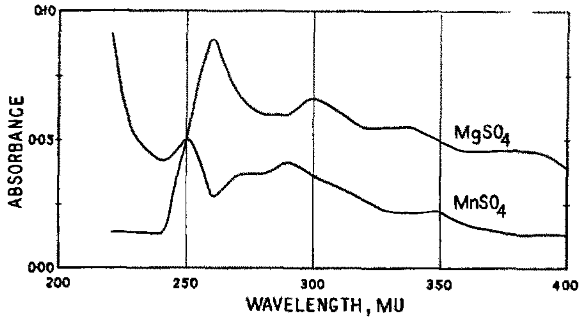

FIG. 2.—Absorbance curves for Mn^{II} and Mg sulphate solutions.

DISCUSSION

The absorbance curves obtained with aqueous solutions of sulphates were rather disappointing. Sulphuric acid samples (9*F* and 18*F*) gave the spectra shown in Fig. 1. The more prominent peak occurs at 260 mμ and the smaller shoulder at 290–300 mμ.

With the solutions of metallic sulphates the spectra varied considerably in appearance. Fig. 2 shows the curves obtained with $MnSO_4 \cdot H_2O$ (*ca.* 5*F*) and $MgSO_4 \cdot 7H_2O$ (*ca.* 5*F*) and Fig. 3 those for $CoSO_4 \cdot 7H_2O$ (*ca.* 0.5*F*) and $NiSO_4 \cdot 6H_2O$ (*ca.* 0.5*F*). The other salts examined (Cd^{++}, K^+, VO^{++}, UO_2^{++}) gave curves which generally decreased in absorbance as the wavelength increased, with no significant maxima.

Bastian, Weberling and Palilla[3] have reported that a solution of $Fe_2(SO_4)_3$ has a peak at 300–305 mμ. Buck, Singhadeja and Rogers[4] found a peak at 267 mμ for a solution of $NiSO_4$ in dilute KCN.

The absorbance curves obtained with $0.001F$ aqueous chromate solutions are given in Fig. 4. The two maxima occur at approximately 270 mμ and 370 mμ. These results are in good agreement with the results reported by Schaumann[5], Davies and Prue[6] and Griffiths, Lott and Symons[7], all of whom reported peaks at 270 mμ and 370 mμ.

Inconclusive results were obtained with the two nitrate solutions examined. A slight increase in absorbance in the 300 mμ region was noted but it was not sufficiently pronounced to permit a definite assignment. Past workers, notably Morton and Riding[8], von Halban[9], Buck, Singhadeja and Rogers[4], have reported that the nitrate ion absorbs in solution at 300–302 mμ.

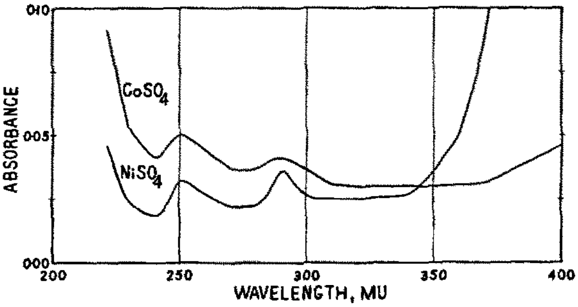

FIG. 3.—Absorbance curves for Co^{II} and Ni^{II} sulphate solutions.

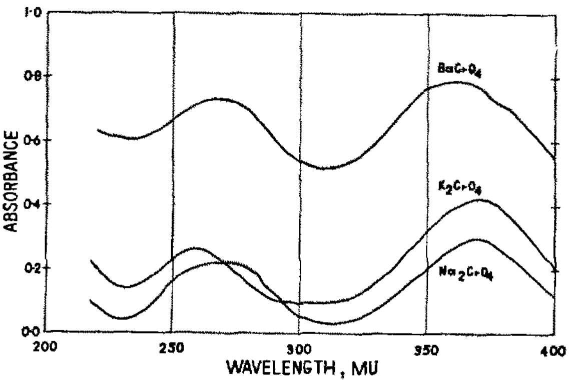

FIG. 4 —Absorbance curves for chromate solutions.

Figs. 5 and 6 show the absorbance curves obtained with the metallic sulphates in potassium bromide discs. In every case, a maximum or at least a levelling effect, was noted in both the 260 mμ and 300 mμ regions.

The curves obtained with the three solid chromate samples are shown in Fig. 7. Maxima at approximately 275 and 375 mμ are evident. Griffiths, Lott and Symons[7] have reported that crystals of $BaCrO_4$ and K_2CrO_4 absorb at 275–280 mμ and at 360–375 mμ.

The curves obtained with the two solid nitrate samples examined are shown in Fig. 8. A maximum at 280–295 mμ was reported by Maslakowez[10] for crystalline KNO_3. Schaumann[5] reported that crystals of $NaNO_3$ absorbed at 2915 Å.

In order to test the practicality of utilising this technique for the qualitative detection of individual inorganic ions, two synthetic mixtures were prepared and examined. The first mixture contained 0.4 mg $CdSO_4$ and 0.2 mg K_2CrO_4 in 400 mg KBr. The absorbance curve for this mixture is shown in Fig. 9 with the tentative assignments indicated. The second mixture contained 0.4 mg K_2SO_4, 0.2 mg K_2CrO_4 and 0.9 mg KNO_3 in 400 mg KBr. The curve for this mixture is shown in Fig. 10, also with the tentative assignments as to the causes of the maxima noted. In both of these mixture curves, no explanation is offered for the extraneous peaks.

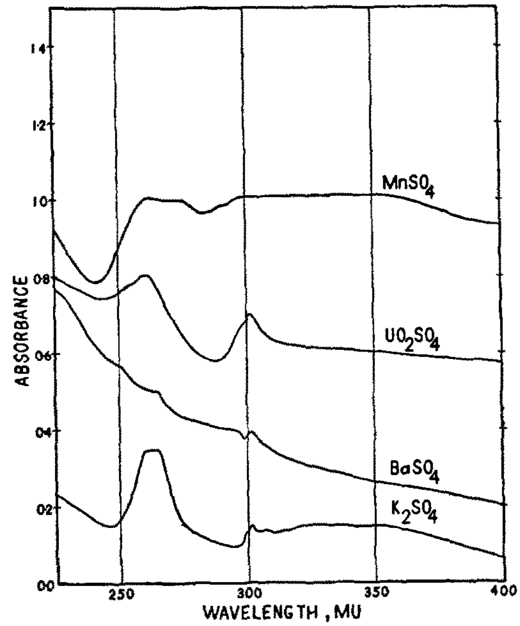

FIG. 5.—Absorbance curves for sulphates in potassium bromide.

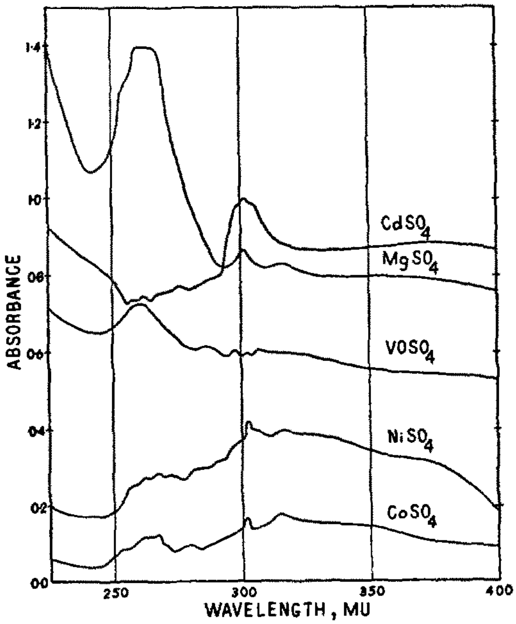

FIG. 6.—Absorbance curves for sulphates in potassium bromide.

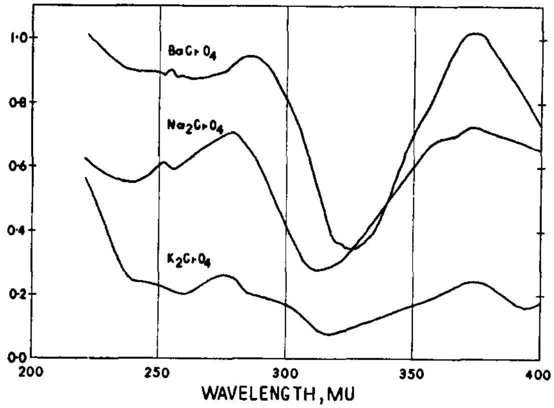

FIG. 7. Absorbance curves for chromates in potassium bromide.

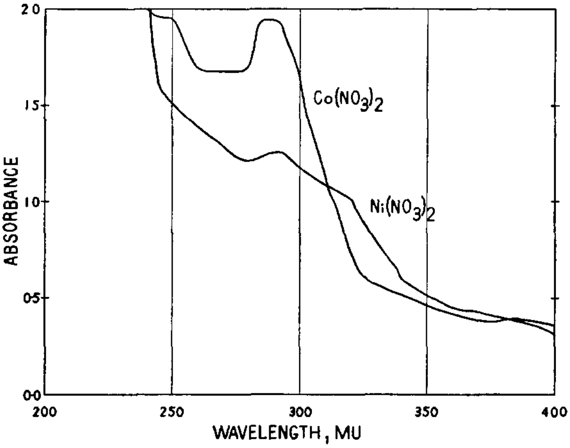

FIG. 8. Absorbance curves for nitrates in potassium bromide.

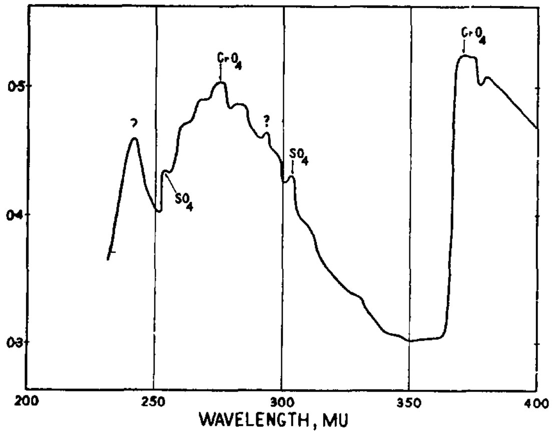

FIG. 9. Absorbance curve for sulphate-chromate mixture in potassium bromide.

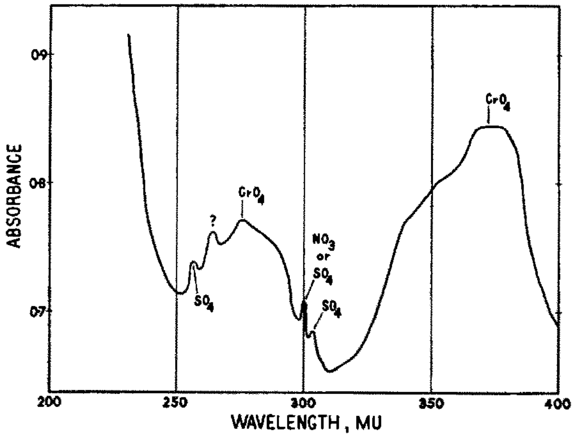

FIG. 10. Absorbance curve for sulphate-chromate-nitrate mixture in potassium bromide.

CONCLUSIONS

On the basis of this preliminary study it appears that the potassium bromide method of sampling inorganic materials for examination in the ultraviolet spectral region does give promising results. Solvent effects are eliminated and the procedure is more rapid than those employed with single crystal samples. The existence of definite absorption bands, apparently attributable to specific ionic groups, recommends this technique to the qualitative analysis of solid mixtures.

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Zusammenfassung—Das Ultraviolettspectrum von neun Sulfaten, drei Chromaten und zwei Nitraten in festem Zustande wurde untersucht, unter Verwendung der der Scheibentechnik. Die Sulfatproben wiesen Absorption im Bereiche 260 und 300 mμ, die Chromate sowohl bei 270 und 370 mμ. Die Nitrate absorbierten bei 290 mμ, aber nur sehr wenig. Der qualitative Nachweis dieser Substanzen in kunstlichen Probemischungen wurde demonstriert.

Résumé—Les spectres ultra-violets de neuf sulfates, trois chromates et deux nitrates à l'état solide ont pu être étudiés par la méthode du disque de KBr. Les échantillons de sulfate montrent une absorption dans les régions 260 et 300 mμ; les chromates à la fois à 270 et à 370 mμ; et les nitrates absorbent faiblement à 290 mμ. L'identification qualitative de ces ions dans des échantillons artificiels a été démontrée.

A new spot test for auric gold with N:N′-di-2-naphthyl-*p*-phenylenediamine

(*Received* 7 *July* 1960)

THE alkyl derivatives of *p*-phenylenediamine are widely used in qualitative microanalysis. These compounds, known as Wurster reagents[1], react with some oxidising ions and substances to give intensively coloured compounds of the meriquinoidal type. Free halogens[2], vanadium[3], manganese[4] and copper[5] are detectable owing to their reaction with dimethyl-*p*-phenylenediamine.

It was found in our laboratory that auric gold and some of the platinum metals—platinum, iridium and ruthenium ions—also oxidise dimethyl-*p*-phenylenediamine to Wurster Red.

In order to find a reagent with more selective analytical properties, we studied the redox behaviour of some alkyl and aryl derivatives of *p*-phenylenediamine. In the course of this investigation we found that N:N′-di-2-naphthyl-*p*-phenylenediamine is a highly selective and sensitive reagent for auric gold.

EXPERIMENTAL

Reagent solution: a saturated acetone solution of N:N′-di-2-naphthyl-*p*-phenylenediamine (an Eastman Organic Chemical product purified by recrystallisation in an acetone–water mixture).

Gold solution: $\frac{1}{194}$ *M* $HAuCl_4$ standard solution prepared by diluting 1 g of $HAuCl_4 \cdot 3H_2O$ (a B.D.H. product) in 500 ml of H_2O containing 2·5 ml of conc HCl.

Procedure

One drop of the neutral or slightly acid (pH value 3–8) test solution is mixed in a depression of a white spot plate with one or two drops of a freshly prepared solution of the reagent. In the presence of auric gold a red-brown precipitate or coloration is formed. The reagent solution itself is faintly yellow-brown; hence with small amounts of auric gold, the colour should be compared with that of a blank test.

Limit of identification: 0·1 μg of gold.

Limit of dilution: 1:500,000.

Interfering ions

Only iron^{III}, cerium^{IV} and osmium^{VIII} cations interfere with the reaction. The interference of cerium^{IV} and iron^{III} ions can easily be eliminated by the addition of some crystals of potassium fluoride, which precipitate Ce^{IV} and mask Fe^{III}. In the presence of the extremely volatile osmium tetroxide, the solution should be boiled before the test.

Most of the anions and even most of the oxidising anions do not interfere with this test. Nevertheless, the ferricyanide and permanganate ions oxidise the reagent similarly to auric gold. Also sulphite and sulphide ions prevent the reaction between gold ions and the reagent owing to their reducing action.

These interferences can be prevented as follows:

(i) In the presence of ferricyanide or of sulphite ions, the test solution should be boiled with H_2O_2 (6%).

(ii) In the presence of permanganate ions, 1 or 2 drops of a 0·1% solution of As_2O_3 and 1 or 2 drops of a 10% solution of Na_2CO_3 (to adjust the pH) should be added.

(iii) The sulphide ions, if present, should be precipitated with zinc carbonate.

Summary—A new selective and sensitive spot test for the detection of auric gold is proposed, based on the redox reaction between the latter and N:N′-di-2-naphthyl-*p*-phenylenediamine.

Zusammenfassung—Eine neue selektive und empfindliche Tüpfelprobe für dreiwertiges Gold wurde angegeben. Die Probe beruht sich an die Redoxreaktion zwischen dreiwertiges Gold und N:N′-di-2-naphthyl-*p*-phenylenediamine.

Résumé—Un nouvel essai à la goutte sensitif et sélectif pour la détection de l'or(III) est proposé. L'essai est basé sur la réaction d'oxyréduction entre l'or et le N:N'-di-2-naphthyl-*p*-phénylènediamine.

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Interference of iron in the determination of 12-tungstophosphoric acid with tri-*n*-butylamine

(*Received* 6 *July* 1960)

IN a recent paper on the determination of tungsten as tris(tributylammonium)12-tungstophosphate[1] we mentioned that the presence of iron complicated the analysis. The nature of the complications is now outlined.

EXPERIMENTAL

Reagent and standard solutions were prepared, and tungstophosphate precipitates formed and separated under the same conditions as before, except that 50% more tributylamine was used for precipitations. Unless otherwise indicated, precipitates were left overnight before filtration.

When solutions containing sodium tungstate and disodium hydrogen phosphate were acidified with hydrochloric acid and iron^{II} sulphate and tributylammonium chloride then added, the onset of precipitation was usually retarded. As the amount of iron^{II} was increased, the weights of precipitates obtained after drying at 140° increased to a maximum. A much smaller amount of iron^{III} gave a similar result. Ignition products of the heaviest precipitates (Table I) appeared to be $Fe_2O_3 \cdot P_2O_5 \cdot 24WO_3$ (200 mg of tungsten = 265·9 mg, including 5·1 mg of iron and 2·8 mg of phosphorus), which suggested that the amine had been co-ordinated about the iron ion in the original precipitates. The precipitate obtained in the experiment with 280 mg of iron^{III} was weight-constant from 105°–150° and contained 18·3, 3·57 and 1·75% of carbon, hydrogen and nitrogen, respectively. The corresponding values for $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40} \cdot 2H_2O$, which might conceivably

TABLE I. EFFECT OF IRON SALTS ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRIBUTYLAMINE
100 Ml of 0·25*N* hydrochloric acid solution contain 200 mg of tungsten^{VI} and 85 mg of phosphate (PO_4)

	Fe^{II}				Fe^{III}		
Iron added, *mg*	25	150	700	1400	25	280	1400
Precipitate obtained at 140°, *mg*	337	347	357	356	355	354	352
Ignition product (750°), *mg*	263	266	267	267	267	266	264
Ratio of weights obtained at 140° and at 750°, R_1	1·28	1·31	1·34	1·33	1·33	1·33	1·33
Iron in ignition product, *mg*	2·4	3·9	4·9	5·6	5·1	—	5·9
Phosphorus in ignition product, *mg*	2·6	3·4	(4·1)	3·2	3·2	—	2·8
Tungsten (approx.) in filtrate, *mg*	0·5	0·5	0·5	0·5	0·5	—	4

Résumé—Un nouvel essai à la goutte sensitif et sélectif pour la détection de l'or(III) est proposé. L'essai est basé sur la réaction d'oxyréduction entre l'or et le N:N'-di-2-naphthyl-*p*-phénylènediamine.

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Interference of iron in the determination of 12-tungstophosphoric acid with tri-*n*-butylamine

(*Received* 6 *July* 1960)

IN a recent paper on the determination of tungsten as tris(tributylammonium)12-tungstophosphate[1] we mentioned that the presence of iron complicated the analysis. The nature of the complications is now outlined.

EXPERIMENTAL

Reagent and standard solutions were prepared, and tungstophosphate precipitates formed and separated under the same conditions as before, except that 50% more tributylamine was used for precipitations. Unless otherwise indicated, precipitates were left overnight before filtration.

When solutions containing sodium tungstate and disodium hydrogen phosphate were acidified with hydrochloric acid and iron^{II} sulphate and tributylammonium chloride then added, the onset of precipitation was usually retarded. As the amount of iron^{II} was increased, the weights of precipitates obtained after drying at 140° increased to a maximum. A much smaller amount of iron^{III} gave a similar result. Ignition products of the heaviest precipitates (Table I) appeared to be $Fe_2O_3{\cdot}P_2O_5{\cdot}24WO_3$ (200 mg of tungsten = 265·9 mg, including 5·1 mg of iron and 2·8 mg of phosphorus), which suggested that the amine had been co-ordinated about the iron ion in the original precipitates. The precipitate obtained in the experiment with 280 mg of iron^{III} was weight-constant from 105°–150° and contained 18·3, 3·57 and 1·75% of carbon, hydrogen and nitrogen, respectively. The corresponding values for $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}{\cdot}2H_2O$, which might conceivably

TABLE I. EFFECT OF IRON SALTS ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRIBUTYLAMINE
100 Ml of 0·25*N* hydrochloric acid solution contain 200 mg of tungsten^{VI} and 85 mg of phosphate (PO_4)

	Fe^{II}				Fe^{III}		
Iron added, *mg*	25	150	700	1400	25	280	1400
Precipitate obtained at 140°, *mg*	337	347	357	356	355	354	352
Ignition product (750°), *mg*	263	266	267	267	267	266	264
Ratio of weights obtained at 140° and at 750°, R_1	1·28	1·31	1·34	1·33	1·33	1·33	1·33
Iron in ignition product, *mg*	2·4	3·9	4·9	5·6	5·1	—	5·9
Phosphorus in ignition product, *mg*	2·6	3·4	(4·1)	3·2	3·2	—	2·8
Tungsten (approx.) in filtrate, *mg*	0·5	0·5	0·5	0·5	0·5	—	4

represent the composition, are 18·4, 3·63 and 1·79%. The use of very large excesses of the amine increased the weights of precipitates by only 1 mg.

The same general effects were observed when 2:4-dimethylquinoline, 8-hydroxyquinoline or cinchonine replaced tributylamine. The cinchonine complex was weight-constant from 105°–200°, analyses for nitrogen and carbon showed that 2·59 molecules of dibasic cinchonine were associated with 12 of tungsten, and the ignition product was apparently $Fe_2O_3{\cdot}P_2O_5{\cdot}24WO_3$.

TABLE II. EFFECT OF VARYING AMOUNTS OF ACID AND PHOSPHATE ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRIBUTYLAMINE IN PRESENCE OF IRON SALTS

200·0 Mg of W = 354·7 mg of $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}{\cdot}2H_2O$ (heated at 140°) = 265·9 mg of $Fe_2O_3{\cdot}P_2O_5{\cdot}24WO_3$; R_1, the ratio of these weights, is 1·334.

200·0 Mg of W = 311·5 mg of $(C_{12}H_{27}N{\cdot}H)_3PW_{12}O_{40}$ (heated at 210°) = 258·6 mg of $P_2O_5{\cdot}24WO_3$; R_2, the ratio of these weights, is 1·204.

X is the weight of ignition product in mg.

Hydrochloric acid	Phosphate (PO_4)	Weight of iron^{III} present, *mg*											
		25			100			280			700		
N	*mg*	X	R_1	R_2	X	R_1	R_2	X	R_1	R_2	X	R_1	R_2
0·2	85	267*	1·33					265*	1·33		262*	1·34	
	425	266†	1·34		264†	1·34		260†	1·34		255†	1·34	
					265	1·34							
	850				257	1·33					248	1·34	
0·5	85										265†	1·34	
	425	264†	1·31		265†	1·34		265†	1·34		261†	1·34	
	850	266	1·33		264	1·34		263†	1·34		259	1·34	
1·0	425										264†	1·33	
	850	263	1·28	1·22	260	1·27		263	1·32		258	1·33	
	1700							251	1·31	1·25	251	1·32	1·26
2·0	850				259	1·26	1·20	259	1·26		258	1·27	
	1700										261	1·26	1·20
					Iron^{II}						Iron^{II}		
2·0	850				260	1·25	1·20				260	1·25	1·20

* Filtration after 1 hr. All other precipitates were filtered the following day.

† 12-Tungstophosphoric acid used.

In further experiments with tributylamine (see Table II) the amounts of acid and phosphate were varied. Results, except those indicated by †, relate to a standard solution prepared by *gradually* acidifying a solution containing sodium tungstate and a 10-fold excess of disodium hydrogen phosphate. Additional phosphate, as orthophosphoric acid, and iron salts were added to acidified solutions, the volumes of which were made 100 ml before precipitation.

Although 12-tungstophosphoric acid that had been degraded by means of an excess of sodium hydroxide solution and then re-formed in presence of additional phosphate by slow or rapid addition of acid, gave with tributylamine the weight of precipitate expected for undegraded material,[1] it was now found that *rapidly* acidified solutions of degraded tungstophosphate, to which ferric chloride and tributylamine were then added, gave variable lower weights of precipitates and values of R_1 than *slowly* acidified solutions, which alone gave the results expected for 12-tungstophosphoric acid plus ferric chloride.

With reference to Table II, R_1 values of 1·33–1·34 allied with values of $X < 265$ mg denoted incomplete precipitation of tungsten. This was associated with high concentrations of iron and phosphate and counteracted somewhat by a higher acid concentration. As a rule, supernatant solutions yielded a little more precipitate after further standing. R_2 values of 1·20 for 2*N* hydrochloric acid solutions indicated, however, that tris(tributylammonium)tungstophosphate was the product of reaction. Here, ignition products contained $<70\ \mu g$ of iron when 100 and 700 mg of iron^{II} were present during precipitation of tungstophosphate but 0·4 and 0·9 mg, respectively, when iron^{III} was used.

A silver reductor column[2] (length 14 cm, diameter 1 cm) containing 18 g of silver was suitable for reduction of at least 100 mg of iron^{III} in a solution containing 12-tungstophosphoric acid. Fifty ml of sample solution (1*N* hydrochloric acid) and appropriate washings were passed through the reductor, and the acid concentration of the blue effluent, which gradually lost its colour on heating in air, was raised to 2*N* before precipitation and separation of tris(tributylammonium)-tungstophosphate as usual. Two hundred mg of tungsten, alone and in presence of 100 mg of iron, yielded 311·6 ± 0·1 mg of the complex. About 0·4 mg of tungsten found in filtrates was balanced by a little silver chloride in the precipitates.

CONCLUSION

Satisfactory determination of 12-tungstophosphate as the tris(tributylammonium) complex is possible in solutions containing iron^{II}, provided that acid concentration is fairly high. A silver reductor is suitable for reducing iron^{III}. With reference to Table II, determination as the aquopentakis(tributylamine)iron^{III} complex might be feasible if the amounts of phosphate, iron and acid present in the solution before precipitation could be so regulated as to ensure values for R_1 and X of 1·33–1·34 and at least 265 mg, respectively.

When tungsten is precipitated as tungstic acid in presence of iron and phosphate, by digestion with acids and addition of cinchonine,[3] contamination with iron may *not* be entirely due to co-precipitation associated with a single precipitation.

Acknowledgement—We thank Dr. R. A. Chalmers of Aberdeen University for recording the thermal behaviour of some precipitates.

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Summary—When 12-tungstophosphoric acid reacts with tri-*n*-butylammonium chloride in presence of iron salts, a precipitate of apparent composition, $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}\cdot nH_2O$, may form. Reduction of iron^{III} to iron^{II} and precipitation in 2*N* hydrochloric acid solution prevent its formation.

Zusammenfassung—Wenn 12-Wolframphosphorsäure mit Tri-n-butylammoniumchlorid in Gegenwart von Eisen(III)salzen zur Reaktion gebracht wird, resultiert ein Niederschlag der scheinbaren Zusammensetzung $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}\cdot nH_2O$ Reduktion des Eisen(III) zu Eisen(II) und Arbeiten in 2 n Salzsäure verhindert die Fällung.

Résumé—Quand l'acide 12-tungstophosphorique réagit avec le chlorure de tri-n-butylammonium en présence de sels de fer, il peut se former un précipité de composition apparante $[Fe(H_2O)(C_{12}H_{27}N)_5$ $PW_{12}O_{40}\cdot nH_2O$. La réduction du fer(III) en fer(II) et le précipitation en solution acide chlorhydrique 2N empêchent sa formation.

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Talanta, 1960, Vol. 5, pp. 131. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

SIR,

I AM sorry that Mr. Greenfield (*Talanta*, 1960 **4**, 147) should think fit to rebuke me for using part of a sentence from his paper to illustrate poor presentation in a paper describing an analytical method. It should have been evident from the incomplete reference I gave, that I was anxious not to appear discourteous. Furthermore, I had no intention of criticising Mr. Greenfield's method: I merely wanted to set down the actual words used by an author.

Since, however, Mr. Greenfield has chosen to defend the type of wording to which I object, I must reply that his instructions quoted in my letter (*Talanta*, 1960, **3**, 272) are not only difficult to carry out, but that they are unnecessarily precise. Since the sodium peroxide is to be added to a solution containing 55 ml (no limits given) of hydrochloric acid (4*N* "accurately" adjusted within unspecified limits) it is difficult to see how the use of even double the quantity of sodium peroxide would have much effect on the normality of the final solution.[1] In any case, a direction such as "between 0·4 and 0·6 grams of sodium peroxide" would have been adequate, more realistic, and therefore, more likely to inspire confidence in the reader.

In answer to Mr. Greenfield's final paragraph I would say that no matter how good a method is, if the directions for carrying it through are in any way inaccurate or obscure the method cannot be expected to work. If, therefore, an author cannot present his method in a manner that an analyst can easily follow and obtain results with the accuracy the author has claimed, he must get someone else to write it for him.

A. A. MOSS

Department of Mineralogy
British Museum (Natural History)
Cromwell Road, London, S.W.7
24 *June* 1960

[1] 1 drop (0·05 ml) 4*N* HCl $\equiv$ 8 mg Na_2O_2.

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BOOK REVIEWS

Methods of Analysis for Petrochemicals. Edited by E. R. LITTMAN. Chemical Publishing Co. Inc., New York, 1958. pp. 384. $12.00.

To a comparatively new industry, such as the petroleum chemical industry, a comprehensive collection of analytical methods applicable to its products would be a very valuable aid. A book of that type would fill the need of many laboratories and would be welcome to most chemists working in this field.

The present volume does not fill this need. It is not a comprehensive collection of analytical methods used in the petroleum chemical industry, since it leaves out whole areas of vital importance. For instance there is hardly a mention of the analysis of hydrocarbon gases, whether by low temperature distillation, by gas-liquid chromatography, or by spectrographic methods. Analysis of ethylene products, with the exception of that of ethyl alcohol, is not dealt with. Such important products as ethylene oxide and its numerous derivatives, polymers of ethylene or propylene, cannot be found amongst the chemicals with which the book is concerned.

The book contains in effect a collection of analytical methods at present in use at the Enjay laboratories. These methods are necessarily confined to the products handled by the Enjay organisation, which is a subsidiary of the Standard Oil of New Jersey group. This is the reason for the very partial coverage of the field.

On the other hand, there are numerous methods of analysis of petroleum, as distinct from petroleum chemical products, such as determinations of flash points, viscosities, aniline points etc. These methods are of relatively minor interest for the analysis of petroleum chemicals.

Within these limitations, which are not clear from its misleading title, the book gives a good number of sound and well tried methods of analysis for a restricted range of petroleum chemicals and also petroleum products. It deals largely with derivatives of propylene, butylenes and aromatics. Many of the methods are the standard procedures of A.S.T.M. with the additional experience and added details, gathered over many years, by the Enjay laboratories. There are many hints and references to small points, so essential in analytical work, revealing the considerable body of experience available to the author of the book. In the description of practical details, very little, if anything, is omitted. This is not so with regard to theoretical background. For instance, in the description of the determination of water in hydrocarbon gases using the Karl Fischer reagent and the dead stop-method, full experimental details are given, but the electrochemical background to the method is not mentioned. Generally there is also a dearth of literature references.

The book is well produced but the price may be considered high by British readers.

H. STEINER

Heterometry. MORDECHAÌ BOBTELSKY. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Co., Amsterdam, 1960. Pp. vii + 229. 42s.

HETEROMETRY is the study of the formation of precipitates from solution by measuring the light absorbancy of the heterogeneous medium at different ratios of reactants. The method has been devised and developed exclusively by the author and his pupils, as a glance down the list of references at the end of this book will show.

The work is split up into ten chapters, the first four of which outline the development and scope of heterometry, its relationship to other physico-chemical methods (turbidimetry, conductimetry, and potentiometry), technique and instrumentation and analytical aspects. The remaining chapters

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There is little that can be said in favour of this book. The main faults, apart from a number of obvious inconsistencies, lie in the immoderate claims made for the method and the amount of space devoted to experimental detail and speculative discussion based on the results. Most of these claims are made in the chapters (VII—X) dealing with the properties of precipitates. From the ratios of one reactant to another which make up precipitates the reader is often presented with reaction mechanisms and detailed structures of the products without reference to supporting evidence from other sources. It is even claimed (p. 187) in discussing dye complexes that a critical point on the heterometric curve, from which the ratio is derived, provides a "deep insight into the electronic structure of the compound".

Heterometric titrimetry would appear to have definite potentialities in chemical analysis, particularly in the rapid determination of minor constituents in mixtures. While the two chapters (V and VI) dealing directly with chemical analysis are probably the best in the book, even here important aspects tend to be obscured by the detail presented.

Many of the faults of this book may be attributed to the author's difficulty with the language in spite of the fact that he had assistance in correcting it. Accordingly there can be little doubt that greater justice would have been done to heterometry if it had been produced under the guidance of an experienced scientific editor.

S. J. LYLE

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

THIS is a series of monographs on the radiochemistry of the elements produced by the sub-committee on radiochemistry of the National Research Council, U.S.A. The series has grown out of a need for up-to-date and specialised information and procedures. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radiochemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

In the latter section, which occupies the major part of the monograph, there is ample evidence that a careful selection of the known radiochemical techniques for each element has been made. Many originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has been covered up to 1959.

Undoubtedly this series will be of particular interest and value to the radiochemist or the analytical chemist. It has, however, also much to offer to the biochemist and physicist who often use radiochemical techniques in the solution of specific problems.

The following monographs in the series are now available:

[1] The Radiochemistry of Arsenic. Harold C. Beard. January 1960 $0.50.
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R. J. MAGEE

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R. J. MAGEE

Principles and Practice of Gas Chromatography. Edited by ROBERT L. PECSOK. John Wiley and Sons, Inc., New York: Chapman and Hall, Ltd., London, 1959. Pp. xii + 226, 54s.

THIS book has its origins in a first course in gas chromatography given at the University of California, Los Angeles in 1959. All important aspects of gas chromatography are touched upon in 150 pages of text divided into thirteen chapters, of which twelve are contributed separately by four authors and one by the editor. There is also a bibliography which is virtually complete up to 1958 and includes some early 1959 references.

Notwithstanding that the book aims at being an introduction to the subject, nowhere is there given a general introduction to technique, and a reader new to the subject would have difficulty in orienting himself. The real value of the book is for the practitioner of the technique who wishes to acquire a clear understanding of the basic elements on which the method is founded. These are very clearly set out, and are always closely related to practical operation. In consequence, the book contains much general information concerning the choice and control of operating conditions which even experienced and well informed gas chromatographers will find of value. It is on this score that the book justifies its existence and enables the reviewer to give it his recommendation. However, it must be said that the present device of having four independent contributors is an inefficient way of achieving this objective. There is much wasteful repetition of material and, with a high-cost book such as this, one becomes rather sensitive about paying a number of times over, as it were, for the same information. Especially irritating in this connection is the fact that some of the chapters are cut short at a point where they promised to become distinguished contributions, presumably because of the lack of space. Again, it is felt that more space could well have been devoted to recent developments such as ionisation detectors and capillary columns, about which very little indeed is said.

The bibliography consists of the titles of publications, listed in alphabetical order of the authors, and classified by the year of publication; it is a striking illustration of the explosive growth of the subject. Unfortunately, the absence of a subject index related to the bibliography greatly limits the value of the compilation of references.

In order to facilitate rapid publication, the book has been reproduced from typescript by the photo-offset method, but the layout is good and the page appearance pleasing.

DESMOND BRENNAN

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NOTICES

Wednesday–Friday 2–4 *November* 1960: Analytical Groups of the New York and North Jersey Sections of the **American Chemical Society,** New York, Delaware Valley, New England and Baltimore-Washington Sections of the **Society for Applied Spectroscopy and Metropolitan Microchemical Society:** *Eastern Analytical Symposium and Instrument Exhibit.* Hotel New Yorker, New York City.

The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities. The exhibition will consist of 65 manufacturers of scientific apparatus and supplies.

For further information about the meeting contact the Publicity Chairman: E. WYNNE, Fisher Scientific Co., P.O. Box 375, Fair Lawn, N.J., U.S.A.

Monday 27 *February–Friday* 3 *March* 1961: Analytical Chemistry Group, Pittsburgh Section, **American Chemical Society** and **Spectroscopy Society of Pittsburgh:** Twelfth Pittsburgh Conference on *Analytical Chemistry and Applied Spectroscopy.* Penn–Sheraton Hotel, Pittsburgh, Penna., U.S.A.

A symposium entitled *New Frontiers in Optics and Spectroscopy* will be sponsored jointly by the **Pittsburgh Conference** and the **Optical Society of America.**

In addition to the programme of technical papers, there will be an exhibition of the newest instrumentation for analysis.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is 15 October 1960.

All correspondence should be addressed to: Dr. WILLIAM F. HARRIS, Programme Chairman, The Twelfth Annual Pittsburgh Conference, Research Laboratories, Westinghouse Electric Corporation, Pittsburgh 35, Penna., U.S.A.

The B.S.I. News announces, amongst others, the following amendment slips to British Standards:

B.S. 1672: *Methods of testing rubber latex: Part* 2: 1954. *Chemical and physical tests. Amendment No.* 2: *PD* 3683 (*Price* 2*s.*)

B.S. 2782: *Methods of testing plastics: Part* 4: 1958. *Analytical methods and viscosity in solution. Amendment No.* 4: *PD* 3709. (Gratis); *Part* 5: 1958. *Miscellaneous methods. Amendment No.* 3: *PD* 3708. (Gratis).

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AMPEROMETRIC DETERMINATION OF GLUCOSE, FRUCTOSE AND SACCHAROSE AT ZERO APPLIED POTENTIAL

E. MICHALSKI, K. CZARNECKI and M. IGNACZAK
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Summary—An indirect amperometric determination of glucose, fructose, and saccharose has been developed. The sugars are oxidised with cerium^{IV} perchlorate in $1N$ perchloric acid at 60°. After cooling, the excess oxidant is titrated with sodium oxalate solution. The end-point is determined amperometrically at zero applied potential.

EXISTING methods for the determination of sugars can be divided into two groups: physical and chemical. The former include the polarimetric, the densitometric and the refractometric methods. The chemical methods are based on the capacity of the sugar for reducing some oxidants. In most cases a base solution containing copper^{I} salts is the oxidant.[1] As a consequence, the determination of sugars is reduced to different methods of determining the resulting copper^{I} oxide. As under these conditions there is no stoichiometric dependence on the quantity of the resulting copper^{I}, oxide, it is necessary to determine it under exactly the same conditions.

It is characteristic of the methods used hitherto that comparatively weak oxidants were employed, causing only a partial oxidation of the sugar. The application of a stronger oxidant can produce a more complete oxidation of the examined compound.

A method of determining glucose, fructose, and saccharose has been developed by the authors, which consists in oxidising the sugars in an acidic medium by means of cerium^{IV} perchlorate.[4]

EXPERIMENTAL

$0{\cdot}1N$ solution of cerium^{IV} perchlorate in $1N$ perchloric acid: The solution of cerium^{IV} perchlorate was prepared according to the method described by Smith and Getz.[2] It was standardised potentiometrically by means of sodium oxalate. The standardised solution was kept in a dark and cool place. It has been established that the normality remains practically unchanged under these conditions.

$0{\cdot}15N$ solution of sodium oxalate in $1N$ perchloric acid: Sodium oxalate was obtained by the neutralisation of a solution of oxalic acid.[3] The substance obtained after drying served as the standard substance. The conventional weight was dissolved in $1N$ perchloric acid.

The solutions of glucose, fructose and saccharose used for the determinations, were prepared from weighed quantities of material recrystallised from ethyl alcohol. The quantities were dissolved in $1N$ perchloric acid.

Apparatus

In order to determine the end-point of the cerimetric titration an amperometric method at zero applied potential was employed. A saturated calomel electrode was used as reference electrode, and a wire of polished platinum (diameter 0·5 mm, length 8 mm) as an indicator electrode. The electrodes were connected with a galvanometer having a sensitivy of 3×10^{-7} A per scale division. During the determinations the indicator electrode was immovable, but the solution was vigorously stirred. The presence of oxygen was found to have no influence on the results.

The determination of sugars has also been performed by means of an amperometric "dead-stop end-point" method. The electrodes employed were made of platinum wire (diameter 1 mm, length 7 mm). The potential difference applied to the electrodes from outside amounted to 50 mV. The changes in the current intensity were observed with a galvanometer of sensitivity $7{\cdot}8 \times 10^{-8}$ A per scale division.

The determination of glucose

The oxidation of glucose with cerium^{IV} perchlorate may be represented by the equation:

$$CH_2OH(CHOH)_4CHO + 12Ce^{4+} + 6H_2O \rightarrow 6HCOOH + 12Ce^{3+} + 12H^+ \qquad (1)$$

The reaction is relatively slow and it does not permit an immediate titration of the sugar to be made. The determination was performed by adding approximately a two-fold excess of the oxidant to a sample of the examined solution taken from the standard sugar solution with a pipette. The mixture was heated for 35 to 45 min in a water bath at 60°. When small quantities of sugar were examined the time of heating was prolonged. After cooling the solution, the excess cerium^{IV} was back-titrated by means of standard sodium oxalate. To establish the end-point an amperometric method at zero applied potential was employed. The measurement of the current was carried out towards the end of the titration when the solution became almost completely discoloured. Based on the results obtained a curve was drawn of the current intensity versus the volume of reagent added (Fig. 1).

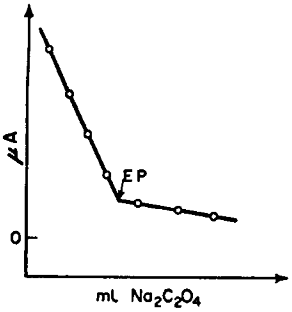

FIG. 1.

To establish the end-point of titration an amperometric "dead-stop end-point" method was also applied. The sudden fall observed in the current intensity at the end-point permits it to be determined without a diagram. The differences between the results obtained by means of both amperometric methods did not exceed experimental error.

By means of the method described 0·6–10 mg of glucose have been determined. Four series of determinations were made, each consisting of 9 to 10 determinations. The results of each series are given in Table I.

TABLE I. AMPEROMETRIC DETERMINATION OF GLUCOSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Glucose Present, *mg*	Glucose Found, mean, *mg*	Mean deviation from mean %error
I	0·1026	0·1487	35	8·44	8·43	0·10
II	0·1026	0·1487	40	3·44	3·43	0·18
III	0·1026	0·1487	45	1·62	1·63	0·55
IV	0·1026	0·1487	45	0·60	0·58	0·75

The determination of fructose

The oxidation of fructose by means of cerium^{IV} perchlorate is according to the equation:

$$CH_2OH(CHOH)_3COCH_2OH + 14Ce^{4+} + 6H_2O \rightarrow 5HCOOH + CO_2 + 14Ce^{3+} + 14H^+ \qquad (2)$$

As in the case of glucose, a two-fold excess of cerium^{IV} perchlorate was added to the examined sugar taken from the standard sugar solution with a pipette. The mixture was heated for 45 min at a temperature of 60°, then the excess of cerium^{IV} was back-titrated with sodium oxalate.

0·6–13 mg of fructose were determined by means of this method. Four series of determinations were made, each of them consisting of 10 to 12 determinations. The results obtained are presented in Table II.

TABLE II. AMPEROMETRIC DETERMINATION OF FRUCTOSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Fructose		Mean deviation from mean %error
				Present, *mg*	Found, mean, *mg*	
I	0·1026	0·1487	45	12·52	12·50	0·09
II	0·1102	0·1487	45	6·57	6·58	0·12
III	0·1102	0·1487	50	2·36	2·35	0·56
IV	0·1102	0·1487	50	0·60	0·62	0·80

The determination of saccharose

Saccharose reacts in a similar way to glucose and fructose. As the reaction takes place in an acidic medium it is preceded by the process of inversion. The products obtained as a result of this process react with cerium^{IV} perchlorate according to equations (1) and (2). The process of oxidation as a whole gives the following overall equation in the case of saccharose:

$$C_{12}H_{22}O_{11} + 26Ce^{4+} + 13H_2O \rightarrow 11HCOOH + CO_2 + 26H^+ + 26Ce^{3+} \qquad (3)$$

As with glucose and fructose, the determination of saccharose was performed by adding an excess of the oxidant to a sample taken from the standard solution with a pipette. The mixture was heated for about 50 min in a water bath at 60°. Then the excess of cerium^{IV} was back-titrated amperometrically. The determination of 0·6–8 mg of saccharose has been performed. Three series of determinations were made, each of them consisting of 10 to 12 determinations. The results obtained are presented in Table III.

TABLE III. AMPEROMETRIC DETERMINATION OF SACCHAROSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Saccharose		Mean deviation from mean %error
				Present, *mg*	Found, mean, *mg*	
I	0·1102	0·1487	45	7·28	7·27	0·21
II	0·1102	0·1487	50	2·00	2·01	0·15
III	0·1102	0·1487	55	0·67	0·65	0·93

CONCLUSION

Milligram quantities of glucose, fructose and saccharose may be determined by oxidising them in an acidic medium with cerium^{IV} perchlorate. The end-point of the reaction has been determined by an amperometric method at zero applied potential, titrating the excess cerium^{IV} perchlorate with sodium oxalate. Several series of determinations of each sugar have been performed, each series consisting of about 10 determinations. The mean deviation from the mean % error has amounted to about 0·2% for quantities of sugar of the order of several mg, about 0·5% for quantities of sugar of the order of 1 mg, and about 0·9% for quantities smaller than 1 mg.

Zusammenfassung—Es wird eine amperometrische Methode zur Bestimmung von Glucose, Fructose und Saccharose beschrieben. Obengenante Zucker werden mit $Ce(ClO_4)_4$ Lösung in 1n Perchlorsäure bei 60°C oxydiert und der Überschuss der Oxydationsmittels durch Rücktitration mit Natriumoxalatlösung zurückgemessen. Endpunkt mit Titration bestimmt man amperometrisch ohne die Aussenspannung.

Résumé—Les auteurs ont élaboré une méthode ampérométrique du dosage de glucose, fructose et de saccharose. Les sucres nommés ont été oxidés en chauffant—environ 60°C—par une solution de perchlorate de cerium(IV) dans 1*N* l'acide perchlorique. L'excès de l'oxydant après le refroidissement a été titré à l'aide de la solution d'oxalate de sodium. Le point d'équivalent était marqué en utilisant une méthode ampérométrique sans applications du potentiel imposé de l'extérieur.

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THE APPLICATION OF METALLOCHROMIC INDICATORS IN COLORIMETRY—I

THE SPECTROPHOTOMETRIC DETERMINATION OF MINUTE AMOUNTS OF COPPER WITH ANALOGUES OF GLYCINE THYMOL BLUE

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Summary—The possibility of application of five different metallochromic derivatives of Thymol Blue (I–V) to the spectrophotometric determination of micro amounts of copper has been studied. The derivative of proline (I), applied in a solution buffered with hexamethylenetetramine and hydrochloric acid, has proved best for this purpose. Absorbance of its copper complex shows only insignificant changes in the pH range from 4·9 to 5·4 and it conforms to Beer's law up to 25 μg of copper^{II} at 595 mμ. Larger quantities of iron^{II}, cobalt^{II}, nickel^{II}, zinc^{II}, lead^{II}, uranium^{VI} and beryllium^{II} interfere.

With the development of chelatometry many new indicators have been recently introduced into chemical analysis, undoubtedly the most important of them being the so-called metallochromic indicators.[1] Their great sensitivity, favourable colour properties and, in some cases, good selectivity are very promising as to their potential application to other fields of analytical chemistry, *e.g.* many colorimetric methods have been developed with the use of these substances.

In the group of "complexone-type" metallochromic indicators only the application of Cresolphthalein Complexone[2] and recently also of Xylenol Orange[3–5] to spectrophotometry have been studied. Other analogous compounds have not been investigated from this standpoint, although many of them are capable of meeting all the requirements necessary for colorimetric reagents. One of the most promising indicators of this type is Glycine Thymol Blue, introduced in recent years into chelatometry.[6] The chelating properties of this substance, as compared with the analogous Methylthymol Blue,[7] are decreased to such an extent by eliminating one carboxymethyl group in the side-chain, that only the reaction with copper is actually applicable; other cations react only weakly or fail to react at all. Analogous condensation products of Thymol Blue with formaldehyde and other aminocarboxylic acids, prepared in connection with the systematic study of new metallochromic indicators,[8] behave similarly. By further modifying the auxiliary functional groups[9] a still higher specificity was reached as compared with Glycine Thymol Blue.

All of the prepared substances are acid-base indicators with the colour properties of the parent dye, *i.e.* Thymol Blue. In an acidic medium, where the original colour of the dye is yellow, they form blue complexes with copper^{II}.[8] The sensitivity of these

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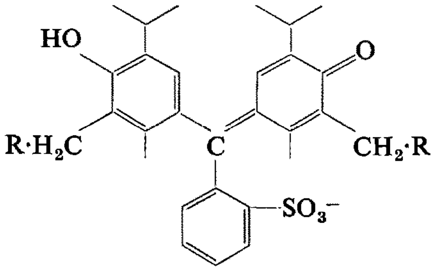
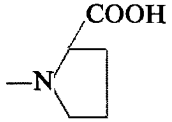
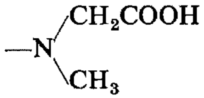
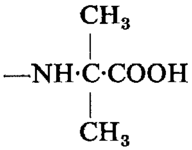
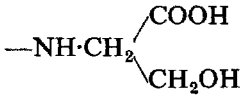
reactions, stability of the colour formed, and sufficient selectivity promise—according to preliminary investigations—the potential use of some of these substances as chromogenic reagents for spectrophotometric determination of copper. From this viewpoint five most satisfactory reagents (I–V) have been studied; the results of this study are reported in this paper.



No.	R	Name
(I)		Proline Thymol Blue
(II)	 $-N{<}^{CH_2COOH}_{CH_3}$	Sarcosine Thymol Blue
(III)	$-NH\cdot CH_2COOH$	Glycine Thymol Blue
(IV)	 $-NH\cdot C(CH_3)_2\cdot COOH$	Methylalanine Thymol Blue
(V)	 $-NH\cdot CH_2{<}^{COOH}_{CH_2OH}$	Serine Thymol Blue

EXPERIMENTAL AND RESULTS

Apparatus and reagents

The absorption spectra of the reagents and their copper complexes were measured by means of a quartz spectrophotometer SF 4 in cells of 1-cm optical path. Other absorption measurements were made on a König-Martens spectrophotometer with an entrance and eye-piece slit width of 0·2 mm. For the pH measurements an Acidimetr AK (Kovodružstvo, Prague), with a high-resistance glass electrode, was used.

0·1 % solutions of reagents (I)–(V) were prepared in double-distilled water; all of these solutions were stable for several weeks. The stock solution (0·001*M*) of copper^{II} was prepared by dissolving 0·2497 g of $CuSO_4\cdot 5H_2O$ (A. R. grade) in double-distilled water and diluting to 1 litre. Working solutions were prepared by appropriate diluting of the stock solution. 0·1*M* solutions of other cations were prepared by dissolving the corresponding salts (A. R. grade). Buffer solutions for the pH range from 4·2 to 6·2 were prepared by mixing a 1*M* solution of hexamethylenetetramine (A. R. grade) and 6*N* hydrochloric acid in the appropriate proportions.

Qualitative test for copper and sensitivity of the reaction

To a 5-ml sample solution of copper buffered with hexamethylenetetramine and hydrochloric acid, 3 drops of the reagent solution were added and the colour formed was compared, after a few sec, with a blank. According to the amount of copper present, the resulting colour was either sky-blue or, with smaller quantities of copper, purple or grey. The sensitivity of the reaction at the optimal pH values is given in Table I.

TABLE I.—SENSITIVITY

Reagent	pH	pD
Proline Thymol Blue	4·9	7·6
Sarcosine Thymol Blue	4·6	7·6
Glycine Thymol Blue	5·4	7·6
Methylalanine Thymol Blue	5·1	7·4
Serine Thymol Blue	6·0	7·4

Absorption spectra

The yellow coloured, slightly acid reagent solutions show an absorption maximum at about 450 mμ. The formation of a copper complex causes a bathochromic shift of about 150 mμ. Fig. 1 shows the absorption spectrum of Proline Thymol Blue (curve 1) and of its copper complex with an excess of the reagent (curve 2) at pH 5·2. Absorption curves of the copper-complexes of all of the compounds studied (I–V) measured against the reagent blanks are illustrated in Fig. 1 and 2.

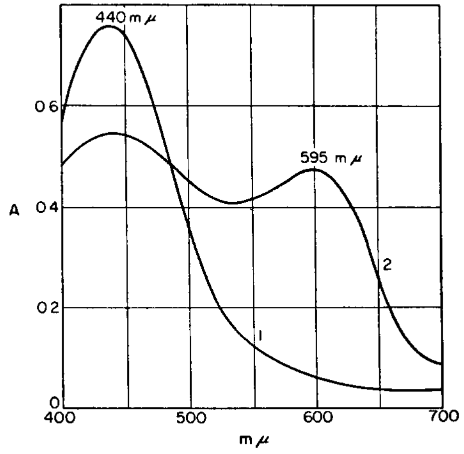


FIG. 1.

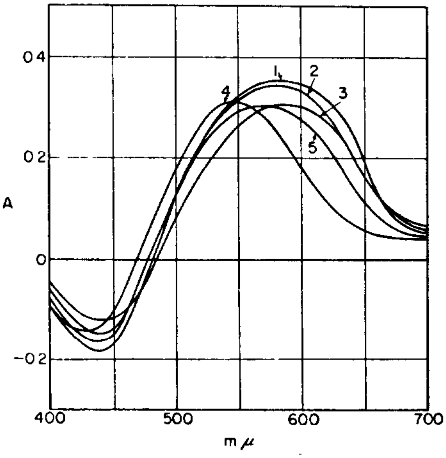


FIG. 2.

Effect of pH and choice of the appropriate buffer

The effect of pH on the sensitivity of the reaction was studied with different buffer solutions. However, their choice was restricted since some of them, *e.g.* citrate, mask the reaction. Hexamethylenetetramine was found to be the most convenient buffer. Acetate buffer is less suitable for it slightly decreases the sensitivity, and gives negative results in the presence of larger amounts of iron$^{\text{III}}$ or tin$^{\text{II}}$.

The relation between the absorption of the copper complex and pH was studied in hexamethylenetetramine buffer at different wavelengths and with an excess of the reagents. Fig. 3 shows the absorbancy plotted against pH at wavelengths of absorption maxima (see Fig. 2) in the pH range from 4·2 to 6·2. All the obtained curves have two branches: the ascending one represents the successive formation of the complex up to a maximum lying at the pH at which the reaction with copper is quantitative. A moderate slope of the second branch is caused by the commencing acid-base change of the reagent blank against which the measurements have been made. From this standpoint, Proline

Thymol Blue has been found to be the most convenient reagent for the spectrophotometric determination of copper, since the pH-curve of this reagent shows only insignificant changes of absorbancy in rather broad limits around pH 5·2.

Calibration curves

The validity of Beer's law has been verified in the hexamethylenetetramine-hydrochloric acid buffer at a reagent concentration of 0·2 ml of a 0·1% solution in a total volume of 25 ml. Measurements were made at wavelengths of the maximum difference in absorbancy of the copper complex against the reagent blank (see Fig. 2), and at two different pH values. Proline Thymol Blue follows Beer's law best of all these reagents. Calibration curves of this dye are illustrated in Fig. 4. Curves No. 1 were obtained with 5-cm cells at pH 4·9 and 5·4, respectively, and conform to Beer's law up to 10 μg of copper^{II} in 25 ml. Calibration curve No. 2 was obtained at the same pH values in 2-cm cells for amounts of copper up to 25 μg in an equal volume. A slight "gooseneck" curvature occurs but even in this case Beer's law is followed well within the limits of error of measurement.

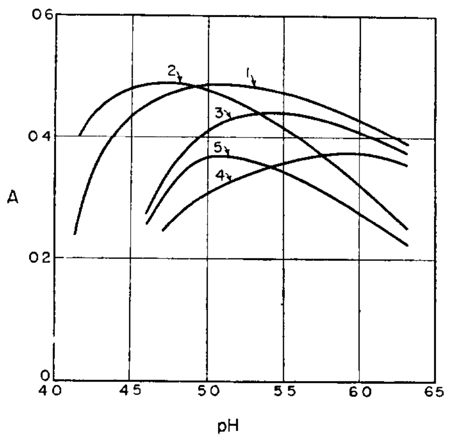


Fig. 3.

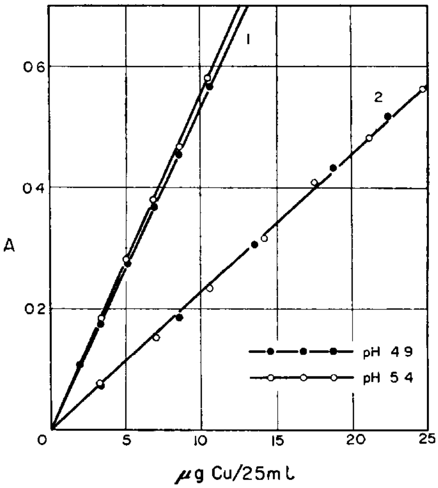


Fig. 4.

Influence of foreign ions

The effect of foreign ions was studied by absorption measurements in the solutions of copper complexes of all of the reagents with 0·2 ppm of copper^{II} at the same wavelengths as in the preceding determination. As interfering were classified those ions causing a greater difference in absorption—in comparison with the absorption of the copper complex alone—than 0·005 units. On the basis of the results obtained the reagents studied may be arranged in the following sequence of increasing sensitivity to foreign ions: Proline Thymol Blue, Methylalanine Thymol Blue, Sarcosine Thymol Blue, Serine Thymol Blue and Glycine Thymol Blue. From this viewpoint Proline Thymol Blue was again found to be the most convenient reagent for the application studied, which under the conditions used for the determination of copper reacts only with cobalt, zinc, nickel, lead, uranium and beryllium. Iron^{II} interferes if present in an approximately 2·5-fold excess; however, this interference may be easily removed by oxidation to the tervalent form and by the subsequent addition of an appropriate quantity of ammonium fluoride. Upper limits for the concentrations of all of the interfering cations allowing the determination of 0·2 ppm of copper^{II} are given in Table II. Chromium^{III} interferes by virtue of its own colour and all cations precipitated under the conditions used prevent the determination of copper.

Of the anions iodides, dithionites, ferro- and ferricyanides, oxalates, citrates, tartrates and all substances giving even weak complexes with copper, interfere.

Strong oxidants and reductants destroy the dye.

Stability of coloration

The stability of the coloured complex of copper with Proline Thymol Blue was studied at the laboratory temperature by measuring the absorption at regular time intervals. The maximal colour developed over a period of a few min and no decrease of absorbance was then observed even after several days.

TABLE II.—INTERFERING IONS

Ion	Added as	Limiting conc., *ppm*	
		pH 4·9	pH 5·4
Fe^{2+}	$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	0·5 1000*	0·5 1000*
Co^{2+}	$CoSO_4{\cdot}7H_2O$	0·8	0·7
UO_2^{2+}	$UO_2(CH_3COO)_2{\cdot}2H_2O$	1·8	0·7
Ni^{2+}	$NiSO_4{\cdot}7H_2O$	7	3
Be^{2+}	$BeSO_4{\cdot}4H_2O$	10	7
Zn^{2+}	$ZnSO_4{\cdot}7H_2O$	15	9
Pb^{2+}	$Pb(NO_3)_2$	40	10

* After oxidation to Fe^{3+} and addition of NH_4F.

DISCUSSION

A large number of reagents for the spectrophotometric determination of copper have been proposed to date, so that the addition of any new ones must be properly justified. There are, in our opinion, serious reasons for which Proline Thymol Blue should be included. Its advantages are:

1. High sensitivity, expressed by the value of pD = 7·6 and a molar extinction coefficient of 19600 at 595 mμ.
2. Absorption of its copper complex sufficiently independent of pH.
3. Favourable properties with regard to interferences from other cations.
4. Practically unlimited stability of the coloration formed.

The results presented in this paper show that only a very few of the reagents previously suggested and used for the spectrophotometric determination of copper can successfully compete with Proline Thymol Blue. By comparison with the sensitivity of other reagents, as expressed by molar extinction coefficients, it follows that only four substances (oxalyldihydrazide, Zincone, dithizone and 1:5-diphenylcarbohydrazide) are better—in this respect—than Proline Thymol Blue (*cf.* [10]). However, Zincone and dithizone show very low specifity so that in applying these reagents a tedious and time-consuming separation of copper from other interfering cations is usually indispensable. The application of diphenylcarbohydrazide is restricted by the low stability of both the reagent solution and the colour produced; it is also necessary to maintain accurately both the pH (a change of 0·01 in pH implies a 2% error in the determination) and the temperature.[10] On the other hand, the absorption of the copper complex of Proline Thymol Blue changes but negligibly over a pH range from 4·9 to 5·4, the reagent is practically of unlimited stability, and only a few cations interfere with the determination.

From this point of view Proline Thymol Blue seems to be very convenient for the determination of minute amounts of copper, especially in biological materials. In this case only the interference of iron^{II} presents a certain difficulty; this difficulty can, however, be obviated by the oxidation of the iron to the tervalent form and by the addition of a small amount of ammonium fluoride.

Zusammenfassung—Die Möglichkeit der Anwendung von fünf verschiedenen metallochromen Thymolblauderivaten /I–V/ für die spektrophotometrische Bestimmung von Cu^{2+}-Mikromengen wurde untersucht. Am besten bewährte sich das Prolinderivat /I/ in Lösungen, die mit Urotropin-Salzsäure gepuffert wurden. Die Absorption des Kupferkomplexes dieses Derivats bleibt in pH-Grenzen 4.9–5.4 praktisch konstant und folgt dem Beerschen Gesetz bis zu 25 μg Kupfer bei 595 mμ. Grössere Mengen von Fe^{2+}-, Co^{2+}-, Ni^{2+}-, Zn^{2+}-, Pb^{2+}-, Be^{2+}- und $UO_2{}^{2+}$-Ionen stören.

Résumé—Les auteurs ont étudié la possibilité d'application de cinq différents dérivés métallochromiques du bleu de thymol au dosage spectrophotométrique de micro-quantités de cuivre. Le dérivé de la proline utilisé en solution tamponnée avec l'héxaméthylènetétramine et l'acide chlorhydrique s'est révélé au mieux pour ce dosage. L'absorption de son complexe avec le cuivre montre seulement des changements insignifiants dans le domaine de pH 4,9–5,4 et obéit à la loi de Beer jusqu'à 25 μg de Cu^{2+} à 595 mμ. De plus grandes quantités de Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} Pb^{2+}, UO_2^{2+} et Be^{2+} gênent.

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THE DETERMINATION OF GALLIUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—Neutron-activation analysis has been applied to the determination of gallium in rocks. The Harwell Pile BEPO has been used as the source of neutrons, and a radiochemical procedure employing carrier chemistry has been utilised to separate the induced gallium activity.

Neutron-activation analyses of gallium in the standard rocks G1 and W1 are reported and compared with results obtained by other analytical methods.

INTRODUCTION

THE geochemistry of gallium has been reviewed by Shaw,[1] and an extensive study of the distribution of the element in rocks, minerals, sediments, and sea water has been reported recently by Burton, Culkin, and Riley.[2]

Various analytical procedures have been employed for the determination of gallium in rocks; spectrographic,[3] spectrophotometric,[4] fluorimetric,[5] and fluorescent X-ray spectrographic[6] methods have been used. Neutron-activation analysis has been successfully employed for the determination of gallium in iron meteorites[7] and in blende,[8] and it was decided to apply this technique to the determination of gallium in rocks.

The principles of neutron-activation analysis have been extensively discussed elsewhere, and the subject has been reviewed recently by Atkins and Smales.[9] Advantages of the method for determining trace elements may be summarised as follows:

Sensitivity. With the advent of high-flux atomic piles, neutron-activation analysis has, for many elements, represented the ultimate in practical sensitivity.

Specificity. The identity of the radionuclide used for the determination can be confirmed by measurements of the decay and energy of its radioactivity, in addition to radiochemical separation.

Contamination. A feature of the neutron-activation method is that analytical samples generally require little pre-treatment before irradiation. Since carriers are usually employed in radiochemical separations, the method is free from difficulties caused by reagent blanks or by contamination from traces of inactive material during radiochemical operations after irradiation.

Separation. If carrier chemistry is used there is no need for radiochemical separation steps to be quantitative, as a correction is made for losses by measurement of chemical yield.

Scale of operation. The use of carriers avoids the difficulties of chemical operations with ultramicro quantities, such as problems of co-precipitation and adsorption.

Standards. It is usually easier to prepare satisfactory comparison standards for neutron-activation analysis than for spectrochemical analysis.

Neutron activation of gallium

Naturally occurring gallium consists of two isotopes, ^{69}Ga(% abundance, $\theta = 60{\cdot}2$) and ^{71}Ga($\theta = 39{\cdot}8\,\%$). On irradiation with neutrons of thermal energies, radioisotopes of gallium are produced by the following nuclear reactions:

$$^{69}\text{Ga} \xrightarrow{\text{n},\gamma} {}^{70}\text{Ga}(t_{\frac{1}{2}} = 21{\cdot}1 \text{ min}) \xrightarrow{\beta^-} {}^{70}\text{Ge (stable)}$$

$$^{71}\text{Ga} \xrightarrow{\text{n},\gamma} {}^{72}\text{Ga}(t_{\frac{1}{2}} = 14{\cdot}3 \text{ hr}) \xrightarrow{\beta^-} {}^{72}\text{Ge (stable)}$$

Isotopic thermal neutron activation cross-sections, σ, for the nuclear reactions are:

$$^{69}\text{Ga}(\text{n},\gamma)^{70}\text{Ga} \qquad \sigma = 1{\cdot}4 \text{ barns}$$

$$^{71}\text{Ga}(\text{n},\gamma)^{72}\text{Ga} \qquad \sigma = 3{\cdot}4 \text{ barns}$$

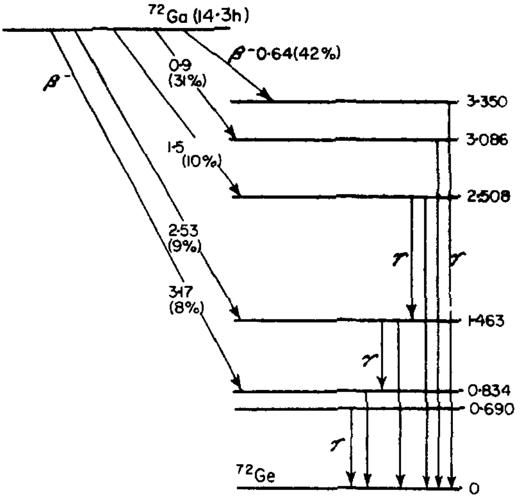

FIG. 1. Decay scheme for ^{72}gallium. Energies in MeV.

The radionuclide 14·3-hour ^{72}Ga was used in the present study. With a neutron flux of 10^{12} neutrons. cm^{-2}. sec^{-1} available in the Harwell Pile BEPO, it has been estimated by Jenkins and Smales[10] that *ca.* 1×10^{-10} g of gallium may be determined under ideal conditions. Since the average abundance of gallium in igneous rocks is about 19 ppm, neutron-activation analysis may be applied in cases where only very small samples of the material are available.

The decay scheme[11] for ^{72}Ga is shown in Fig. 1.

EXPERIMENTAL

Irradiation

All rock samples were available in a finely powdered condition, and were given no preliminary treatment before neutron-irradiation. Suitable quantities, usually about 0·5 g, of the powdered material were weighed out accurately into silica tubes of internal diameter 6 mm, and the tubes were immediately sealed. Standards were prepared by weighing out 0·1–0·2-ml aliquots of a dilute standard solution of gallium (100 mg of Ga/litre in 1*M* HNO_3) into silica tubes of internal diameter 4 mm. Samples and standards were packed side by side, with silica wool, in a standard screw-top aluminium can 3 in. long by 1 in. diameter, and were sent to the Atomic Energy Research Establishment, Harwell, for irradiation. Irradiation was in the Pile BEPO at pile factor 10, and was for 15 hr.

On delivery from Harwell after irradiation, the samples and standards were allowed to "cool" for 1 day and then were analysed radiochemically for ^{72}Ga.

Radiochemical separation

The radiogallium was separated from other elements in the irradiated rock samples by a modification of the procedure of Morris and Brewer.[8] The rock samples were dissolved by digesting with hydrofluoric acid and fuming with perchloric acid. Carrier chemistry was used in the separation procedure, and an excellent first decontamination step involved the extraction of gallium into ether from 5·5*M* hydrochloric acid. The relatively few elements extracted along with the gallium were then removed by scavenging with antimony trisulphide and ferric hydroxide. The gallium was finally precipitated and weighed as the 8-hydroxyquinolate.

A rather similar procedure has been employed recently by Bowen[12] in the analysis of biological material.

Reagents

Ga carrier: 10 mg of Ga/ml (added as $GaCl_3$ in dilute HCl)—standardised.
Fe carrier: 2 mg of Fe/ml (added as $FeCl_3{\cdot}6H_2O$ in very dilute HCl).
Sb carrier: 10 mg of Sb/ml (added as $SbCl_3$ in sufficient HCl to give a clear solution).

HF: 40%.
$HClO_4$: 9*M*.
HNO_3: 16*M*.
HNO_3: 6*M*.
HCl: 6*M*.
HCl: 1*M*.
Ether: pre-treated with 5·5*M* HCl.
HCl: 5·5*M* pre-treated with ether.
NH_4OH: 6*M*.
NaOH: 6*M*.
H_2S: generator.
Manoxol OT (British Drug Houses): 0·1% aqueous solution.
8-Hydroxyquinoline: 1% solution in 2*M* CH_3CO_2H.
$CH_3CO_2NH_4$: 6*M*.

Preparation and standardisation of the gallium carrier

Dissolve 5 g of pure gallium metal in dilute HCl and dilute to 500 ml.

Pipette 5 ml of the carrier solution into a 500-ml beaker, add 200 ml of H_2O, and warm to 70°. Add 35 ml of the 1% 8-hydroxyquinoline reagent, followed by the dropwise addition of 6*M* $CH_3CO_2NH_4$ with continuous swirling until a permanent yellow precipitate is formed. Add a further 1 ml of 6*M* $CH_3CO_2NH_4$ and continue swirling for 1 min, then allow to cool. Filter the granular precipitate through a sintered-glass crucible of medium porosity and wash with hot water. Dry to constant weight in an oven at 110°, and weigh.

Standardisations as the 8-hydroxyquinolate give results which are reproducible, but which may be a little higher[13] than the values obtained by standardisation as Ga_2O_3. Since gallium is finally weighed as the 8-hydroxyquinolate in the radiochemical procedure, the carrier is standardised gravimetrically through this compound.

Radiochemical separation procedure for the rock samples

Step 1: Remove the silica irradiation tubes containing the rock samples from the can, open them at the constriction, and transfer the contents to 60-ml platinum crucibles. Wash out the tubes with a little warm 6*M* HNO_3 and transfer the washings quantitatively to the crucibles. To a sample in a platinum crucible add 2 ml of standard Ga carrier. Cover loosely with a platinum lid and gently warm for a few min.

Step 2: Add 10 ml of 40% HF, cover the crucible with the platinum lid, and digest on a steam-bath until the sample is dissolved. Add 3 ml of 9*M* $HClO_4$ and 2 ml of 16*M* HNO_3, and heat the mixture till white fumes of $HClO_4$ begin to be given off, taking care to avoid spattering. Replace the cover loosely, and continue to heat for 5 min at a temperature such that the $HClO_4$ fumes moderately, but does not evaporate rapidly. Heat for 5–10 min longer, adding 1 ml of $9M$ $HClO_4$. Finally evaporate carefully almost to dryness. Extract the residue with hot water. Filter and discard any residue. Collect the filtrate in a 50-ml centrifuge tube and precipitate hydroxides by addition of $6M$ NH_4OH. Centrifuge and discard the supernate.

Step 3: Take up the residue in 15 ml of $6M$ HCl and filter, collecting the filtrate in a 50-ml centrifuge tube. Extract the gallium from the solution by agitating with 15 ml of ether pre-treated with $5{\cdot}5M$ HCl. Transfer the ether phase to a clean 50-ml tube and wash it twice with 10-ml portions of $5{\cdot}5M$ HCl saturated with ether. Discard the aqueous phases. Extract the gallium from the ether phase by equilibrating with an equal volume of H_2O. Draw off and retain the aqueous phase.

Step 4: Remove ether from the final solution by heating on a water-bath. Add 1 ml of Sb carrier and acidify with $6M$ HCl until the solution is clear. Boil and pass H_2S through the hot solution. Centrifuge and decant the clear supernatant solution into a clean 50-ml centrifuge tube. Boil to expel H_2S.

Step 5: Add $6M$ NaOH until the solution has a hydroxide concentration of 1-$2M$. Add 1 drop of Manoxol OT solution, heat to boiling, and add 1 ml of Fe carrier dropwise. Digest for 30 min. Filter through a Whatman No. 541 filter paper and discard the precipitate.

Step 6: Just acidify the solution with $1M$ HCl and dilute to 20 ml with H_2O. Heat to 70° and add 12 ml of 1% 8-hydroxyquinoline reagent. Add $6M$ $CH_3CO_2NH_4$ drop by drop with continuous stirring until a permanent yellow precipitate is formed, and then add 1 ml more. Continue stirring for 1 min. Wash the precipitate with 10 ml of warm H_2O and two 5-ml portions of cold water. Slurry the precipitate with H_2O on to a weighed aluminium counting tray (A.E.R.E. Cat. No. 4-3/1068), using a transfer pipette. Ensure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 30 min and weigh.

Treatment of the irradiated gallium standards

At a suitable time open the irradiation tubes containing the standards. By means of a drop-pipette drawn out almost to a point, transfer the gallium solution quantitatively to a 50-ml centrifuge tube and rinse thoroughly with hot $2M$ HCl. Add 2 ml of standard Ga carrier and mix thoroughly. Dilute to about 35 ml with H_2O and adjust to pH 1. Precipitate gallium with 8-hydroxyquinoline and mount for counting as in *Step 6* above.

Measurement of radioactivity of the final precipitates

The final precipitates of gallium 8-hydroxyquinolate from the rock samples and the standards were counted under similar conditions with a Geiger-Müller counter of the EHM 2/S type, associated with conventional electronic equipment. At least 10^4 counts were recorded when possible. All measured counting rates were corrected for paralysis, background, and chemical yield. No self-absorption corrections were necessary with the range of weights of gallium 8-hydroxyquinolate obtained in the radio-chemical procedure. Decay curves of samples and standards were measured and corresponded with the published half-life of ^{72}Ga, so confirming the radiochemical purity of the gallium—*e.g.* see Fig. 2. Extrapolation of the decay curves to zero time or to any arbitrary time, gave activity values for sample and standard from which the gallium content of the original material could be found.

RESULTS

The results of neutron-activation analyses of the granite G1 and the diabase W1, which have been suggested as international standards for the determination of both major and minor constituents of igneous rocks,[14] are given in Table I. The results may be compared with those obtained by other workers using different analytical methods (Table II.)

DISCUSSION

In the neutron-activation analysis of gallium in rocks consideration must be given to the fact that elements other than gallium, on irradiation, undergo nuclear reactions

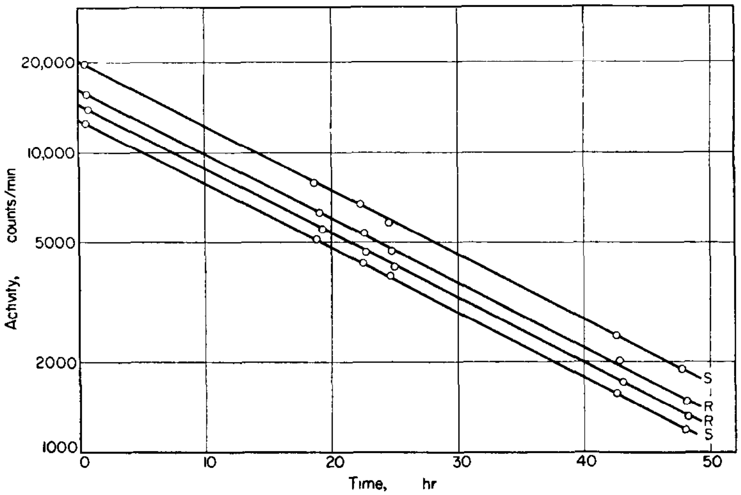

FIG. 2. Decay curves of final precipitates: S, from gallium standards. R, from samples of rock.

TABLE I. GALLIUM CONTENTS OF THE STANDARD GRANITE G1 AND THE STANDARD DIABASE W1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G 1, *ppm*	W 1, *ppm*
21·2	17·5
21·2	18·4
19·5	
21·6	

TABLE II. OTHER RESULTS FOR THE GALLIUM CONTENTS OF THE STANDARD ROCKS G1 AND W1

Method	G1, *ppm* Ga	W1, *ppm* Ga	Analysts	
Spectrographic	20	15	Mitchell	see Ahrens[3]
Spectrographic	18	12	Murata	
Spectrographic	19	13	Gorfinkle and Ahrens	
Spectrographic	15	20	Nockolds	
Spectrographic	18	11	Shaw and Webber	
Spectrographic	23	23	McKenzie *et al.*[6]	
Chemical and fluorimetric	15	15	Hey, see Ahrens[3]	
Spectrophotometric	21·3	21·5	Culkin and Riley[4]	
Fluorescent X-ray spectrographic	20	24	McKenzie *et al.*[6]	
	av. 19 ± 3	av. 17 ± 5		

In addition to the above results, Hamaguchi *et al.*[15] have obtained the value 13·6 ± 1·2 ppm for the gallium content of W1 by a spectrographic method. Semi-quantitative spectrographic analyses by Harvey (see Ahrens[3]) give for G1 10 ppm Ga and for W1 20 ppm Ga.

leading to the formation of gallium isotopes. The elements germanium, arsenic, zinc, and uranium need consideration in this respect.

Germanium may give rise to ^{72}Ga on irradiation with fast neutrons (of which there is a proportion, about 17% of the thermal neutron flux,[16] under the irradiation conditions employed in BEPO) by the reaction ^{72}Ge(n,p)^{72}Ga. The mean cross-section for this reaction with the pile distribution of fast neutrons may be estimated theoretically[17] to be 0·42 millibarns. Taking this value for the cross section, it may be calculated that if a rock contains 7 ppm of germanium* the apparent gallium content due to this secondary transformation is only *ca.* 10^{-4} ppm. Germanium may also give rise to ^{72}Ga from the thermal neutron irradiation by the process

$$^{70}\mathrm{Ge}(n,\gamma)^{71}\mathrm{Ge} \xrightarrow{\mathrm{EC}} {}^{71}\mathrm{Ga}(n,\gamma)^{72}\mathrm{Ga}.$$

A previous study of this sequence[19] shows that it is of no consequence in the analysis of gallium in rocks. Yet a further nuclear reaction whereby germanium may yield ^{72}Ga is ^{72}Ge(γ,p)^{72}Ga, but this is unlikely to be significant.

Arsenic may yield ^{72}Ga with fast neutrons by the reaction ^{75}As(n,α)^{72}Ga. Taking a theoretically calculated value of the cross-section for this reaction, 0·04 barns, and assuming[18] that the average arsenic content of a rock is 5 ppm, it can be calculated that the spurious gallium content due to this reaction is 0·02 ppm.

The formation of ^{72}Ga from zinc in rocks by the process

$$^{70}\mathrm{Zn}(n,\gamma)^{71}\mathrm{Zn} \xrightarrow{\beta^-} {}^{71}\mathrm{Ga}(n,\gamma)^{72}\mathrm{Ga}$$

can be shown by calculation to be negligible.[19]

Another possible mode of formation of ^{72}Ga is by the slow-neutron fission of uranium. The fission yield of ^{72}Ga is very low, however, and since there is only about 4 ppm of uranium in an average rock,[18] interference with the activation analysis of gallium is negligible.

Any interference of importance due to the production of gallium radio-isotopes other than ^{72}Ga would have been apparent from the decay measurements made on the counted samples from rock specimens.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Gallium in Gestein herangezogen. Der Harwell-Reaktor BEPO wurde als Neutronenquelle verwendet und radiochemische Methoden, wie Trägerfällungen wurden herangezogen um die erzeugte Galliumaktivität zu isolieren. Resultate nach dem neuen Verfahren wurden mit denen nach anderenAnalysenmethoden erhaltenen für Standardgesteinsproben G1 und W1 verglichen.

Résumé—L'analyse par activation par les neutrons a été appliquée au dosage du gallium dans les roches, la pile BEPO de Harwell a été utilisée comme source de neutrons et un procédé radiochimique employant la chimie des entraîneurs a été utilisé pour séparer l'activité induite du gallium. Les analyses par activation par les neutrons du gallium dans les roches étalons G1 et W1 sont décrites et comparées avec les résultats obtenus par d'autres méthodes analytiques.

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* This is the figure quoted by Rankama and Sahama[18] for the average abundance of germanium in igneous rocks. A more recent value for the crustal abundance, due to Burton *et al.*,[2] is 1·7 ppm Ge.

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FERRIMETRIC DETERMINATION OF URANIUM^{IV} USING RHODAMINE 6G AS FLUORESCENT INDICATOR

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Summary—Experimental conditions have been developed for the titration of uranium^{IV} with iron^{III} alum solution, using Rhodamine 6G as a fluorescent indicator. The titration is best carried out at 98–100° in a 2-3*N* hydrochloric acid medium, under filtered ultraviolet light, using 2·0 ml of 0·05% Rhodamine 6G solution for 30 ml of the titration mixture. A slight excess of iron^{III} solution quenches the greenish-yellow fluorescence of the dye through inner filter action. With the titration assembly described here, it is possible to determine uranium^{IV} with an accuracy of about 0·4%. This method appears to be more convenient than the potentiometric titration or the method employing potassium thiocyanate as internal indicator.

Evidence is also presented to show that the reaction between uranium^{IV} and iron^{III} is slow at room temperature.

FROM a consideration of redox potentials, iron^{III} sulphate and iron^{III} chloride are much less powerful oxidising agents than cerium^{IV} salts, potassium permanganate, potassium dichromate, or even sodium vanadate. It is, therefore, obvious that iron^{III} salts have not been widely employed as oxidants in titrimetric analysis. However, they have been so used in a few instances by employing higher temperatures. The determination of tin^{II} chloride with iron^{III} chloride is perhaps the earliest example of the analytical applications of iron^{III} chloride as a titrimetric reagent.[1,2,3] Next in importance are to be mentioned the determination of titanium^{III} and chromium^{II}.[4,5,6,7,8] Bradbury and Edwards[9] employed the direct titration between mercury^{I} nitrate and iron^{III} alum in the presence of excess thiocyanate for analytical purposes. A more detailed examination of this reaction was made by Belcher and West[10] and by Burriel and Lucena.[11] Pugh[12] has recommended mercury^{I} perchlorate in place of mercury^{I} nitrate. Uranium^{IV} has also been determined by titration with iron^{III} at 98–100°.

The indicators that have so far been used in titrations with iron^{III} include thiocyanate, methylene blue, indigo carmine, phenosafranine and cacotheline. No one appears to have so far used Rhodamine 6G as a fluorescent indicator in titrations involving iron^{III} as an oxidant. The present investigation is concerned with the titration of uranium^{IV} with iron^{III} in a hydrochloric acid medium.

Auger[13] appears to have been the earliest person to propose the titrimetric determination of uranium^{IV} with iron^{III} using potassium thiocyanate as indicator. Vortmann and Binder[14] determined iron^{III}with uranium^{IV} sulphate by titration to the disappearance of the colour of ferrithiocyanate. Weiss and Blum[15] carried out the titration of uranium^{IV} with iron^{III} potentiometrically at an elevated temperature, not exceeding 70°, in an atmosphere of carbon dioxide. They stated that the addition of ammonium thiocyanate to the mixture is essential, believing that ammonium thiocyanate does not alter the potential of the system but acts as a catalyst. Belcher, Gibbons and West[16] found that the reverse titration of iron^{III} with uranium^{IV} gives trouble at 60° and they preferred a slow titration in the cold with a potentiometric end-point. In the potentiometric titration, Issa and Elsherif[17] found that it is necessary to wait for 11–14 min at the end-point if the titration is performed in a 5–7N overall hydrochloric acid concentration at 20°, but only for 1 min if the titration is carried out at 60°. Cellini and Lopez[18] determined uranium^{IV} by titration with iron^{III} sulphate in a 0·1N sulphuric acid medium at room temperature, in an inert atmosphere. Rodden[19] recommended the titration of uranium^{IV} to be carried out below 90° using either ammonium thiocyanate as internal indicator or by potentiometry or by amperometry. Korach, Nessle, Sinclair and Casto[21] have studied the rate of oxidation of uranium^{IV} with iron^{III} by means of the absorption maximum of uranium^{IV} at 650 mμ, and believe that the rate of oxidation of uranium^{IV} by iron^{III} in 5% sulphuric acid is rapid at room temperature. They expressed the opinion that the electrometric titration of uranium^{IV} with iron^{III} should be feasible at room temperature, if some way could be found of speeding up the rate of establishment of potential equilibrium at the electrode. But the results cited by Rodden[20] on the amperometric titration of uranium^{IV} with iron^{III} indicate that the reaction is rather slow. It is stated that the errors obtained are "due to incomplete attainment of chemical equilibrium" and that the percentage error increases with the use of more and more dilute solutions.

EXPERIMENTS AND OBSERVATIONS

Preparation of Reagents: (*a*) The uranium^{IV} solution used in this investigation is prepared by reducing uranium^{VI} acetate in a Jones reductor and passing air through the reduced solution for 10 min to oxidise any uranium^{III} formed to uranium^{IV}. The strength of the uranium^{IV} solution is adjusted to be about 0·05N, with the concentration of sulphuric acid remaining at about 1·0N. (*b*) About 0·05N solution of iron^{III} is prepared from an AnalaR B.D.H. sample of ferric alum dissolved in 2–3N hydrochloric acid and standardised by reduction in a Jones reductor and titration with standard ceric sulphate solution. (*c*) A 0·05% solution of B.D.H. Rhodamine 6G is prepared in water. The solution has been found to be quite stable for 1 week, and for longer periods if treated with a drop or two of chloroform.

In view of the above, it appears that the question remains unsettled, whether the reaction between uranium^{IV} and iron^{III} is sufficiently rapid for analytical purposes. We have made a study of the problem by two methods.

In the first method we have made use of a very dilute solution of ferriin (oxidised ferroin) to indicate the progress of the reaction. In a blank experiment, 50 ml of $10^{-5}M$ ferriin solution (containing sulphuric acid at a 2N overall concentration) is treated with 1·0 ml of $5 \times 10^{-4}N$ uranium^{IV} solution (in 2N sulphuric acid). It is noted that in 10 min, the mixture develops a very slight red colour due to the reduction of ferriin. In another experiment the same mixture of ferriin and uranium^{IV} is treated with 1·0 ml of $5 \times 10^{-2}N$ iron^{III} sulphate solution (in 2N sulphuric acid). This mixture is found to develop a strong red colour in 10 sec. The first experiment shows that the reduction of ferriin by uranium^{IV} is *very* slow. This result, taken along with the result of the second experiment, shows that the strong red colour appearing in the second experiment is due to the formation of iron^{II} by the interaction of uranium^{IV} and iron^{III}. It is well known that even a trace of iron^{II} gives an intense red colour with ferriin. The speed of the development of the red colour in the second experiment will, therefore, be an indication of the speed of interaction of uranium^{IV} and iron^{III}. A large number of such experiments have been made with varying concentrations of uranium^{IV} and iron^{III}; the results are given in Tables I and II.

From Tables I and II, it is seen that the speed of the reaction is dependent on the concentrations of both uranium^{IV} and iron^{III}. It will also be evident that the reaction is very slow at concentrations of uranium^{IV} and iron^{III} encountered near the equivalence point of a volumetric titration.

The second method employed by us to obtain qualitative information on the speed of the reaction between uranium^{IV} and iron^{III} consists in the use of a fluorescent indicator, namely Rhodamine 6G.

TABLE I

Volume of uranium^{IV} solution, X *ml*	Time required for the development of a red colour, *sec*
1·0	10
0·50	25
0·25	35

50 ml of $10^{-5}M$ ferriin in $2N$ sulphuric acid
+1 ml of $5 \times 10^{-3}N$ iron^{III} in $2N$ sulphuric acid.
+X ml of $5 \times 10^{-4}N$ uranium^{IV} in $2N$ sulphuric acid.

TABLE II

Volume of iron^{III} solution, X *ml*	Time required for the development of a red colour, *sec*
1·0	10
0·5	30
0·2	60
0·1	90
0·05	140

50 ml of $10^{-5}M$ ferriin in $2N$ sulphuric acid
+1 ml of $5 \times 10^{-4}N$ uranium^{IV} in $2N$ sulphuric acid
+X ml of $5 \times 10^{-3}N$ iron^{III} in $2N$ sulphuric acid

From preliminary experiments with a 0·0005 % solution of Rhodamine 6G, we have made the following observations:

(1) It has a greenish-yellow fluorescence in a 1–4*N* hydrochloric acid medium in the diffused light of the laboratory.

(2) If the acid concentration is increased beyond 4*N*, the fluorescence intensity decreases but it is still marked under filtered ultraviolet light (<400 mμ).

(3) The intensity of fluorescence appears to be lower at 90° than at 28° in a 3–6*N* hydrochloric acid medium, while a rise of temperature appears to be without much effect on the fluorescence intensity in a 1–3*N* hydrochloric acid medium.

(4) The intensity of fluorescence in filtered ultraviolet light is not affected by fairly large concentrations of sodium chloride (1–4 g of salt per 100 ml).

(5) The addition of a small quantity of iron^{III} markedly quenches the greenish-yellow fluorescence of the dye in filtered ultraviolet light, but not the greenish-yellow fluorescence of the dye in daylight.

(6) The quenching effect of iron^{III} is much more pronounced in a hydrochloric acid medium than in a sulphuric acid medium. The minimum amount of iron^{III} required to effect complete quenching of the greenish-yellow fluorescence in a 30-ml volume of a 0·0005 % solution of the dye in 6*N* hydrochloric acid has been found to correspond to 0·12 ml of 0·05*N* iron^{III} solution, when the flask containing the mixture is kept at a distance of 20 in. from the lamp in the apparatus described here. With a 2*N* hydrochloric acid solution of the dye, the minimum amount of iron^{III} required to produce complete quenching corresponds to 0·16 ml of the same iron^{III} solution. Working with sulphuric acid solutions of the dye, we have found that the minimum amounts of iron^{III} required to produce complete quenching correspond to 4 ml and 5 ml of the same iron^{III} in 6*N* and 2*N* sulphuric acid solutions, respectively. These observations can be explained from the optical absorption curves of iron^{III} in hydrochloric acid and sulphuric acid, respectively. The optical absorption for iron^{III} in the region 340–400 mμ is much greater in an hydrochloric acid medium than in a sulphuric acid medium. This difference is more and more accentuated as the acid concentration is increased up to 6*N*.

We have made the interesting observation that the quenching action of iron^{III} can be counteracted by the addition of a suitable quantity of uranium^{IV} and allowing to stand for sufficient time. This indicates that (1) the quenching action of iron^{III} is due to a physical effect, (2) the fluorescence re-appears when the iron^{III} is destroyed by reaction with uranium^{IV}, and (3) the reaction between iron^{III} and uranium^{IV} is slow, as the restoration of fluorescence requires time and is not instantaneous after the addition of uranium^{IV}.

The following experiments have been conducted to ascertain, qualitatively, the speed of the reaction between uranium^{IV} and iron^{III} in a hydrochloric acid medium. Five ml of 0·04*N* uranium^{IV} solution are mixed with 15 ml of concentrated hydrochloric acid and 1·0 ml of 0·05% Rhodamine 6G and the mixture diluted to 40 ml. This solution is treated with varying volumes (X ml) of 0·05*N* iron^{III} solution. It was noticed that, in each case, the fluorescence of the mixture was quenched immediately after the addition of the iron^{III} solution but it reappeared after some time. The time required for re-appearance of the fluorescence was noted in each case. The results are presented in Table III.

TABLE III

Volume of iron^{III} solution, X *ml*	Time required for the re-appearance of a fluorescence, *min*
2·0	11
1·0	8
0·8	6
0·6	5
0·4	4
0·2	3

Temperature 28°

In the above experiments, the time required for the re-appearance of fluorescence is evidently the time required for the reduction of iron^{III} by uranium^{IV}. These experiments, therefore, lead us to the conclusion that the reaction between iron^{III} and uranium^{IV} is slow at 28°. In another set of experiments, 0·4 ml of iron^{III} solution is mixed with 15 ml of concentrated hydrochloric acid and 1 ml of 0·05% Rhodamine 6G and the mixture diluted to 40 ml. This mixture (which does not show any fluorescence) is treated with varying volumes (Y ml) of 0·04*N* uranium^{IV} solution in 2*N* sulphuric acid. A fluorescence appears in the mixture after some time. The time required for the appearance of the bright fluorescence of the dye is noted in each case. The results are given in Table IV.

TABLE IV

Volume of uranium^{IV} solution, Y *ml*	Time required for the appearance of a fluorescence, *min*
1·0	14
2·0	9
3·0	7
5·0	4

The results in Table IV also show that the reaction between iron^{III} and uranium^{IV} is slow at room temperature and that the speed of the reaction increases as the uranium^{IV} concentration is increased, while keeping the concentration of iron^{III} constant.

Experiments similar to those involved in Tables III and IV, but conducted at 98–100°, lead us to the conclusion that the reaction between uranium^{IV} and iron^{III} is very fast at that temperature. Hence it is possible to carry out the titration of iron^{III} with uranium^{IV} or *vice versa* using Rhodamine 6G as a fluorescent indicator.

The apparatus employed by us in the fluorimetric titration has been assembled as shown in Fig. 1. Light from a Philips 125 W "Germicidal lamp" U (run on 220 V, a. c. mains), mounted horizontally, passes through an iris diaphram D on to a condensing lens L_1. After passing through L_1 it is rendered parallel by lens L_2. A narrow pencil of light from this lens passes through a second iris diaphram D_2 and falls on the titration mixture contained in a 100-ml Pyrex glass beaker V mounted on a B.T.L. magnetic stirrer hot plate H (P is the paddle). The entire assembly is enclosed in a box painted black on the inside and provided with suitable shutters. The side of the box opposite the titration beaker at A has a small aperture, which enables the fluorescent light from the beaker to be observed in a direction perpendicular to the incident light, by a person sitting in a comfortable position. The neck of the beaker passes through a hole in the right-end top of the box, as shown in the figure. The mouth of the beaker is fitted with a stopper having three holes. Through two holes of this stopper are fitted the inlet and exit tubes for passage of carbon dioxide, while through the middle hole passes the nozzle of a micro burette B. The Philips "Germicidal lamp" transmits mostly ultraviolet light with a trace of violet radiation.

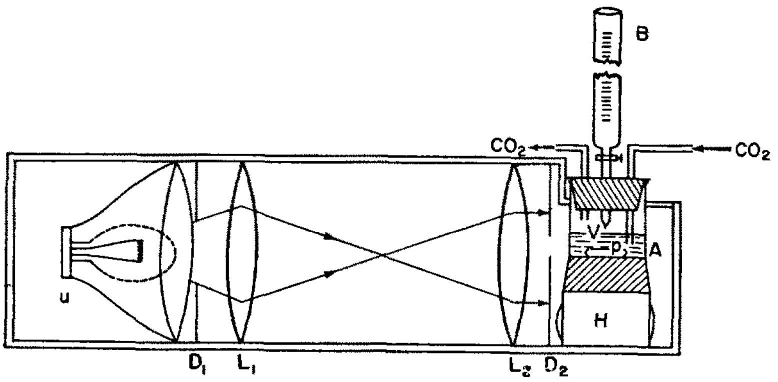

FIG. 1.—Titration assembly.

Both Rhodamine 6G and iron^{III} chloride strongly absorb the light emitted by the germicidal lamp. The fluorescence emitted by Rhodamine 6G in a 5–6N hydrochloric acid solution appears greenish-yellow under this light, both at room temperature and also at 98°. When 1 drop of 0·05N iron^{III} solution is added to 30–40 ml of the mixture, containing Rhodamine 6G, the fluorescence is noticed to disappear at A, while the fluorescence is still observable in the solution near the point of entry of the light.

For the fluorescence to disappear throughout the entire mixture, the addition of 3 drops (about 0·12 ml) of 0·05N iron^{III} solution is necessary under the experimental conditions described above. Hence, 0·12 ml of 0·05N iron^{III} solution may be taken as the blank correction in a fluorimetric titration if one takes the end-point as the disappearance of fluorescence throughout the entire solution, but 0·04 ml as the correction if one takes the disappearance of the fluorescence at A. The blank correction depends upon the concentration of the iron^{III} solution, the intensity of the light, the distance of the flask from the light source and the volume of the titration mixture, as well as the acidity of the solution. If the titration is carried out in 2–3N hydrochloric acid, a correction of 0·16 ml of 0·05N iron^{III} solution is necessary if one takes the quenching of fluorescence throughout the mixture as the end-point, and a correction of 0·04 ml if one takes the quenching at A as the end-point. In actual practice, titrations in a 2–3N hydrochloric acid medium have been found more convenient, taking the quenching of the fluorescence at A as indicating the end-point of the titration.

Influence of hydrochloric acid concentration

We have noticed that the titration becomes increasingly difficult as the acid concentration is increased beyond 5–6N. This is presumably due to the fact that the speed of the reaction diminishes with an increase in hydrochloric acid concentration. At hydrochloric acid concentrations higher than 5–6N, the quenching of fluorescence is noted at a titre lower than the theoretical. The difference in the observed and theoretical titres increases with increasing acid concentration. Moreover, it has been noticed that the fluorescence does not return, even after standing for 10 to 15 min in spite of the low titres. These results could be understood in the light of the fact that the potential of the U_N/U^{VI} system increases with an increase in the concentration of hydrochloric acid. The experimentally observed titres and the corresponding uranium potentials for different hydrochloric acid concentrations are given in Table V.

TABLE V

Concentration of hydrochloric acid, *moles/l*	U^{IV}/U^{VI} potentials, *mV*	Fe^{III}/Fe^{II} potentials, *mV*	Observed titre, *ml*	Blank correction for overall quenching, *ml*	Correct titre, *ml*
2	530*	680†	4·02	0·16	3·86
3	530*	670†	4·01	0·16	3·85
4	530*	660†	4·01	0·16	3·85
5	535*	—	3·98	0·12	3·86
6	535*	—	3·97	0·12	3·85
7	560*	—	3·78	0·08	3·70

* Computed from the graph given by Issa and Elsherif[17]
† Smith and Richter[22]

The hydrochloric acid concentrations given here can only be approximate as the mixture loses hydrochloric acid when heated at the higher acid concentrations.

It has been observed by us that when the acid concentration is below 2*N*, the quenching effect is not very prominent, with the result that slightly higher titres are obtained. In solutions which are more than 4*N* in hydrochloric acid, the end-point detection is somewhat less sharp, although accurate titres can be obtained with practice.

Prescribed procedure

Using the apparatus described above, in which the distance of the flask from the lamp is about 20 in., we have found that it is convenient to carry out the titration of uranium^{IV} with iron^{III} in a 2–3*N* hydrochloric acid medium at 98–100°. It is also convenient to take the quenching at A to indicate the end-point of the titration. In such titrations, the blank correction corresponds to 0·04 ml of 0·05*N* iron^{III} solution for a titration mixture of 30 ml. Some typical results are given in Table VI. These show that the error of determination is within 0·4%. It is recommended that 2·0 ml of 0·05% aqueous solution of Rhodamine 6G are added to 30 ml of the titration mixture.

TABLE VI

Amount of uranium^{IV} taken, *millimoles*	Amount of uranium^{IV} found, *millimoles*
0·250	0·248
0·375	0·374
0·500	0·502
0·560	0·558
0·780	0·778
0·805	0·808

Interferences

Since uranium^{IV} prepared by reduction of a uranium^{VI} salt in the Jones reductor is contaminated with zinc sulphate, we have studied the interference of zinc sulphate in the fluorimetric titration procedure here proposed. A number of titrations have been made with varying quantities of zinc sulphate added in addition to what has already been introduced in the Jones reductor. The results presented in Table VII show that zinc sulphate does not interfere.

Similar studies with chrome alum showed that the addition of 0·02–0·2 g of chrome alum does not interfere with the titration, but it has been observed that when a larger amount (0·5 to 1·0 g) is present, the dark green colour of chromium^{III} masks the greenish-yellow fluorescence of the dye.

TABLE VII

Amount of $ZnSO_4 \cdot 7H_2O$ added, *g*	Volume of iron^{III} solution required, *ml*
1·0	4·15
2·0	4·16
3·0	4·16
4·0	4·13
5·0	4·15

5 ml U^{IV} solution $\equiv$ 4·16 ml of Fe^{III} solution

Metals like vanadium and molybdenum, which are reduced in the Jones reductor to lower oxidation states oxidisable by iron^{III}, should be absent.

Zusammenfassung—Experimentelle Bedingungen zur Titration von Uran(VI) mit Eisenalaunlösung unter Verwendung von Rodamin-6G als Fluorescenz-indicator wurden ausgearbeitet. Die Titration wird am besten bei 98–100°C in 2–3n Salzsäure, unter filtriertem UV-Licht, nach zusatz von 2·0 ml einer 0·05% Rodamin-6G-Lösung für je 30 ml Titrationslösung, vollzogen. Ein geringer Überschuss von Eisen(III) lösung löscht die grünlichgelbe Fluorescenz des Indicators. Mit der beschriebenen Titrationsanordnung ist es möglich Uran mit einer Genauigkeit von etwa 0·4% zu bestimmen. Die Methode ist besser geeignet als das übliche Verfahren mit Thiocyanat als Indicator. Es wird gezeigt, dass die Reaktion zwischen Uran(VI) und Eisen(III) bei Zimmertemperatur nur langsam verläuft.

Résumé—Les auteurs ont élaboré les conditions expérimentales de titrage de l'uranium (VI) avec une solution d'alun ferrique en utilisant la rhodamine 6G comme indicateur fluorescent. Le titrage est effectué à 98°–100° en milieu acide chlorhydrique 2N–3N, sous lumière ultra-violette filtrée, en utilisant 2,0 ml de la solution de rhodamine 6G à 0,05 pour cent pour 30 ml du mélange de titrage. Un faible excès de la solution de fer (III) fait disparaître la fluorescence jaune verdâtre du colorant par action de filtre interne. Avec le montage décrit, il est possible de doser l'uranium (VI) avec une précision d'environ 0,4 pour cent. Cette méthode paraît être plus commode que le titrage potentiométrique ou la méthode employant du thiocyanate de potassium comme indicateur interne. Les auteurs démontrent aussi que la réaction entre l'uranium (VI) et le fer (III) est lente à la température ordinaire.

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THE PHOTOMETRIC DETERMINATION OF ALCOHOLS BY MEANS OF VANADIUM OXINATE

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Summary—Vanadium oxinate dissolved in such organic solvents as chloroform and nitrobenzene can be successfully used for the photometric determination of micromolar quantities of various alcohols. The sensitivity depends upon the dielectric constant of the solvent and the concentration of the reagent. Suggestions are made for using the reaction to estimate the relative reactivity of a given alcohol and the steric effect about the alcoholic OH. The reaction can also be used to differentiate alcohol isomers.

INTRODUCTION

VANADIUM oxinate dissolves to give solutions of different colours in different solvents. In solvents such as acetic anhydride, amyl acetate, benzene, toluene, the solutions, like the solid, are dark violet, while in acidic solvents such as acetic acid and phenol they are blue. Furthermore, a red colour is characteristic of hydroxylic solvents. Therefore the red colour which vanadium oxinate produces in commercial chloroform is due to ethyl alcohol which has been added to the chloroform as stabiliser. This was pointed out by Buscarons and others,[1] who proved that a chloroform preparation which has been purified by repeated washing with water is coloured dark violet instead of red on addition of the oxinate. It has also been shown by the present author that while, by the addition of vanadium oxinate, a pure sample of an ester such as amyl acetate or benzyl acetate is coloured dark violet without any shade of red, some samples of the same esters are coloured red by the same oxinate, undoubtedly due to the presence of alcoholic impurity.

These facts suggest that the functional group of an alcohol has a specific affinity for vanadium oxinate, an affinity which is strong enough to produce an alcohol-vanadium oxinate association characterised by a red colour.

It has proved possible to utilise this red colour for detecting and even for determining alcohols. Thus in 1949 Buscarons *et al.*[1,2] demonstrated the usefulness of vanadium oxinate as a reagent for detecting a small amount of alcohol. In 1957 Kudo and Aoki[3] proposed vanadium oxinate in xylene-acetic acid as a reagent for alcohol detection and actually detected the alcoholic OH present in sterols such as testosterone and œstradiol. Furthermore, Maruta and Iwama[4] were able to determine photometrically aliphatic alcohols higher than hexyl alcohol by using Kudo and Iwama's reagent with slight modification.

The aim of the present investigation was to establish more elaborate methods for alcohol determination, using the same colour reaction. The nature of the colour of the alcohol–vanadium oxinate associate was therefore critically examined to find the factors and conditions which determine or control its development and stability.

REAGENTS AND APPARATUS

Vanadium oxinate: Precipitated from an acetic acid-acetate medium and washed with water and finally recrystallised from chloroform.

Oxine: GR.

Chloroform: Shake 500 ml of chloroform with 100 ml of 1*N* sulphuric acid containing 1 g of potassium chromate. Wash the organic layer, first with 100 ml of 1*N* sodium hydroxide and then 4 times with distilled water. The purified chloroform is dehydrated and is kept in a dark bottle, preferably in a dark cold place.

Other organic solvents: GR. If necessary, shake the solvent with distilled water to eliminate any alcoholic impurity and dehydrate.

*Vanadium oxinate solution:** In the case of chloroform and nitrobenzene, 1 μmol of vanadium oxinate per ml of solvent, containing about 1 mg of oxine per ml of solution, is used. In the case of the other solvents, which dissolve a smaller amount of vanadium oxinate, saturated vanadium oxinate solution, containing about 1 mg of oxine per ml of solution, is used.

Beckman DU spectrophotometer.

EXPERIMENTAL AND DISCUSSION

Spectrum of alcohol-vanadium oxinate associate

The first approach was to establish the difference spectrum between the absorption curve for the oxinate in an indifferent solvent (E_1) and that for the same solution to which an excess of an alcohol has been added (E_2).

The tested alcohols were those from ethyl alcohol to amyl alcohol and the indifferent solvents tested were benzene, toluene, xylene, nitrobenzene and chloroform.

The difference spectrum of the amyl alcohol-chloroform system (Fig. 1), representing an absolute value of $E_1 - E_2$, is characterised by two maxima with peaks at 470 mμ and 635 mμ. It is important that irrespective of the nature of the alcohol and the solvent, the positions of these two maxima remain unchanged, while the value $E_1 - E_2$ varies greatly with the amounts of alcohol added and the kind of solvent used. The value increases with the amount of alcohol and decreases with increase in the dielectric constant of the solvent.

This suggests the existence of the equilibrium:

$$\text{Vanadium oxinate} + \text{Alcohol} \rightleftharpoons \text{Vanadium oxinate-alcohol.}$$

Increase of the dielectric constant of the medium would favour dissociation, the point of equilibrium shifting to the left, to produce a decrease in the value of $E_1 - E_2$; while increase of the concentration of alcohol or vanadium oxinate would cause the equilibrium to move to the right, with an increase in $E_1 - E_2$ value. This view is supported by Fig. 2, in which are shown some examples of standard curves for amyl alcohol.

Calculation of the $\Delta\varepsilon_{635}$ value, defined as

$$\Delta\varepsilon_{635} = \frac{E_1 - E_2}{c \cdot d}$$

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* A solution of vanadium oxinate in xylene-acetic acid[3,4] is blue and is best for the qualitative test for alcohols, because the colour change from blue to red can be more easily observed than the colour change from dark violet to red. On the other hand, the stability of the reagent is not so great in an acidic medium and fading of the reagent occurs to some extent even in the course of the reaction between alcohol and the reagent, thus producing a larger blank value. In the present study, vanadium oxinate is dissolved in various inert solvents containing some oxine in excess. The reagent thus prepared is very stable and no appreciable change in colour is observed at least for several days at room temperature, and even at 70° it is stable for more than 12 min.

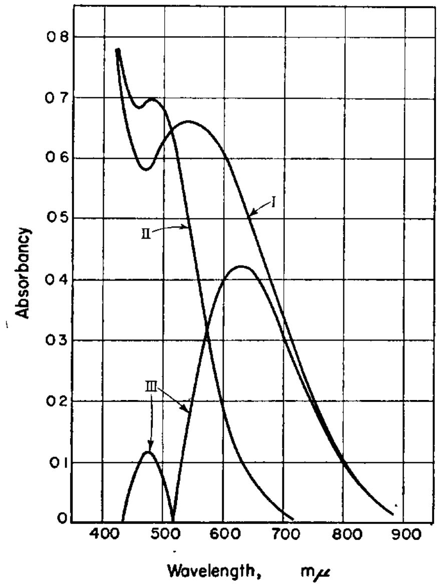

FIG. 1.—Absorption spectra of vanadium oxinate in chloroform (cell depth: 1·0 cm)
I—2 × $10^{-4}M$ vanadium oxinate in the absence of alcohol.
II—2 × $10^{-4}M$ vanadium oxinate in the presence of excess amyl alcohol.
III—Absolute value of (I—II).

in which c is the molar concentration of alcohol and d is cell depth in cm, and E_1 and E_2 are absorbancies at 635 mμ of reagent itself and of reagent in the presence of alcohol respectively, is also important.

In Table I are listed the values as determined for several alcohols. The values vary over a short range from 43·7 for benzyl alcohol to 95 for *n*-octyl alcohol, apart from 10·5 for *tert*butyl alcohol. The exceptionally low $\Delta\varepsilon_{635}$ value for *tert*butyl alcohol reflects the weak reactivity of the OH group of this alcohol.

This relationship appears to hold widely and the measurement of $\Delta\varepsilon_{635}$ for various

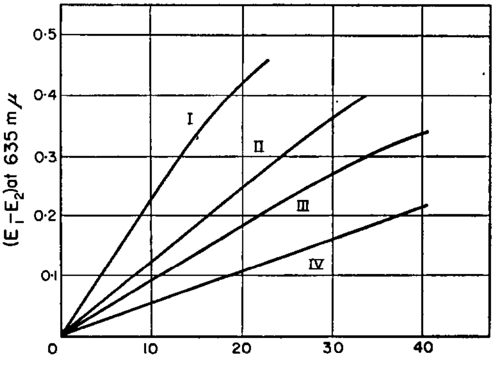

FIG. 2.—Influence of reagent concentration and solvent on the colour
I—4 μmol of vanadium oxinate in 10 ml of chloroform.
II—2 μmol of vanadium oxinate in 10 ml of chloroform.
III—5 μmol of vanadium oxinate in 10 ml of nitrobenzene.
IV—2·5 μmol of vanadium oxinate in 10 ml of nitrobenzene.

TABLE I.—$\Delta\varepsilon_{635}$ OF SOME ALCOHOLS AND ALCOHOL–ETHERS*

5 μmol of vanadium oxinate in 10 ml of nitrobenzene; heating at 70° for 10 min.

Compound	$\Delta\varepsilon_{635}$
Methyl alcohol	60·0
Ethyl alcohol	59·3
n-Propyl alcohol	65·3
n-Butyl alcohol	94·3
tert-Butyl alcohol	10·5
iso-Amyl alcohol	94·9
n-Octyl alcohol	95·0
Benzyl alcohol	43·7
Ethyleneglycolmonobutylether	37·8
Ethyleneglycolmonomethylether	34·0

* Mean values of the results obtained for 10, 20 and 40 μmol of each alcohol in 10 ml of nitrobenzene.

alcohols offers a basis for ascertaining the reactivity of the OH group of these organic substances and the steric hindrance around their OH group. Moreover it is noteworthy that knowledge of molecular weight, together with the $\Delta\varepsilon_{635}$ value, allows differentiation of alcohol isomers. For example, *n*-butyl alcohol can be thus easily distinguished from *tert*-butyl alcohol.

Of special interest is the fact that the value is nearly constant for normal alcohols with more than four carbon atoms, showing the possibility of determining collectively the quantity of alcohol, in moles, in a mixed sample of these different kinds of alcohols.

Colour development and stability

The development of the colour is complete within about 3 hours at room temperature irrespective of the solvent. As shown by nitrobenzene (Fig. 3), heating

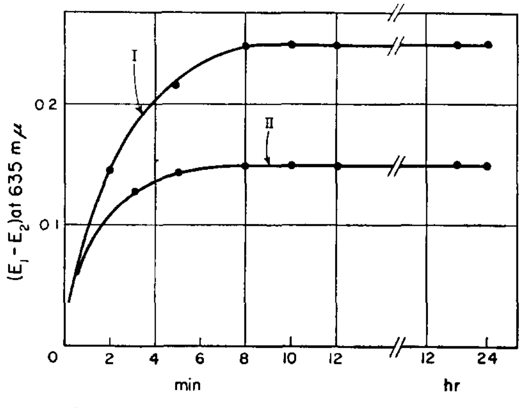

FIG. 3.—Time necessary for complete colour development for *n*-propyl alcohol at 70° and colour stability at room temperature.

I—5 μmol of vanadium oxinate and 40 μmol of *n*-propyl alcohol in 10 ml of nitrobenzene, cell depth: 1·0 cm.

II—2·5 μmol of vanadium oxinate and 40 μmol of *n*-propyl alcohol in 10 ml of nitrobenzene, cell depth: 1·0 cm.

shortens the time. Thus 8 min are sufficient for full development of colour at 70° and 12 min heating at this temperature causes no deterioration of the colour. Therefore for rapid determination a solvent with a high boiling point such as toluene, xylene or nitrobenzene is preferable. Of these, nitrobenzene is best, since it dissolves a greater amount of vanadium oxinate, thereby ensuring the determination of a wider range of alcohol concentration.

The colour developed is stable for at least 24 hours after development if excess oxine protects the colour; this otherwise tends to fade because of deterioration of the vanadium oxinate used as the reagent.

From these results the principles to be taken into consideration for a satisfactory alcohol determination would appear to be:

(1) A solvent with a low dielectric constant is preferable for the determination of smaller amounts of alcohol.

(2) Excess oxine favours stability both of the reagent and of the colour developed.

(3) For a rapid determination a solvent with a high boiling point is more satisfactory.

RECOMMENDED PROCEDURES

Based on the above considerations three photometric methods for determining alcoholic OH content by using vanadium oxinate have been established. The appropriate one may be chosen to suit the requirements.

1. *Rapid method*

Add 5–50 μmol of alcohol to 5 ml of a nitrobenzene solution of vanadium oxinate. Add nitrobenzene to give a total volume of 10 ml. Heat the solution for 10 minutes in a water bath at 70°. Cool with tap water. Measure the absorbancy at 635 mμ, and obtain the equivalence of alcoholic OH, from a previously constructed standard curve.

2. *Sensitive method*

Add 1–20 μmol of alcohol to 5 ml of chloroform solution of vanadium oxinate. Add chloroform to give a total volume of 10 ml. Set aside for 3 hours at 30°. Measure the absorbancy at 635 mμ. Determine the OH content from a previously constructed standard curve.

3. *Determination of alcohols dissolved in organic solvents*

(*a*) *Alcohols in a solvent with high boiling point:* Construct a standard curve using a 1:1 mixture of the solvent in question and nitrobenzene. Add 5 ml of a nitrobenzene solution of vanadium oxinate to 5 ml of sample solution containing 5–50 μmol of alcohol. Heat for 10 minutes at 70°. Then proceed as given in method 1.

(*b*) *Alcohols in a solvent with low boiling point:* Proceed as in (*a*), but use a chloroform solution of vanadium oxinate and do not heat: maintain for 3 hours at 30° before measuring the absorbancy at 635 mμ.

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Zusammenfassung—Für der photometrischen Bestimmung der Mikromolmenge verschiedener Alkoholen vorschlagt man das in solchen organischen Lösungsmittel wie Chloroform und Nitrobenzol gelöste Vanadinoxinat. Die Empfindlichkeit hängt von der Dielektrizitätskonstante des solvents und der Konzentration des Reagenses ab. Diese Reaktion gewährt eine Methode zur Abschätzung der relativen Reaktivität des gegebenen Alkohols und des sterischen Effeckts um OH des Alkohols. Die Reaktion kann auch zur Differenzierung zwischen isomeren Alkoholen verwendet werden.

Résumé—Pour le dosage photométrique d'une quantité micromole de divers alcools, on propose l'emploi de l'oxinate de vanadium dissous dans des solvants organiques tels que le chloroforme et le

nitrobenzène. La sensibilité dépend de la constante diélectrique du solvant et de la concentration du réactif. Cette reaction donne un moyen d'évaluer la réactivité relative d'un alcool et l'effet stérique au voisinage de OH alcoolique. La réaction peut aussi être utilisée pour différencier des alcools isomères.

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THE SEQUENTIAL ANALYSIS OF LONG RANGE FALLOUT DEBRIS

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Summary—A method for the determination of the principal radionuclides of Sr, Ba, Ce, Cs, Y, Zr, Nb, and W in single fallout samples containing bulk Si, Fe, and Ca is presented. The sample and added carriers are dissolved by fusion with sodium carbonate. The melt is leached first with hot water and then with hydrochloric acid. W and Cs are recovered from the water leach. Sr, Ba, Y, and the heavier rare earths appear in the hydrochloric acid leach. Ce is found in the leach residue and Nb in both the residue and the hydrochloric acid leach. The Zr and Nb in the residue are separated from Ce by absorption on an anion-exchanger from hydrochloric acid. The Zr and Nb in the hydrochloric acid leach are separated from Sr and Ba by precipitation of Sr and Ba as nitrates and then separated from Y and the heavier rare earths by absorption on the anion-exchanger. The combined Zr fractions are eluted with dilute hydrochloric acid and Nb with a hydrochloric-hydrofluoric acid mixture.

INTRODUCTION

THE chief mechanism by which radiation doses are delivered to the general population from detonations of nuclear weapons is the off-site deposition of radioactive debris. This hazard has been studied by many means, including an extensive empirical method based on gross β-activity monitoring.[1] The final practical approach, however, is the radiochemical determination of each nuclide. Many authors have summarised techniques for individual fission and neutron irradiation products.[2-4] Others have devised schemes for the determination of groups of these nuclides from single samples.[5-8] In general, all are based on specialised innovations of classical, ion-exchange, and solvent extraction chemistry used in conjunction with radiometric techniques.

A majority of these methods are limited to relatively simple sample matrices or consider only long-lived fission products. However, recent fallout distribution theory[9] suggests the presence of many shorter lived nuclides in long range fallout and the most widely used sampling systems[10,11] collect considerable quantities of insoluble silicon, iron, sulphate and phosphate compounds in the time and space necessary for the accumulation of detectable activities. The method presented is an integration of many reported techniques and several newer procedures, which permits the joint assay of the radionuclides of strontium, caesium, barium, tungsten, zirconium, niobium, and the rare earths from single samples containing up to ten grams of inert substances.

The nuclides listed are determined in association with milligram quantities of inactive carriers to provide media for chemical operations and recovery determinations. Interchange between radioactive and carrier atoms in their respective molecules is achieved by fusion with sodium carbonate. Compounds which are not attacked in the melt are then equilibrated by digestion with mineral acids.

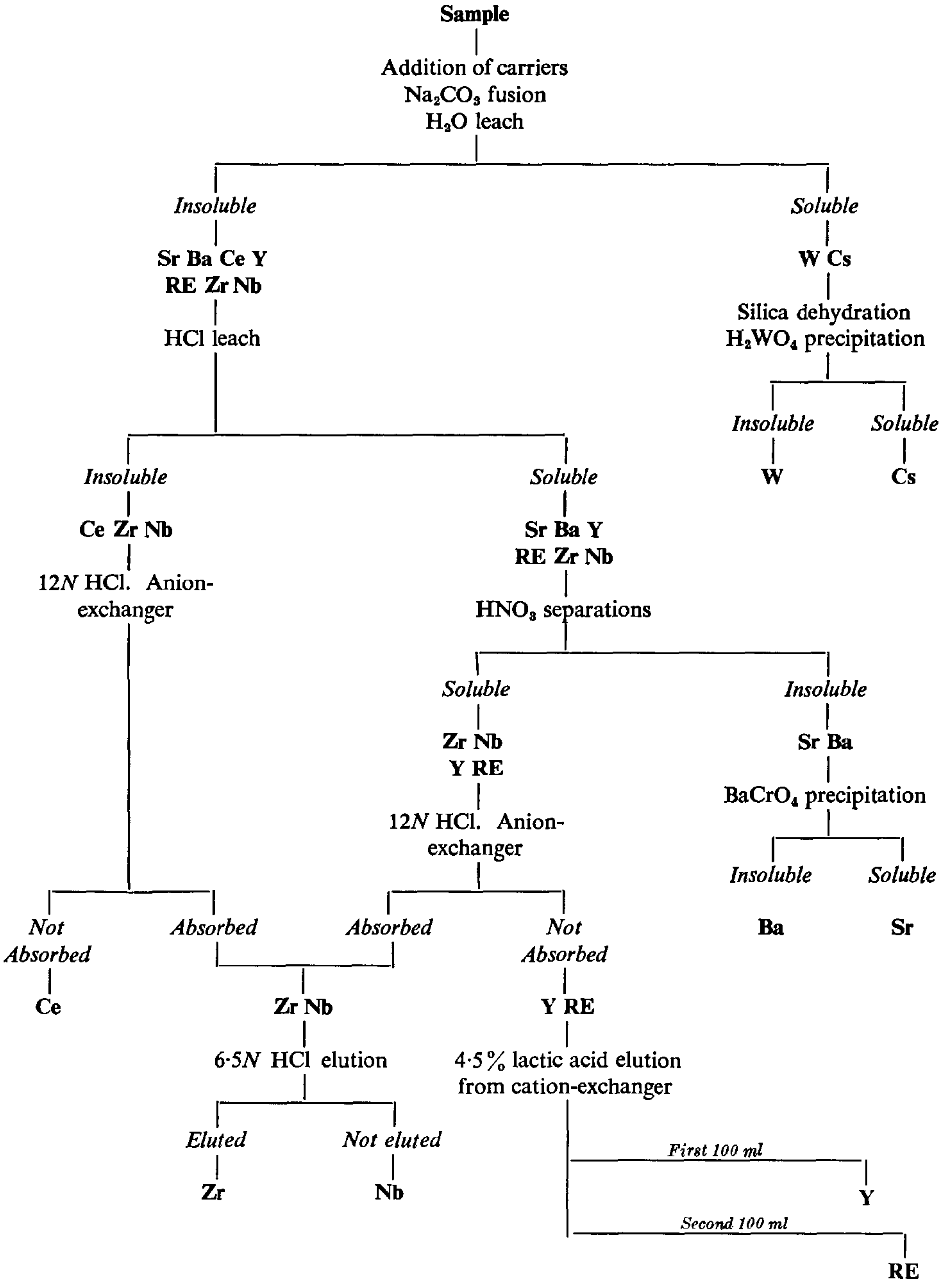

FIG. 1.—Flow chart.

The fundamental separations are illustrated in Fig. 1. Most of the precipitations shown are drawn from adaptations of classical procedures compiled by many authors.[12-15] The radiochemical separation of strontium and barium with 75% nitric acid was discussed by Fresco, Hardy and Welford.[16] The separations based on exchange of anionic chloride complexes were described by Kraus and Moore.[17] The cation-exchange separation of the rare earths was suggested by Cuninghame *et al.*[18]

Final purifications are performed by routine procedures in use in many laboratories.[2,3] Tungsten is purified by an anion-exchange method developed from work reported by Collins and Welford.[19] Caesium is collected by the method of Ewing.[20] Radiometric determinations are carried out with standard β- and γ- radiation detector techniques.[3,4]

EXPERIMENTAL

Reagents

Mineral acids—Unless otherwise noted, acid volumes cited refer to concentrated analytical grades.

Strontium carrier solution—Dissolve 24·2 g of $Sr(NO_3)_2$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of strontium as the oxide.

Barium carrier solution—Dissolve 15·2 g $BaCl_2$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of barium as the sulphate.

Cerium carrier solution—Dissolve 31·0 g $Ce(NO_3)_3.6H_2O$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of cerium as the oxide.

Zirconium carrier solution—Dissolve 3·53 g $ZrOCl_2.8H_2O$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of zirconium as the oxide.

Tungsten carrier solution—Dissolve 16·0 g Na_2WO_4 in H_2O. Dilute solution to 1 litre with H_2O. Standardise by gravimetric determination of tungsten as the 8-hydroxyquinolate.

Caesium carrier solution—Dissolve 25·4 g CsCl in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of caesium as the chloroplatinate.

Lanthanum carrier solution—Dissolve 31·2 g $La(NO_3)_3$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of lanthanum as the oxalate.

Yttrium carrier solution—Dissolve 21·6 g of $Y(NO_3)_3.6H_2O$ in H_2O. Dilute solution to 500 ml with H_2O. (Decontaminate by TBP extraction, if necessary.)[4] Standardise by gravimetric determination of yttrium as the oxalate.

Niobium carrier solution—Dissolve 1 g Nb metal in saturated aqueous oxalic acid solution. Dilute solution to 1 litre with saturated aqueous oxalic acid solution. Standardise by gravimetric determination of niobium as the oxide.

Sodium carbonate wash solution—Dissolve 50 g Na_2CO_3 in H_2O. Dilute solution to 1 litre with H_2O.

Cinchonine solution—Dissolve 125 g cinchonine in 6*N* HCl. Dilute solution to 1 litre with 6*N* HCl.

Cinchonine wash solution—Dilute 10 ml of cinchonine solution to 1 litre with H_2O.

Acetic acid solution—Dilute 345 ml glacial acetic acid to 1 litre with H_2O.

Ammonium acetate solution—Dissolve 463 g ammonium acetate in H_2O. Dilute solution to 1 litre with H_2O.

8-*Hydroxyquinoline solution*—Dissolve 50 g 8-hydroxyquinoline in 2*M* acetic acid. Dilute solution to 1 litre with 2*M* acetic acid.

8-*Hydroxyquinoline wash solution*—Add 50 ml of ammonium acetate solution and 25 ml of acetic acid solution to 10 ml of 8-hydroxyquinoline solution. Dilute mixture to 1 litre with H_2O.

Sodium chromate solution—Dissolve 48·6 g Na_2CrO_4 in H_2O. Dilute solution to 1 litre with H_2O.

Mandelic acid solution—Dissolve 160 g mandelic acid in H_2O. Dilute solution to 1 litre with H_2O.

Mandelic acid wash solution—Dissolve 50 g mandelic acid in 20 ml of HCl. Dilute solution to 1 litre with H_2O.

Iodic acid solution—Dissolve 61·6 g of HIO_3 in H_2O. Dilute solution to 1 litre with H_2O.

Iodic acid wash solution—Dilute 50 ml of iodic acid solution to 100 ml with 20% HNO_3.

Lactic acid solution I—Dilute commercial grade lactic acid (85%) to 4·25% with H_2O. Titrate to pH 3·5 with NH_4OH using pH meter. (For solutions that must be stored, 19 ml of phenol per litre is added to prevent deterioration oflactic acid.)

Lactic acid solution II—Titrate lactic acid solution I to pH 3·7 with NH_4OH.

Citric acid solution—Dissolve 50 g citric acid in H_2O. Titrate to pH 7·0 with NH_4OH using pH meter. Dilute solution to 1 litre with H_2O.

Chloroplatinic acid solution—Dissolve 10 g of chloroplatinic acid in H_2O. Dilute solution to 100 ml with H_2O.

Aerosol solution—Dissolve 1 g of Aerosol OT in H_2O. Dilute solution to 1 litre with H_2O.

Special apparatus

Sample mounting—Final precipitates are filtered through tared glass-fibre filter paper for weighing. The samples are then mounted on plastic discs, covered with Mylar film and secured with plastic rings. Specifications are given in USAEC Report No. NYO-4700.[4]

β- and γ-Counters—Standard mica windowed Geiger-Müller tubes are used for β-counting and the Baird well-type scintillation counter for γ-counting.[4]

Ion-exchange columns

The ion-exchange column vessel used is shown in Fig. 2. The dimensions are given in inches. A wad of glass wool is used to support the resin bed. Resins are wet-sieved, aqueous and non-aqueous extracted on receipt and stored in distilled water until required.[4]

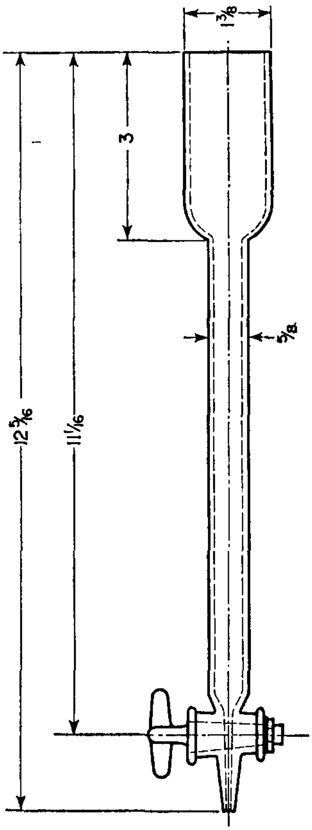

Fig. 2.—Ion exchange column.

Tungsten column—Transfer 10 ml of wet settled Dowex 1 X-4 (50–100 mesh) Cl^- form to the column. Allow the resin bed to settle, and pass 100 ml of 1*N* HCl at a flow-rate not exceeding 5 ml per min through the bed. Pass the sample solution through.

Zirconium column—Transfer 20 ml of wet-settled Dowex 1 X-2 (50–100 mesh) Cl^- form to the ion-exchange column. Allow the resin bed to settle, and pass 150 ml of HCl through at a flow-rate not exceeding 3 ml per min. Add 1 ml of Nb carrier solution directly to the resin bed and wash with 100 ml of HCl. Pass the sample solution through. To regenerate, pass 250 ml of 0·5*N* HCl through the resin bed at a flow-rate not exceeding 5 ml per min.

Yttrium column—Transfer 10 ml of wet-settled Dowex 50 X-8 (200–400 mesh) H^+ form to the ion-exchange column. Allow the resin bed to settle, and pass 100 ml of lactic acid solution I through the resin bed at a flow-rate not exceeding 3 ml per min. Pass the sample through. To regenerate, pass 100 ml of citric acid solution and 100 ml of water through the resin bed at flow-rates no exceeding 5 ml per min.

PROCEDURES

Section 1A—*Group separations*

Procedure	*Remarks*
1. Transfer the sample to a platinum dish and ignite at 500°.	Destruction of organic material.
2. Add 1 ml of Sr, Ba, Ce, Zr, W, and Cs carrier solutions and 2 ml of NH_4OH.	
3. Dry at 110°, weigh and fuse with five times the sample weight of Na_2CO_3.	Dissolution and equilibration of sample and carriers.
4. Grind the melt thoroughly and transfer to a 600-ml beaker. Dissolve any remaining material in hot water and wash into the beaker.	
5. Add 200 ml of water, digest with stirring for 1 hr. Cool and filter over Whatman No. 42 filter paper.	H_2O extraction of W and Cs.
6. Wash with sodium carbonate wash solution. Collect filtrate and washings in a 600-ml beaker and reserve for step 1, Section 3A.	Filtrate is reserved for W and Cs analysis.
7. Dissolve the precipitate on the filter paper with 1 : 1 HCl and collect the solution in a 400-ml beaker. Transfer the paper and insoluble material to a platinum crucible and reserve for step 1, Section 1B.	HCl dissolution of carbonate. Precipitate reserved for insoluble residue treatment.
8. To the filtrate, add 25 ml of HCl and evaporate to dryness. Add 10 ml of HCl to the residue. Heat on hot plate for 5 min. Add 100 ml of distilled water, heat to boiling, cool and filter over Whatman No. 40 filter paper. Wash thoroughly with hot 1 : 9 HCl. Add the paper and residue to the platinum crucible from step 7. Collect filtrate and washings in a 250-ml beaker and reserve for step 1, Section 2A.	Dehydration of silica. Combination of insoluble residues. Filtrate and washings reserved for strontium separations.

Section 1B—*Treatment of insoluble residues*

1. Dry the papers and residues from steps 7 and 8, Section 1A, at 110° and ash at 500°.	Destruction of filter paper.
2. Add 2 ml of H_2SO_4 and 10 ml of HF and evaporate to SO_3 fumes.	Volatilisation of silica.
3. Transfer to a 100-ml beaker and add 10 ml of HCl and 10 ml of HNO_3. Evaporate to SO_3 fumes. Transfer to a 40-ml centrifuge tube and dilute to 20 ml. Cool and centrifuge. Decant supernate into a 40-ml centrifuge tube and discard precipitate.	Dissolution of insoluble oxides.
4. Adjust to pH 10 with NH_4OH. Digest, cool and centrifuge. Discard supernate.	Collection of Zr and Ce.
5. To the precipitate add 10 ml of HCl and reserve for step 4, Section 4A.	

Section 2A—*Strontium*

1. Add 1 ml of yttrium carrier and evaporate the solution from step 8, Section 1A to less than 20 ml. Add 10 ml of distilled water.

Procedure	*Remarks*
2. With mechanical stirring, slowly add 100 ml of fuming nitric acid. Stir for 45 minutes. Cool and filter over glass-fibre filter paper.	Collection of Sr and Ba as nitrates.
3. Collect the filtrate in a 250-ml beaker and reserve for step 1, Section 4A. Dissolve the precipitate with distilled water and collect in a 150-ml beaker.	Reserve filtrate for Zr, Y, and Nb analysis.
4. Evaporate to dryness. Add 12 ml of distilled water and with constant stirring add 40 ml of fuming nitric acid.	
5. Cool and filter over glass-fibre filter paper. Combine filtrate with filtrate from step 3.	Separation of Sr and Ba from Ca.
6. Dissolve the nitrate precipitate with distilled water, collect in a 40-ml centrifuge tube and add 1 ml of yttrium carrier.	
7. Heat in a water bath at 90°. Adjust to pH 8 with NH_4OH. Cool, centrifuge, and decant the supernate into a centrifuge tube. Record the time.	First milking of ^{90}Y and ^{140}La
8. Dissolve the precipitate with 3–5 drops of HCl. Add 10 ml of distilled water and repeat step 7. Combine supernates. Discard the precipitate.	
9. To the combined supernates, add 1 ml of $6M$ acetic acid and 2 ml of $6M$ ammonium acetate solution. Adjust to pH 5·5 with HCl or NH_4OH. Heat in a water bath at ~90°. Add 1 ml of sodium chromate solution. Digest with occasional stirring for 10–15 min. Cool. Centrifuge.	Separation of Ba from Sr.
10. Decant the supernate into a polyethylene bottle. Add 2–3 drops of HCl and 1 ml of yttrium carrier solution. Allow solution to stand for 2 weeks.	Equilibration of ^{90}Sr and ^{90}Y.
11. Dissolve the precipitate from step 9 with 5 ml of $0{\cdot}5N$ HCl. Transfer to a polyethylene bottle and add 1 ml of lanthanum carrier. Store for 10 days and reserve for step 1, Section 2B.	Equilibration of ^{140}Ba and ^{140}La.
12. Transfer the equilibrated solution from step 10 to a 40-ml centrifuge tube. Heat in a water bath. Adjust to pH 8 with NH_4OH and add 6 drops of 30% H_2O_2. Heat with occasional stirring for 15 min. Cool. Centrifuge. Record hour and date.	Second milking of ^{90}Y.
13. Transfer the supernate to a 100-ml beaker, and reserve for step 16. Dissolve the precipitate with 3 drops of HCl and dilute to 20 ml with water.	
14. Heat in a water bath. Adjust to pH 8 with NH_4OH. Cool. Centrifuge. Combine supernate with that from step 13 and reserve for step 16.	Purification of Y.
15. Dissolve the precipitate with 3 drops of concentrated HCl. Add 20 ml of distilled water. Heat in a water bath and add 1 ml of saturated oxalic acid. Digest with occasional stirring for 5 min. Cool, filter, dry, and mount. Discard filtrate.	Final precipitation of ^{90}Y as the oxalate.
16. Heat the combined supernates from step 14 to just below the boiling point. Add 10 ml of a saturated solution of sodium carbonate with stirring. Cool and filter over a weighed filter. Wash precipitate with Na_2CO_3 wash solution. Dry, weigh, mount, and count.	Final precipitation of Sr as the carbonate.

Section 2B—*Barium*

1. Transfer the solution from step 11, Section 2A to a 40-ml centrifuge tube. Dilute to 20 ml. Heat and add 3 drops	Dissolved $BaCrO_4$ precipitate.

Procedure	*Remarks*
of H_2SO_4, allow to stand for 1 hr. Centrifuge. Record hour and date.	Separation of Ba and La.
2. Transfer the supernate to a centrifuge tube. Adjust to pH 10 with NH_4OH. Add 6 drops of 30% H_2O_2. Digest in water bath for 20 min. Cool. Centrifuge, discard supernate. Wash precipitate with H_2O. Discard wash.	Collection of La as the hydroxide.
3. Dissolve the precipitate with 3 drops of HCl. Dilute to 20 ml. Heat. Add 1 ml of saturated $H_2C_2O_4$. Digest for 15 min with stirring.	Final precipitation of La as the oxalate.
4. Cool. Filter through glass-fibre filter paper. Dry, mount, and count.	
5. Slurry the precipitate from step 1 with 0·5*N* HCl. Filter through a weighed glass-fibre filter paper washing with H_2O. Dry and weigh.	Gravimetric determination of Ba as the sulphate.

Section 3A—*Tungsten*

1. Acidify the solution from step 6, Section 1A, with HCl and add a 100-ml excess. Evaporate to dryness. Add 100-ml of HCl, evaporate to dryness and bake.	Dehydration of silica.
2. Slurry with 500 ml of hot water and heat to just below boiling on a sand bath. Add 20 ml of HCl, 10 ml of HNO_3 and 10 ml of cinchonine solution.	Precipitation of W as the acid.
3. Add 10 ml of wet paper pulp. Digest with occasional stirring for 1 hr.	Coagulation of H_2WO_4.
4. Allow solution to cool to room temperature. Filter over No. 42 Whatman filter paper. Wash the precipitate with hot cinchonine wash solution. Collect the filtrate in a 600-ml beaker and reserve for step 1, Section 3B.	Reserve for Cs analysis.
5. Transfer the filter and precipitate to a platinum crucible. Dry at 110° and ignite at 500°.	Destruction of filter paper.
6. Add 5 ml of HNO_3 and 20 ml of HF to crucible. Evaporate to dryness. Cool.	Volatilisation of silica.
7. Add 1 ml of 6*M* NaOH. Heat and transfer to a 40-ml centrifuge tube using distilled water.	Dissolution of H_2WO_4.
8. Adjust the volume to 20 ml with distilled water and add 10 ml of HNO_3.	
9. Digest for 1 hr in a water bath at 95°. Cool and centrifuge. Decant and discard the supernate.	Re-precipitation of W as the acid.
10. Add to the precipitate 1 ml of 6*M* NaOH. Heat in a water bath at 95° to effect solution. Add 3 ml of saturated tartaric acid solution and adjust the volume to ~15 ml with 1*N* HCl.	Complexing of W for anion-exchange purification.
11. Pass the solution through a prepared Dowex 1 X-4 column* at a flow-rate of 0·5 ml per min. Wash the resin bed with 100 ml of 1*N* HCl. Discard waste and wash solutions.	Exchange of W-tartrate complex.
12. Transfer the resin to a platinum crucible. Dry at 110°. Ignite at 500°.	Destruction of resin and tartrate radical.
13. Add 2–3 ml of NH_4OH dropwise, and 5 ml of water. Digest.	
14. Transfer the solution to a 100-ml beaker with water and dilute to ~50 ml.	

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* See preparation of tungsten column under *Special Apparatus*.

Procedure	*Remarks*
15. Add 1 ml of 6*M* acetic acid solution and 2 ml of 6*M* ammonium acetate solution, adjusting to pH 5·5, if necessary, with HCl.	
16. Heat at 90° on a sand bath and add 2 drops of 0·1% Aerosol solution. Add 3 ml of 8-hydroxyquinoline solution. Stir the solution for 2 min. Cool.	Final precipitation of W as the hydroxyquinolate.
17. Filter over a weighed filter paper. Wash with 8-hydroxyquinoline wash solution. Dry at 110°. Weigh, mount and count.	

Section 3B—*Caesium*

1. To the filtrate from step 4, Section 3A, add 50 ml of HCl. Evaporate the solution carefully to dryness, and char organic material. Ignite at 500°	Filtrate from precipitation of H_2WO_4.
2. Dissolve the salts in 200 ml of distilled water. Add 50 ml of HCl. Evaporate to dryness.	Dehydration of silica.
3. Dissolve in 100 ml of distilled water. Filter over No. 42 Whatman paper. Wash the residue with hot 5% HCl. Discard the residue.	
4. Add 4 ml of chloroplatinic acid solution. Stir for 1 hr. Allow to stand overnight in a refrigerator. Filter over a weighed filter. Weigh, mount, and count.	Final precipitation of Cs as the chloroplatinate.

Section 4A—*Zirconium*

1. Evaporate the solution from step 3, Section 2A, to less than 20 ml and transfer to a 40-ml centrifuge tube. Adjust to pH 10 with NH_4OH. Digest, cool, and centrifuge. Discard supernate.	Filtrate from nitric acid collection step. Collection of hydroxides.
2. Wash the precipitate twice with 20-ml portions of H_2O. Discard the wash solutions. Dissolve the precipitate with 10 ml of HCl.	Complexing of Zr-Nb for anion-exchange separation.
3. Pass the solution through a prepared Dowex 1 X-2 column.* Wash with 100 ml of HCl. Collect the effluent and wash solution in a 250-ml beaker and reserve for step 1, Section 5B.	Separation of Y from Zr-Nb. Reserve for Y determination.
4. Pass the solution from step 5, Section 1B, through the same resin column used in step 3. Wash with 100 ml of HCl. Collect the effluent and wash solution in a 250-ml beaker and reserve for step 1, Section 5A.	Separation of Ce from Zr-Nb. Reserve for Ce determination.
5. Pass through the column 100 ml 6·5*N* HCl. Reserve the column for step 1, Section 4B. Collect the effluent in a 250-ml beaker and evaporate to 10–20 ml.	Elution of Zr. Reserve column for Nb determination.
6. Transfer to a 40-ml centrifuge tube and adjust to pH 10 with NH_4OH. Digest, cool and centrifuge. Discard the supernate. Dissolve the precipitate with 3 ml of HCl. Add 25 ml of H_2O and 4 ml of 16% mandelic acid.	Final precipitation of Zr as the mandelate.
7. Heat at 95° for 45 min with occasional stirring. Cool and filter over weighed glass-fibre filter paper. Wash the precipitate with mandelic acid wash solution. Dry at 110°, weigh, mount, and count.	

Section 4B—*Niobium*

1. Pass through the resin column from step 5, Section 4A, 100 ml of 4·5*N* HCl–0·06*N* HF. Collect in a 250-ml beaker.	Elution of Nb from resin column. Collection of Nb as the hydroxide.

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* See preparation of zirconium column under *Special Apparatus*.

Procedure	*Remarks*
Adjust to pH 10 with NH_4OH. Heat for 5 min on hot plate.	
2. Filter over Whatman No. 40 filter paper. Discard the filtrate. Dry and ignite the precipitate at 500°. Transfer the material to a 5-ml glass vial, and count.	Preparation of Nb for γ-counting.
Section 5A—*Cerium*	
1. Evaporate the solution from step 4, Section 4A, to approximately 20 ml and transfer to a 40-ml centrifuge tube. Adjust to pH 9 with NH_4OH. Digest, cool and centrifuge. Discard the supernate.	Effluent and wash solutions from Zr and Nb adsorption. Collection of Ce and rare earths as hydroxides.
2. Dissolve the precipitate with 10 ml of HNO_3, add 0·3 ml of 30% H_2O_2 and allow 5 min for reaction time.	Dissolved hydroxides from column effluent. Reduction of Ce^{IV} to Ce^{III}.
3. Add 20 ml HIO_3, cool and centrifuge. Decant the supernate into a 40-ml Lusteroid centrifuge tube and discard the precipitate.	Scavenging step to remove traces of Zr, Th, or Po.
4. To the supernate, add 5 ml of HF with stirring. Centrifuge and discard the supernate.	Collection of Ce and rare earths as fluorides.
5. Slurry the precipitate with 1 ml of saturated boric acid, add 5 ml of HNO_3 and transfer to a 40-ml centrifuge tube. Dissolve the precipitate by heating and adjust to pH 9 with NH_4OH. Cool and centrifuge. Discard the supernate.	Collection of Ce and rare earths as hydroxides.
6. Dissolve the precipitate in 10 ml of HNO_3. Add 20 ml of HIO_3 and immerse in an ice bath. Add 1 ml of $NaBrO_3$ solution, allow to digest for 10 min. Centrifuge. Discard the supernate.	Oxidation of Ce^{III} and precipitation of cerium as the iodate.
7. Dissolve the precipitate with 10 ml of HNO_3, 3 drops of HCl, and 3 drops of H_2O_2. Boil off the peroxide and cool in ice bath. Add 20 ml of HIO_3 and 1 ml of $NaBrO_3$.	Re-precipitation of $Ce(IO_3)_4$.
8. Cool. Filter over weighed glass-fibre filter paper. Weigh, mount, and count.	
Section 5B—*Yttrium*	
1. Evaporate the solution from step 3, Section 4A, to 20 ml and transfer to a 40-ml Lusterloid centrifuge tube. Adjust to pH 8 with NH_4OH. Digest, cool, and centrifuge. Discard the supernate.	Collection of Y and rare earths as the hydroxides.
2. Dissolve the precipitate in 10 ml of HNO_3 and dilute with water to about 30 ml. Add 5 ml of HF. Stir and digest for 15 min at room temperature. Centrifuge, decant, and discard the supernate.	Collection of Y and rare earths as the fluorides.
3. Slurry the precipitate with 1 ml of saturated boric acid, add 5 ml of HNO_3 and transfer to a 40-ml centrifuge tube. Dissolve the precipitate by heating and adjust to pH 9 with NH_4OH. Cool and centrifuge. Discard the supernate.	Collection of Y and rare earths as hydroxides.
4. Dissolve the precipitate with 3 drops of HCl. Add 3 ml of 4·25% lactic acid (pH 3·5).	
5. Pass the solution through a prepared* Dowex 50 X-8 column. Wash the centrifuge tube with two 5-ml portions of hot water, passing each through the column. Discard waste and wash solutions. Pass 100 ml of the lactic acid solution (pH 3·5) through the column.	Separation of Y from rare earths.

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* See preparation of yttrium column under *Special Apparatus*.

Procedure	*Remarks*
6. Collect eluant in a 150-ml beaker to which 1 ml of saturated oxalic acid has been added. Reserve the column for step 1, Section 6.	
7. Digest with occasional stirring for 10 min. Cool and filter over weighed glass-fibre filter paper. Wash the precipitate with distilled water. Dry, weigh, mount, and count.	Final precipitation of Y as oxalate.
Section 6—Rare earths	
1. Pass through the column from step 5, Section 5B, 100 ml of 4·25% lactic acid, pH 3·7. Collect the eluant in a 150-ml beaker to which 1 ml of lanthanum carrier has been added.	Elution of rare earths.
2. Digest for 10 min. Add 1 ml of saturated oxalic acid. Cool, filter, mount, and count.	Final precipitation of rare earths using La as carrier.

DISCUSSION

Yields of the various elements from experimental samples are listed in Table I. The matrices were composed of 1- and 2-gram aliquots of representative United States soils with known quantities of activities and carriers added. In all cases the results of gravimetric and radiometric recovery measurements agree within the probable error of their determination, indicating that equilibration takes place before chemical losses occur. Results of tracer studies indicate that ^{95}Nb generally follows zirconium carrier and that its recovery is more reproducible when niobium carrier is not used until the final stages of the procedure.

TABLE 1. RESULTS OF GRAVIMETRIC AND RADIOMETRIC ANALYSES

Element	Number of analyses performed	Average % recovery	
		Gravimetric	Radiometric
Sr	36	83	77
Cs	24	79	77
Ce	20	83	80
Y	10	86	82
Zr	24	88	80
W	72	72	76
Nb	24	—	90

Cross contamination analyses were conducted on most of the recovery samples using β-absorption[21] and decay study[22] techniques. In no case was more than 0·001% of any added alien activity detected in a finally precipitated elemental fraction.

The method has also been used satisfactorily for the comprehensive analysis of more than 200 actual fallout samples collected in New York City.[23] Since bulk quantities of iron, silica and calcium were handled without interference, many other biospheric sample types are within the scope of the procedure. In addition, with some alterations, the analyses of other individual rare earths, ruthenium, iodine and molybdenum are possible.

Zusammenfassung—Eine Methode wird beschrieben zur Bestimmung der wichtigsten Radionucleide von Sr, Ba, Ce, Cs, Y, Zr, Nb und W in einer einzigen "Fallout"-Probe, die als Hauptmestandteile

Si, Fe und Ca enhält. Die Probe wird nach Zusatz von Trägermaterial mit Natriumcarbonat geschmolzen und der Schmelzkuchen erst mit Wasser und dann mit Salzsäure ausgezogen. W und Cs werden aus dem wässrigen Auszug gewonnen. Sr, Ba, Y und die schwereren seltenen Erden scheinen im salzsauren Auszug auf. Ce wird im Auszugsrückstand gefunden, während Zr und Nb sowohl im Rückstand als auch im Säureextrakt vorhanden sind. Zr und Nb aus dem Ruckstand werden von Ce durch Adsorption an einem Anionenaustauscher aus salzsaurer Lösung getrennt. Das im sauren Extrakt enthaltene Zr und Nb wird von Sr und Ba durch Fällung der letzteren als Nitrate getrennt und dann vom Y und den schwereren seltenen Erden durch Anionenaustauscher separiert. Die kombinierten Zr-Fraktionen werden mit verdünnter Salzsäure und das Nb mit Salzsäure-Flussäure eluiert.

Résumé—Les auteurs présentent une méthode de dosage des principaux radioéléments de Sr, Ba, Ce, Cs, Y, Zr, Nb et W dans des échantillons contenant de grandes quantités de Si, Fe et Ca. L'échantillon et les supports ajoutés sont dissous par fusion avec du carbonate de sodium. La masse fondue est lavée d'abord avec de l'eau bouillante, puis avec de l'acide chlorhydrique. W et Cs sont récupérés à partir de l'eau de lavage. Sr, Ba, Y et les terres rares plus lourdes apparaissent dans l'acide chlorhydrique de lavage. Ce est trouvé dans le résidu de lavage et Zr et Nb à la fois dans le résidu et dans l'acide chlorhydrique de lavage. Zr et Nb dans le résidu sont séparés de Ce par absorption sur un échangeur d'anions à partir d'acide chlorhydrique.

Zr et Nb dans l'acide chlorhydrique de lavage sont séparés de Sr et Ba par précipitation de Sr et Ba à l'état de nitrates, et ensuite séparés de Y et des terres rares plus lourdes par absorption sur un échangeur d'anions. Les fractions de Zr combinées sont éluées avec de l'acide chlorhydrique dilué et Nb avec un mélange acide chlorhydrique-acide fluorhydrique.

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CHLORITE AS AN OXIDISING AGENT IN TITRIMETRIC ANALYSIS

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Summary—The possibilities of using a solution of sodium chlorite as an oxidising agent in titrimetric analysis have been investigated. Such a solution, in the absence of light, is chronometrically stable and convenient for the direct titration of sulphite (in applying the titre to a known solution of sulphite); iron, by its reduction to iron^{II} with tin^{II} chloride (the result to be read from the difference between the potential-jump corresponding to iron^{II} × tin^{II} and the first jump corresponding to tin^{II}); arsenite; iodide. The titration is generally carried out in an acidic medium, with the occasional application of catalysts such as potassium iodate.

INTRODUCTION

THE possibility of using sodium chlorite in chemical analysis has been known for some time. Yet there are in the literature very few references to using that substance as a titrimetric reagent. A priority for applying chlorites in titrimetric analysis has been claimed by Levi.[1] The latter was also the first author to deal with the problem of the stability of chlorite solutions.[2]

Levi and his co-workers also occupied themselves with obtaining the chlorites of the alkali and the alkaline earth metals.[3,4] They described, too, both the reductimetric and oxidimetric use of chlorite in chemical analysis.[5] On the one hand they used chlorite as a reducing agent for the quantitative determination of permanganate.[6] On the other hand, however, they state that chlorite quantitatively oxidises arsenite, stannite and antimonite in an alkaline medium,[7] as well as sulphite. The question of oxidising thiosulphate[7] with chlorite is discussed. Jackson and Parsons[8,9] proposed a method of determining sulphite with chlorite. Yntema and Fleming[10] discussed the quantitative oxidation of iodide to iodate with chlorite; and Brown[11] reported on the application of chlorite to the titrimetric determination of arsenite.

An indirect analysis with application of chlorite is proposed by Paul and Singh.[12] These authors consider that a series of reducing substances might be quantitatively determined by means of their pre-oxidation with iodine monochloride, the liberated iodine being subsequently oxidised by a standard solution of chlorite to IBr_2^-, in the presence of potassium bromide. However, they give no further details or results.

In a general way it may be stated that the literature pertaining to the use of chlorite in titrimetric analysis is scarce and, moreover, it often suggests some doubts.

The oxidation potential of chlorite has been studied by Holst,[13] then by Flis[14] over a wide range of pH. The data given by them are concordant. Comparing the potential values given by Holst and Flis with that of the redox potential in the systems discussed by the authors mentioned before, it seems, in some cases, improbable to admit the possibility of a quantitative oxidation, especially in such a medium as described. It would, therefore, be of much interest on the one hand to re-examine the redox systems already described and on the other hand to establish the possibility of quantitative oxidation with chlorite of a series of other reducing substances.

EXPERIMENTAL

Reagents

Titrant: Technical sodium chlorite solutions were employed ($NaClO_2$ content about 80%, with impurities of $NaClO_3$, NaCl, NaOH).

After storing 0·1*N* chlorite solution for a long time, both out of light and exposed to light, it has been found that with light excluded the solution remains perfectly stable for a period of not less than 3 months (see Table 1).

TABLE I.—STABILITY TEST OF 0·1*N* SODIUM CHLORITE SOLUTION

Time, *days*	Normality of $NaClO_2$ solution protected against light	Normality of $NaClO_2$ solution exposed to light action
0	0·9905	0·9905
1	0·9905	0·9905
2	0·9905	0·9802
3	0·9905	0·9200
5	0·9905	0·9103
8	0·9905	0·9056
10	0·9904	0·8925
15	0·9904	0·8632
30	0·9904	0·8332
60	0·9904	0·8245
90	0·9904	0·8115

Standardisation of sodium chlorite solution

The equivalent weight of chlorite is 1/4 of its molecular weight according to the equation:

$$ClO_2^- + 4H^+ + 4e \rightarrow Cl^- + 2H_2O$$

The standardisation of chlorite solution was carried out by the method due to Bray.[15] A measured quantity of chlorite solution (10 ml) was treated with 15 ml of 10% potassium iodide solution and 10 ml of 2*N* sulphuric acid, diluted with 65 ml of water, and the liberated iodine immediately titrated with 0·1*N* sodium thiosulphate solution. For titration purposes in an acidic medium, the standardisation of chlorite solution was carried out in a solution of the same acid concentration as used in the experiments. The thiosulphate solution was standardised by means of dichromate.

Apparatus

Quantitative titration of reducing substances with sodium chlorite was carried out by potentiometric titration with the electrode system: platinum-saturated calomel. The electromotive force of the system was measured with a direct-reading pH-meter ("Orion," Hungarian made), or, more accurately, with a compensating method using a pH-meter with an electronic amplifier ("Ridan," Polish made). The latter method ensured a titration accuracy within a limit of 1 mV. The results were computed after the method of Hahn.[16] The characteristic graphs of the titration are shown in Fig. 1.

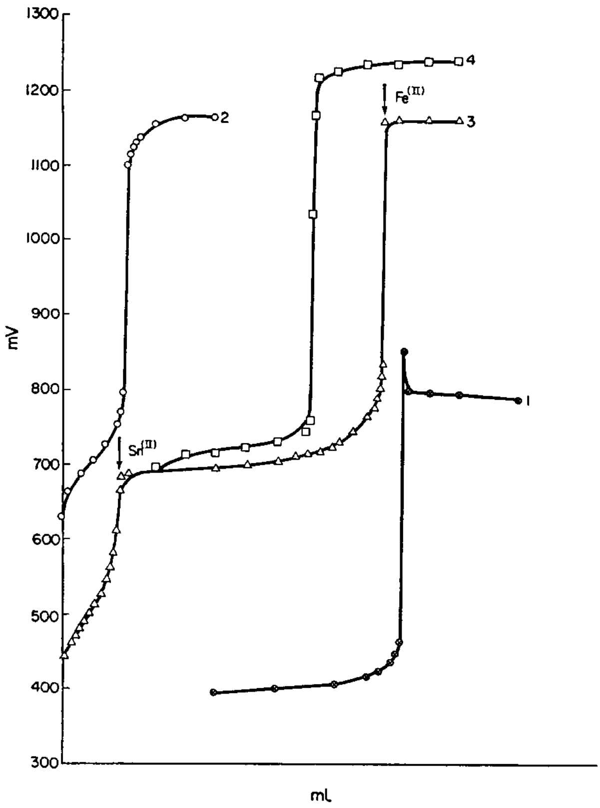

FIG. 1.—Some titration curves obtained with sodium chlorite solution.

1. Titration of sulphite (pH 4·08)
2. Titration of iodide (2*N* H_2SO_4)
3. Titration of Fe^{II} with Sn^{II} present in excess (2*N* HCl + 2*N* H_2SO_4 + KI)
4. Titration of arsenite (2*N* HCl + KIO_3).

RESULTS AND DISCUSSION

Oxidation of sulphite

The study of the possibility of titration of sulphite with chlorite was initiated by checking the method proposed by Jackson and Parsons.[9] These authors considered the reaction:

$$ClO_2^- + 2SO_3^{2-} \rightarrow Cl^- + 2SO_4^{2-}$$

to be too slow for analytical purposes; they stated that a small addition of potassium iodide results in a considerable acceleration. Supposing that oxidation of sulphite with chlorite occurs indirectly through the following reactions:

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O$$

$$2H_2O + 2I_2 + 2SO_3^{2-} \rightarrow 2SO_4^{2-} + 4I^- + 4H^+$$

then they are applying the classical titration of sulphite in an acetic acid medium using the chlorite solution with starch as indicator.

The determination of sulphite, performed according to the above method, yielded results which were too low compared with those by the iodometric method which was

TABLE II.—DETERMINATION OF SULPHITE

Concentration of sulphite determined iodometrically (100%)	Concentration of sulphite determined with $NaClO_2$ (by the present method)															
	Medium															
	0·1*N* H_2SO_4		pH 1·98		pH 2·87		pH 4·07		pH 4·56		pH 5·1		pH 6·09		pH 7·02	
mol/l.	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%
0·0327	0·0225	68·81	0·02475	75·69	0·02975	90·89	0·03075	94·04	0·03080	94·19	0·02625	80·27	0·0240	73·39	0·02180	66·27
0·0421	0·0293	69·50	0·03199	76·00	0·03789	90·00	0·03957	94·00	0·03968	94·25	0·03347	79·50	0·03069	72·90	0·02779	66·00
0·0500	0·0338	67·50	0·03745	74·90	0·04550	91·00	0·04705	94·10	0·04707	94·15	0·04025	80·50	0·03690	73·80	0·03260	65·20

taken as a standard method. The error in the above-described method amounted to about 17%. It seems evident that acidifying a sulphite solution with even a weak acid, such as acetic acid, causes its decomposition with loss of gaseous sulphur dioxide. In order to eliminate this source of error, the possibilities of quantitative oxidation of sulphite with chlorite within the pH range of 1 to 7 were examined. The concentration of sulphite solution was determined by the iodometric method.

Buffer solutions used in the analysis in order to keep the desired pH of the titrated solution were prepared according to Britton and Robinson and their pH was determined by the compensation method.

The results shown in Table II confirm the preceding observations. In a medium with a pH of below 4, decomposition of sulphite takes place with loss of sulphur dioxide, and this is increased in proportion as the pH of the titrated solution is lowered. In a medium of pH above 5 sulphite oxidation is very slow and the results obtained are likewise too low.

The optimal pH range for the titration proved to be from 4 to 4·6. Within these pH limits the reaction occurs with a rate sufficient for analytical purposes, whereupon the results obtained are so reproducible that in standardising the chlorite solution with a sulphite solution of a known concentration, it is possible to put this method into practice.

Oxidation of iodide

In starting tests of titrating iodide with chlorite it was assumed that the reaction would be:

$$4KI + NaClO_2 + 2H_2SO_4 \rightarrow 2I_2 + NaCl + 2K_2SO_4 + 2H_2O$$

The potential of the redox system

$$I_2 + 2e \rightleftharpoons 2I^-$$

amounts to 0·535 V.

From that background, tests have been made of the titration of iodide with chlorite in an acidic medium. Diluted (about 0·02N) iodide solutions were prepared with a view to preventing a volatisation of the liberated iodine. The concentration of the iodide solution was determined by titration with iodate using Andrews' method. For the titration, 0·1N and 0·02N solutions of sodium chlorite were used. Oxidation of iodide was carried out in a sulphuric acid medium (0·01N, 0·2N, 1N, 2N and 4$N H_2SO_4$).

TABLE III.—DETERMINATION OF IODIDE

Concentration of iodide determined by titration with iodate	Concentration of iodide determined with $NaClO_2$ (by the present method)							
	0·1N solution of $NaClO_2$					0·02N $NaClO_2$ solution		
	Medium							
	4N H_2SO_4	2N H_2SO_4	1N H_2SO_4	0·2N H_2SO_4	0·01N H_2SO_4	2N H_2SO_4	1N H_2SO_4	0·2N H_2SO_4
mol/l.	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*
0·02067		0·02075						
0·02058	0·02061	0·02061	0·02062	0·02061	0·0224	0·02075	0·02076	0·0224
0·02058		0·02068	0·02061	0·02062	0·0231	0·02076	0·02069	0·0224
0·02058		0·02061	0·02061	0·02061		0·02065	0·02070	0·0213
0·02058		0·02061	0·02062	0·02061				0·0210
				0·02062				0·0216

As seen from Table III, the titration of iodide with chlorite gave entirely satisfactory results. Chlorite, in an acidic medium, oxidises iodide to iodine. Nevertheless, stress must be placed on the necessity of keeping a sufficiently high acidity in the medium. For, when using $0{\cdot}1N$ sodium chlorite for oxidising purposes in $0{\cdot}01N$ sulphuric acid solution, a slow stabilisation of potential of the titrated system will take place, as well as retardation of the potential-jump. Reproducible results are then no longer obtainable. The same effect is to be observed when using $0{\cdot}02N$ sodium chlorite in a $0{\cdot}2N$ sulphuric acid medium. At a higher degree of acidity the potential of the titrated system is instantaneously stabilised, and the potential-jump (260–300 mV) takes place at the correct point.

In the second part of this experimental series, tests were made of oxidising iodide to iodate with chlorite according to the work of Yntema and Fleming.[10] These authors consider that the difference of the potentials of the systems ClO_2^-/Cl^-(1·56 V) and IO_3^-/I^-(1·085 V) is sufficient for carrying out a titration. However, they do not take into consideration that such a high oxidising power as that of the system ClO_2^-/Cl^- is only obtainable in a strongly acidic medium. On the contrary, in a medium of pH 5–6 like that of their experiments, the potential is considerably lower.

Iodide was titrated in an acidic medium as well as in solutions with a higher pH (5, 5·5 and 6) following the Yntema–Fleming method. A series of tests was also made of titrating chlorite with iodide. In none of these cases were reproducible results obtained. According to our experiences, it has been found that:

1. During the titration in an acidic medium, the iodine separated in the first phase (the first potential-jump) became oxidised proportionally following the addition of consecutive portions of the reagent to the I^+ ion (the colour of the solution was changing from reddish-brown to pink-red and the liquid gave no blue tint with starch). Then, the coloration of the solution disappeared with a simultaneous appearance of an odour of chlorine dioxide. At that moment a second potential-jump took place. Following the addition of further portions of the reagent, the potential fell abruptly (Fig. 2).

2. During the titration within the pH limits of 5–6, there was no liberation of iodine. The potential rose regularly, with no appearance of a potential-jump corresponding to the oxidation of iodide to iodine. Following the addition of further portions of reagent, just prior to the end-point a slight yellow-brown coloration appeared (this was caused by the liberation of iodine, which was proved by the addition of starch), afterwards changing to pink I^+, whereupon the coloration disappeared and simultaneously a potential-jump occurred with the manifestation of a chlorine dioxide odour.

3. During the titration in an acidic medium as well as at a pH of 5–8, it was observed that the position of the end-point depends on the rate at which the titration has been carried out. The slower the reagent was added, the smaller the quantity used up to the moment of the potential-jump, and *vice versa.* The reaction rate may be estimated at pH 5·5 from the result of an experiment where a measured quantity of iodide solution was treated with chlorite in excess; the liquid was mixed and its potential measured every few min. The potential-jump occurred only after 30 min, with the simultaneous manifestation of a chlorine dioxide odour.

From the above observations it was concluded that a potential-jump takes place in the titration system at the moment when chlorine dioxide appeared in the solution, following decomposition of chlorite, rather than at the moment of complete oxidation of iodide to iodate. Indeed, according to Flis,[14] the reaction

$$ClO_2^- \rightarrow ClO_2 + e$$

already occurs within a medium of pH $< 6{\cdot}5$ and the potential of such a system, within the limits of pH of 4–8, is 0·934 V. Accordingly, the possibility of quantitatively oxidising iodide to iodate by chlorite seems to be problematical.

Oxidation of iron^{II}

The redox potential of the system

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

is high and amounts to 0·77 V. It could, therefore, be reasoned that the oxidation of iron^{II} to iron^{III} with chlorite would find its only chance of realisation in a strongly acidic medium. The concentration of the iron^{II} solution was determined by a manganometric method. The iron^{III} compounds were reduced with tin^{II} chloride. Therefore, at the outset, the conditions were settled for the quantitative oxidation of tin^{II} with chlorite. It has been stated that the potential of the titrated system become stabilised in the quickest possible way in a 2N solution of sulphuric acid. The potential-jump was very distinct and covered about 600 mV (450 → 1100 mV)

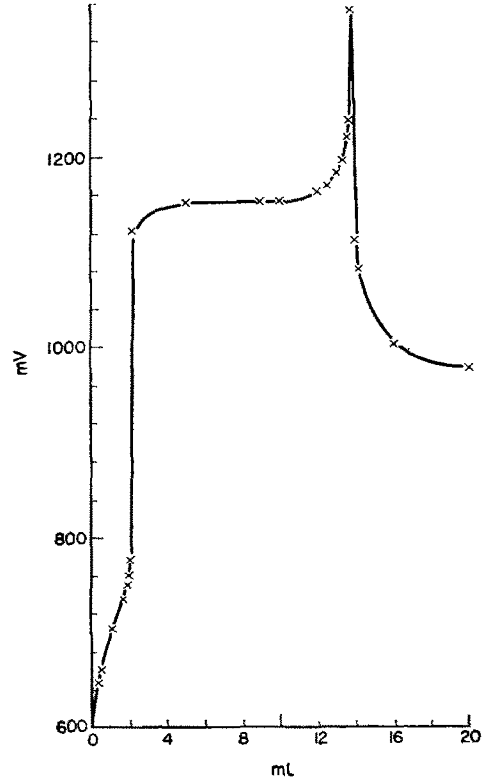

FIG. 2.—Oxidation curve of iodide to iodate with 0·1N solution of sodium chlorite (1N H_2SO_4)

A very small addition of potassium iodide as a catalyst improved the titration conditions and the results of the determination. The tests of titrating an iron^{II} salt solution with chlorite were carried out in a hydrochloric acid medium (5·5*N*, 2*N* and 1*N*) and in a sulphuric acid medium (2*N* and 1*N*). The results of the experiments are given in Table IV. During the titration two potential-jumps were obtained, the first one for tin^{II}, the second for iron^{II}. The titration in sulphuric acid medium gives a retarded potential-jump and thereby too high results are obtained. The potential of the system, after the first jump, stabilises slowly; the reaction rate for oxidising iron with chlorite in this medium is too small for analytical purposes.

TABLE IV.—DETERMINATION OF IRON

Concentration of iron determined by manganometric method	Concentration of iron determined with $NaClO_2$ (by the present method)						
	Medium						
	5·5*N* HCl	2*N* HCl	1*N* HCl	2*N* H_2SO_4	1*N* H_2SO_4	2*N* HCl + 2*N* H_2SO_4 without a catalyst	2*N* HCl + 2*N* H_2SO_4 with KI present as catalyst
equiv./l.	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*
0·0762				0·0917	0·0912		
0·0781	0·0735	0·0793				0·0793	0·0783
0·0781	0·0735					0·0798	0·0780
0·1694	0·1560	0·1680	0·1690			0·1750	0·1698
0·1694	0·1560	0·1710	0·1700			0·1740	0·1692
0·1694	0·1554	0·1708				0·1732	0·1696
0·1694	0·1574					0·1740	0·1694

The tests of the titration in the presence of hydrochloric acid confirmed the observations made in studying the system Sn^{II}/ClO_2^-. The potential of the system, up to the first jump corresponding to tin^{II}, stabilised slowly, whereas in the second phase of titration this occurred instantaneously. In the tests in which 5·5*N* hydrochloric acid was used, the potential-jump, corresponding to the oxidation of iron^{II}, took place too early. It seems probable that with such a high acidity the decomposition rate of chlorite to form chlorine dioxide is higher than the rate of oxidation of iron^{II}. Thus the observed potential-jump corresponds rather to the first reaction. During the titration of iron^{II} in a medium of 2*N* and 1*N* hydrochloric acid the potential-jump took place at the correct point.

Because of these observations there was applied, in a further series of tests, a mixed medium of the two acids (sulphuric and the hydrochloric acids), with the particular provision that the reduction of iron^{III} with tin^{II} chloride was carried out in a 2*N* solution of hydrochloric acid, 2*N* sulphuric acid being added just before the titration. Within this titration series, the potential of the system, during the whole titration time stabilised very quickly but the results of the determination were too high. Therefore, according to the observations derived from the tests for the quantitative oxidation of tin^{II} an addition of potassium iodide as catalyst was applied, and satisfactory results obtained. The potential of the system, during the entire titration time, stabilised quickly, and the precision of the determination, as seen from Table IV, was fully sufficient. It was also observed in a complete series of tests that a chlorine dioxide odour, which is perceivable even in very small concentrations, showed itself only after the end-point of the titration was attained. It is a proof that the oxidation reaction of iron^{II} with chlorite is completed quantitatively.

Oxidation of arsenite

Brown,[11] like many other authors,[15,17,18,19,20] found that the reaction:

$$NaClO_2 + 2HAsO_2 + 2H_2O \rightarrow NaCl + 2H_3AsO_4$$

is very slow; however, in the presence of a catalyst—osmium tetroxide—the reaction develops a rate sufficient for analytical purposes. Brown titrated chlorite with a solution of sodium arsenite at pH 8·2 in the presence of osmium tetroxide. He defined the cited pH as an optimum, since with a lower pH a decomposition of chlorite takes place with liberation of chlorine dioxide, and with a higher pH the reaction is too slow. Further, he stated that at pH 8·2 an reverse titration, when applying potentiometric analysis, gives no result, as proportionally with addition of the reagent, a gradual rise of the potential of the system takes place, without any jump of potential.

The series of experiments with quantitative oxidation of arsenite was started by checking Brown's method, whereupon a confirmation of his results was obtained. Next, the possibility of determining arsenite with chlorite in the absence of a catalyst was examined. The redox-potential of the system

$$H_3AsO_4 + 2H^+ + 2e \rightarrow HAsO_2 + 2H_2O$$

amounts to 0·559 V. The oxidation of arsenite with chlorite was carried out in an acidic medium. The concentration of sodium arsenite solution (about 0·1*N*) was determined iodometrically. The oxidation of arsenite was carried out in a hydrochloric acid (5·5*N*, 2*N* and 1*N*) and in a sulphuric acid (2*N*) medium. 0·1*N* sodium chlorite solution was employed as titrant. The results are given in Table V.

TABLE V.—DETERMINATION OF ARSENITE

Concentration of arsenite determined iodometrically	Concentration of arsenite determined with $NaClO_2$ (by the present method)								
	Medium								
	5·5*N* HCl				2*N* HCl				1*N* HCl
	without a catalyst	with KIO_3	with ICl	with KI	without a catalyst	with KIO_3	with ICl	with KI	without a catalyst
equiv./l.	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*
0·0518	0·0528	0·0518	0·0528	0·0528	0·0529	0·0518			0·0568
0·0518	0·0519	0·0515	0·0528	0·0530	0·0538	0·0515			0·0560
0·0518	0·0519	0·0516	0·0523		0·0538	0·0517			
0·0518	0·0528				0·0553				
0·0518	0·0523								
0·0504	0·0506	0·0501							
0·0504	0·0506	0·0503							
0·0504	0·0506								
0·0610	0·0610	0·0608	0·0610	0·0613			0·0625	0·0623	
0·0610	0·0610	0·0608	0·0610	0·0613			0·0620		

During the titration in a hydrochloric acid medium, the stabilisation speed of the potential of the titrated system was dependent on the acidity of the medium. The use of 5·5*N* and 2*N* hydrochloric acid was found to be most favourable. With these two concentrations of hydrochloric acid, the rate of stabilisation of the potential was equal to the speed of this process with the iodometric method. The potential-jump, in all cases, was very distinct and amounted to about 250–300 mV. Nevertheless, this jump occurred at the correct point only with a titration in a 5·5*N* solution of hydrochloric acid. With lower concentrations of acid, the jump was retarded. Further, it was found that the addition of a small amount of potassium iodate has a catalysing action on the oxidation reaction of arsenite in a hydrochloric acid medium. This observation allowed the quantitative determination of arsenite to be made in a $2N$ solution of hydrochloric acid. The addition of potassium iodide or iodine monochloride did not influence the process. Attempts to titrate arsenite in a sulphuric acid solution gave no results. Indeed, the potential of the titrated solution rose regularly and revealed no jump.

It may be concluded from the experiments performed that, in a medium of $5{\cdot}5N$ or $2N$ hydrochloric acid, with the addition of potassium iodate as a catalyst, a quantitative determination of arsenite with chlorite can be carried out with sufficient precision.

Further experiments in the application of chlorite as an oxidising agent as well as the use of redox indicators in these titrations are being made.

Zusammenfassung—Möglichkeiten Natriumchloritlösungen als oxydierendes Agens in der Massanalyse zu verwenden wurden untersucht. Es wird angegeben, dass solche Lösungen unter Ausschluss von Licht für einige Zeit stabil sind. Sie sind geeignet zur direkten potentiometrischen Titration von Sulfite, Eisen(III) (nach Reduktion zu Eisen(II) mit $SnCl_2$), Arsen(III) und Jodid. Die Titrationen werden im allgemeinen in säurem Medium durchgeführt wobei manchmal Katalysatoren, wie z.B. KJO_3 verwendet werden.

Résumé—Les auteurs ont étudié la possibilité d'utiliser des solutions de chlorite de sodium comme agent oxydant dans l'analyse titrimétrique. De telles solutions en l'absence de lumière sont stables pendant un certain temps, et conviennent pour le titrage potentiométrique direct du sulfite, du fer (III) (après réduction en fer (II) par $SnCl_2$), de l'arsenic (III) et de l'iodure. Le titrage est effectué généralement en milieu acide, quelquefois en utilisant des catalyseurs tels que KIO_3.

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THE RAPID DETERMINATION OF WATER OF HYDRATION IN MAGNESIUM PERCHLORATE DESICCANT

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Summary—The efficiency of "anhydrous" magnesium perchlorate as a desiccant, and its capacity in absorption of water vapour, ammonia gas, alcohol vapour, and other highly volatile organic vapours, is dependent upon the extent to which its water of hydration is removed in preparation for commercial distribution. American Chemical Society "Reagent Chemicals" specifications call for not more than 10% water as a maximum tolerance. The product is, by intent, not ordinarily manufactured for distribution in the completely dehydrated form and regularly contains approximately 5% unremoved water of hydration. This is the regular practice to insure a less friable granular structure than would result from complete dehydration. The method here described for the determination of its water content is rapid in application, sufficiently accurate for all practical demand, and requires very simple apparatus and manipulative details.

INTRODUCTION

MAGNESIUM perchlorate is obtained as the hexahydrate upon crystallisation from boiling saturated solution in water. By proper treatment in this process, its crystal aggregate is readily controlled in particle size for subsequent dehydration to give the ideal condition for its many analytical applications. In the successful elimination of combined water, vacuum drying is the most practical technique. This dehydration results in the following stepwise elimination of water:

$$\begin{aligned} &Mg(ClO_4)_2{\cdot}6H_2O \rightarrow Mg(ClO_4)_2{\cdot}4H_2O \\ &\qquad \rightarrow Mg(ClO_4)_2{\cdot}2H_2O \rightarrow Mg(ClO_4)_2 \text{ anhydrous} \end{aligned}$$

For the purpose of providing high porosity without alteration in chosen particle size, these dehydrations must be carried out without the various hydrates fusing in their own water of hydration. This demands stepwise dehydration and the final stage must be done in a good vacuum and at temperatures between 200 and 250°. Anhydrous granular magnesium perchlorate owes its dehydration efficiency to two distinct properties, the one based upon its high degree of porosity, and the other upon its re-hydration accompanied by high heat exchange in the latter process. The anhydrous material absorbs ammonia with greater heat interchange than occurs with water absorption. As in the absorption of water, ammonia forms the analogous di-, tetra- and hexa-ammoniates. The diammoniate is not dissociated with heat below approximately 200°, at which temperature it gives no odour of ammonia.

Magnesium perchlorate as a desiccant has been made commercially available for a period of almost 40 years.[1] Its many analytical and industrial applications are well known.[2] The dew-point of a gas with which its dehydration is at equilibrium is less than liquid air temperature. Magnesium perchlorate dihydrate cannot be further dehydrated in contact with phosphorus pentoxide[3] at any temperature at which the phosphorus desiccant is applicable and at temperatures under 150°. Since dry ammonia gas displaces the water of hydration from magnesium perchlorate, the ammoniates have greater stability than the hydrates.

Magnesium perchlorate is highly soluble in water and almost all organic solvents.

EXPERIMENTAL

Apparatus

Silvered Dewar Flask, 62·5 mm wide inside and 110 mm deep, capacity 300 ml.

Centigrade thermometer 0–100°.

Paraffined cork stopper, one hole for thermometer insertion, to fit top of Dewar.

A cylinder of filter paper 44 mm in diameter and 75 mm tall open at top. These are made from a rectangular piece cut from an 18·5-cm circular filter (a 100 × 150-mm section). Roll the paper on a template and fold around the bottom for closure. Use a small piece of masking tape for holding the side section and bottom in position. These containers are used to contain samples for test, weight 1·4 g.

A reasonably sensitive small platform balance. An Ohaus 700-g capacity balance was adequate for making weighings to the nearest 100 mg. A 100-ml graduated cylinder was used for water measurement.

Reagents

Water and the sample to be tested are the only reagents involved.

Analytical procedure

To the Dewar flask add 75 ml of water, put the thermometer and paraffined cork in place, and at equilibrium read the temperature. Place a 20·0-g sample of the magnesium perchlorate to be tested in the cylindrical paper container, and fold in the top. Drop the sample into the Dewar, insert the thermometer and cork cover, and at equilibrium measure the temperature rise in the Dewar flask. Stir by a gentle circular motion of the Dewar to ensure complete solution of sample.

From a calibration curve provided by the procedure to be described below determine the % of water left in the perchlorate drier. The dihydrate of magnesium perchlorate contains 13·9 % water of hydration. The temperature rise for 20 g of the exact dihydrate under the conditions described is 17·6°. For 20 g of anhydrous magnesium perchlorate it is 37·5°. The slope of the calibration curve is approximately 45°. The temperature increase for each removal of 1 % of water of hydration is approximately 2·7°. The accuracy is approximately ±0·2 % in water content determined. Duplicate determinations of temperature measurement are quite easily attained. Greater precision is not necessary.

Preparation of calibration data

Dry carefully 125–150-g batches of magnesium perchlorate hexahydrate in an electrically heated tube heater under vacuum of 0·25 mm and at stepwise increase in temperature starting at 125°. At 165°–170° the dehydration is complete to the formation of the dihydrate. For removal of the last two molecules of water, a temperature of 200°–225° is required and time intervals of 16–24 hr under continuous evacuation of less than 1 mm pressure. Pass the samples thus prepared at various time intervals several times through a 4-mesh sieve and allow to cool in a 500-ml plastic cap bottle in a desiccator charged with the same desiccant.

Weigh samples of 4–6 g into porcelain boats (16 × 1000 mm), using a ground-glass stoppered weighing pig. Determine their water content by complete dehydration at 225°–250° in vacuo. Determine the weight of the boat contents again, thus defining the residual water of hydration. When analyses of the reference standards were made in duplicate, the results shown graphically in Fig. 1, were obtained.

As would be predicted, the increase in temperature of solution in water for the range 13·9–0·0 % of water is a straight line function within the range covered by the transformation $Mg(ClO_4)_2 \cdot 2H_2O$ to anhydrous desiccant.

The variation in temperature rise with each increase in % water found is indicated for the analytical purpose intended in Table I.

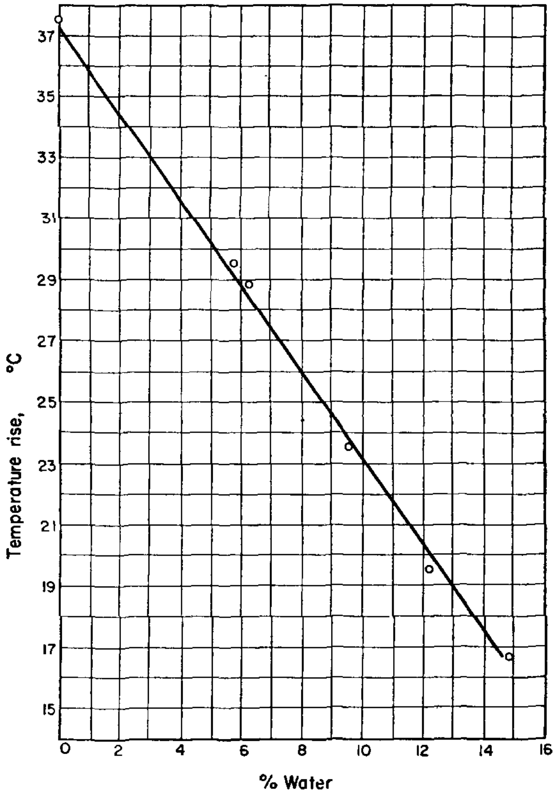

FIG. 1.

TABLE I.—TABULATION OF THE DATA SHOWN IN THE GRAPH OF FIGURE 1. TEMPERATURE VS. WATER CONTENT

Water found, %	Temp. rise, °*C*	Water found, %	Temp. rise °*C*	Water found, %	Temp. rise °*C*
0·0	37·5	6·0	28·9	11·0	21·7
1·0	35·9	7·0	27·4	12·0	20·3
2·0	34·5	8·0	26·0	13·0	19·0
3·0	33·1	9·0	24·6	13·9	17·7
4·0	31·6	10·0	23·2		
5·0	30·2				

DISCUSSION

The purpose of the filter paper sample-container is to bring about retarded solution of the sample in water. Failure to use such a procedure, particularly for water contents of 1–5 %, causes loss of heat through transformation of some of the water content of the Dewar flask to steam. The thermometer often shows a temperature rise much in excess of the equilibrium value due to local heating. A steady reading, with complete solution of the sample, is ordinarily obtained after 20–25 sec. The contents of a reagent bottle of desiccant before analysis for its water content should be passed through a coarse sieve several times before sampling to insure uniformity. A sample bottle with even a tight-fitting screw top and paper or other type liner will be found in extended periods of shelf-life to admit sufficient water to the desiccant to alter the true water content of the original product on its top layer.

The regeneration of spent magnesium perchlorate by heating and evacuation, if porosity and granulation are to be maintained, is not a simple operation. Contamination of spent reagent with organic impurities, especially if acidic in reaction, may give rise to material decomposition. Unless such contamination is known to be absent such regeneration is ill advised.

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DETERMINATION OF LEAD, CADMIUM AND ZINC IONS IN LARGE EXCESS OF INDIUM ION USING THE ALTERNATING CURRENT POLAROGRAPH

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(*Received* 10 *February* 1960)

Summary—Lead, cadmium or zinc ions in the presence of a large excess of indium ion can be determined, without removal of excess indium and dissolved oxygen, by means of the alternating current polarograph in supporting electrolytes such as nitric acid or phosphoric acid.

INTRODUCTION

SINCE the half-wave potentials of indium and cadmium ions are very close to each other, their separation being about 0·1 ∼ 0·2 V in KBr or KCl electrolyte solution, their polarographic determination is regarded as being comparatively difficult using the conventional d.c. polarograph. But a.c. polarograms of these metallic ions show well-separated reduction waves in the same supporting electrolyte solutions, when the concentrations of the elements are almost equal.

However, when the concentration ratio of indium ion to cadmium ion becomes large, the reduction wave of cadmium ion is not so easily separated from that of indium ion, even by the a.c. polarographic method. Although it is possible to apply the suppression method to the indium ion using dissolved oxygen, this method is not very effective for separating the cadmium wave from the indium wave when indium is present in large excess (over 0·2 *mM*). It is therefore necessary to find another suitable electrolyte solution for the separation of cadmium and indium ion, such that in it either the potential of indium ion moves towards a more negative potential than that of cadmium ion, or the indium ion is reduced irreversibly so that its peak height is decreased as much as possible. In the present study, phosphoric acid was found to be a suitable electrolyte for the separation of the reduction waves of the ions, and it permits determination of cadmium, lead and zinc ions in the presence of a large excess of indium ion by means of a.c. polarography.

EXPERIMENTAL

Reagent and apparatus

Indium nitrate is prepared by dissolution of indium metal (99·9%) in nitric acid (specially pure), evaporation on the water-bath to dryness and dissolution in the appropriate amount of distilled water to give 1*M* $In(NO_3)_3$ solution. Lead nitrate, thallium nitrate, cadmium sulphate and lead nitrate used as the metallic ions to be determined are specially purified grade. Phosphoric acid, nitric acid or ammonium nitrate used for the supporting electrolyte are also specially purified grade.

The d.c. and a.c. polarographs employed in the present experiment have already been described.[1] In the a.c. polarograph R_s and C_s are respectively 0·5 KΩ and 0·2 μF. The reference electrode (1*N* calomel electrode) is connected through agar–agar with the polarographic solution; the mercury flow from the capillary is 2·79 mg/sec; the drop time in 0·5*N* nitric acid at −1·0 V is 4·3 sec/drop.

1. *A.c. polarograms in various electrolytes*

(a) *Ammonium nitrate electrolyte:* From the d.c. polarogram of indium in 0·5*M* ammonium nitrate solution (pH 2), it is found that the reduction wave appears at about −0·53 V and its electrode

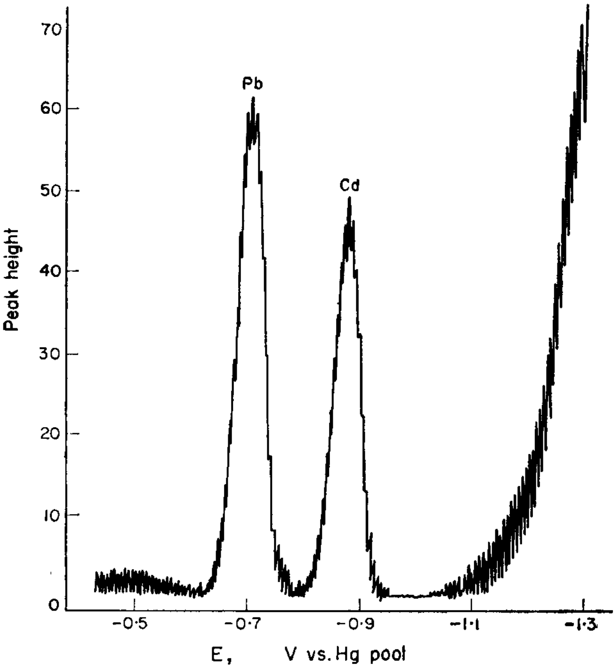

FIG. 1.—A.c. polarograms of lead, cadmium and zinc ions in the presence of large excess of indium ion (in 0·5*M* NH_4NO_3). (0·25 *mM* Cd and Pb; 0·5 *mM* Zn; 10 *mM* In, 25°).

reaction proceeds irreversibly as shown by the slope of the reduction waves. In agreement with this, the a.c. polarogram of indium has a very low peak height, as shown in Fig. 1, in comparison with those shown by 0·25 m*M* lead or cadmium ions. However, it is evident that the peak height of cadmium is affected by that of indium, although the peak height of lead is not so affected. This appears from the calibration curves for lead and cadmium, shown in Fig. 2, in which the lead curve is a straight line passing through the origin, but the cadmium curve, although a straight line, does not pass through

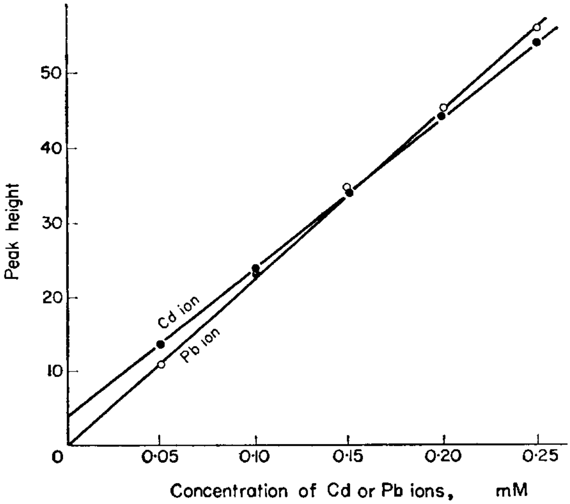

FIG. 2.—Calibration curves for cadmium and lead ions in the presence of large excess of indium (10 *mM*) in 0·5 *M* NH_4NO_3 solution (25°) (● Cd ion; ○ Pb ion).

the origin. The peak heights are expressed by measuring the distance of the top of the peak from the curve for supporting electrolyte alone in the a.c. polarogram of the metallic ion. The reduction wave of zinc overlaps the hydrogen discharge wave, so that it is impossible to determine zinc together with lead and cadmium in ammonium nitrate electrolyte solution.

(b) *Nitric acid electrolyte:* Since the a.c. polarogram for indium shows a reversible wave in 0·5*N* nitric acid solution, its peak appearing at about −0·8 V vs. N.C.E., the presence of indium does not affect the reduction waves of cadmium and lead, as shown in Fig. 3. The reduction wave for zinc is obscured owing to the hydrogen discharge wave, making the polarographic determination of zinc impossible.

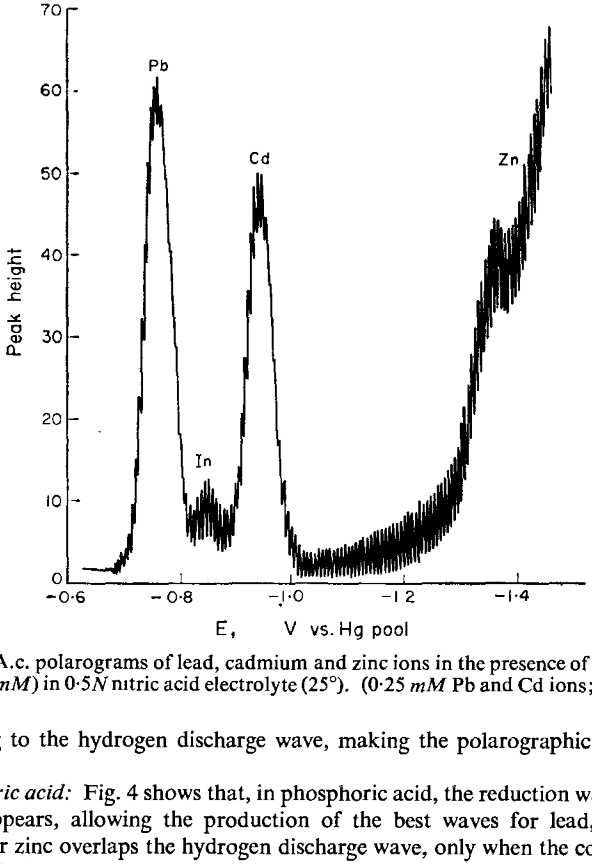

FIG. 3.—A.c. polarograms of lead, cadmium and zinc ions in the presence of large excess of indium (10 *mM*) in 0·5*N* nitric acid electrolyte (25°). (0·25 *mM* Pb and Cd ions; 0·5 *mM* Zn ion).

(c) *Phosphoric acid:* Fig. 4 shows that, in phosphoric acid, the reduction wave for indium [0·07*M*, $In(NO_3)_3$] disappears, allowing the production of the best waves for lead, cadmium and zinc.

The wave for zinc overlaps the hydrogen discharge wave, only when the concentration of indium increases excessively, *i.e.* more than 0·07*M*. Fig. 5 shows an example of the a.c. polarogram when the concentration of indium is 0·33*M*. In such a case there is no effect on the waves for lead and cadmium.

Fig. 6 gives the calibration curves for lead, cadmium and zinc in the presence of 20 *mM* indium nitrate in 1*M* phosphoric acid and indicates the good linear relationship between the metal ions and peak heights, provided that their concentrations are in the range 0·25 ~ 0·05 *mM*.

2. *Effect of the presence of other ions*

(a) *Effect of thallium on the waves of lead and cadmium:* The wave for thallium lies between those of lead and cadmium. Therefore the waves for lead and cadmium are both influenced by the thallium wave, becoming higher than in individual solutions of each ion. Fig. 7 shows this situation in phosphoric acid electrolyte and indicates that the influence is more pronounced in the lead wave than in that of cadmium. The increase in peak height almost equals the overlap of the thallium wave with those of lead or cadmium. Such overlapping is probably due to the fact that the peak potential of thallium is closer to that of lead than to that of cadmium. This influence was found with nitric acid or ammonium nitrate, as well as with phosphoric acid as supporting electrolyte.

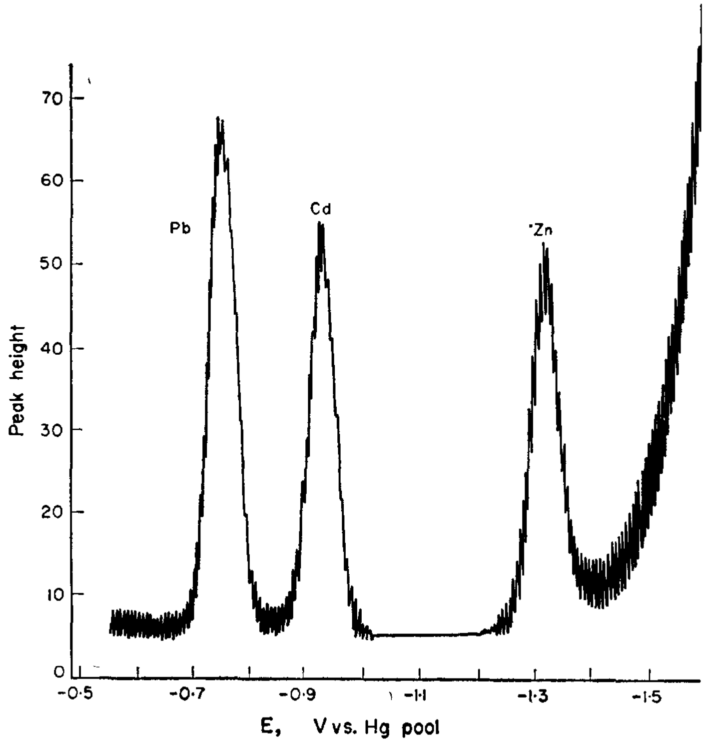

FIG. 4.—A.c. polarograms of lead, cadmium and zinc ions in $1M$ phosphoric acid electrolyte (25°). (0·25 mM Cd and Pb; 0·5 mM Zn; 0·07M In).

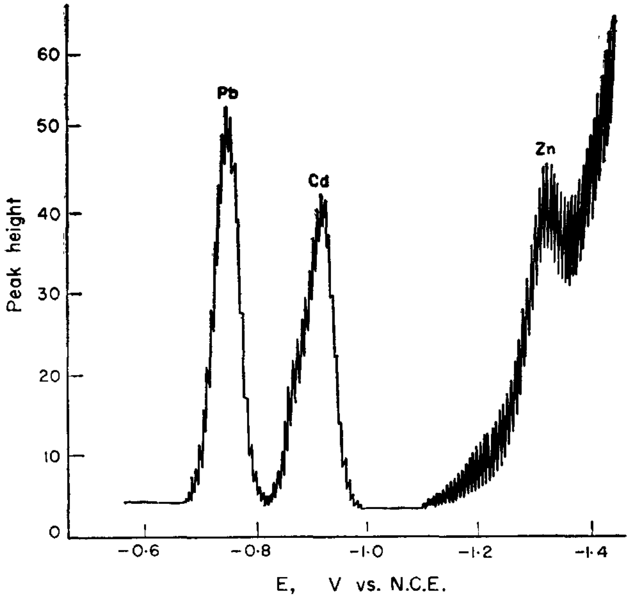

FIG. 5.—A.c. polarograms of lead, cadmium and zinc ions in $1M$ phosphoric acid (25°). (0·2 mM Pb and Cd; 0·4 mM Zn; 0·33M In).

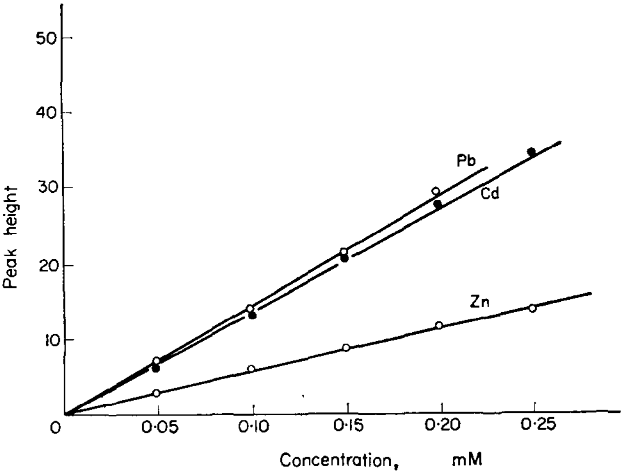

FIG. 6.—Calibration curves for lead, cadmium and zinc ions in the presence of 20 *mM* indium nitrate in 1*M* phosphoric acid (20°). (10 scale units of peak height equal 0·2 mV).

(b) *Effect of halide ion on the peak height of indium:* If halide is present in a supporting electrolyte such as nitric acid, phosphoric acid or ammonium nitrate, the indium wave appears between the waves of lead and cadmium. Such a medium influences the waves of lead and cadmium if the concentration of indium ion is large. In Table I the effect of chloride and iodide on the indium wave (concentration 0·16 *mM*) is shown.

The influence of iodide ion is even more marked at very low concentration than that of chloride ion.

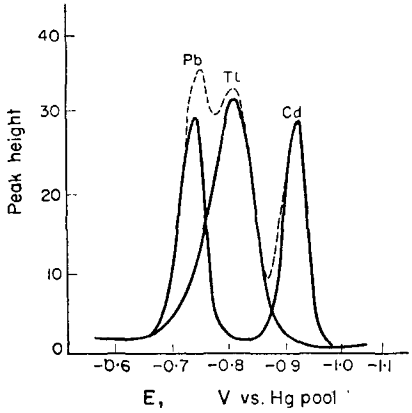

FIG. 7. A.c. polarograms of lead and cadmium ions with (– – –) and without (—) thallium ion in large excess of indium ion (10 *mM*). (0·2 *mM* Cd and Pb; 0·4 *mM* Tl. 20°).

DISCUSSION

In a supporting electrolyte of 1*M* phosphoric acid, it was found[2] that indium ion is present as a soluble complex ion with phosphoric acid such as $[In(HPO_4)]^{(3-2n)+}$ or $[In(H_2PO_4)_n]^{(3-n)+}$. This complexing of the indium ion is the cause of the disappearance of the indium wave at a more positive potential than the reduction potential of the hydrogen ion.

In a supporting electrolyte of nitric acid,[3] indium ion forms an aquo-complex such as $[In(H_2O)_6]^{3+}$. This complex also causes the disappearance of the indium wave.

TABLE I. EFFECT OF THE CONCENTRATION OF HALIDE ION UPON THE PEAK HEIGHT OF INDIUM ION

Conc. of halogen ion, *M*	Cl^- in			I^- in 0·5*M* NH_4NO_3
	1*M* NH_4NO_3	0·5*M* NH_4NO_3	1*M* H_3PO_4	
$0{\cdot}5 \times 10^{-1}$	6·8	—	—	—
1×10^{-1}	9·5	14·5	7·5	—
2×10^{-1}	20·8	22·5	15·5	—
3×10^{-1}	24·0	30·0	21·5	—
4×10^{-1}	32·0	—	—	—
$0{\cdot}2 \times 10^{-4}$	—	—	—	1·5
$0{\cdot}5 \times 10^{-4}$	—	—	—	2·0
1×10^{-4}	—	—	—	3·5
$2{\cdot}5 \times 10^{-4}$	—	—	—	7·5
5×10^{-4}	—	—	—	10·5

But an irreversible reduction wave for indium appears at —0·6 V vs. N.C.E. in ammonium nitrate electrolyte (pH 2) and disappears when the electrolyte solution is acidified by nitric acid to the extent of 0·1*N*. The irreversible reduction wave is therefore thought to be due to the formation of a basic aquo-complex such as $[In(H_2O)_5(OH)]^{2+}$, which is implied by the study of Cozzi and Vivorelli.[3]

This basic complex is reduced at a more positive potential than the aquo-complex and when the electrolyte solution is acidified, it releases the co-ordinated OH group, resulting in the formation of the aquo-complex, which is reduced at a more negative potential than the former basic aquo-complex. Indium ion tends to form a halogeno-complex with halide ion, which complex is reduced at a more positive potential than the aquo-complex, resulting in the appearance of a reversible wave with a distinctly higher peak in the a.c. polarogram.

If the aquo-, basic aquo- or phosphoric complexes of indium ion described above exist in the presence of halide ion, indium ion forms more stable complexes than these and shows a higher peak with increase in the concentration of halide ion.

The effect of halide ion on the reduction wave of indium ion varies in accordance with the difference between the stabilities of the complexes and their halogeno-complexes. Also the effect of iodide ion is more pronounced than that of chloride ion.

Zusammenfassung—Blei, Cadmium und Zink können in Gegenwart eines grossen Überschusses von Indium ohne Entfernung von gelöstem Sauerstoff bestimmt werden, wenn man mit Wechselstrom-polarographie in einer Grundlösung aus Sälpeter- oder Phosphorsäure arbeitet.

Résumé—Les ions du plomb, du calcium ou du zinc peuvent être dosés en présence d'un grand excès d'ion de l'indium sans élimination de l'excès d'indium ou de l'oxygène dissous si le dosage est réalisé à l'aide d'un polarographe à courant alternatif dans un électrolyte support tel que l'acide nitrique ou l'acide phosphorique.

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DETECTION OF MONOBASIC PHOSPHORUS ACID ESTERS BY CONVERSION TO CHOLINESTERASE INHIBITORS

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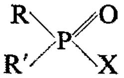
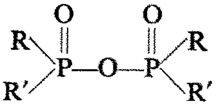
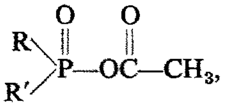
Summary—Many monobasic acids of quinquevalent phosphorus form cholinesterase inhibitors when exposed to ketene. Based upon this finding, a sensitive test to detect the presence of these compounds on filter paper has been developed. Seventeen out of nineteen of these acids tested gave positive results. Negative results obtained with the remaining two are attributable to steric factors or to the high hydrolysis rate of the acetylated product. Only one of eighteen phosphorus compounds other than the monobasic acids examined, namely *n*-butylphosphonic acid, gave a positive test; an explanation is offered to account for this exception.

WITH the demonstration by Cook[1] that very sensitive cholinesterase inhibition tests could be applied directly to paper chromatograms, a new approach to the detection of enzymatically inactive compounds, by the *in situ* conversion to active cholinesterase inhibitors, became attractive.

Compounds of the type  $RR'P(=O)X$ (R and R′ are alkyl or alkoxy) are generally active cholinesterase inhibitors[2] if the hydrolysis product HX has a pK_a less than 7. Thus, conversion of a monobasic acid of quinquevalent phosphorus to a derivative satisfying this requirement should permit use of an enzymatic method.

Procedures for converting the acids to two classes of derivatives of the required type, namely  $RR'P(=O)\text{—O—}P(=O)RR'$ I and  $RR'P(=O)\text{—OC(=O)—}CH_3$, II were selected for study because the reactions were well known[3,4] and because compounds of these classes are good cholinesterase inhibitors (*e.g.* tetra-ethylpyrophosphate and diethylacetylphosphate). Lack of sufficient information precluded selection of either class over the other on the basis of relatively superior inhibitory power. The preparation of I can be accomplished by reaction of the appropriate monobasic acid with N:N′-disubstituted carbodi-imide,[3] while II can be made with the acid and ketene; of the two reagents, only the latter can be removed, if in excess, by volatilisation at a relatively low temperature. Moreover, the ketene method may be expected to yield twice as many moles of enzyme inhibitor as the carbodi-imide method. Based on these considerations, as well as on a few comparison tests, ketene was made the reagent of choice.

The product of reaction of ketene with a monobasic acid of phosphorus, under the conditions used here, is believed to be II; if, in fact, it were I, then II would most

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probably be an intermediate in its formation. Assuming that I can be formed from II by reaction with a second molecule of the monobasic phosphorus acid, the likelihood of this second step would be minimised where the concentration of acid was quite small and that of ketene relatively high. A determination of the initial pseudo-first order rate constants at pH 7, by Michel's enzyme inhibition technique,[5] for the hydrolysis of authentic samples of I and II (R = ethyl, R′ = ethoxy) showed about a four-fold difference in hydrolysis rates ($k_{obs} = 0{\cdot}0042$ and $0{\cdot}018\ min^{-1}$, respectively). An extract of filter paper which had been impregnated with the corresponding acid and exposed to ketene gave an initial hydrolysis rate constant ($0{\cdot}019\ min^{-1}$) well in agreement with the supposition that II is the principal product in the phosphorus acid-ketene reaction.

The results of tests on 36 organophosphorus compounds are shown in Table I. In each case, the paper was spotted with 1 μg per cm^2 of the compound in methanol. Positive tests were also obtained with the sodium salt of *iso*propylmethylphosphonic acid and the di*cyclo*hexylamine salt of di-*iso*propylphosphoric acid.

DISCUSSION

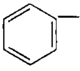
Cholinesterase hydrolyses acetylcholine to choline and acetic acid. In an unbuffered system, the latter product causes the indicator, bromothymol blue, to change from a blue to a yellow colour. The persistence of a blue colour indicates the presence of an enzyme inhibitor. In an atmosphere of high moisture content, or on over-exposure to ketene, the acid background is high (due, presumably, to the reaction between ketene and water to form acetic acid). In such cases, a larger quantity of enzyme spray solution will be required to give the overall blue colour specified in the procedure and will lead to decreased sensitivity of the test. Minimal quantities of spray reagent are required and maximum sensitivity is obtained if the paper is exposed to ketene, generated at a rate of from 10–40 mg/min, for 5 minutes. If too much acidic material is present at the phosphorus acid site, it may be necessary to neutralise the excess acidity before spotting or to use less of the phosphorus compound in order to achieve the desired overall blue colour.

Initially, the technique described by Cook,[1] in which four identical sized strips of filter paper, each containing a single reagent, are placed one on top of the other, was tried. Because of diffusion of the spots on the paper and attenuation of the spots among the four strips, the sensitivity was not good. The sensitivity of the test was improved significantly when enzyme, substrate, base and indicator were combined as a single spray reagent and one strip of paper was used.

Colorimetric and fluorescent acid-base indicators, other than bromothymol blue, were examined. None was more satisfactory.

Positive tests were given by 1 μg per cm^2 of all monobasic phosphorus acid esters after reaction with ketene, with the exception of dimethylphosphate and ethyl*iso*propylphosphonate. The failure of dimethylphosphate to behave like other monobasic phosphoric ester acids is possibly due to (*a*) the rapid hydrolysis rate of acetyldimethylphosphate or (*b*) the low rate of reaction of the acetylated compound with the esterases in horse serum. While there is no direct evidence on either of these possibilities, it is known that the hydrolysis constant of tetramethylpyrophosphate is 10 times that of TEPP[6] and its inhibitory power towards human plasma esterase 1/2500 that of TEPP.[7] The one monobasic phosphonate ester which gave a negative response

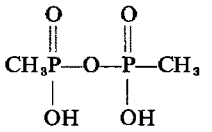
TABLE I. COMPOUNDS TESTED BY KETENE TEST

		Test result[a]	Sensitivity[d], $\mu g/cm^2$
Dibasic phosphate esters	$CH_3OPO(OH)_2$	—	
	$nC_3H_7OPO(OH)_2$	—	
	$iC_3H_7OPO(OH)_2$	—	
	$nC_4H_9OPO(OH)_2$	—	
Monobasic phosphate esters	$(CH_3O)_2PO(OH)$	—	
	$(C_2H_5O)_2PO(OH)$	±	1·0
	$(iC_3H_7O)_2PO(OH)$[b]	+	0·2
	$(nC_4H_9O)_2PO(OH)$	+	0·5
Neutral phosphate ester	$(C_2H_5O)_3PO$	—	
Dibasic phosphonic acids	$CH_3PO(OH)_2$	—	
	$nC_4H_9PO(OH)_2$	+	0·5
	$nC_{16}H_{33}PO(OH)_2$	—	
	—$PO(OH)_2$	—	
Monobasic phosphonate esters	$CH_3P(OCH_3)O(OH)$	+	0·5
	$CH_3P(OC_2H_5)O(OH)$	+	0·05
	$CH_3P(OC_3H_7i)O(OH)$[c]	+	0·05
	$CH_3P(OC_4H_9n)O(OH)$	+	0·05
	$C_2H_5P(OCH_3)O(OH)$	+	0·2
	$C_2H_5P(OC_2H_5)O(OH)$	+	0·2
	$C_2H_5P(OC_2H_5)O(OH)$	+	0·2
	$C_2H_5P(OC_3H_7i)O(OH)$	+	0·2
	$C_2H_5P(OC_4H_9n)O(OH)$	+	0·05
	$iC_3H_7P(OC_2H_5)O(OH)$[e]	—	
	$iC_3H_7P(OC_4H_9n)O(OH)$	+	0·5
	$nC_4H_9P(OCH_3)O(OH)$	+	0·05
	$nC_4H_9P(OC_2H_5)O(OH)$	+	0·05
	$nC_4H_9P(OC_4H_9n)O(OH)$	+	0·02
Neutral phosphonate esters	$CH_3(OC_3H_7i)_2PO$	—	
	$C_2H_5(OC_2H_5)_2PO$	—	
	$nC_4H_9(OC_2H_5)_2PO$	—	
	$nC_4H_9(OC_4H_9n)_2PO$	—	
Dialkyl phosphites	$(CH_3O)_2POH$	—	
	$(C_2H_5O)_2POH$	—	
Trialkyl phosphites	$(CH_3O)_3P$	—	
	$(C_2H_5O)_3P$	—	
	$(nC_4H_9O)_3P$	—	

to this test (as well as another which gave a relatively weak test) contains a bulky *iso*propyl group directly attached to the phosphorus atom; the sensitivity of enzymatic reactions to steric effects is well known.

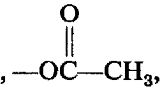
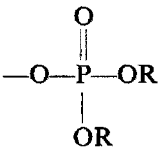
All compounds which were not expected to form anticholinesterase compounds

TABLE 1 (*continued*)

		Test result[a]	Sensitivity[d], *μg/cm*^{2}
Dibasic aryl phosphorus acid	$C_6H_5P(OH)_2$	—	
Phosphinic acids	$CH_3(C_2H_5)PO(OH)$	+	0·1
	$CH_3(nC_3H_7)PO(OH)$	+	0·1
Pyrophosphonic acid	 $CH_3P(=O)(OH)—O—P(=O)(OH)—CH_3$	—	

[a] — = negative ± = faintly positive; + = positive.
[b] The di*cyclo*hexylamine salt of this compound also gave a positive test.
[c] The sodium salt of this compound also gave a positive test.
[d] Smallest quantity necessary to give a faintly positive test.
[e] Gave a positive test with 2 *μg* per cm^2.

upon reaction with ketene, such as neutral phosphate and phosphonate esters, dibasic phosphate esters, dibasic phosponic acids, and phosphites gave negative tests with the exception of the dibasic *n*-butylphosphonic acid. It is to be expected that certain dibasic phosphonic and phosphoric acid esters will, after treatment with ketene, react with esterases (as was found with dibasic *n*-butylphosphonic acid). The basis for this statement is as follows: It has been shown that there is a relationship between the rate of the reaction of a given phosphorus ester or anhydride with the enzyme and hydrolysis rate of the compound,[8] the more easily hydrolysable compounds being the more rapid reactants with the enzyme. If, however, the hydrolysis rate is too high, the phosphate will have decomposed on the paper before it can react with the enzyme. One may expect, then, that a plot of the reactivity of a phosphorus compound with the enzyme in this test against the hydrolysis rate of the phosphorus ester will be bell-shaped in character, with both the extremely rapidly and the very slowly hydrolysing esters exhibiting low reactivity with the enzyme. All compounds capable of reacting with ketene to form anhydrides which will hydrolyse at intermediate rates (rates which would fall in the dome portion of the curve described above) will, in all probability, also exhibit some activity in the enzyme reaction.

The rate of hydrolysis of phosphorus esters will depend upon the nature of the groups attached to the phosphorus. For simple phosphate esters it has been shown that the rate of alkaline hydrolysis decreases as the size of the alkyl substituent increases, presumably due to the operation of steric factors.[9] The leaving group also affects the hydrolysis rate; the rate being higher as the acidity of the leaving group increases. For example, esters (or anhydrides) having leaving groups —F,  $—OC(=O)—CH_3$,  $—O—P(=O)(OR)—OR$ etc. have high rates of hydrolysis; those in which the leaving group is

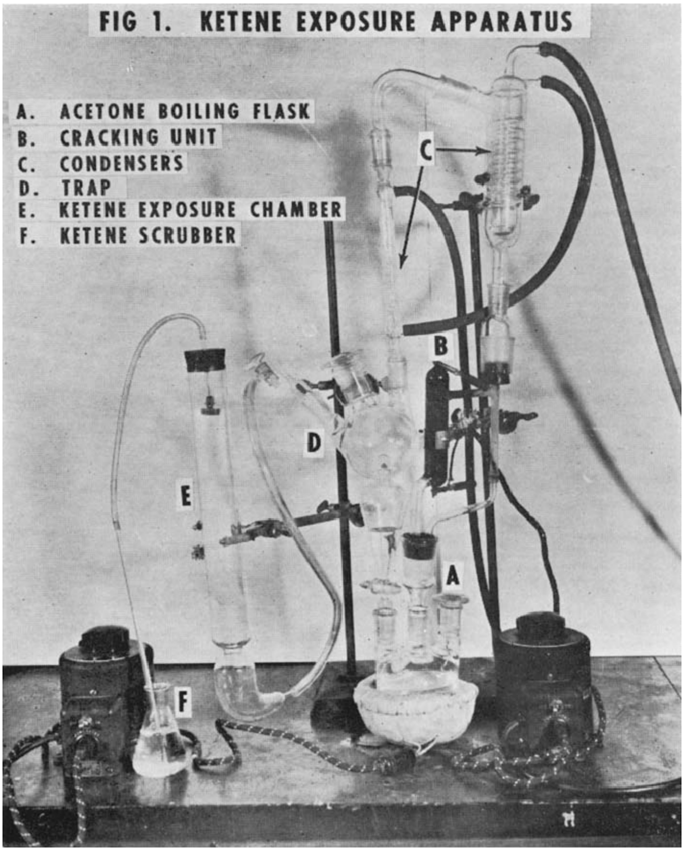
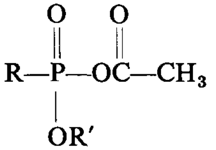
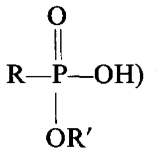
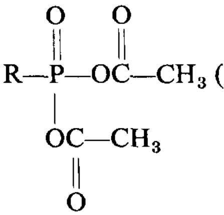


FIG 1. KETENE EXPOSURE APPARATUS

A. ACETONE BOILING FLASK
B. CRACKING UNIT
C. CONDENSERS
D. TRAP
E. KETENE EXPOSURE CHAMBER
F. KETENE SCRUBBER

SR or OR have relatively low hydrolysis rates. If, now, two such highly acidic leaving groups are present in a single molecule, then the loss of one of these groups is very rapid. Thus, for example, the expulsion of one fluorine atom (as its ion) from methylphosphonodifluoridate is almost instantaneous; the hydrolysis of *iso*propylmethylphosphonofluoridate is rapid, but slow by comparison with the difluoro compound. In both cases, the hydrolytic products are no longer active anticholinesterases.

By analogy, it would be expected that  $R-\underset{\underset{OR'}{|}}{\overset{\overset{O}{\|}}{P}}-O\overset{\overset{O}{\|}}{C}-CH_3$ (the reaction product between ketene and  $R-\underset{\underset{OR'}{|}}{\overset{\overset{O}{\|}}{P}}-OH$) would hydrolyse rapidly but not instantaneously, and that the rate of hydrolysis would decrease as the alkyl group R (or R′) became larger. The compound  $R-\underset{\underset{\underset{\underset{O}{\|}}{OC-CH_3}}{|}}{\overset{\overset{O}{\|}}{P}}-O\overset{\overset{O}{\|}}{C}-CH_3$ (where R is the same alkyl group as in the monacetyl ester) would be expected to hydrolyse much more rapidly by comparison. If the alkyl groups in a diacetyl ester were of sufficient bulk, and the alkyl group in a monoacetyl ester sufficiently small, it would appear that there might be two compounds, one a diacetyl ester, the other a monoacetyl ester, of comparable rates of hydrolysis, both capable of exhibiting activity against the enzyme.

Sym-dimethylpyrophosphonate, which gave a negative test using the procedure described here, behaved as one would predict from the foregoing discussion. The product of reaction of dimethylpyrophosphonate with ketene, namely dimethyldiacetylpyrophosphonate, which contains two highly electronegative groups, would be expected to hydrolyse instantaneously to the inactive acid ester.

The choice of horse serum as the source of cholinesterase rested upon factors such as availability, cost and known sensitivity to a large group of pyro-esters (in the absence of information on the corresponding acetylesters). But it is well known that the reactivities of different organophosphorus compounds with esterases derived from various sources are not the same. For example, tetramethylpyrophosphate is more active against the cholinesterase in mouse brain than against the enzyme in human serum, while the reverse relationship holds for tetra-ethylpyrophosphate.[7] Hence, for the detection of special groups of acids of phosphorus, it may be advisable to use different enzyme sources.

EXPERIMENTAL

Apparatus and equipment

A diagram of the equipment is shown in Fig. 1. The ketene generator was constructed according to the directions of Wang and Schueler.[10] The apparatus was calibrated for ketene delivery by the method of Vogel.[11] The spray bottle was manufactured by Kontes Glass Co.

Reagents

Enzyme spray solution (freshly prepared) consists of 1 part by volume of horse serum (available from Pitman-Moore) plus 1 part by volume of 1·2% aqueous acetylcholine chloride plus 0·4 part by volume of 2·5% bromothymol blue in 0·1*N* NaOH.

Some of the organophosphorus compounds were kindly supplied *gratis* by Hooker Electrochemical Co. and the Victor Chemical Works. Other compounds were synthesised by Food Machinery Co., Fairfield Div. under contract to the U.S. Army Chemical Corps.

Procedure

The paper strip, spotted with a solution of the organophosphorus compound in absolute methanol, is placed in an oven for 5 min at 125° to remove the organic solvent completely. (Failure to eliminate the organic solvent results in the formation of products which strongly interfere in the test. While it was not the primary purpose of this research to investigate the use of the test in applications to particular chromatographic systems, it has been found that the condition described herein, *i.e.* oven heating for 5 min at 125°, is adequate for the following reagent grade solvents: methanol, ethanol, 2-propanol, 1-butanol, acetonitrile and water.) The strip is placed in the ketene exposure chamber for 5 min, with the apparatus set to deliver from 10 to 40 mg of ketene per min. *For operating directions and precautions to be observed in operation of the ketene generator, the reader is urged to consult the original article by Wang and Schueler.*[10] The paper is removed, heated in an oven for 1 min at 125° to remove excess ketene, sprayed with the enzyme spray solution to an overall blue colour and placed between two flat sheets of glass. The presence of an anticholinesterase is indicated by the persistence of a dark blue spot while the background is changing colour (usually from blue to yellow) during the course of about 30 min.

Zusammenfassung—Viele monobasische Säuren des fünfwertigen Phosphors bilden Cholinesterase-inhibitoren wenn sie Keten ausgesetzt werden. Diese Beobachtung wurde zur empfindlichen Nachweis dieser Verbindungen auf Tüpfelpapier ausgewertet. Siebzehn solcher Säuren (aus neunzehn untersuchten) gaben positive Reaktion. Die negativen Ergebnisse der verbleibende zwei werden auf sterische Faktoren oder zu hohe Hydrolysengeschwindigkeit der azetylierten Produkte zurückgeführt. Nur eine einzige der achtzehn nicht monobasischen Säuren gab einen positiven Test, nämlich n-Butylphosphonsäure. Eine Erklärung für dieses Verhalten wird gegeben.

Résumé—Beaucoup d'acides monobasiques du phosphore pentavalent forment des inhibiteurs cholinestérase quand ils sont exposés aux cétènes. Un test sensible, basé sur cette découverte, a été élaboré pour déceler la présence de ces composés sur papier filtre. Dix-sept parmi les dix-neuf acides testés donnaient des résultats positifs. Les résultats négatifs obtenus avec les deux autres acides sont attribués aux facteurs stériques ou à la grande vitesse d'hydrolyse du produit acétylé. Seul un des dix-huit acides du phosphore examinés, autres que les acides monobasiques, à savoir, l'acide n-butylphosphorique, donnait un test positif; une explication est proposée pour interpréter cette exception.

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COULOMETRIC TITRATION OF IRON^{II} BY ELECTROLYTICALLY GENERATED BROMINE

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Summary—Iron^{II} reacts with bromine more smoothly in acetic acid-sodium acetate medium than in sulphuric acid medium, producing a marked potential change at the end-point. The titration curves and the reaction velocities of the reaction have been studied with regard to various compositions of the electrolytic solution. It was found that iron^{II} from 0·01 meq to 0·1 meq could be titrated coulometrically with less than about 1% error, if the electrolytic solution contained 0·1M potassium bromate, 1N acetic acid and 0·2N sodium hydroxide.

INTRODUCTION

THE coulometric titration of iron^{II} is one of the earliest examples of this type of method in chemical analysis. As the titrating reagent, Furman, Cooke and Reilley[1] used cerium^{IV} generated electrolytically from cerium^{III}; and Tutundžić and Mladenović[2] used permanganate ion generated electrolytically from manganese sulphate in sulphuric acid. Those methods are not considered to be particularly useful for continuous coulometric titration, although theoretically they should be versatile. Furman's method is associated with troublesome recovery of the valuable cerium^{IV} from the effluent electrolytic solution; Tutundžić's method is faced with the difficult problem of adopting the best conditions for avoidance of the generation of manganese dioxide or manganese^{III} as well as permanganate ion and yet keep the electrolytic current efficiency at 100%. The electrolytic current must change continuously in conjunction with the concentration of the component to be determined in the sample stream. It is therefore very difficult, in continuous coulometric titration, to hold the electrolytic current efficiency at 100% over the wide range of the charge density on the surface of the generating electrode.

Electrolytically generated bromine is extensively employed as an oxidising agent in coulometric titration, but the reaction of bromine with iron^{II} is too slow to be useful, in comparison with conventional titration. The present authors discovered that bromine reacts more rapidly with iron^{II} in acetic acid-sodium acetate medium than in sulphuric acid medium and studied the titration curve of these reactions. In consequence a new coulometric titration of iron^{II} by electrolytically generated bromine, in a medium of a suitable composition, has been established.

APPARATUS AND REAGENTS

The apparatus used in the present work has already been described.[3] The constant-current source and the direct-reading potentiometer are both of the electronic type, constructed in our laboratory. The electrolytic time is measured by an integral-type stop-watch. The titration apparatus is shown in Fig. 1. The generating anode and cathode are both made of platinum, the former being 20 × 20 mm^2, and the latter a platinum spiral immersed in 15% ammonium sulphate solution, separated by a sintered-silica disc from the anode solution.

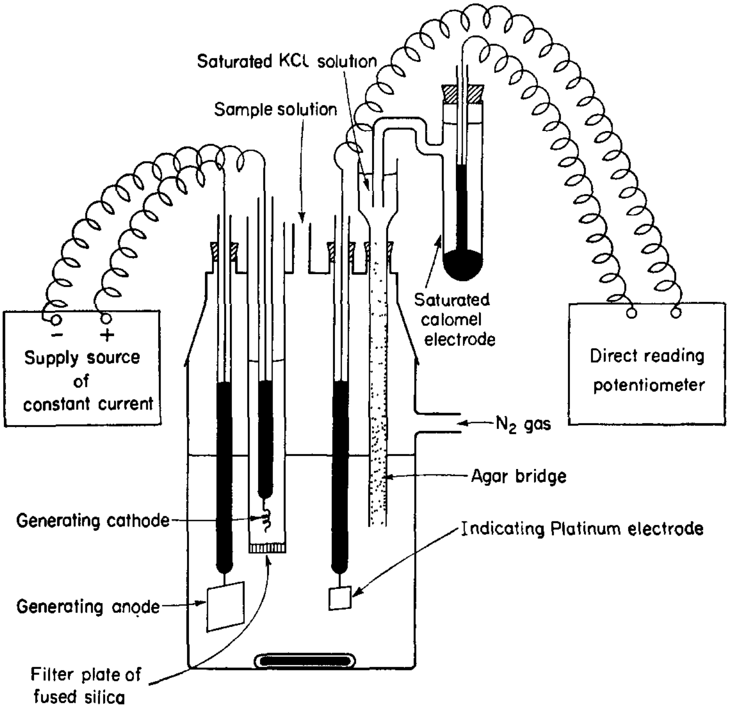

FIG. 1.—Apparatus for coulometric titration.

Fig. 2 shows the constant-current generator circuit. The electrolytic current flows through resistances R_2 and R_3, the iR drop across which is the input of a conventional voltage regulator circuit. By holding the iR drop across R_2 and R_3 constant, the voltage regulator circuit supplies a constant output to the cell. The electrolytic current is controlled to the desired value by adjusting R_3.

The indicating electrode is a platinum plate (15 × 15 mm^2) and the reference electrode a saturated calomel electrode, which is connected to the electrolytic solution through saturated potassium chloride solution and an agar bridge. The indicator circuit, as shown in Fig. 3, is constructed with a bridge, the

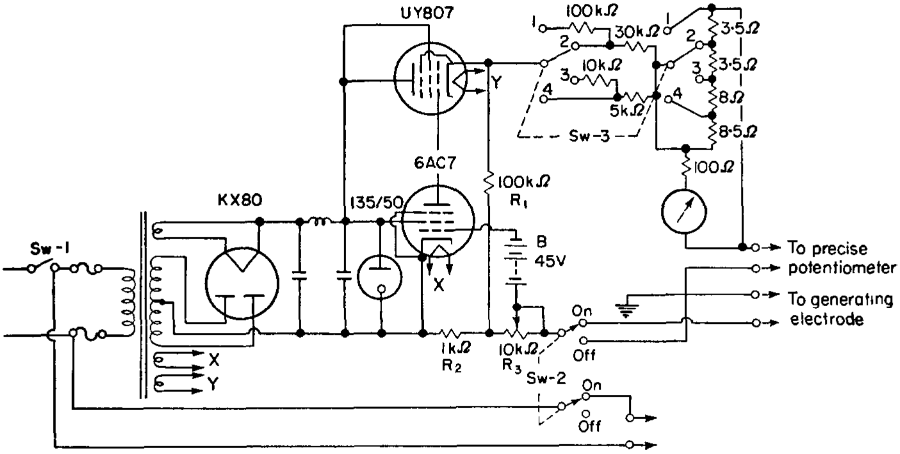

FIG. 2.—Constant-current generator circuit for coulometric titration.

components being two vacuum tubes (6SJ7) and two resistances (R_2 and R_3). This circuit is very stable towards fluctuations of the supplied voltage.

All the reagents used were of commercial special grade and water was purified by an ion-exchange resin. The electrolytic solution was prepared by dissolving 120 g of acetic acid and 8 g (or 16 g) of sodium hydroxide in 500 ml of purified water to which 24 g of potassium bromide was added, and making the solution up to 1 litre with purified water. The solution in the generating cathode chamber was prepared by dissolving 150 g of ammonium sulphate in 850 g of purified water. The sample solution (iron^{II} solution) is made from a stock solution prepared by dissolving 39·3 g of ferrous ammonium sulphate in 1*N* sulphuric acid, making up to 1 litre and standardising with potassium permanganate standard solution.

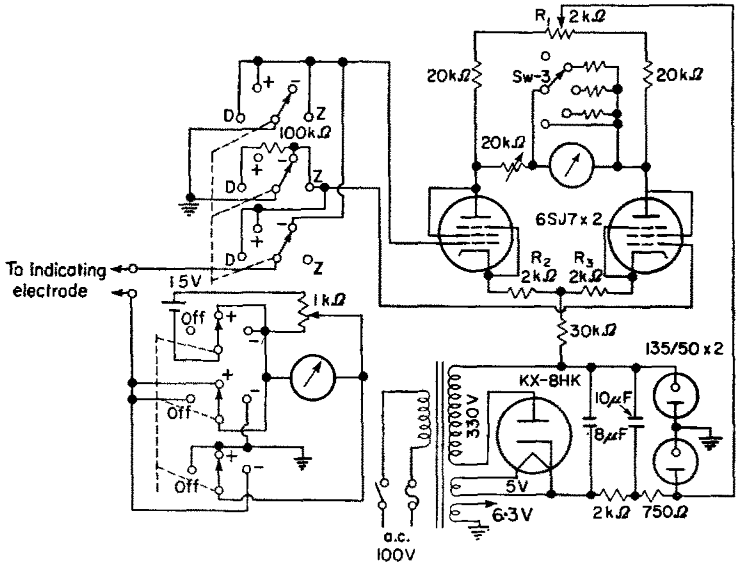

FIG. 3.—Circuit diagram for indicator system.

EXPERIMENTAL AND RESULTS

1. *Titration curve*

The reaction of bromine with iron^{II} is very slow in sulphuric acid solution, requiring several hours for the reaction of the bromine generated in five minutes, as shown in curve A, Fig. 4. Various other solutions of the compositions cited in Table I were examined.

Table I shows the pH values and the voltages at the end-point for the various compositions. The titration curves were obtained by plotting each indicated voltage after electrolytic oxidation for 20 sec at an electrolytic current of 10 mA. The solution being titrated was prepared by adding 2 ml of 0·01*M* ferrous ammonium sulphate to 100 ml of the cited electrolytic solution. Fig. 4 shows the titration curves. The titration curve of B is very similar to that of A and the titration curve of C to that of D. The titration curves of E and G almost coincide with that of F. Therefore only the curves of A, D, and F are shown in Fig. 4.

Probably because of precipitation of ferric hydroxide, the titrated solution gradually becomes brownish during the titration and more and more turbid with increase of sodium hydroxide (the increase of pH). Fig. 4 shows that the indicated voltages of all the solutions coincide very well after passing the end-point. Therefore it is concluded voltage rises above 0·5 V vs. S.C.E. and does not return to that voltage. Typical results are shown in Table II.

Table II shows that the errors are always positive and relatively smaller (average error 5·6%) in 0·2*N* sodium hydroxide than in 0·4*N* sodium hydroxide. On the other hand the error becomes greater in more dilute sodium hydroxide solution, so that the desirable concentrations in the electrolytic solution is 0·2*N* sodium hydroxide. The calibration curve is shown in Fig. 6, which shows a linear relationship between coulombs (the electrolytic time at constant current) and the concentration of iron^{II}, if the electrolytic solution contains 0·2*N* sodium hydroxide, 0·1*M* potassium bromide and 1*N* acetic acid. Provided that the coulomb value is corrected by a factor of 0·9466 as a titration factor, the coulometrically titrated value of iron^{II} has only an error ranging within ±1%

TABLE II. COULOMETRIC TITRATION OF Fe^{2+} WITH ELECTRO-GENERATED BROMINE AT 9·92 mA ELECTROLYTIC CURRENT (POTENTIOMETRIC END-POINT DETECTION)

Electrolyte	No. of trials	Taken, *meq* × 10^3	Found, *meq* × 10^3	Error, %	Standard deviation, %
0·1*M* KBr + 0·2*N* NaOH + 1*N* CH_3COOH	4	8·851	9·488	+7·19	1·53
	4	17·702	18·576	+4·94	1·58
	4	35·404	37·418	+5·68	0·69
	4	53·106	56·076	+5·59	0·51
	4	88·51	92·78	+4·82	0·44
0·1*M* KBr + 0·4*N* NaOH + 1*N* CH_3COOH	4	19·282	23·263	+20·65	2·28
	2	38·564	49·137	+27·42	—
	2	57·846	80·593	+39·32	—
	1	77·128	108·760	+41·01	—

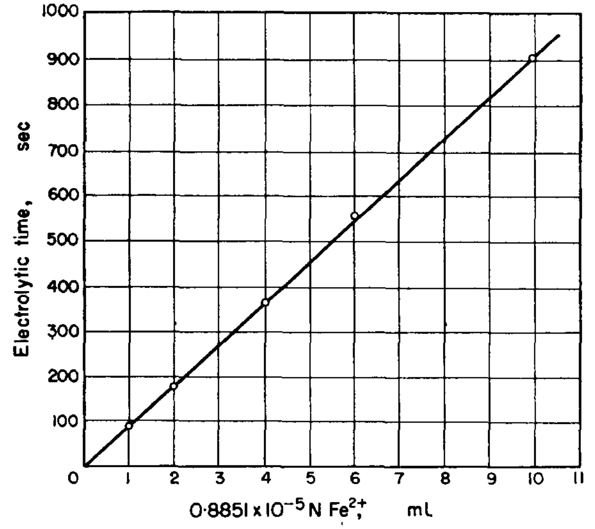

FIG. 6.—Relationship between quantity of iron^{II} and bromine generating time.

4. *Coulometric titration (dead-stop method)*

The vacuum-tube potentiometer used allows the use of a dead-stop method for the end-point detection. By changing the switch, the electric current between the indicating electrodes is, as shown in Fig. 7, passed through the fixed resistance (100 KΩ), which voltage drop can be read with a vacuum tube potentiometer. The indicating electrodes are platinum plates, 15 × 15 mm^2 and 10 × 5 mm^2, between which the voltage of 0·4 ~ 0·5 V is applied. (The applied voltage is far less than 0·4 V when the indicating current is running, because of the voltage depression due to the resistance of 100 KΩ.) The cathode acts as an indicating electrode. The indicating current flows because of depolarisation in the presence of iron^{II}, stops because of the polarisation at the end-point, and passes again because of depolarisation caused by liberated bromine after the end-point. Therefore the titration curve is sharply V-shaped at the end-point, this corresponding to the minimum of the titration curve.

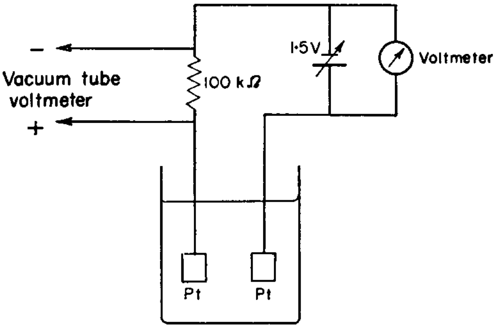

FIG. 7.—Schematic diagram for amperometric detection of end-point.

TABLE III. COULOMETRIC TITRATION OF Fe^{2+} WITH ELECTRO-GENERATED BROMINE (AMPEROMETRIC END-POINT DETECTION)

Taken, *meq* × 10^3	Found, *meq* × 10^3	Error, %
8·644	9·098	+5·25
8·851	9·350	+5·69
17·288	17·990	+4·06
17·392	18·092	+4·02
17·702	18·609	+5·11
34·576	35·979	+4·06
54·175	51·864	+4·46

Table III shows the result when iron^{II} is titrated with bromine generated at 10 mA in an electrolyte containing 0·1*M* KBr, 1*N* CH_3COOH and 0·2*N* NaOH.

Zusammenfassung—Die Reaktion zwischen Eisen (II) und Brom verläuft in einem Medium von Essigsäure-Natriumazetat viel glatter als in Schwefelsäure. Dies bewirkt einen sehr gut ausgeprägten Sprung in der potentiometrischen Titrationskurve. Die Kurve sowie die Reaktionsgeschwindigkeiten der Reaktionen wurden studiert. Es wurde gezeigt dass Eisen(II)-Mengen von 0·01 bis 0·1 Milliäquivalenten coulometrisch mit etwa 1 % Fehler titriert werden können, wenn die Lösung 0·1 m in Kaliumbromat, 1 n in Essigsäure und 0·2 n in Natronlauge ist.

Résumé—L'ion ferreux réagit sur le brome plus facilement en milieu acide acétique-acétate de sodium qu'en milieu acide sulfurique; il en résulte une variation nette du potentiel au point équivalent. Les courbes de titrage et les vitesses de cette réaction ont été étudiées, et les auteurs ont montré qu'il était possible de titrer de 0,0 à 0,1 milliéquivalent de fer ferreux par coulométrie à environ 1% près si la solution électrolytique contient du bromate de potassium 0,1 M, de l'acide acétique N et de la soude 0,2 N.

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UN RÉACTIF DÉFINI DE DIAZOCOPULATION, LE 3-PHENYL 5-NITROSAMINO 1,2,4-THIODIAZOLE OU PHENITRAZOLE

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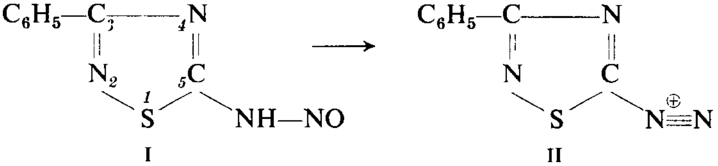
Résumé—Le 3-phényl 5-nitrosamino 1,2,4-thiodiazole ou *phénitrazole* permet de réaliser des diazocopulations dans des conditions parfaitement définies. En milieu acide, il se déshydrate en effet en un diazoïque que l'on condense d'emblée sur des phénols ou des amines aromatiques. Ce réactif permet encore de révéler les aldéhydes dont les phénylhydrazones correspondantes conduisent à des formazans. Les colorations obtenues autorisent le plus souvent des dosages à l'échelle du centième de milligramme.

PARMI les 5-nitrosamino 1,2,4-thiodiazoles connus, le dérivé 3-phénylé, I, offre l'avantage d'une stabilité satisfaisante, contrairement à ses analogues méthylé ou méthoxylé[2]. Ces nitrosamines se déshydratent en milieu acide pour conduire aux sels de diazonium correspondants[2,3]. Ainsi, le composé I, que nous proposons de nommer *phénitrazole*, fournit le diazoïque II dont la réactivité a déjà été mise à profit pour réaliser des condensations sur les pyrroles[6].



I
Phénitrazole

II

Selon nos recherches, l'emploi du phénitrazole se révèle avantageux en analyse. En effet, par simple déshydratation effectuée directement dans le milieu de condensation, ce réactif nous a permis de réaliser des diazocopulations dans des conditions parfaitement définies, contrairement aux solutions de diazoïques usuelles dont la composition est difficile à reproduire. De plus, avec ce sel de diazonium, on n'observe pas de coloration des témoins.

Les *phénols*, par action du phénitrazole en présence d'acide perchlorique, forment des azoïques dont la coloration est observée en milieu alcalin (Tableau I). Dans le cas du phénol ordinaire, la comparaison des résultats obtenus avec les réactifs usuels et avec le nouveau réactif est en faveur de ce dernier. Ainsi, pour obtenir une densité optique de 0,3 (cuve de 1 cm), il faut mettre en jeu 15 à 30 μg de phénol avec les diazoïques de la *p*-nitraniline ou de l'acide sulfanilique et seulement 5 μg avec le phénitrazole. L'emploi du phénitrazole conduit par ailleurs à une méthode quantitative permettant des dosages à l'échelle du centième de milligramme.

TABLEAU I. APPLICATION DIRECTE AUX PHENOLS ET AUX ARYLAMINES

	Coloration	λ max., mμ	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, μg
A-Phénols			
o-Aminophénol	rose	515	21
m-Aminophénol	rouge	520	7
p-Aminophénol	rose	515	45
Gaïacol	rouge-violet	530	5
Hydroquinone	brun	420	65
α-Naphtol	violet	550	7
β-Naphtol	violet	540	12
Phénol	rouge	515	4
Phloroglucinol	rouge	500	10
Pyrocatéchol	violet	530	12
Résorcinol	rouge orangé	500	5
Salicylaldéhyde	jaune	380	40
B-Arylamines et divers			
Aniline*	orangé	495	28
Diméthylaniline	rose violacé	535	6
Méthylaniline*	rose	510	27
Carbazole*	bleu	590	7
Indole*	orangé	470	9

* 5 minutes de contact à 0° en milieu acide.

Des colorations sont également obtenues à partir des *arylamines* (Tableau I) tandis que les alcoylamines ne sont pas révélées. Parmi les composés hétérocycliques que nous avons essayés, seuls l'indole et le carbazole ont réagi. L'histidine, l'histamine, la théophylline, la caféine, l'adénine, la thymine et la guanine, qui se condensent avec les sels de diazonium usuels, ne développent pas de coloration dans le cas présent.

Enfin, le phénitrazole, par action des phénylhydrazones, se prête à la condensation en formazans déjà décrite pour d'autres sels de diazonium[4,5]. Les *aldéhydes* peuvent être ainsi décelés et dosés (Tableau II), les cétones et sucres usuels étant sans action.

TABLEAU II. APPLICATION INDIRECTE AUX ALDEHYDES

Aldéhydes	Coloration	λ max., mμ	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, μg
Acétaldéhyde	Orangé	490	44
Acide glyoxylique (sel de sodium)	Orangé	490	40
Benzaldéhyde	Violet	550	23
Formaldéhyde	Orangé	490	3
Furfuraldéhyde	Orangé	510	22
Glyoxal (monohydrate)	Orangé	490	14
Propionaldéhyde	Orangé	490	105
Vanilline	Violet	565	92

PARTIE EXPERIMENTALE

(avec Mlles G. Clement et S. Venard)

Le 3-phényl 5-amino thiodiazole et son dérivé nitrosé (phénitrazole) sont préparés selon Goerdeler.[1,2]

Phénols et arylamines

A 1 cm^3 de solution alcoolique du phénol, on ajoute 1 cm^3 de solution alcoolique à 0,4 pour cent de phénitrazole et 1 cm^3 d'acide perchlorique (55° Bé). Après 5 minutes de repos à température ordinaire, on refroidit dans la glace et ajoute 3 cm^3 de solution aqueuse à 20 pour cent de soude également glacée. On effectue la mesure sur photomètre après 5 minutes à température ordinaire.

Aldéhydes

Le réactif est obtenu par mélange de volumes égaux d'acide perchlorique (55° Bé) et de solution alcoolique à 0,4 pour cent de phénitrazole. On maintient à 0° pendant 5 minutes avant emploi.

A 1 cm^3 de solution alcoolique d'aldéhyde, on ajoute 0,5 cm^3 de solution aqueuse à 0,5 pour cent de chlorhydrate de phénylhydrazine, abandonne pendant 20 minutes à température ordinaire, refroidit à 0°, ajoute 1 cm^3 de réactif puis, après 5 minutes à 0°, 3 cm^3 de solution aqueuse à 20 pour cent de soude. La lecture sur photomètre est effectuée après 5 minutes de repos à 0°.

Summary—3-Phenyl-5-nitrosamino-1:2:4-thiodiazole, or *phenitrazole*, allows diazo coupling to be carried out in precisely defined conditions. In acid medium it dehydrates to a diazo compound which may be condensed directly with phenols or aromatic amines. The reagent enables the detection of aldehydes of which the corresponding phenylhydrazones lead to formazans. The colorations obtained allow the determination of amounts of the order of hundredths of a milligram.

Zusammenfassung—3-Phenyl-5-nitrosamino-1,2,4-thiodiazol (Phenitrazol) gestattet Diazokupplung unter genau definierten Bedingungen. In saurem Medium dehydriert die Verbindung zu einer Diazoverbindung, die direkt mit Phenolen oder aromatischen Aminen kondensieren kann. Das Reagens ermöglicht die Bestimmung von Aldehyden, deren entsprechende Phenylhydrazone zur Bildung von Formazanen führen. Die erhaltene Färbung gestattet die Bestimmung von Mengen in der Grössenordnung einiger Hundeertstel Milligramm.

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SUR UN PRINCIPE DE COLORIMETRIE EN MILIEU NON AQUEUX. SON APPLICATION A L'ANALYSE ORGANIQUE FONCTIONNELLE

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Résumé—En milieu non aqueux, il est possible de caractériser la fonction hydroxyle, le carbonyle ou le groupe amine primaire aliphatique. On procède à la formation d'un dérivé (ester, hydrazone ou arylamine) présentant des groupes nitrés aromatiques puis, sans extraction ni élimination de l'excès de réactif, on développe par une base organique en diméthylformamide une coloration caractéristique. Des dosages peuvent être ainsi effectués sur quelques centièmes de milligramme.

L'ÉTUDE des réactions colorées en absence d'eau n'a été l'objet, jusqu'ici, que de recherches fragmentaires. On peut, à titre d'exemple, citer le cas des malonylurées que l'on identifie sous forme de complexes métalliques obtenus en milieu anhydre. De même, en présence de bases, les dérivés nitrés aromatiques conduisent, selon le solvant, à des absorptions variables en position et en intensité.[1]

Il nous est apparu possible de donner une extension plus large à la notion de colorimétrie en milieu non aqueux et de l'appliquer à l'analyse organique fonctionnelle. Le but de nos essais a été de procéder à la formation d'un dérivé puis, par l'emploi d'un solvant, de développer d'emblée une coloration, sans extraction préalable ni élimination de l'excès de réactif.

Nous décrivons ici ces colorimétries nouvelles. Les exemples rapportés intéressent la fonction hydroxyle, le carbonyle et le groupe amine primaire aliphatique. Les dérivés retenus (esters, hydrazones, arylamines) présentent des groupes nitrés aromatiques que l'on révèle par la pipérazine ou l'hydrate de benzyltriméthylammonium. A partir des amines, il est également possible de former des bases de Schiff comportant un reste diméthylaminé aromatique sensible à l'action du nitrométhane. L'effet du solvant apparaît alors décisif. Ainsi en diméthylformamide, les esters dinitrobenzoïques se colorent par la pipérazine tandis que l'acide dinitré lui-même n'est pas révélé; en alcool, il n'apparaît aucune coloration ni avec l'acide ni avec ses esters.

Alcools primaires et secondaires

L'estérification par le chlorure de 3,5-dinitro benzoyle suivie d'une réaction avec l'acétone a déjà été mise à profit pour doser colorimétriquement les alcools.[2] Mais cette méthode exige, en particulier, une séparation préalable et quantitative de l'ester.

Aprés acylation en présence de pyridine, une solution de pipérazine dans le diméthylformamide développe une coloration rouge (510 mμ) qui n'est pas observée en absence de corps hydroxylés. Dans les mêmes conditions, les amines ne sont pas révélées et les phénols ne conduisent qu'à une coloration fugace.

La méthode peut être quantitative (Tableau I). Il convient alors d'effectuer les

TABLEAU I

Alcools	Prise d'essai pour obtenir une densité optique de 0,3 à 510 mμ en cuve de 1 cm, μg
Ethanol	9
Butanol-1	15
Butanol-2	17
Cholestérol	75
Epi-déhydroandrostérone	65
Testostérone	60

lectures photométriques à température constante pour éviter tout phénomène de thermochromie. En pratique, 50 μg de 3,5-dinitrobenzoate d'éthyle conduisent, dans nos conditions opératoires, à une densité optique de 0,65 à 0° et de 0,15 à 50°, en cuve de 1 cm.

Composés carbonylés

Les *p*-nitrophénylhydrazones sont colorées en milieu alcalin et l'intensité de la coloration varie avec le solvant.[1b] Selon nos essais, l'hydrate de benzyltriméthylammonium en solution dans le diméthylformamide permet de rendre la réaction sélective. On obtient des colorations rouges ou violettes et des dosages peuvent être effectués sur quelques centièmes de mg (Tableau II).

Amines primaires aliphatiques

On sait que l'on forme des dérivés dinitrophénylés par action du 1-fluoro 2,4-dinitro benzène sur le groupe amine primaire. Nous avons observé que l'arrangement *m*-dinitré peut alors être révélé et dosé en milieu non aqueux par l'hydrate de benzyltriméthylammonium qui fournit une coloration rouge orangé (Tableau III). Dans les mêmes conditions, les amines secondaires (diéthyl-, dipropyl- et dibenzyl-amine) ne réagissent que faiblement. Les amines aliphatiques tertiaires et les aryl-amines ne sont pas décelées.

Si l'on condense le *p*-diméthylamino cinnamaldéhyde sur les amines primaires aliphatiques, en choisissant le nitrométhane comme solvant, on observe des colorations orangées. Cette réaction permet également des dosages sur 5 à 20 μg (Tableau III).

PARTIE EXPERIMENTALE

(avec Mlle G. CLEMENT)

ALCOOLS PRIMAIRES ET SECONDAIRES

Réactifs

Solution à 5 pour cent de chlorure de 3,5-dinitrobenzoyle dans le benzène.

Solution à 25 pour cent d'hexahydrate de pipérazine dans le diméthylformamide.

Mode opératoire

La prise d'essai dissoute dans 0,1 ml de mélange à parties égales de pyridine et de benzène, est ajoutée à 0,1 ml de solution de chlorure de 3,5-dinitrobenzoyle puis abandonnée pendant vingt minutes à 18–22°. On introduit ensuite 0,1 ml de pyridine à la même température puis, après cinq minutes, 5 ml de solution de pipérazine également portée à 18–22°. La lecture est effectuée à 510 mμ.

TABLEAU II

Composés carbonylés	Temps de chauffage à 70°, *min*	Couleur	λ max., *mμ*	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, *μg*
Aldéhydes				
Acétaldéhyde	30	rouge	510	40
Diphénylacroléine	20	bleu violet	570	10
Formaldéhyde	20	rouge	500	8
Glyoxal (monohydrate)	30	bleu	690	3
Pipéronal	20	violet	540	8,5
Propionaldéhyde	30	rouge	510	50
Salicylaldéhyde	20	violet	550	7,5
Vanilline	20	bleu violet	570	9,5
Sucres				
Glucose	20	rouge	510	50 → 0,04*
Ribose	20	rouge	510	50 → 0,06
Cétones simples				
Acétone	30	rouge	510	6
Acétophénone	30	violet	540	26
Acétylacétate d'éthyle	30	rouge	510	50 → 0,1
Acétylacétone	30	rouge	510	50 → 0,03
Benzile	30	violet	550	80
Benzophénone	30	rouge	510	50 → 0,08
Camphre	30	rouge	510	50 → 0,05
Cyclohexanone	20	rouge	510	10,5
Cyclopentanone	30	rouge	510	16,5
Diacétyle	30	violet-bleu	560 680	17,5 13,5
α-Ionone	30	violet	540	19
Méthyléthylcétone	30	rouge	510	10
Cétones stéroïdes				
Acide déhydrocholique	30	rouge	510	42
Androstane 17β-ol 3-one	30	rouge	510	30
$\Delta^{1,4}$-Androstadiène 3,17-dione	30	bleu-violet	560	25
Δ^{4}-Androstène 3,17-dione	20	violet	540	18
Cortisone	20	violet	540	22,5
1-Déhydrocortisone	30	violet	555	24
Déhydro *épi*-androstérone	30	rouge	510	50 → 0,08
1-Déhydrohydrocortisone	30	violet	555	30
Dexaméthasone	30	violet	560	33
Hydrocortisone	20	violet	540	23
Progestérone	20	violet	540	18,5
Testostérone	20	violet	540	19
Δ^{1}-Testostérone (acétate)	30	violet	540	35

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* Avec une prise d'essai de 50 μg, la densité optique est de 0,04.

TABLEAU III

Amines	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm	
	Réaction au 1-fluoro 2,4-dinitrobenzène (495 mμ)	Réaction au diméthylaminocinnamaldéhyde (475 mμ)
Ethylamine	8 μg	12 μg
Propylamine	8 μg	7,5 μg
Benzylamine	22 μg*	20 μg
Cyclohexylamine	22 μg	18 μg
Ethanolamine	11 μg	11 μg

* $\lambda_{max.}$ = 525 mμ dans le cas de la benzylamine.

COMPOSÉS CARBONYLÉS

Réactifs

Solution à 0,040 g pour cent de *p*-nitrophénylhydrazine dans l'éthanol absolu contenant 0,1 pour cent d'acide chlorhydrique concentré.

Solution fraîchement préparée à 0,4 pour cent d'hydroxyde de benzyltriméthylammonium dans le diméthylformamide, obtenue en diluant à 1 pour cent dans le solvant la solution aqueuse à 40 pour cent d'hydroxyde d'ammonium quaternaire.*

Mode opératoire

A 0,5 ml de solution dans l'éthanol du composé carbonylé, on ajoute 0,5 ml de réactif à la *p*-nitrophénylhydrazine et chauffe à 70° pendant dix à trente minutes. On refroidit puis dilue par 9 ml de solution de benzyltriméthylammonium dans le diméthylformamide.

AMINES PRIMAIRES ALIPHATIQUES

(*a*) *Par le 1-fluoro 2,4-dinitrobenzène*

Réactifs

Solution à 0,025 pour cent de 1-fluoro 2,4-dinitrobenzène dans le diméthylformamide.

Solution fraîchement préparée à 0,4 pour cent d'hydroxyde de benzyltriméthylammonium dans le diméthylformamide, obtenue en diluant à 1 pour cent dans le solvant la solution aqueuse à 40 pour cent d'hydroxyde d'ammonium quaternaire.*

Mode opératoire

A 1 ml de solution d'amine dans le diméthylformamide, on ajoute 0,5 ml de solution de fluorodinitrobenzène, abandonne pendant dix minutes à température ordinaire et ajoute 4,5 ml de solution de benzyltriméthylammonium et 0,1 ml d'eau. La lecture est effectuée après cinq minutes de repos, à 495 mμ.

(*b*) *Par le diméthylaminocinnamaldéhyde*

Dans 2 ml de solution d'amine dans le nitrométhane (ou dans 0,1 ml d'éthanol en ajoutant 2 ml de nitrométhane), on introduit 2 ml de solution à 0,05 pour cent de diméthylaminocinnamaldéhyde dans le nitrométhane, chauffe pendant vingt-cinq minutes au bain-marie bouillant, refroidit et complète à 10 ml avec du nitrométhane. La lecture est effectuée à 475 mμ.

* On peut également utiliser une solution à 30–35 pour cent d'hydroxyde obtenu à partir de bromure ou d'iodure d'ammonium quaternaire. A 5,5 g de bromure ou à 6,6 g d'iodure, en solution dans 10 cm^3 d'eau, on ajoute 5 g de Ag_2O. Après une heure d'agitation, on filtre, abandonne pendant 24 heures puis on ajoute 0,5 g de noir décolorant, agite pendant 5 minutes et filtre de nouveau.

Summary—In non-aqueous medium it is possible to characterise the hydroxyl, the carbonyl and the aliphatic primary amino groups, by formation of a derivative (an ester, hydrazone or arylamine) containing nitro groups. Without either extraction or elimination of the excess of reagent, a characteristic coloration is developed in dimethylformamide by using an organic base. Determinations are possible on the hundredths of a milligram scale.

Zusammenfassung—In nichtwässrigen Medium ist es möglich Hydroxyl-Carbonyl- und primäre aliphatische Aminogruppen durch Bildung eines Derivates (Ester, Hydrazon oder Arylamin), das eine Nitrogruppe enthält, zu charakterisieren. Ohne extraction oder Entfernung des Reagensüberschusses wird in Dimethylformamid eine charakteristische Färbung erzielt, wenn eine organische Base angewendet wird. Bestimmung im Hundertstel-milligrammbereich sind möglich.

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A NEW SELECTIVE METALLOCHROMIC REAGENT FOR THE DETECTION AND CHELATOMETRIC DETERMINATION OF CALCIUM

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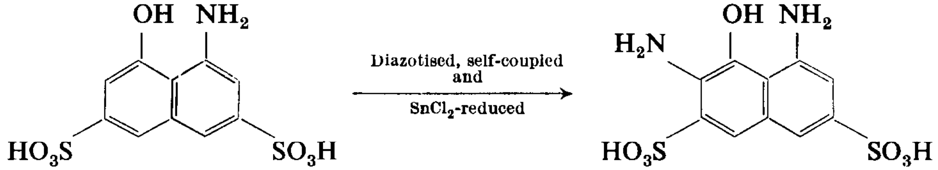
Summary—A new reagent, Calcichrome, which gives a highly sensitive colour reaction with calcium ions in alkaline solution, has been synthesised. Neither barium, strontium nor magnesium react with the reagent, which is therefore proposed as a selective spot-test reagent for calcium. In addition, Calcichrome may be used as a metallochromic indicator for the accurate complexometric titration of calcium in the presence of at least twelve-fold amounts of barium. *Trans*-1:2-diaminocyclohexane-N:N:N′:N′-tetra-acetic acid is used as titrant since it is the only complexan available which is sufficiently selective in its reactivity towards calcium and barium.

Few satisfactory methods are available for the detection and determination of calcium in the presence of the other alkaline-earth elements and magnesium. Glyoxal-bis (2-hydroxyanil) is the only reagent known to us which can be used, without chemical separation, for the detection of calcium in the presence of barium and strontium.[1] All three alkaline earths give a red precipitate with the reagent, but only the calcium complex is extracted from aqueous solutions into a chloroform phase.

In the course of an extensive survey of the complexometric indicator properties of polyhydroxyazo dyes, part of which has already been published,[2,3] we have observed certain relationships between molecular structure and indicator action. In the course of subsequent investigations based on this experience we isolated the self-coupling reaction product of diazotised H-acid (8-hydroxyl-1-aminonaphthalene-3:6-disulphonic acid) and examined its indicator properties. Whilst more work requires to be done on the structure of this reagent, the present paper describes the synthesis, properties and some of the applications of this new reagent which is specific for calcium within the alkaline earth group. Thus we have used it as a spot-test for the detection of calcium in the presence of barium and strontium and for the titration of calcium in the presence of a large excess of soluble barium salts.

DISCUSSION

The self-coupling reaction product of diazotised H-acid was first described in the early German literature. In Friedländer's compilation[4] the opinion was expressed that the composition of the product was such that one or possibly two diazotised H-acid



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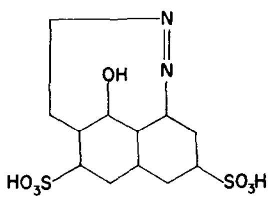
units were involved. It was reported that reduction with stannous chloride yielded only 1:7-diamino-8-naphthol-3:6-disulphonic acid. No other product could be isolated.

From the above evidence self-coupling had definitely taken place; moreover it was also observed that once the diazonium salt had been made alkaline, acidification yielded only a reversible blue to red colour-change and no trace of the original diazonium salt. Friedländer therefore proposed two possible structures:—



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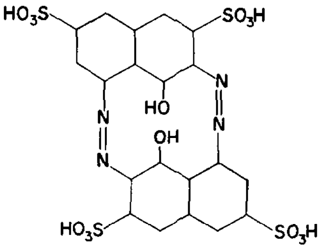

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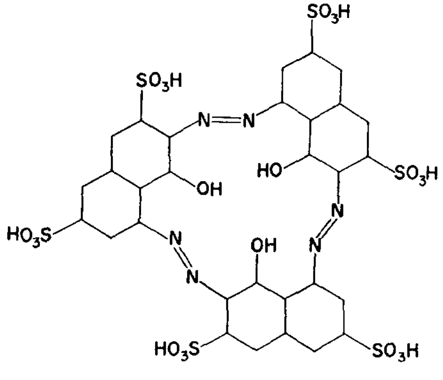
However, consideration of the stereochemistry involved in these structures suggested to us that their existence was highly improbable and this was borne out when attempts were made to build molecular models of such compounds. We have found, however, that it is easily possible for a scale model molecule to be formed in which three diazotised H-acid units are coupled together by 1–7 azo linkages. This produces a virtually planar ring structure in which the hydroxyl groups are closely crowded together in the centre of the molecule.



Probable stucture

A preliminary series of experiments designed to establish the structure of such a molecule, *cyclo*-tris-7-(1-azo-8-hydroxynaphthalene-3:6-disulphonic acid), has yielded some results which substantiate the hypothesis of formation of a trimer of diazotised H-acid, but more refined experiments are required before a definite conclusion can be stated. Some of this evidence is presented in outline below, but meanwhile, the practical significance of this new metallochromic reagent justifies publication of its synthesis, an account of its reactions with cations, and details of its application to certain analytical problems.

SYNTHESIS

1-Amino-8-naphthol-3:6-disulphonic acid may be diazotised in hydrochloric acid solution and self-coupled by pouring the solution into strong sodium hydroxide, when a deep-blue solution is obtained. Acidification of the reaction mixture with hydrochloric acid changes the colour of the solution to red and precipitation of the crude product is virtually complete after 12 hr. For use as an indicator or a spot reagent, the compound may be purified sufficiently by suspending in methanol and gassing out with HCl. The filtered solution may then be evaporated to crystallisation under reduced pressure on a water bath. Purification is also obtained by dissolution of the crude product in water, and precipitation and isolation of the lead salt. The latter is suspended in water and the bulk of the lead is precipitated therefrom as $PbCl_2$; the last traces are removed with H_2S, which in turn is removed by passage of nitrogen, and the product is obtained by concentration of the filtered aqueous solution under reduced pressure. The product thus obtained which contains only a very small amount of sodium, and is free from lead and chloride, is believed to be the virtually pure free acid form of the reagent.

It is thought that a superior purification procedure may be possible and this will be reported later when details are given of the structure of the compound.

ACID-BASE AND METALLOCHROMIC REACTIONS

The chemical properties of the reagent, *cyclo*-tris-7-(1-azo-8-hydroxynaphthalene-3:6-disulphonic acid), hereafter referred to as Calcichrome, were examined with a 0·5% aqueous solution of the reagent. The reagent is coloured crimson in the pH range 2–8·5, purple at pH 10–11·5, blue at pH 13 and dark red in strong alkali: This observation agrees with our supposition that the molecule contains three ionisable protons which would not be expected to dissociate fully till a high pH had been attained.

The metallochromic properties of the reagent were examined with 37 cations each in six different buffers corresponding to pH 2, 4·6, 7, 10, 11·5, and 13. The ions concerned were Al, As^{III}, Ag, Ba, Be, Bi, Ca, Cd, Ce^{III} and Ce^{IV}, Co, Cr^{III}, Cu^{I} and Cu^{II}, Fe^{II} and Fe^{III}, Ga, Hg^{I} and Hg^{II}, In, La, Mg, Mn, Ni, Pb, Sb, Sn^{II} and Sn^{IV}, Sr, Th, Ti^{III}, U^{IV} and U^{VI}, V^{IV} and V^{V}, Zn, Zr. These tests were carried out in small test tubes containing 1 ml of distilled water and 2 drops of 0·1 N solutions of the metal ions. Two drops of pH adjusting solution were added and the contents were mixed and treated with 2 drops of Calcichrome. The colour of the solution was noted and if it differed from that produced by the buffer alone, 3 drops of 0·1M EDTA were added and any colour change recorded. The essential points are noted in Table I.

Only eight ions yield coloured products with the reagent under these conditions and in strongly alkaline solutions, pH 13, *only* calcium forms a coloured product. Neither magnesium nor the other two alkaline earths give a colour reaction with Calcichrome under these conditions and consequently this reaction can be used as the basis of a specific spot-test procedure for Ca^{2+} in the presence of other ions. Ordinary strontium salts usually contain sufficient calcium to yield a faint pink colour but spectrographically pure strontium salts yield no colour.

SPECIFIC SPOT-TEST FOR CALCIUM

With a $1 \times 10^{-4}M$ solution of Calcichrome in water and the procedure recommended below it was shown that on a spot plate unequivocal detection of calcium by

TABLE I

Metal ion	pH	Colour Change	
		Metal ion	EDTA (excess)
Ba	10	Red	Purple
	11·5	Red	Purple
Ca	10	Red	Purple
	11·5	Red	Purple
	13	Red	Blue
Cd	11·5	Red	Purple
Cu^{I} and Cu^{II}	4·6	Purple	Red
	7	Purple	Red
La	10	Red	Purple
	11·5	Red	Purple
Mg	10	Red	Purple
	11·5	Red	Purple
V^{IV}	4·6	Blue	Red
	7	Blue	Red
Zn	10	Red	Purple
	11·5	Red	Purple

the naked eye under normal laboratory conditions could be obtained with 0·25 μg at a dilution limit of 1:1,000,000. When the alkalinity of the test medium is greater than $4 \times 10^{-2}N$ there is a loss of sensitivity, and when less than $2 \times 10^{-2}N$ the blanks give a purple rather than a blue colour, with consequent loss of colour contrast. At one stage a solution of the reagent in 0·1*N* NaOH was used in order to simplify the procedure but this was abandoned when this formulation of the reagent was found to deteriorate after a few days.

Precipitates of some heavy metal hydroxides adsorb the reagent and give a purple colour even in the absence of calcium, but it was found that by treatment with hydrogen sulphide in acetone these interferences could be overcome within certain limits. Some cations inhibit the colour formation with the calcium quite markedly when present in large excess, though they themselves do not form coloured products. Thus, the following molar proportions of ions interfere in this way: Ba, 35: Mg, 20: Na (chloride), 1000. Almost complete inhibition was also caused by the following molar proportions of the anions PO_4^{3-}, 5: $(COO)_2^{2-}$, 10: SO_4^{2-}, 800; fluoride does not appear to interfere.

The recommended procedure can be used to detect 1 part of calcium at the $10^{-4}M$ level in the presence of 8 parts each (molar proportion) of Ba, Sr, Cu, Zn, Cd, Mg, *i.e.*, a total of 48 parts of the other ions present in the sample solution. An identical test could be produced if the H_2S–in–acetone treatment were replaced by acetone and thioacetamide, but if the acetone-sulphide is omitted both test and blank solutions give purple colours. The function of the acetone is discussed in the following section.

REACTION OF CALCICHROME WITH Ca^{2+} IONS

Fig. 1 shows the absorption spectra of the metal-free indicator and its calcium solution at pH ≈ 13. From this it will be observed that the addition of calcium produces a hypsochromic shift of the wavelength of maximum absorption equivalent to *ca.* 80 mμ. Only a cursory examination has so far been made to verify the exact nature of the molecule itself and its calcium chelate since difficulty was experienced in obtaining a sample of the dye of sufficient purity to give an accurate ultimate analysis in view of its rather high molecular weight. A preliminary examination by Job's method (*cf.* Fig. 2) shows however that the ratio of calcium ions to H-acid units in the molecule corresponds to 1:3. This may be interpreted as some indication that the cyclic trimer structure is most likely. We attribute the absence of colour reaction of Calcichrome with barium and strontium in part to the known tendency of these ions to form weaker complexes than calcium, but more largely to the size of the chelate "cage" at the centre of the molecule, the larger ionic radii of these ions, and their consequent inability to approach the closely crowded hydroxyl groups.

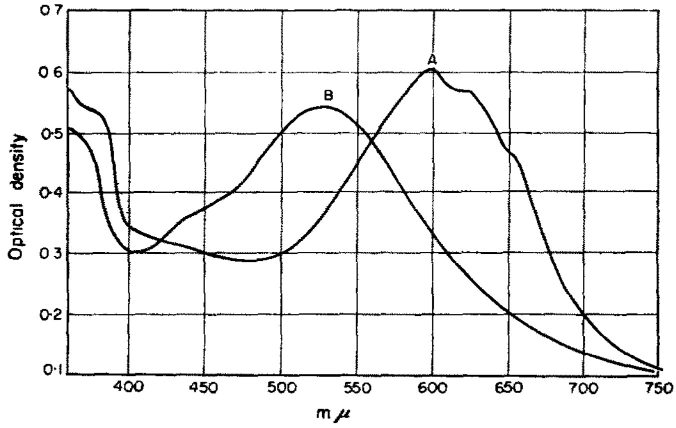


FIG. 1. Absorption spectra at pH > 12
(a) Metal-free reagent
(b) Calcium chelate

TITRATION OF CALCIUM IN PRESENCE OF BARIUM

There is now no lack of suitable indicators for the complexometric titration of calcium, but none is sufficiently selective in its behaviour to permit the titration of calcium in the presence of the other alkaline earths. The reactions of Calcichrome suggest that it should be applicable to the problem. However, because of the unselective reactivity of EDTA it would appear that a specific indicator would do little to solve the problem since the complexan will react with the other alkaline earths before the calcium has been completely titrated. The logarithms of the instability constants of the calcium and barium chelates of EDTA are 10·6 and 7·8 respectively. An examination of published log K values for other complexans shows that for *trans*-1:2-diaminocyclohexanetetra-acetic acid (CDTA) the log K values for the calcium and barium chelates are 12·5 and 7·99 respectively. This separation of 4·51

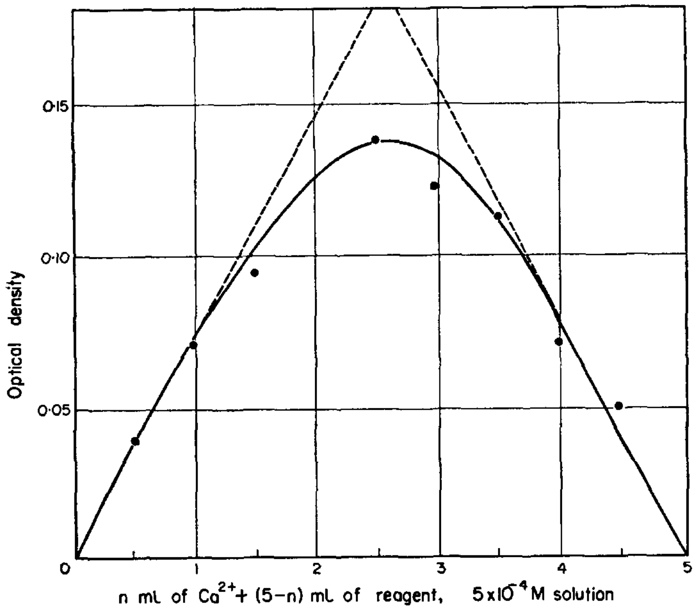


FIG. 2. Corrected plot of continuous variations experiment on Ca^{2+} chelate of reagent pH ≈ 12. $\lambda = 520$ mμ

TABLE II. RECOVERY OF 10·00 ml OF $2 \times 10^{-2}M$ Ca^{2+} IN PRESENCE OF Ba^{2+}

$2 \times 10^{-2}M$ $BaCl_2$ added, *ml*	Ba^{2+}/Ca^{2+} ratio	Recovery of Ca^{2+}, *ml*	Quality of end-point
0·00	0	10·00 10·00 10·00	Colour change complete over 3 drops. Rapid and sharp end-points.
5·00	0·5	10·00 10·02 10·00	Colour change complete over 3 drops. Rapid and sharp end-points.
10·00	1	10·00 10·00 10·04	Colour changes over 4 drops. Fairly rapid and sharp.
25·00	2·5	10·00 10·00 10·02	Colour changes over 5 drops. Sluggish but still sharp.
25·00 ml of $1 \times 10^{-1}M$ Ba^{2+}	12·5	10·04 10·00 10·00	Colour changes over 5 drops. Sluggish but still sharp.

units is better than that to be obtained with any other available complexan and consequently we have used it as a titrimetric reagent.

First of all the indicator action was examined in the EDTA titration of $2 \times 10^{-2}M$ and $10^{-2}M$ calcium solutions, and compared against Acid Alizarin Black SN (AABSN, Colour Index Mordant Black 25) which in our experience is the best calcium indicator currently available for dilute solution work.[3] Both indicators furnished identical titres though the end-point with Calcichrome was not as sharp as with AABSN. The latter gave a 1-drop colour change, whereas Calcichrome changed colour over 4 drops with the $1 \times 10^{-2}M$ solution. Even though it can be used for calcium in strongly alkaline solutions Calcichrome is not very suitable for the titration of calcium in the presence of magnesium. Solutions of calcium were next titrated with $2 \times 10^{-2}M$ CDTA with satisfactory results, and subsequently with calcium solutions containing varying amounts of barium. The results of these experiments are summarised in Table II. When the barium was present in fairly large proportions there was a tendency for sluggish end-points to be obtained and for the recovery to be very slightly high. As the colour showed signs of changing just before the end-point, the titrant was added dropwise at 10-sec intervals over the last few drops. Despite this sluggishness, however, there was no difficulty in obtaining a specific and accurate titration of calcium in the presence of a twelve-fold amount of barium.

TITRATION OF CALCIUM IN PRESENCE OF STRONTIUM

Since we could find no data relating to the stability constant of the CDTA-Sr^{2+} chelate we repeated the above experiments in an attempt to determine calcium in the presence of strontium. However, high recoveries were obtained and it was apparent that an appreciable amount of strontium was titrating with calcium. Several other complexans were examined without success, namely N:N′-bis-hydroxyethylethylenediamine-N:N′-diacetic acid (HEEDDA), N-hydroxyethyl-ethylenediamine-N:N′:N′-triacetic acid (HEEDTA), 1:2-diamino*cyclo*pentane-N:N:N′:N′-tetra-acetic acid (CPDTA)[5] and 1:2-diamino*cyclo*heptane-N:N:N′:N′-tetra-acetic acid (CHDTA).[5]

Attempts were made to overcome the interference of strontium in the calcium titration by precipitating the former as its insoluble sulphate. A procedure based essentially on that of Scott and Furman[6] was therefore applied, in which ammonium sulphate was employed as the reagent. It was found that the results for calcium were virtually quantitative whether or not the strontium sulphate was removed by filtration (*cf.* Table III). The resultant large concentration of electrolyte in the solution caused some inhibition of the indicator action, but this was overcome to a certain extent by addition of acetone. This expedient was adopted since it has been observed that the addition of miscible organic solvents stabilises complexes in solution whereas the addition of electrolyte has a weakening effect.[7] Thus we sought to balance the two effects against each other.

Precipitation with sodium sulphate and sulphuric acid yielded less reproducible results, but precipitation from homogeneous solutions *via* hydrolysis of sulphamic acid, with its resultant larger crystals of strontium sulphate, yielded slightly superior results though the gain in accuracy was small relative to the much greater time factor involved. Consequently only the ammonium sulphate procedure is reported here. Because of its obvious limitation in terms of absolute precision and accuracy this last procedure is not included as a recommended method for the determination of calcium in the presence of strontium, but rather as a rapid procedure which gives a tolerably good result when the time factor is more important than accuracy.

TABLE III. RECOVERY OF CALCIUM IN PRESENCE OF STRONTIUM BY CDTA TITRATION WITH CALCICHROME AS INDICATOR

$2 \times 10^{-2}M$ calcium solution taken, *ml*	$2 \times 10^{-2}M$ strontium solution added, *ml*	$2 \times 10^{-2}M$ calcium solution found, *ml*
10·00	0·00	10·00
5·00	5·00	4·85 5·00 5·05 5·05 5·30
10·00	5·00	9·70 10·00 9·86 9·80
15·00	5·00	14·85 15·05 15·00 14·95 15·05

TITRATION OF CALCIUM IN PRESENCE OF OTHER METALS

It was found that 0·5 molar proportions of zinc, lead, arsenic and antimony did not affect the accuracy of the calcium determination provided sufficient sodium hydroxide was added to form their amphoteric salts.

CONCLUSIONS

Whilst a fair amount of work remains to be done to establish firmly the exact structure of this new metallochromic reagent for calcium, the above experiments provide a highly selective and sensitive reagent for the detection of calcium. They also illustrate the necessity to use a selective complexan in conjunction with a specific indicator to obtain true specificity of titration. To the best of our knowledge the above method is the only direct titrimetric procedure which has been devised for the accurate titration of calcium in the presence of soluble barium.

EXPERIMENTAL

Synthesis of Calcichrome

5*N* hydrochloric acid (500 ml) is cooled in ice to below 5° and treated with a 30% solution of sodium nitrite (23 ml). The mixture is stirred continuously and kept below 5° whilst a suspension of 1-amino-8-naphthol-3:6-disulphonic acid monosodium salt sesquihydrate (H-acid) (37 g) in water (150 ml) is added in small portions over a period of 15 min. The reaction mixture is stirred for a further 30 min, and then the suspension of the yellow diazonium salt is poured in a thin stream with constant stirring into cold 4*N* sodium hydroxide (1 litre). Self-coupling takes place immediately, but the mixture should be stirred for a further 30 minutes to ensure complete reaction. To the alkaline solution is added sufficient concentrated hydrochloric acid to make it just acid; the colour changes to red and after 12 hr the impure product is filtered off and dried over solid sodium hydroxide. The impure product consists of the acid sodium salt with some sodium chloride. It may be rendered pure enough for reagent use by the following method.

The impure product is stirred with ethanol (1 litre) and hydrogen chloride gas is bubbled gently through the mixture to saturation. The free acid reagent dissolves in the alcohol and the residue of sodium chloride is removed by filtration. The solution is evaporated under vacuum on a water bath and when the product separates out it may be filtered off at the pump, sucked dry and finally dried *in vacuo* over sodium hydroxide.

Spot test for calcium

Reagents: 1N Sodium hydroxide: 0·1N Sodium hydroxide: Acetone saturated with washed and dried H_2S: 0·1% *Calcichrome Solution* (*ca.* 1 × $10^{-4}M$) aqueous.

(*a*) *Direct Procedure:* Place 4–5 drops of test solution on the spot-plate, add 1 drop (2 if necessary as shown by blank) of 0·1*N* sodium hydroxide and 1 drop of Calcichrome reagent solution. Prepare a blank similarly with 4–5 drops of water in place of the test solution. The latter should have a blue colour free of any trace of red. The presence of calcium will be revealed by a definite red coloration.

(*b*) *Procedure for Calcium in presence of ions which interfere with or inhibit the reaction as used above:* Place in a small centrifuge-tube test solution (1·0 ml), acetone saturated with hydrogen sulphide (0·5 ml) and 1 *N* sodium hydroxide (0·2 ml). Shake the mixture for 10 sec and centrifuge to give a clear solution. Place 5 drops (0·2 ml) of the supernatant solution on a spot-plate and to this add 1 drop of 0·1*N* sodium hydroxide to give a final alkalinity of approximately 3 × $10^{-2}N$. Add 1 drop of the reagent solution to the test spot and stir with a small glass rod. After 10 sec compare the colour of the spot with that of a "blank" spot in which the test solution is replaced by distilled water. The presence of calcium in the test solution is indicated by the pink colour of the spot; the "blank" is pale blue.

The acetone saturated with hydrogen sulphide may be replaced by pure acetone (0·5 ml) and thioacetamide (0·05 g).

Complexometric titration of calcium in presence of barium

Reagents: 2 × $10^{-2}M$ *CDTA*: 6·88 g of free acid dissolved in 50 ml of 1*N* sodium hydroxide and made up to 1 litre. Standardise against pure 2 × $10^{-2}M$ calcium chloride solution. *Indicator solution*, 0·5% in water: *Sodium hydroxide*, 1*N*:

Procedure: The test solution should be approximately 2 × $10^{-2}M$ with respect to the concentration of calcium. Pipette 10·00 ml of test solution into a 250-ml conical flask. Make the volume up to 100 ml by the addition of distilled water, and to the solution add 1*N* sodium hydroxide (10 ml) and 3 drops of indicator solution. Titrate the solution against the standard CDTA to the pink to blue end-point. Add the titrant slowly when approaching the end-point. Variations of the above volumes may be made so long as the sodium hydroxide concentration is maintained at *ca.* 0·1*N*.

Rapid titration of calcium in presence of strontium (method of limited precision)

Reagents: 2 × $10^{-2}M$ solutions of *Calcium chloride, Strontium chloride, CDTA: Ammonium sulphate,* 0·2*M*: *Calcichrome indicator solution*, 0·5% *aqueous: Acetone: Sodium hydroxide*, 1*N*.

Procedure: Pipette measured amounts of 2 × $10^{-2}M$ solutions of calcium and strontium chlorides into a 250-ml conical flask and dilute the contents to 50 ml. Bring the contents of the flask to boiling point and add 5 ml of 0·2*M* ammonium sulphate dropwise to the boiling solution over a period of *ca.* 2 min. Simmer the mixture for a further 10 min then allow to cool for 30 min. Add 20 ml of acetone, 6 ml of 1*N* sodium hydroxide and 4–5 drops of indicator solution. Finally titrate the solution to the sluggish pink to blue end-point.

Acknowledgments—We are grateful to the Clayton Aniline Company for the provision of a research grant to one of us (R. A. C.) and wish to express our thanks to Professor R. Belcher for many helpful suggestions.

Zusammenfassung—Ein neues Reagens, Calcichrome, wurde synthetisiert. Das Reagens gibt eine hochempfindliche Farbreaktion mit Calcium in alkalischer Lösung. Barium, Strontium und Magnesium reagieren nicht. Das Reagens wird daher zum selektiven Tüpfelnachweis von Calcium vorgeschlagen. Zusätzlich kann Calcichrome als metallochromer indicator zur komplexometrischen Bestimmung von Calcium in Gegenwart von wenigstens zwölffachem Überschuss an Barium verwendet werden. Trans-1,2-diaminocyclohexantetraessigsäure wird als Titrationsmittel verwendet, da es das einzige erhältliche Komplexan ist, das hinreichende Selektivität in Bezug auf die Reaktion mit Calcium und Barium zeigt.

Résumé—L'auteur a fait la synthèse d'un nouveau réactif—Calcichrome—qui donne une réaction colorée très sensible avec les ions calcium en solution alcaline. Ni le baryum, ni le strontium, ni le magnésium ne réagissent sur le réactif, qui est, pour cette raison, proposé comme réactif sélectif d'essai par touches du calcium. De plus le Calcichrome peut être utilisé comme indicateur métallochromique pour le titrage complexométrique précis du calcium en présence de quantités au moins 12 fois plus grandes de baryum. L'acide trans-1-2-diaminocyclohexane-N-N-N′-N′-tétracétique est utilisé comme agent titrant car il est le seul complexant convenable qui soit suffisamment sélectif dans sa réactivité vis à vis du calcium et du baryum.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—II

THORIUM

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Summary—A comparison has been made of the precipitation of thorium with 8-hydroxyquinoline by the direct method of addition of reagent and by precipitation from homogeneous solution by generation of the reagent from 8-acetoxyquinoline. The latter reagent produces a thorium precipitate with superior physical characteristics. Separation studies using cerium^{III} as a diverse ion also indicate the superiority of the method using 8-acetoxyquinoline. Further studies of thorium 8-hydroxyquinolate, precipitated by either method, indicate that ignition to thorium oxide is a reliable way to conclude the determination. Methods involving weighing or brominating the 8-hydroxyquinolate generally furnish erroneous results.

INTRODUCTION

8-HYDROXYQUINOLINE is a widely used reagent for the precipitation of many metals. In 1929 it was recommended for thorium,[1] 2–100 mg, the determination being concluded either by weighing or brominating the 8-hydroxyquinolate. The formula[2,3] of the thorium chelate is reported to be $Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)$. At 110° the chelate is said to retain its molecule of crystallisation.[2,4] There is some question about the temperature at which the molecule of crystallisation is removed because the temperature ranges reported for weighing $Th(C_9H_6NO)_4$ are 150–160°,[5] 160–170°,[1,2] and 275–345°.[4]

The present investigation was undertaken to study the precipitation of thorium from homogeneous solution using 8-acetoxyquinoline as a source of 8-hydroxyquinoline and to compare it with the conventional precipitation method. A further objective of the investigation was to study the usual methods used to conclude the determination, *i.e.*, weighing or brominating the precipitate or ignition to thorium oxide.

EXPERIMENTAL

Reagents

Unless otherwise specified, all chemicals were reagent grade.

Thorium: About 5 g of $Th(NO_3)_4{\cdot}4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, N.J.) were dissolved in 200 ml of water to which were added 10 ml of concentrated hydrochloric acid and 25 g of ammonium chloride. The resulting solution was filtered and diluted to 400 ml and 5% hexamethylenetetramine[6] solution (freshly prepared) was added dropwise, until pH 6 was reached. The thorium precipitate was washed with hot 1% ammonium chloride solution, dissolved in a slight excess of hydrochloric acid, and the solution diluted to 2 litres. The concentration of thorium was determined by precipitation with hexamethylenetetramine[6] followed by ignition to the oxide.

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Rare earths: The source of cerium was either $Ce(NO_3)_3\,6H_2O$ (Eimer and Amend Company, New York, N.Y.) or $(NH_4)_2Ce(NO_3)_6$ (G. F. Smith Chemical Company, Columbus, Ohio). From these compounds, cerium^{III} chloride solutions were prepared. Solutions of yttrium chloride and lanthanum chloride were prepared from yttrium oxide (Research Chemicals Inc., Burbank, Calif.) and lanthanum oxalate (Lindsay Light and Chemical Company, West Chicago, Ill.).

8-*Hydroxyquinoline:* The solution used was made by dissolving 2·5 g of the reagent (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, N.J.) in 6 ml of glacial acetic acid and diluting with water to 100 ml.

8-*Acetoxyquinoline:* This reagent was prepared by the method of Salesin and Gordon[7] for use in the present investigation but has since become available from Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Michigan.

Precipitation of thorium with 8-acetoxyquinoline

Preliminary investigations were made to determine the appropriate concentrations of reagents, the temperature of reaction, and the pH, which would result in the quantitative precipitation of thorium 8-hydroxyquinolate in a form with desirable physical characteristics. The quantity of 8-acetoxyquinoline used was three times the stoichiometric amount required.

Below pH 4·0, no precipitate formed, and at pH 4·5, precipitation was not quantitative. The rate of precipitation increased with pH and with temperature. At pH 6·5, the precipitate became somewhat gelatinous. Desirable results were obtained by precipitation in the pH range, 5·0–6·0, and at 50°; the precipitate was obtained in the form of spherical orange-coloured particles. At room temperature and at pH 5·5, smaller particles more uniform in size and more yellow in colour were obtained. Yttrium, lanthanum, and cerium^{III} were found to precipitate at a pH somewhat above 6·0. The best results for the precipitation of thorium for analytical purposes were obtained using pH 5·0 and 50°, and by increasing the quantity of 8-acetoxyquinoline to four times the stoichiometric amount required.

Photomicrographs of thorium 8-hydroxyquinolate are shown in Fig. 1.

Procedure: Dissolve 8-acetoxyquinoline (four times the stoichiometric quantity required for the thorium) in 20 ml of 1:1 acetic acid. Add a solution of thorium containing 10–50 mg and dilute to 100–500 ml, the final volume being proportional to the quantity of thorium present. Adjust the pH to 5·0 with 1:1 ammonium hydroxide and then warm the solution at 50° for 2 hr. Cool, filter, and wash the precipitate with a minimum of cold water. Ignite to thorium oxide.

Precipitation of thorium with 8-hydroxyquinoline

Method used: Five ml of 2*N* acetic acid were added to the solution containing 10–50 mg of thorium in a volume of 100–500 ml, the final volume being proportional to the quantity of thorium present. Then 8-hydroxyquinoline solution, 6 ml for each 10 mg of thorium present, was added. The solution was then heated to 90° and 50 ml of 2*N* ammonium acetate solution was added with continuous stirring. The solution was cooled to room temperature before filtering.

Determination of thorium in the precipitate

Because, as will be discussed later, there was some question regarding the composition of the precipitate, it was desirable in many of the determinations to minimise solubility losses due to the use of wash solution. Thus, precipitates were frequently transferred to a filter with the repeated use of the filtrate itself. After complete transfer to the filter medium, the precipitate was then washed with two small portions of cold water before either being weighed or brominated. In other cases, transfer and washing of the precipitate were effected wholly with a minimum of cold water. At 110° precipitates were dried for 3–5 hr; at higher temperatures they were dried for approximately 10 hr.

Where bromination was used, the titrimetric procedure[8] given in *Analytical Chemistry of the Manhattan Project* was used.

In some cases, precipitation of a known amount of thorium was effected with a known excess either of 8-hydroxyquinoline or 8-acetoxyquinoline. After precipitation, the reaction mixture was diluted in a volumetric flask and an aliquot of the supernatant liquid, obtained by filtration through a dry filter, was analysed for residual reagent by bromination and titration. From these results, the composition of the precipitate could be determined.

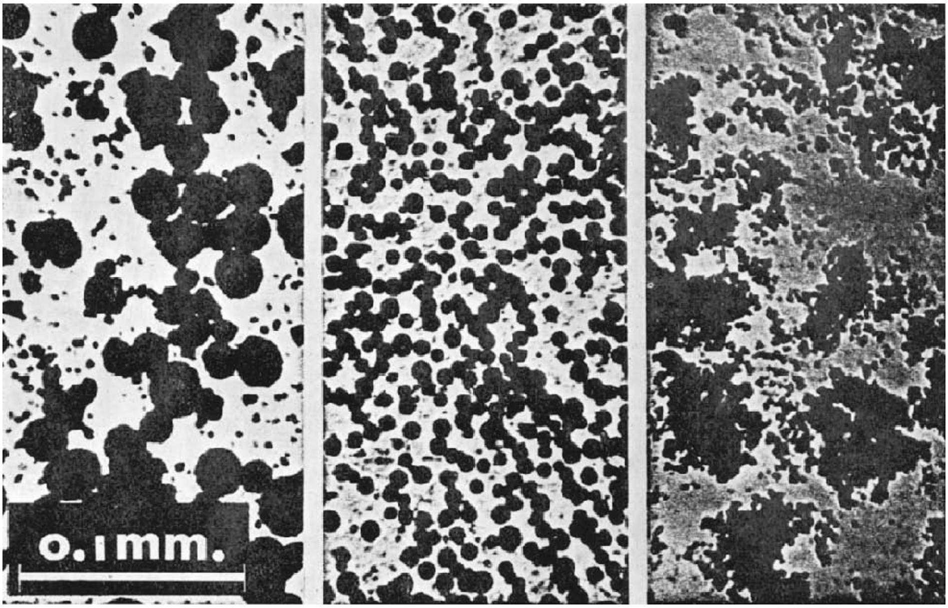

FIG. 1.—Photomicrographs of thorium 8-hydroxyquinolate (all photomicrographs are at same magnification.)
(*a*) method of PFHS at pH 5·0 and at 50°.
(*b*) method of PFHS at pH 5·5 and at room temperature.
(*c*) conventional method of precipitation.

Separation of thorium and cerium

Thorium was precipitated in the presence of cerium^{III} and the precipitate was decomposed with a mixture of 10 ml of concentrated nitric acid and 3 ml of concentrated perchloric acid by heating to fumes of the latter. The cerium in the resulting solution was then determined colorimetrically with *o*-phenanthroline[9] using a Beckman DU spectrophotometer with 1-cm cells.

RESULTS AND DISCUSSION

The composition of the precipitate, determined as previously described by using known quantities both of thorium and the reagent is shown in Table I. The uncertain composition of the precipitate is quite obvious; in particular, there appears to be less than the one molecule of crystallisation of 8-hydroxyquinoline as has been previously reported by others. The results shown in Table I are in general confirmed by the more usual determinations in which the precipitates were separated by filtration. Parts A and B of Table II show less than one molecule of crystallisation regardless of whether the precipitate is analysed by bromination without previously drying, or weighed after being dried at 110°.

TABLE I. COMPOSITION OF THE THORIUM PRECIPITATE

Formula assumed = $Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)_x$

Precipitation with 8-*hydroxyquinoline* (6 *determinations*)

$x = 1{\cdot}16, 0{\cdot}89, 0{\cdot}91, 0{\cdot}97, 0{\cdot}83, 1{\cdot}01$

Precipitation with 8-*acetoxyquinoline* (2 *determinations*)

$x = 0{\cdot}80, 0{\cdot}87$

As is also shown by the high results of Part B of Table II, further drying at 165° did not remove all of the 8-hydroxyquinoline of crystallisation. The exception is the one conventional precipitation with 14 mg of thorium, but as will be seen subsequently there is a somewhat slightly different response to drying shown by precipitates obtained by the two different methods of precipitation.

When the drying temperature was changed to 180°, the results obtained were quite satisfactory, as is shown in Part C of Table II. Somewhat better results are indicated for the PFHS method, but the results are not conclusive.

The results of Part D of Table II and their summary in Table III confirm the previous observation that satisfactory results can be obtained by drying the precipitate at 180°. Again, the slightly lower results obtained for the conventionally produced precipitate are evident. The degradation of the precipitate is apparent if the precipitate is dried at 190° or higher. It is difficult to correlate the results obtained here at 295° and at 345° with the recommendation of 275–345°[4] as a drying temperature even though the latter derives from thermogravimetric data. It is often inadvisable to compare a thermogravimetric observation with results obtained by a conventional weighing procedure. However, it would appear from the overwhelming evidence obtained in the present study not only that the thermogravimetric experiment ought to be repeated, but particularly that the recommendation of 275–345° as a drying temperature be ignored where a conventional drying and weighing procedure is to be employed. On the other hand, the close tolerance required for drying the precipitate, *i.e.* within a narrow range close to 180°, is certainly something of a handicap.

With either method of precipitation, excellent results were obtained as shown in Table IV when the precipitate is ignited to thorium oxide.

TABLE II. DETERMINATION OF THORIUM BY WEIGHING AND/OR BROMINATION OF THE 8-HYDROXYQUINOLATE

A. By bromination of the precipitate[a] *without prior drying*

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)	
		$Th(C_9H_6NO)_4 \cdot (C_9H_6NOH)$	Th
PFHS	69·9	−11·2	−2·8
PFHS	14·0	−1·8	−0·5
PFHS	14·0	−2·8	−0·7
Conventional	14·0	−11·6	−2·8
Conventional	14·0	−6·5	−1·6
Conventional	14·0	−3·6	−0·9
Conventional	14·0	−1·5	−0·4
Conventional	14·0	−1·4	−0·4
Conventional	14·0	+2·4	+0·6
Conventional	28·0	−2·9	−0·8

B. By weighing the precipitate[b] *dried first at* 110 ± 1° *and later at* 165 ± 5° *followed by bromination*

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)					
		110°		165°			
				Weighing		Bromination	
		$Th(C_9H_6NO)_4 \cdot (C_9H_6NOH)$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th
PFHS	69·9	−19·5	−4·9	+14·7	+4·2	+14·7	+4·2
PFHS	69·9	−17·7	−4·4	+14·6	+4·1	+20·7	+5·9
PFHS	69·9	−17·3	−4·3	+15·7	+4·5	+19·3	+5·5
Conventional	14·0	−3·3	−0·8	−1·7	−0·5	−1·3	−0·4
Conventional	14·0	−3·5	−0·9	—	—	—	—
Conventional	14·0	−4·0	−1·0	—	—	—	—

C. By weighing the $Th(C_9H_6NO)_4$ *precipitate*[b] *dried at* 180 ± 5° *followed by bromination*

Method of precipitation	Th taken (*mg*)	Difference found (*mg* of Th)	
		By weighing	By bromination
PFHS	14·0	0·0	0·0
PFHS	14·0	−0·1	−0·1
PFHS	14·0	+0·1	—
PFHS	14·0	−0·1	—
PFHS	14·0	−0·6	—
PFHS	28·0	+0·1	—
Conventional	14·0	−0·3	0·0
Conventional	14·0	−0·4	—
Conventional	14·0	−0·2	—
Conventional	28·0	−0·3	−0·5
Conventional	28·0	−0·3	−0·1

D. By weighing the precipitate[b] after consecutive drying at various temperatures

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)													
		110 ± 1°		180 ± 5°		190 ± 5°.		200 ± 5°.		245 ± 5°.		295 ± 5°.		345 ± 5°.	
		$Th(C_9H_6NO)_4 \cdot (C_9H_6NOH)$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th
PFHS	20·1	−3·9	−0·9	−0·3	−0·1	−0·9	−0·3	−2·0	−0·6	−6·2	−1·8	−38·4	−11·0	−46·5	−13·3
PFHS	20·1	−3·9	−0·9	+0·1	0·0	−0·8	−0·2	−1·8	−0·5	−5·7	−1·6	−33·6	−9·6	−46·2	−13·2
PFHS	20·1	−4·5	−1·0	−0·2	−0·1	−1·2	−0·3	−2·2	−0·6	−8·0	−2·3	−21·2	−6·1	−45·3	−12·9
PFHS	2·0	−0·1	0·0	−0·1	0·0	—	—	−2·9	−0·8	−4·2	−1·2	—	—	—	—
PFHS	1·0	+1·0	+0·2	−0·1	0·0	—	—	—	—	—	—	—	—	—	—
Conventional	20·1	−1·3	−0·3	−0·8	−0·2	−2·0	−0·6	−3·7	−1·1	−10·8	−3·1	−46·7	−13·4	−47·2	−13·5
Conventional	20·1	−4·4	−1·1	−1·0	−0·3	−2·2	−0·6	−3·7	−1·1	−9·7	−2·8	−35·5	−10·2	−46·5	−13·3
Conventional	20·1	−1·8	−0·4	0·0	0·0	−1·7	−0·5	−2·9	−0·8	−8·5	−2·4	−34·5	−9·9	−46·5	−13·3

[a] Precipitate washed thoroughly with cold water.

[b] Precipitate transferred with filtrate to minimize possible solubility losses and finally washed with two small portions of cold water.

TABLE III. AVERAGE RATIO, THEORETICAL QUANTITY OF 8-HYDROXYQUINATE EXPECTED: EXPERIMENTAL QUANTITY FOUND AT VARIOUS DRYING TEMPERATURES

20·1 mg Thorium taken (from Table II, D).

Temperature, °*C*	Ratio	
	PFHS	Conventional
110	1·052	1·032
180	1·001	1·009
190	1·014	1·029
200	1·029	1·051
245	1·10	1·16
295	1·80	2·25
345	2·91	3·00

TABLE IV. DETERMINATION OF THORIUM BY IGNITION OF 8-HYDROXYQUINOLATE[a] TO THORIUM OXIDE

Method of precipitation	Thorium taken (*mg*)	Difference (*mg* of Th)
Conventional	14·0	0·00
Conventional	14·0	0·00
PFHS	14·0	0·1
PFHS	69·9	0·3
PFHS	69·9	0·0
PFHS	139·8	1·0

[a] See note *b* of Table II.

The separation of thorium and cerium is quite satisfactory, as the results of Table V indicate. In view also of the observation that lanthanum and yttrium do not precipitate until a pH slightly greater than 6·0 is reached, it would seem that the PFHS method could furnish an excellent separation of thorium from many of the rare earths. While the separation of thorium from other diverse ions was not studied, the present method can be expected to give better results than are obtainable with the conventional use of 8-hydroxyquinoline.

TABLE V. SEPARATION OF THORIUM FROM CERIUM[a]

Method of precipitation	Thorium taken (*mg*)	Cerium taken (*mg*)	Cerium found in precipitate (*mg*)
Conventional	50·3	50	0·082
PFHS	50·3	50	0·043
Conventional	50·3	250	0·37
PFHS	50·3	250	0·18
PFHS	50·3	500	0·28

[a] Precipitate washed thoroughly with cold water.

CONCLUSIONS

The information of the present study indicates that ignition of thorium 8-hydroxyquinolate to the oxide is a reliable method of concluding the determination. While the PFHS method indicates that good results can also be obtained by drying the 8-hydroxyquinolate at 180 ± 5°, the close control of temperature represents a disadvantage. In general, with this one exception, it would seem best to avoid methods of concluding the determination of thorium which involve weighing or brominating the 8-hydroxyquinolate.

The separation of thorium from the rare earths using PFHS appears promising.

Zusammenfassung—Die Thorium-oxinat niederschläge, nach zwei verschiedenen Fällungsmethoden erhalten, wurden verglichen. Die physikalischen Eigenschaften des Oxinatniederschlages erhalten durch homogene Fällung mittels Hydrolyse von 8-Acetoxychinolin sind wesentlich günstiger als die eines Niederschlages erhalten durch direkte Fällung mittels Oxin. Trennungen von Cer als Fremdion zeigten ebenfalls die Uberlegenheit des Niederschlages aus homogener Lösung. Weitere Untersuchungen ergaben, dass die Veraschung des Niederschlages zu Thoriumoxyd ein zuverlässiger Weg zum Abschluss der Analyse ist. Direktes Auswägen des Oxinates oder massanalytische Bestimmung mittels Brom führen im allgemeinen zu fehlerhaften Resultaten.

Résumé—Les auteurs ont fait une comparaison de la précipitation du thorium par la 8-hydroxyquinoléine, d'une part par la méthode directe d'addition du réactif, d'autre part par précipitation en solution homogène par production du réactif à partir de 8-acetoxyquinoléine-Ce dernier réactif donne un précipité de thorium qui a des caractéristiques physiques supérieures. Des études de séparation utilisant le cérium (III) indiquent aussi la supériorité de la méthode employant la 8-acétoxyquinoléine. Des études ultérieures du 8-hydroxyquinolate de thorium, précipité par l'une ou l'autre méthode, indiquent que la calcination à l'état d'oxyde de thorium est un procédé sûr pour terminer le dosage. Les méthodes faisant intervenir des pesées ou la bromuration du 8-hydroxyquinolate donnent généralement des résultats erronés.

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PHOTOMETRIC DETERMINATION OF TELLURIUM WITH BISMUTHIOL II

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Summary—A method for the photometric determination of tellurium based on the extraction of the yellow-coloured complex of tellurium with bismuthiol II is presented. The described method permits the determination of as little as 0·01 % of tellurium in ores directly without preliminary separation. After the isolation of the element by reduction with tin^{II} chloride even smaller amounts can be determined.

INTRODUCTION

TELLURIUM is the least abundant of the sulphur group of the elements, its percentage in the earth's crust being estimated[41] to the extent of $1 \cdot 10^{-6}$%. Although it is found native, in most cases it is in the form of its compounds. In its minerals, which are rare, tellurium occurs as the tellurite, tellurate, and most frequently as the telluride. Its affinity to various metals decreases in the following order:[42]

Au—Ag—Hg—Bi—Ni—Pb—Cu.

Tellurium is found associated with selenium, especially in sulphide ores from which it is transferred to ashes during metallurgical processing and to anode slimes during the electrolytical refining of metals. These ashes and slimes constitute the chief sources for its production.[40]

Colorimetric procedures for the determination of small amounts of tellurium in ores are usually preceded by the isolation of the element from a large sample by reduction to the elemental state. Gravimetric and titrimetric procedures are unsuitable for such small amounts.

The first colorimetric method was elaborated by Pierson,[38] who reduces tellurium compounds to the element with mercury^{I} chloride and estimates the amount of tellurium present by comparing the colour of the mercury^{I} chloride with standards similarly prepared. Volkov[48] and Zemel[50] precipitate the element with tin^{II} chloride in the form of a coloured sol in the presence of a protective colloid; Johnson, Kwan and Westlake[18] recommend hypophosphorous acid for reduction. Johnson and Andersen[16] measure the tellurium sol in the ultraviolet region in which the measurement is more sensitive. The coloured halides of quadrivalent tellurium have been also used for determination. Hanson, Bradbury and Carlton[13] measure the solutions of tellurium in concentrated hydrochloric acid, Fletcher and Wardle[10] employ hydrobromic acid, while Johnson and Kwan[17] carry out their measurements in hydriodic acid. Geiersberger and Durst[11] utilise the brown coloration of a solution of caesium iodotellurite for determination. Metallic tellurium dissolves in concentrated sulphuric acid to give the purple addition compound $Te{\cdot}SO_3$, and this was used by Wiberley, Bassett, Burrill and Lyng[49] for the colorimetric determination of the element. Scott and Leonard[43] recommend the measurement of the absorption of telluric acid in the ultraviolet region. Some organic reagents have been also proposed for the determination. Thus, Jílek and Vřešťál[15] apply thiourea, which yields a yellow solution with tellurium. The photometric procedure of Gotô and Kakita[12] is based on the extraction of the yellow complex of tellurium with diethyldithiocarbamate; Bode[1] performs the above reaction in the presence of EDTA and potassium cyanide. Shcherbov and Ivankova[46] extract the complex of chlorotellurous acid and rhodamine B and determine tellurium fluorometrically. Ingamells and Sandell[14] use an indirect procedure based on an induced reaction of the element with ferri-phenanthroline.

The present paper is devoted to the reaction of tellurium with bismuthiol II (mercaptophenylthiolthiadiazolone), which was applied to the photometric determination of the element.

Bismuthiol II was introduced to analytical chemistry by Dubský, Okáč and Trtílek[7] as a micro reagent for the detection of bismuth, and its reactions were further studied by the same authors.[5,6,8,9] Later, the reagent was utilised for the gravimetric determination of mercury,[47] bismuth,[20,21] lead,[26] palladium,[22] platinum,[23] silver,[27,34] thallium,[28] copper,[29] cadmium,[30] arsenic,[31] and antimony,[31] for the separation of arsenic, antimony, and tin[31] from each other, for the separation of gold[23] and silver[32] from the platinum metals, and for certain separations within the platinum group.

Titrimetric procedures using bismuthiol II are based on several principles: bismuth,[24] lead,[33] and cadmium[30] can be determined by dissolving the isolated precipitate of the element with bismuthiol II in EDTA and back-titrating the excess of the latter with a standard solution of a magnesium salt, using Eriochrome Black T as indicator. Analogously, the precipitates of palladium[24] and silver[33] can be dissolved in potassium cyanide, the excess of which is back-titrated with silver nitrate and potassium iodide as indicator. Bismuthiol II may be used as a titrimetric reagent in the amperometric determination of silver,[3] lead,[3] mercury,[3] copper,[4] and cadmium.[4] Bismuth[4] is determined indirectly by back-titrating the excess of bismuthiol II with a mercury^{II} salt. The excess of a standard solution of bismutiol II can be titrated oxidimetrically with iodine monochloride[2] using potentiometric indication as, for instance, in the determination of copper and silver.

As a colorimetric reagent bismuthiol II was used only in the case of bismuth[20] and palladium.[25] In both methods the colour intensity of coloured complexes held in solution by a protective colloid is measured. Extraction-photometric procedures have not been described up to now. Although a number of the above cited papers describe the effect of nearly all elements, the behaviour of selenium and tellurium towards bismuthiol II has not been reported.

EXPERIMENTAL

Apparatus

The absorption spectrum of the yellow-coloured complex was investigated with a Zeiss universal spectrophotometer in 1-cm cells, using a hydrogen lamp and NaCl-prism.

All other measurements were carried out with an Elpho-Pulfrich photometer in 2-cm cells using a tungsten lamp, an EGS photocell and a violet 415-mμ filters with a spectral band of 31 mμ.

The pH of the buffer solutions was measured with an Ionoscop potentiometer with a built-in Weston element. A platinum indicating electrode and a saturated calomel reference electrode were used in the quinhydrone method.

Reagents

Tellurium stock solution: 0·1000 g of crushed metallic tellurium (Johnson, Matthey and Sons, London) was dissolved, with warming, in 10 ml of concentrated nitric acid; the resulting solution was evaporated on a water bath to dryness. The residue was taken up with concentrated hydrochloric acid (200 ml in total) and distilled water, cooled to 20°, and diluted to 1000 ml. From this stock solution, containing 100 μg of tellurium per ml, the working solution was prepared by diluting 200 ml to 1000 ml with distilled water. The working solution contains 20 μg of tellurium per ml.

Selenium solution: 0·14 g of selenium dioxide (Johnson, Matthey and Sons, London) was dissolved in water and made up to 100 ml with distilled water. 1 ml corresponds to approximately 1 mg of selenium.

Bismuthiol II solution: 1 g of bismuthiol II (the potassium salt of 5-mercapto-3-phenyl-2-thiol-1:3:4-thiadiazolone-2, p.a.; Lachema, m.p. 244–247°) was dissolved in distilled water and diluted to 100 ml. The solution was saturated for about 5 min with nitrogen from a cylinder and stored in a tightly stoppered bottle. The nitrogen was previously freed from traces of oxygen by absorption in an alkaline solution of pyrogallol containing 5 g of pyrogallol and 20 g of potassium hydroxide in 100 ml.

Thymol blue solution: 0·1 g of solid indicator plus 1 pellet of sodium hydroxide were dissolved, with warming, in about 20 ml of water and diluted to 100 ml in the usual manner.

Acetate buffer solution: 123 g of anhydrous sodium acetate (pure, remelted; Lachema) was dissolved in about 200 ml of boiling water, treated with 485 ml of glacial acetic acid (p.a.; Lachema), cooled, and diluted to 1000 ml with distilled water.

Tin^{II} chloride solution: 50 g of tin^{II} chloride dihydrate (p.a. Lachema) was boiled with 40 ml of hydrochloric acid (1:1) until the solution became clear. The solution was cooled and made up to 100 ml with distilled water.

Hydrobromic acid: The commercial product (40–48%) was redistilled with the addition of about 1 g of hydrazine sulphate per litre. The constant boiling acid was collected and stored in a dark bottle.

RESULTS

During preliminary tests it was found that, with bismuthiol II in feebly acid solution, tellurium and selenium yield yellow precipitates. A buffered acetic acid solution, however, remained clear and colourless. Tellurium, and partially also selenium, could be extracted with organic solvents in the form of yellow solutions.

In the present paper the extractibility of the tellurium complex was used for its photometric determination. Benzene was selected as the most suitable extraction agent.

Determination of the absorption maximum

The yellow coloured complex in benzene was measured at different wavelengths in a 1-cm cell with a spectrophotometer, using water in the reference cell. From Fig. 1 it can be seen that the maximum absorption of the yellow complex is attained at 335 mμ. However, at this wavelength the absorption of the blank is also maximal. For this reason all subsequent measurements were carried out in the visible region of the spectrum, which does not require an expensive spectrophotometer and is more suitable for routine work. All other measurements were made with an Elpho-Pulfrich photometer and a violet 415-mμ filter.

Influence of pH of the solution

To neutralised solutions of tellurium (100 μg), acetate or monochloracetate buffer mixtures and a solution of the reagent were added. The resulting solutions were extracted with a 10-ml portion of benzene. The readings of the extracts are plotted against the pH of the buffer solution used. As can be seen from Fig. 2 the extinction increases with decreasing pH and is maximal at pH values lower than 4·3. At pH 4·0 about 0·5 hr after the addition of the reagent a yellow precipitate of the complex is gradually formed in the aqueous phase. At higher acidities the precipitate was formed almost immediately and caused lower extinction readings of the benzene extract.

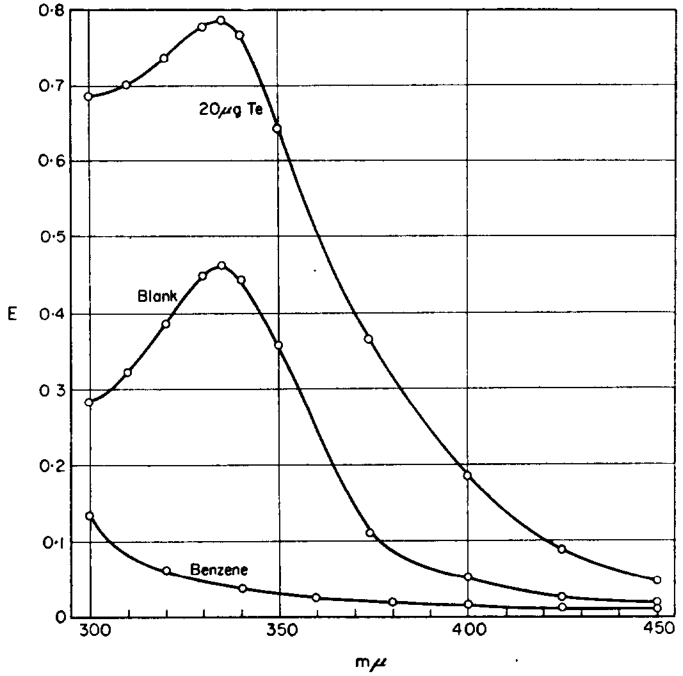

FIG. 1.—Dependence of extinction upon wavelength.

It was necessary, therefore, to extract immediately after the addition of the reagent. From Fig. 2 it is evident that the extinction is maximal in the range of pH 4·3 to 3·3. The formation of an analogous complex of selenium with bismuthiol II is shifted to higher acidities. At a pH of 4·15, which was selected as most suitable, the extinction is maximal, interference by selenium is slight, and no precipitation takes place in the aqueous phase. A buffer solution possessing this pH can be obtained by mixing acetic acid and sodium acetate in the molar ratio 8·5: 1·5. Ten ml of the buffer solution, which is 10*M* in acetate, were used in all subsequent measurements.

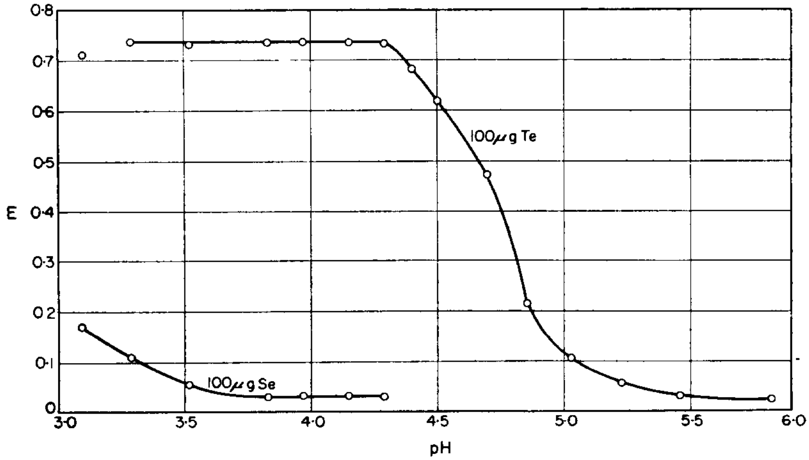

FIG. 2.—Dependence of extinction upon pH.

Influence of concentration of the reagent

To 50 ml of solution, representing 100 μg of tellurium, 10 ml of buffer solution and a freshly prepared solution of the reagent in amounts ranging from 0·2 to 4 ml were added. The solution was extracted with 10 ml of benzene and the extract measured against water. As can be seen from Fig. 3 maximum extinction is attained by the use of 2 ml of a 1 % solution of the reagent and it does not change upon further addition of the reagent. The apparent slight tendency to enhance the extinction is caused by the somewhat higher extinction of the blank. Further, it was found that the consumption of reagent increases with an increasing volume of the aqueous phase. Aqueous solutions of bismuthiol II are subject to gradual oxidation by air, resulting in the formation of a turbidity or even a precipitate. This decomposition of the reagent does not substantially influence the determination. In all subsequent measurements 3 ml of a 1 % solution of the reagent were used, which is sufficient even if the volume of the aqueous phase is 100 ml. It is feasible to pass nitrogen through the freshly prepared solution and to stopper the flask tightly after each withdrawl of reagent or to repeat the bubbling from time to time. A solution through which nitrogen had been passed and which was kept in a tightly stoppered flask remained clear and usable for 6 months.

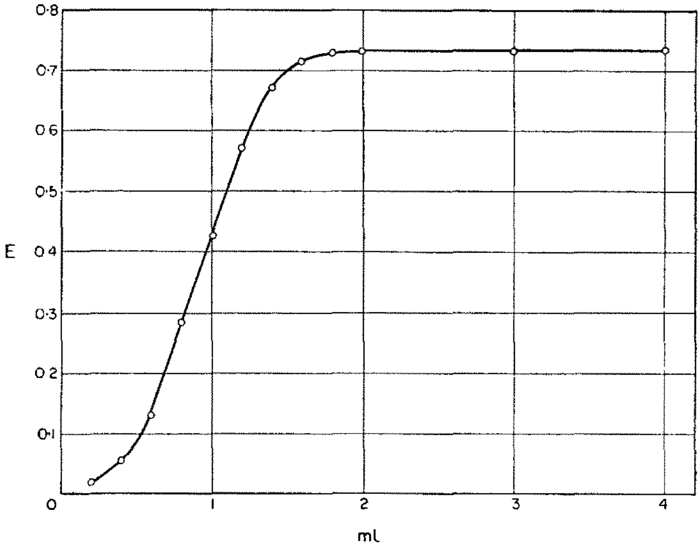

FIG. 3.—Dependence of extinction upon amount of reagent added.

Stability of coloration

The stability of coloration of the yellow complex of tellurium with bismuthiol II was investigated by measuring its extinction at regular intervals. A benzene extract of the complex, corresponding to 100 μg of tellurium, did not exhibit the slightest change during 3 hr. However, all vessels in which the complex is kept must be completely air-tight to avoid the volatilisation of benzene. Practically the same extinction reading was obtained if the extract was left in contact with the aqueous layer in the separatory funnel for 3 hr.

Effect of number of extractions on the coloured complex

Fifty ml of solution, containing 100 μg of tellurium, were treated with 10 ml of acetate buffer mixture, 3 ml of 1 % solution of bismuthiol II, and extracted with 10 ml of benzene. After the separation of the phases, the aqueous layer was extracted with another 10 ml of benzene. The second extract exhibited the same extinction as the blank which is proof that the complex of tellurium with bismuthiol II is extracted quantitatively by a single extraction. To obtain quickly a quite clear extract, the benzene layer was filtered through a small filtering funnel in the stem of which a plug of glass wool has been inserted. (Alternatively, a clear benzene extract can be obtained by centrifuging.) The extraction was performed in separatory funnels whose stems have been shortened to approximately 1 cm.

General procedure

To approximately 50 ml of a feebly acid solution in a 100-ml separatory funnel, containing 0–100 μg of tellurium, add 1 ml of a 10 % solution of EDTA and 5 drops of a 0·1 % solution of thymol blue and neutralise with ammonium hydroxide (1 :1) until the indicator turns yellow. Treat with 10 ml of acetate buffer solution, swirl, add 3 ml of a 1 % solution of bismuthiol II and extract for 1 min with 10 ml of benzene added from a pipette (the pipette is filled by means of a rubber bulb possessing a single conical vent). Allow the phases to separate, draw off the aqueous layer and discard it. Pour the benzene layer through the neck of the separatory funnel into a small filtering funnel into the stem of which a plug of glass wool has been inserted, and collect the clear filtrate directly into a dry 2-cm photometric cell. Obtain the extinction with a suitable photometer, using a violet filter and distilled water in the reference cell.

Calibration curve

For the construction of the calibration curve treat 0, 1, 2, 3, 4, and 5 ml of the working solution, containing 20 μg of tellurium per ml, as indicated above. The calibration curve obtained in the visible region of the spectrum by the use of a 415-mμ filter does not exactly follow linearity but it is quite reproducible (Fig. 4).

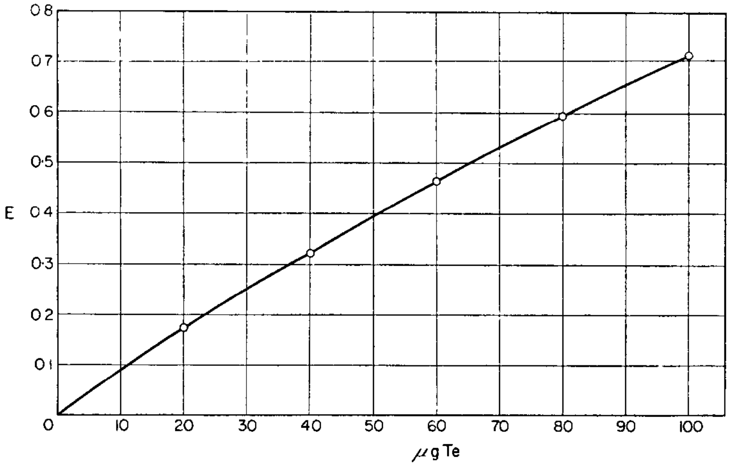

FIG. 4.—Calibration curve of tellurium with bismuthiol II in 10 ml of benzene.

Influence of foreign ions

Solutions containing 100 μg of tellurium and generally 10 mg of a foreign element were treated with 1 ml of a 10 % solution of EDTA to avoid precipitation of elements

TABLE I.—DETERMINATION OF 100 μg OF TELLURIUM IN THE PRESENCE OF FOREIGN IONS

Element	Amount of element, *mg*	Form added	Te found, *μg*	Relative error, %
Ag*	10	$AgNO_3$	—	—
	1**		96	−4
	0·1**		99	−1
Al	10	$KAl(SO_4)_2\cdot 12H_2O$	101	+1
As	10	K_3AsO_3	99·5	−0·5
	10	$Na_2HAsO_4\cdot 7H_2O$	99·5	−0·5
Au*	0·1	$HAuCl_4\cdot 4H_2O$	107	+7
Ba	10	$BaCl_2\cdot 2H_2O$	100	±0·0
Be†	10	$BeSO_4\cdot 4H_2O$	102	+2
Bi	10	$Bi(NO_3)_3\cdot 5H_2O$	101·5	+1·5
Ca	10	$CaCl_2\cdot 6H_2O$	101·5	+1·5
Cd	10	$CdSO_4\cdot 8/3H_2O$	100	±0·0
Ce	10	$CeCl_3$	100	±0·0
Co	10	$CoCl_2\cdot 6H_2O$	101·5	+1·5
Cr†	10	$CrCl_3$	98·5	−1·5
Cs	10	$CsCl$	100	±0·0
Cu	10	$CuSO_4\cdot 5H_2O$	102	+2
Dy	10	$DyCl_3$	101	+1
Er	10	$ErCl_3\cdot 6H_2O$	100	±0·0
Eu	10	$Eu_2(SO_4)_3\cdot 8H_2O$	100·5	+0·5
Fe	10	$FeCl_3\cdot 6H_2O$	100	±0·0
	50§		101	+1
Ga	10	$Ga_2(SO_4)_3$	101	+1
Gd	10	$GdCl_3$	101	+1
Ge	10	$GeCl_4$	99·5	−0·5
Hf	10	$Hf(SO_4)_2$	100	±0·0
Hg*	10	$HgCl_2$	—	—
	0·1		96·5	−3·5
Ho	10	$HoCl_3\cdot 6H_2O$	100	±0·0
In	10	$In_2(SO_4)_3$	100	±0·0
Ir¶	1	$IrCl_4$	98	−2
K	10	K_2SO_4	100	±0·0
La	10	$LaCl_3$	99	−1
Li	10	$Li_2SO_4\cdot H_2O$	100	±0·0
Lu	10	$LuCl_3$	100·5	+0·5
Mg	10	$MgCl_2\cdot 6H_2O$	100	±0·0
Mn	10	$MnSO_4\cdot 5H_2O$	102·5	+2·5
Mo	10	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	±0·0
Na	10	$NaCl$	100	±0·0
Nb¶	1	oxalate	100·5	+0·5
Nd	10	$NdCl_3\cdot 6H_2O$	100	±0·0
NH_4	10	NH_4NO_3	100	±0·0
Ni	10	$NiCl_2\cdot 6H_2O$	101·5	+1·5
Os*	1	OsO_4	—	—
	0·1		97	−3
Pb	10	$Pb(NO_3)_2$	102	+2
Pd*	1	$PdCl_2$	—	—
	0·1		99·5	−0·5
Pr	10	$PrCl_3\cdot 6H_2O$	100	±0·0

TABLE I (CONTINUED)

Element	Amount of element, *mg*	Form added	Te found, *µg*	Relative error, %
Pt*	1	$PtCl_4{\cdot}8H_2O$	—	—
	0·1		105	+5
Rb	10	RbCl	100	±0·0
Re	10	Re_2O_7	100	±0·0
Rh	1	$RhCl_3{\cdot}4H_2O$	97·5	−2·5
Ru	1	$RuCl_3$	102	+2
Sb†	10	$SbCl_3$	101·5	+1·5
Sc	10	$ScCl_3$	101·5	+1·5
Se	5	SeO_2	112	+12
	4		109	+9
	3		108	+8
	2		105	+5
	1		102	+2
Sm	10	$SmCl_3{\cdot}6H_2O$	99	−1
Sn	10	$(NH_4)_2SnCl_6$	99	−1
Sr	10	$SrCl_2$	100·5	+0·5
Ta¶	1	oxalate	100·5	+0·5
Tb	10	$TbCl_3$	100	±0·0
Th	10	$Th(NO_3)_4{\cdot}4H_2O$	99·5	−0·5
Ti†	10	$TiCl_4$	101	+1
Tl*	10	Tl_2SO_4	—	—
	0·5		99·5	−0·5
Tm	10	$TmCl_3{\cdot}7H_2O$	101	+1
U	10	$UO_2(NO_3)_2{\cdot}6H_2O$	100	±0·0
V	1	NH_4VO_3	101	+1
W†	10	$Na_2WO_4{\cdot}2H_2O$	102	+2
Y	10	$YCl_3{\cdot}6H_2O$	99	−1
Yb	10	$YbCl_3{\cdot}6H_2O$	100	±0·0
Zn	10	$ZnSO_4{\cdot}7H_2O$	101·5	+1·5
Zr	10	$ZrOCl_2{\cdot}8H_2O$	100.0	±0·0
Phosphate	100‡	$NH_4H_2PO_4$	100·5	+0·5
Nitrate	5000‡	NH_4NO_3	100	±0·0
Oxalate	1000‡	$H_2C_2O_4{\cdot}2H_2O$	100	±0·0
Sulphate	4000‡	K_2SO_4	100	±0·0

* precipitates
† 100 mg of oxalic acid added
‡ weight of compound added
¶ amount of ammonia required for neutralisation added to buffer solution
§ 5 ml of a 10% solution of EDTA added
** 0·5 ml of HCl (1 : 1) added; reagent added after 10 min

of the hydrogen sulphide group by the reagent and the hydrolysis of certain elements during neutralisation. To some ions, which are easily hydrolysed even in the presence of EDTA, a small quantity of ammonium oxalate was added. In the case of niobium, tantalum and iridium, the amount of ammonium hydroxide required for neutralisation (determined in a separate aliquot) was added directly to the buffer solution to avoid local over-alkalisation. The solutions were treated further as described in the general procedure. From the results listed in Table I it is seen that under the above conditions, besides tellurium, only selenium is extracted in the form of a yellow complex. In comparison with tellurium, its rate of extraction is low and can often be neglected. Oxidising ions such as Au^{III}, Pt^{IV}, V^{V}, nitrites and other oxidising anions were found to yield a yellow extract, since the coloured oxidation product of bismuthiol II is also extracted. Under the conditions described, *i.e.* even in the presence of EDTA, the following elements are precipitated by bismuthiol II: Ag^{I}, Au^{III}, Hg^{II}, Os^{VIII}, Pd^{II}, Pt^{IV}, and Tl^{I}. Larger amounts of these elements must be removed. Among a number of anions investigated, fluoride, tartarate, citrate, and dithionite could not be used as screening agents, because low results for tellurium ensue in their presence.

Application of the method

Since the determination of tellurium with bismuthiol II is sensitive and in the presence of EDTA selective, tellurium can be determined in a number of cases directly without preliminary separations. Using an aliquot corresponding to 100 mg, the method may be applied to the determination of as little as 0·01 % of the element in ores, especially pyrites.

With ores low in tellurium it is feasible to isolate tellurium by reduction to the element with tin^{II} chloride in the presence of a small amount of selenium (1 mg) as collector.

Selenium and mercury can be removed from the obtained precipitate as the volatile bromides by evaporation with hydrobromic acid and bromine.[10,35,37] No loss of tellurium occurred if the evaporation was carried out on a water bath in the presence of a small amount of sulphuric acid.

After decomposition with sulphuric acid, silver and thallium may be removed as the insoluble chlorides by the addition of hydrochloric acid. Contrary to silver, any thallium that survives does not affect the determination. If the final solution contains only a small amount of chlorides (0·5 ml of HCl 1:1), the remaining silver is precipitated approximately 10 min after neutralisation and addition of the buffer solution.

The behaviour of gold in the analysis of auriferous pyrites and concentrates is rather interesting. Since the gold content at times amounted to 500 g/t, it was necessary to deal with its removal. Several procedures are recommended in the literature to effect its removal already during decomposition. The statements concerning their applicability are, however, often conflicting. According to Volkov[48] gold is not dissolved by attack with nitric acid but dissolves during the evaporation with sulphuric acid necessary for the subsequent isolation of tellurium and selenium with tin^{II} chloride. For this reason the above author proposes to decompose the sample with nitric acid, to filter off the insoluble residue, and only then to fume off the filtrate with sulphuric acid. Zemel,[50] on the other hand, states that gold is dissolved by the action of nitric acid but it is again precipitated during the evaporation with sulphuric acid which causes its reduction.

On checking these procedures it was found that the finely dispersed gold in the ore partially dissolves in nitric acid even when diluted 1:1. Further, it was found that tervalent gold is reduced to the element if its solutions are evaporated to white fumes of sulphuric acid. This procedure cannot, however, be used for quantitative purposes. In our opinion the precipitation of elemental gold is not to be attributed to a reducing effect of sulphuric acid but to the thermal decomposition of auric acid. This observation is in agreement with the experiments of Polukarov[39] who recommends isolation of the gold by selective reduction with hydrazine sulphate. Other authors also prefer to remove gold by a preliminary separation step with, for instance, ferrous sulphate,[45] nitrite,[19] or hydroquinone.[44]

Gold is known to remain quantitatively in the insoluble residue after the decomposition of ores with sulphuric acid, which fact has been used for its isolation and gravimetric determination.[36] Experiments showed that this mode of attack, in which telluride is oxidised to tellurite by sulphuric acid, is quantitative for tellurium and it may be used for the determination of the element. Thus, it is possible to remove all of the gold and to obtain the tellurium quantitatively as the sulphate by a single operation. A sulphuric acid solution is not only needed for the reduction of tellurium to the elemental state but is also suitable for its direct determination.

Platinum metals which interfere with the determination of tellurium were not contained in the analysed ores and, therefore, their removal has not been dealt with.

Based on the above facts the following procedure can be recommended for the analysis of sulphide ores.

Decomposition of ores

Transfer 1 g of a 200-mesh sample to a 200-ml conical flask, and add, with constant rotating, 7 ml of concentrated sulphuric acid, cover with a clock glass and heat on a sand bath, first moderately for about 5 min, then to boiling with occasional swirling. Decomposition is complete when the mixture assumes a light coloration and part of the sublimed sulphur is condensed in the upper part of the flask. After about 30 min remove from the sand bath, cool, carefully add approximately 50 ml of water, and boil until the soluble sulphates have dissolved (about 10 min).

Direct determination of tellurium

This procedure may be used for the determination of as little as 0·01 % of tellurium, provided the ore does not contain excessive amounts of selenium or other interfering elements.

Pour the sulphuric acid solution into a 100-ml calibrated flask, cool, dilute to the mark, and mix. Filter the solution through a dry filter paper of close texture and discard the first few ml. Transfer 10 ml of the clear filtrate, by means of a pipette, to a 100-ml separatory funnel, dilute to about 50 ml with distilled water, add 5 ml of a 10% solution of EDTA and proceed as outlined in the general procedure. From the extinction reading obtained subtract that produced by a blank carried through all of the steps of the procedure.

Determination of tellurium after its separation

This procedure is suitable for the determination of amounts as low as 0·001 % of tellurium, even if appreciable amounts of selenium and other interfering elements are present.

Decompose 1 g of the sample with the aid of sulphuric acid in the manner already described, boil with water until soluble salts have dissolved, cool, filter through a filter paper of close texture into a 250-ml low-form beaker, and wash the insoluble residue with distilled water until the volume of the filtrate is 70–80 ml. Treat the filtrate with 10 ml of hydrochloric acid (1:1), then collect any precipitated silver (or thallium) on a small filter paper and wash moderately with water. Dilute the filtrate to 100–120 ml, add 1 ml of a 0·14% solution of selenium dioxide, heat to boiling and precipitate by the dropwise addition of a 50% solution of tin^{II} chloride until the yellow colour of iron^{III} chloride is removed (the solution assumes a light colour which can be seen even if the solution is turbid by precipitated selenium and tellurium), then add 1 ml in excess (in most cases a total amount of only 2–3 ml is required). Cover the beaker with a clock glass and heat on a water bath for 3 to 4 hr. Remove from the bath and let stand at room temperature overnight. Filter the precipitated selenium and tellurium with suction through a porcelain filtering crucible, wash with hydrochloric acid (1:9) containing 1 ml of a 50% solution of tin^{II} chloride per litre, and finally with water. To the precipitate in the filtering crucible add 5 ml of concentrated hydrobromic acid and 3 to 5 drops of 30% hydrogen peroxide. Since the precipitate tends to creep, moisten the walls of the crucible with the same acid by means of a short stirring rod. When solution is complete, filter into the original beaker. Again add 5 ml of hydrobromic acid and a few drops hydrogen peroxide to the crucible and filter and wash with distilled water. Treat the filtrate with 1 ml of sulphuric acid(1:1) and evaporate on a water bath until only sulphuric acid is left. Dilute with a few ml of water, again add 5 ml of hydrobromic acid and 3 to 5 drops of hydrogen peroxide and evaporate as before. Dilute, cool, transfer the solution to a 100-ml separatory funnel, dilute to approximately 50 ml, add in the following order, 0·5 ml of hydrochloric acid (1 : 1), 1 ml of a 10% solution of EDTA, and proceed as indicated in the general procedure. If silver is present, the reagent is added 10 min after the addition of the buffer solution. From the obtained extinction reading subtract that produced by a blank carried through all of the steps of the procedure.

In case the sample contains more than 100 μg of tellurium, transfer the sulphuric acid solution to a 100-ml calibrated flask, and take a corresponding aliquot for the determination.

The presented method was checked by a modified procedure of the iodide method of Johnson and Kwan.[17] Table II shows some results obtained with both procedures of the present method *i.e.* directly and after separation of tellurium. It can be seen that the results are quite reproducible and in good agreement with the mean value of the check method.

TABLE II.—DETERMINATION OF TELLURIUM IN ORES

Sample No.	Tellurium found, %		
	With bismuthiol II		With iodide
	After separation	Directly	
1	0·016 0·018	0·018 0·019	0·017
2	0·025 0·024	0·026 0·027	0·025
3	0·014 0·015	0·013 0·016	0·014
4	0·015 0·015	0·017 0·016	0·016

Acknowledgement—The author thanks Mr. Harry Matschina, Prague, for the translation of the present paper.

Zusammenfassung—Ein photometrisches Verfahren zur Bestimmung des Tellurs beruhend auf der Extraktion des gelben Komplexes von Tellur mit Bismuthiol II wird beschrieben. Das Verfahren ermöglicht es, Tellur bis herab zu 0·01 % direkt nach dem Aufschluss mit Schwefelsäure ohne vorangehende Trennung zu bestimmen. Nach Isolierung des Tellurs mit Zinn(II)-chlorid können noch kleinere Mengen bestimmt werden.

Résumé—L'auteur décrit une méthode de dosage photométrique du tellure, fondée sur l'extraction du complèxe jaune du tellure avec le bismuthiole II. La méthode permet le dosage de quantités aussi faibles que 0·01 % de tellure dans les minerais directement après décomposition, sans séparations préliminaires. Après isolement du tellure par le chlorure stanneux des quantités encore plus faibles peuvent être dosées.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—IV

THE DETERMINATION OF COBALT

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Summary—A method is described for the determination of cobalt in beryllium or beryllium oxide by extraction of the cobalt thiocyanate complex with acetylacetone (2:4-pentanedione). The method is accurate to ±2% or 2 μg of cobalt, whichever is greater. Of the 68 elements investigated only manganese and chromium interfere in 10 mg amounts. No interference was observed when 1 g of each had been removed by ion-exchange or volatilisation (of chromium only) before extraction.

INTRODUCTION

A CHEMICAL method is presented which is specific for cobalt within the limits investigated. No interference was caused by at least 10-mg amounts of 66 elements. The presence of 5 or 10 mg of manganese or chromium caused a slight interference, giving results approximately 6% high for 100 μg of cobalt. One g of manganese and/or chromium has been successfully removed by ion-exchange, resulting in no observable interference. This method is accurate to ±2% or 2 μg of cobalt, whichever is greater.

The method adopted is a modification of one presented by Brown and Steinbach.[2] The sample is dissolved as previously described,[1] citric acid is added to prevent the precipitation of beryllium, and the pH is adjusted to $4{\cdot}0 \pm 0{\cdot}1$. This solution is extracted with acetylacetone (2:4-pentanedione) to remove beryllium and other elements. After removal of the organic phase, sodium thiocyanate is added to the aqueous phase and the cobalt thiocyanate complex extracted with acetylacetone. The absorbance of the organic extract, measured at 625 mμ, is a linear function of the cobalt concentration, at least from 0–8 μg of cobalt per ml, and is constant for at least 2 weeks.

EXPERIMENTAL

Apparatus

Cary Model 14 Recording Spectrophotometer and 50-mm cells.

International Clinical Centrifuge and 15-ml glass-stoppered centrifuge tubes. Beckman pH meter, Model H-2, and combination 14-cm electrode (single probe).

Reagents

De-ionised water, used throughout.

Standard cobalt solution: dissolve 250 mg of cobalt in 6*M* sulphuric acid with 5 drops of nitric acid added initially. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 10 μg of cobalt per ml.

Acetylacetone, (2:4-pentanedione): B.P. 136–139°. The acetylacetone as obtained from the supplier may have a slight yellow colour, probably due to small amounts of iron. This material can be used without further treatment, except for the preparation of the sodium thiocyanate solution and the extraction of the cobalt thiocyanate complex. It is recommended that the acetylacetone be distilled for these uses. It is economical to recover the used acetylacetone by distillation.

Sodium thiocyanate solution, 6M: dissolve 486 g of reagent grade sodium thiocyanate in 380 ml of water, filter immediately and dilute the filtrate to 1 litre with distilled acetylacetone (350 ml).

Citric acid, 50% (w/v).

Hydrochloric acid, (Sp. gr. 1·19, 12*M*).

Nitric acid (Sp. gr. 1·42, 15*M*).

Perchloric acid, 70%.

Sulphuric acid, (Sp. gr. 1·84, 18*M*).

Sodium hydroxide, 50% w/v.

Dowex 1-X8, (50–100 mesh).

Procedure

Dissolve a sample containing about 100 μg of cobalt according to the directions previously given.[1] (If more than 5 mg of manganese or manganese and chromium are known to be present, the solution should be evaporated to dryness and taken up in 9*M* hydrochloric acid. Pass this solution through a column 14 cm high by 1 cm diameter of Dowex 1-X8 in the chloride form. Wash the column with three 15-ml portions of 9*M* hydrochloric acid. Discard the eluate and washings. Wash the column with four 15-ml portions of 0·1*M* sulphuric acid. Collect this eluate and carry it through the following procedure. If more than 1 mg of chromium and less than 1 mg of manganese are present, volatilise the chromium as chromyl chloride in the usual manner and evaporate to dryness. Chromium slowly forms an extractable acetylacetonate which interferes with the determination of cobalt. Thus, it is advisable to complete the analysis as rapidly as possible, when the presence of trace amounts of chromium is suspected.)

Add sufficient acid to have present 5 ml of hydrochloric acid and 10 ml of sulphuric acid. Add 5 ml of 50% citric acid and adjust the pH to 4·0 ± 0·1 with 50% sodium hydroxide. If necessary, heat to redissolve any precipitated beryllium, cool, re-adjust the pH and transfer to a 250-ml separatory funnel. Extract by shaking for 1·5 min with 20-ml portions of acetylacetone until the acetylacetone remains colourless. Discard the organic layers. Check the pH and re-adjust to 4·0 ± 0·1. Again extract with 20-ml portions of acetylacetone until the organic phase is colourless. Add 30 ml of 6*M* sodium thiocyanate and 25 ml of distilled acetylacetone. Shake for 1·5 min. Allow the phases to separate, discard the aqueous phase and drain the organic phase into a 25-ml calibrated flask and dilute to 25 ml with acetylacetone. Centrifuge in glass-stoppered tubes and measure the absorbance at 625 mμ in 50-mm cells, using acetylacetone in the reference cell. Determine the cobalt concentration by reference to a standard curve obtained by carrying known amounts of cobalt through the above procedure. A blank and standard should be carried through the entire procedure. If the absorbance of the sample does not fall on the calibration curve, the sample may be diluted with acetylacetone or the absorbance may be measured using a shorter cell length.

Extraction of the cobalt thiocyanate complex

The cobalt thiocyanate is extracted from an aqueous phase containing 2·5 g of citric acid, 5 ml of 12*M* hydrochloric acid, 7 ml of 18*M* sulphuric acid, sufficient 50% sodium hydroxide to make the pH = 4·0, and 30 ml of 6*M* sodium thiocyanate, in a volume of 175–200 ml. This solution is nearly saturated with acetylacetone.

The cobalt thiocyanate is extracted with 25 ml of acetylacetone. The effect of salt concentration on the solubility of acetylacetone in water makes it necessary to dilute the extract containing the cobalt thiocyanate complex to a definite volume with additional acetylacetone. In spite of the unfavourable phase ratio more than 98% of the cobalt complex is extracted in this manner. The distribution coefficient of the cobalt thiocyanate complex between these two phases is 580 ± 22. This value is independent of the initial cobalt concentration, at least between 0·1 and 5·3 μg/ml.

Brown and Steinbach[2] reported the use of various sources of thiocyanate ion, such as barium, potassium, and ammonium thiocyanates. The first two reagents were unsuitable in this method since they gave precipitates of their sulphates. Ammonium thiocyanate was considered unsuitable because of its lack of purity and instability in acid media. Sodium thiocyanate was used because it overcame these difficulties.

Measurement of the cobalt thiocyanate complex

The colour of the cobalt thiocyanate complex in acetylacetone is stable for at least 2 weeks, whereas it fades in a few hr in some of the more commonly used solvents including acetone, methyl *iso*butyl ketone, or chloroform. The molar absorptivity of the cobalt complex at 625 mμ was found to be 1877 ± 11. The absorbance is a linear function of concentration, at least from 0–8 μg of cobalt per ml acetylacetone.

The absorbance of the cobalt thiocyanate complex is independent of the aqueous thiocyanate concentration between 1·0 and 1·5*M*. Below 1·0*M* thiocyanate the absorbance decreases with decreasing thiocyanate concentration.

Effect of other elements

In testing the effect of other elements on the determination of cobalt by the procedure described, the elements were added to a solution containing the appropriate amounts of beryllium sulphate, sulphuric, hydrochloric and citric acids. Brown and Steinbach tested their method in the presence of unreported amounts of only 8 different metal ions. It was, therefore, deemed necessary to investigate the effects of other possible impurities. No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, Sb^{V}, As^{III}, As^{V}, Ba, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cu^{II}, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Hg^{II}, Mo^{VI}, Nd, Ni, Nb, Pd^{IV}, P(as $PO_4^{\equiv}$), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Sr, Ta, Te^{IV}, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, Ti^{IV}, W^{VI}, U^{VI}, V^{V}, Yb, Y, Zn, or Zr; 100 mg of F^-, 10 ml of 3*M* nitrate, 10 ml of 2*M* perchlorate, or 10 ml of 2*M* acetate. Results are about 6% high when 10 mg of chromium or manganese are present. Therefore, if either or both of these last two elements are present, they should be removed as described.

Apparently, all of the elements investigated which form coloured thiocyanates are removed by the preliminary acetylacetone extraction except nickel, cobalt and platinum. The nickel thiocyanate is not soluble in acetylacetone and does not, therefore, interfere with the determination of cobalt. Some or all of the platinum thiocyanate is extracted with acetylacetone. It does not absorb at 625 mμ, at least at the level investigated; however, it changes the colour of the extract from blue to green.

APPLICATION OF THE METHOD

A sample of beryllium oxide analysed for cobalt using this procedure was found to contain less than 1 ppm of cobalt. When 1-g samples of this oxide were "spiked" with 100 μg of cobalt, recoveries of 100% ± 2% were obtained indicating the applicability of this method in the presence of large amounts of beryllium.

Blank values corresponding to 0–1 μg of cobalt were obtained with the amounts of reagents used during the analysis.

Results obtained when the method was applied to New Brunswick Atomic Energy Commission Laboratory standard samples of beryllium and beryllium oxide are shown in Table I.

Table I.—Analysis of NBL Standards

Sample	Co found, *ppm*	Average, *ppm*	Nominal Co present[c], *ppm*
Be 85	4·0, 4·3	4·15[a]	4
86	21·7, 20·9	21·3[b]	22
87	6·9, 6·8	6·85	7
88	8·4	8·4	8
BeO 72-1	7·3, 7·2	7·25	7·2
−2	3·6, 3·6	3·6	3·6
−3	1·8, 1·8	1·8	1·8
−4	0·76, 0·65	0·70	0·72
−5	0·0 , 0·0	0·0	0·0

[a] Analysis of 10-g samples gave 5·2 and 5·2 ppm of Co.

[b] Analysis of 5-g samples gave 22·7 and 24·7 ppm of Co.

[c] Nominal values for BeO are based on additions to base material, for Be on chemical analysis.

Zusammenfassung—Eine Methode zur Bestimmung von Cobalt in Beryllium oder Berylliumoxyd durch Extraktion von Cobalthiocyanat mit Acetylacetone (2:4-Pentandion) wird beschrieben. Die Methode ist auf ± 2% oder 2 Mikrogramm genau, was immer der höhere Wert ist. Von 68 studierten Fremdionen stören lediglich Mangan und Chrom in Mengen von 10 mg. Keine Störungen wurden festgestellt wenn 1 g deise beideu Ionen durch Ionenaustauscher oder Verfluchtigen (im Falle von Chrom) vor der Extraktion entfernt wurden.

Résumé—Les auteurs décrivent une méthode de dosage du cobalt dans le beryllium ou l'oxyde de beryllium par extraction du complexe thiocyanate de cobalt par l'acétylacétone (2-4 pentanedione). La méthode est précise à ±2% près ou jusqu'à 2 microgrammes de cobalt. Parmi les 68 éléments étudiés, seuls le manganèse et le chrome gênent pour des quantités de 10 mg. Aucune gêne n'est observée quand 1 g de chacun de ces corps a été éliminé par échange d'ion ou volatilisation (du chrome seulement) avant l'extraction.

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ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—V*

A SPECTROPHOTOMETRIC STUDY OF THE BISMUTH-XYLENOL ORANGE COMPLEX

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(*Received* 28 *June* 1960)

Summary—The red bismuth-Xylenol Orange complex has been studied spectrophotometrically. It offers a sensitive and selective reaction for determining traces of bismuth. The complex has an absorption maximum at 540 to 545 mμ and requires a rather narrow acidity range (0·08 to 0·15N) for maximum colour development. It is a 1:1 complex and has a formation constant of 2·8 × 10^5 under the conditions studied. Chloride masks the complex.

XYLENOL Orange forms a red coloured complex with bismuth in an acid medium. The coloured complex is stable and can be used as a basis for the determination of traces of bismuth. This paper reports on the conditions for the colour development of the complex, its composition, its formation constant, and the interference. Since only chloride masks the bismuth-Xylenol Orange complex,[1] bismuth may be determined selectively based on this specific masking.

APPARATUS AND REAGENTS

Standard bismuth solution

Appropriate standard solutions were prepared from a stock bismuth solution in 1N sulphuric acid. The stock solution from pure bismuth metal was standardised by EDTA titration.[2] From the stock solution, a 20 μg per ml bismuth solution was prepared in 0·1N sulphuric acid solution containing 0·15 g of tartaric acid per litre.

Other apparatus and reagents are the same as those reported previously.[1]

PROCEDURE

Calibration curve

Pipette 20 to 100 μg of bismuth into a 25-ml calibrated flask. Add 4 ml of 0·05% Xylenol Orange in 0·1N sulphuric acid, dilute to the mark with 0·1N sulphuric acid and mix. Measure the absorbance at 545 mμ using the reagent blank. Beer's law is followed. The molar absorptivity was found to be 24,000.

RESULTS

Absorption spectra

The spectra for Xylenol Orange and its bismuth complex are shown in Fig. 1. The maximum absorption of the complex is at 540 to 545 mμ.

Effect of acidity

Fig. 2 shows that the optimum sulphuric acid concentration for the colour development of the bismuth complex is 0·08 to 0·15N. In general, perchloric acid

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* Part IV: *Talanta*, 1959, 3, 147.

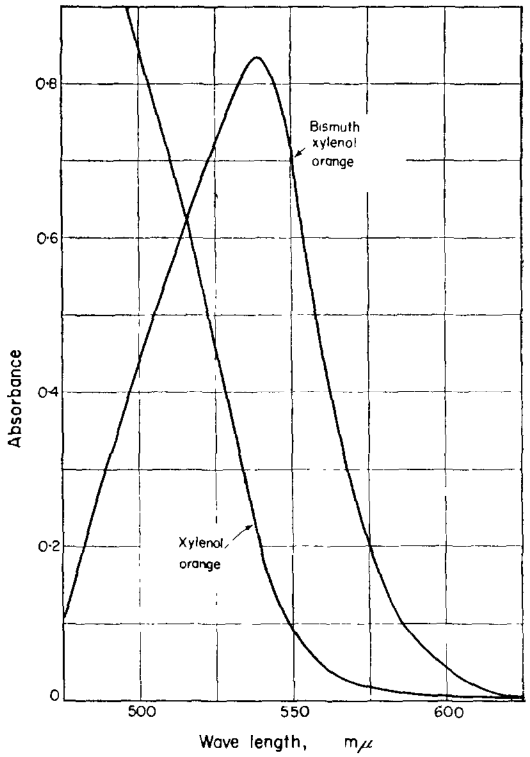
0·8
0·6
0·4
0·2
0
Absorbance
500
550
600
Wave length, mμ
Bismuth xylenol orange
Xylenol orange

FIG. 1.

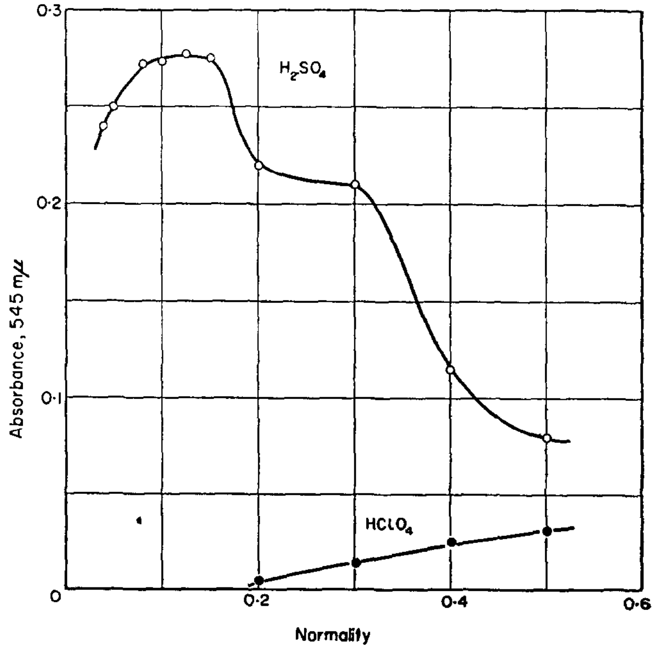
0·3
0·2
0·1
0
Absorbance, 545 mμ
0·2
0·4
0·6
Normality
H_2SO_4
$HClO_4$

FIG. 2.

inhibits the formation of the bismuth-Xylenol Orange complex; however, the absorbance increases slightly above 0·2*N* perchloric acid. As expected, hydrochloric acid can completely mask the formation of the bismuth-Xylenol Orange complex.

Effect of amount of Xylenol Orange

Fig. 3 shows that for 120 μg of bismuth, 3 to 4 ml of 0·05% Xylenol Orange solution are required. Contrary to the previous cases of the colour development of the Xylenol Orange complexes of zirconium, hafnium, and iron, large amounts (more than 4 ml of 0·05%) of Xylenol Orange do not tend to decrease the absorbance.

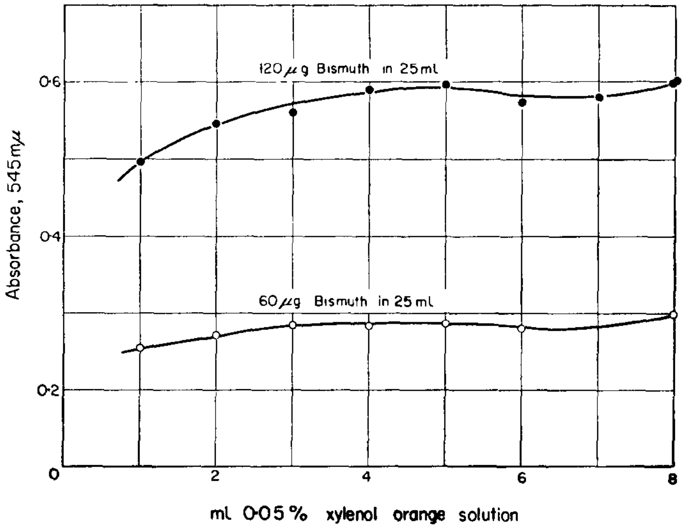

FIG. 3.

Complex formation

Like zirconium, hafnium, and iron, bismuth also forms a 1:1 complex with Xylenol Orange as indicated by Job's method (Fig. 4). The formation constant was calculated from the curves shown in Fig. 4, based on the method used previously.[3] It was found to be $2·8 \times 10^5$ in 0·1*N* sulphuric acid. Because of its low formation constant, it is easily understood why Xylenol Orange has been successfully used as an indicator in the EDTA titration of bismuth in a rather acidic medium.

Effect of chloride

It is well known that halides form quite strong complexes with bismuth. Approximately 14 millimoles of chloride are required to completely mask 40 μg of bismuth, and 16 millimoles for 100 μg of bismuth. Since chloride does not affect the colour of the Xylenol Orange complexes of zirconium, hafnium, and iron, tin, etc., such specific masking by chloride may be used to determine bismuth in the presence of other metals which also give coloured complexes with Xylenol Orange. For instance, the determination of bismuth in the presence of zirconium may be conducted by measuring the change in the absorbance of the sample solution caused by the addition of chloride. The change is equivalent to the bismuth present (see Table I).

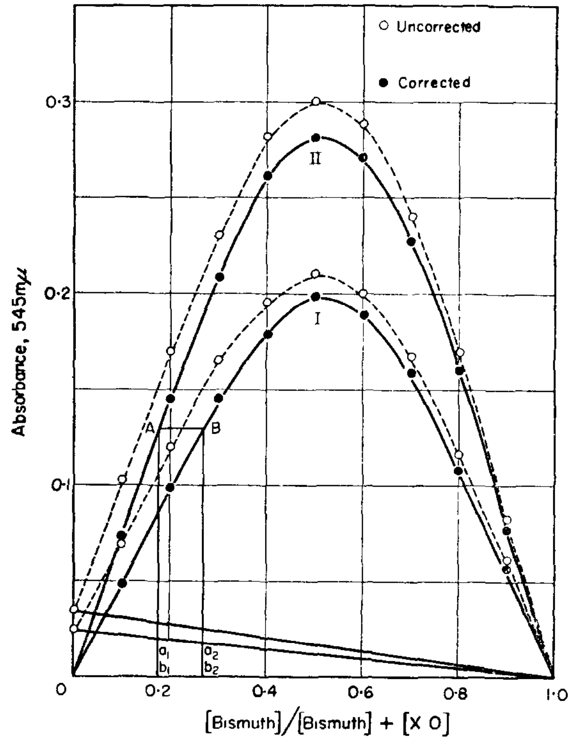

FIG. 4.

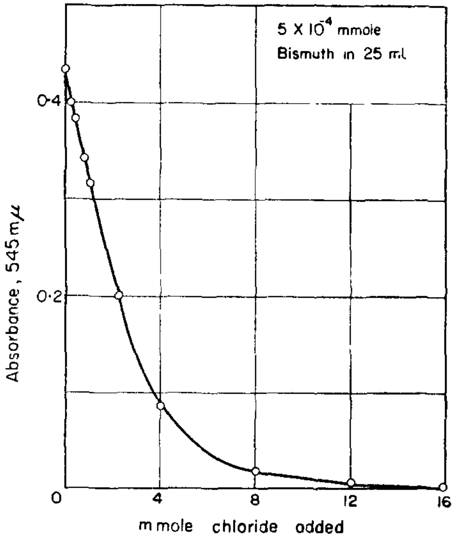

FIG. 5.

Effect of tartaric acid

Fig. 6 shows that tartaric acid has a slight effect on the absorbance. Citric acid shows a similar effect. Both tartaric acid and citric acid mask the Xylenol Orange

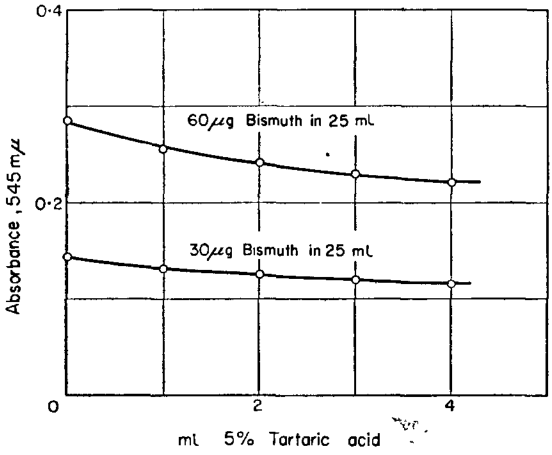

FIG. 6.

complexes of zirconium, hafnium, tin, and antimony (Xylenol Orange is insensitive to antimony). In the case of determining bismuth in the presence of tin, citric acid or tartaric acid may be added as a masking agent; however, approximately the same amount of citric acid or tartaric acid should also be added to the standard bismuth solution in order to compensate for its effect.

TABLE I. EFFECT OF FOREIGN IONS

. Taken: 40 μg of bismuth

Ion	Amount added	Bismuth recovery, %	Remark
Aluminium	1 mmole	100·0	
Manganese$^{\text{II}}$	1 mmole	100·1	
Niobium	5×10^{-4} mmole	100·5	1 mmole citric acid added
Niobium	5×10^{-4} mmole	244	no citric acid added
Molybdenum$^{\text{VI}}$	0·1 mg	191	no H_2O_2 added
Molybdenum$^{\text{VI}}$	0·1 mg	101·1	3 ml 30% H_2P_2 added
Antimony$^{\text{III}}$	1×10^{-3} mmole	130	
Antimony$^{\text{III}}$	1×10^{-3} mmole	99·5	1 mmole citric acid added
Tin$^{\text{II}}$	5×10^{-4} mmole	265	
Tin$^{\text{II}}$	5×10^{-4} mmole	101·5	1 mmole citric acid added
Iron$^{\text{III}}$	40 μg	99·2	2 ml 1% ascorbic acid added
Zirconium	10 μg	180	
Zirconium[a]	10 μg	102·5	

[a] When determining bismuth in the mixture of bismuth and zirconium, two equal aliquots were used; to one was added 14 mmoles of chloride and to the other no chloride was added. The bismuth was calculated based on the difference between the two absorbances obtained.

Interference study

Only a few metals in a $0{\cdot}1N$ sulphuric acid medium produce a red colour with Xylenol Orange.[1] Table I indicates the extent of the effect of these interfering ions on the determination of bismuth. Some of the interfering metals can be completely or partially masked by appropriate masking agents. Fluoride and thioglycollic acid show a slight masking effect on the bismuth-Xylenol Orange complex.

The Xylenol Orange solution and its bismuth complex are stable for at least 1 week without appreciable change. The dithiocarbamate method for bismuth[4] is sensitive and highly selective, but its bismuth complex is not very stable. It was found that the Xylenol Orange method is simple and sensitive for the determination of traces of bismuth in bismuth-manganese thin film used in the electronic industry.

Zusammenfassung—Der rote Wismut-Xylenolorange-Komplex wurde photometrisch untersucht. Er bildet die Grundlage zu einer empfindlichen und selektiven Wismutbestimmung. Der Komplex zeigt ein Absorptionsmaximum bei 540–545 mμ und benötigt einen ziemlich nahen Aciditätsbereich (0·08–0·15 n) zur höchsten Farbentwicklung. Der Komplex hat die Zusammensetzung 1:1 und eine Bildungskonstante von $2{\cdot}8 \times 10^5$ (unter den studierten Bedingungen). Chlorid maskiert.

Résumé—Le complexe rouge bismuth-xylénol orange a été étudié par spectrophotométrie. Il offre une réaction sensible et sélective pour le dosage de traces de bismuth. Le complexe a un maximum d'absorption à 540–545 mμ et nécessite un domaine d'acidité assez étroit (0,08 à 0,15 N) pour obtenir une coloration maximum. C'est un complexe 1-1 qui a une constante de formation de $2{,}8 \,.\, 10^5$ dans les conditions indiquées. Le chlorure masque le complexe.

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THE FLUOROMETRIC DETERMINATION OF *o*-PHTHALIC ACID

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Summary—A fluorometric procedure for the determination of *o*-phthalic acid by conversion to fluorescein is described. The optimum amount of *o*-phthalic acid for application of the method is 50–5000 μg. The determination can be carried out with a relative error of less than 5% even when significant quantities of common *o*-phthalic acid contaminants are present.

THE condensation of 1:2-dicarboxylic acids with resorcinol to yield dyes of the fluorescein type has been noted by Feigl[1] and the fluorescent compounds formed have been used for the qualitative identification of 1:2-dicarboxylic acid structures.

Barr[2] has made a successful quantitative application of this type of reaction in developing fluorometric procedures for the determination of succinic and malic acids.

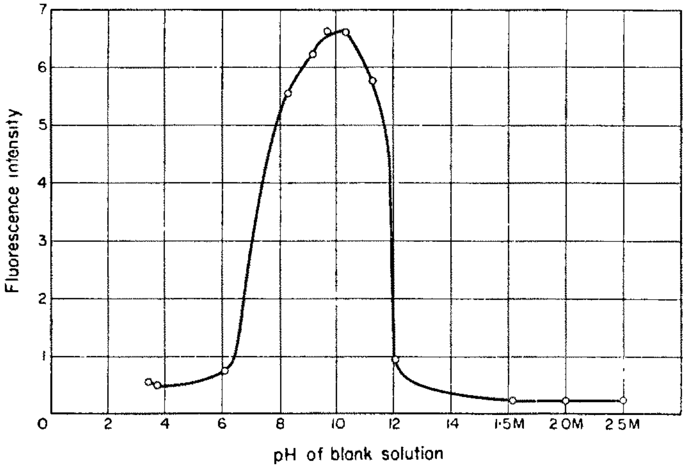

FIG. 1.—Effect of pH on blank fluorescence.

In attempting to apply this reaction to the quantitative determination of *o*-phthalic acid, difficulty was encountered in controlling the deep blue blank fluorescence resulting from the reaction between resorcinol and concentrated sulphuric acid. The fluorescence resulting from this reaction is so intense that the reaction has been recommended by Denigès[3] as a qualitative test for the identification of resorcinol. Fortunately, however, the blank fluorescence intensity is highly dependent upon pH (Fig. 1) while the greenish-yellow fluorescence of fluorescein solutions is completely pH independent above pH 6 (Fig. 2). Consequently, if the fluorescence intensity

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measurements are made in strongly alkaline solution, the blank fluorescence is almost completely suppressed and does not interfere with the determination.

Both Feigl and Barr recommend the use of freshly sublimed resorcinol as a means of minimising blank fluorescence. This procedure did not appreciably lower the blank fluorescence in strongly alkaline (2*M* NaOH) solution as is shown by the comparative results in Table I. The samples used in this study were 1·0-ml aliquot portions of an *o*-phthalic acid solution containing 1·0 mg per ml.

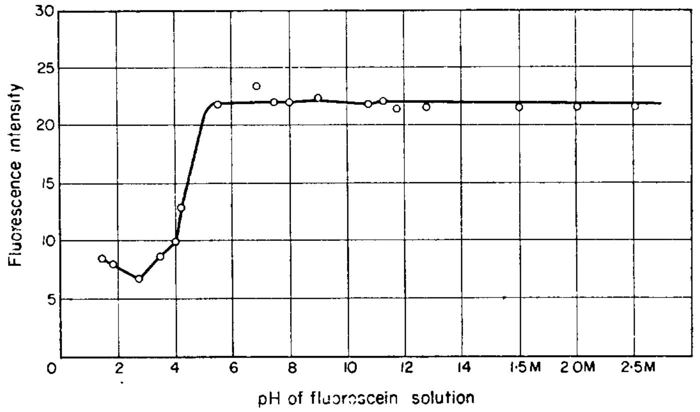

FIG. 2.—Effect of pH on sample fluorescence.

The difference noted between the average results obtained is deemed insignificant because it is within the limits of reproducibility of the method.

The elimination of the sublimation procedure from the method reduces the time required for the over-all procedure by approximately two and one-half hours.

TABLE I. SUBLIMED RESORCINOL VS UNSUBLIMED

Freshly Sublimed		Unsublimed (C.P.)	
Sample fluorescence*	Blank fluorescence*	Sample fluorescence*	Blank fluorescence*
14·3	0·12	14·5	0·21
14·5	0·11	14·3	0·21
14·5	0·12	14·5	0·15
14·3	0·20	14·5	0·19
14·5	0·30	14·0	0·24
14·5	0·20	14·5	0·24
14·5	0·22	14·2	0·18
Ave. = 14·44	Ave. = 0·18	Ave. = 14·36	Ave. = 0·20

* Instrument readings.

REAGENTS AND INSTRUMENTS

The reagents required are: chemically pure resorcinol, pure concentrated sulphuric acid and a solution of approximately 2*M* sodium hydroxide.

The direct reading fluorometer used was constructed in this laboratory employing the line operated

Photovolt Electronic Photometer, model 501-M, in conjunction with a cell compartment and lamp-housing constructed along the lines suggested by C. E. White.[4] The photometer was equipped with the Photovolt "C" phototube which has maximum sensitivity in the range 300–600 mμ.

The primary filter employed was the Corning No. 5840 and the secondary filter combination consisted of the Green Corning Filter No. 4015 used in conjunction with the ultraviolet filter from the Lumetron Model 402-EF instrument. This filter was employed to prevent scattered ultraviolet light from striking the photocell.

EXPERIMENTAL PROCEDURE

An aqueous solution of *o*-phthalic acid should be used. Therefore, if a solid sample is to be determined, dissolve a weighed amount in a measured volume of water, using a small amount of sodium hydroxide to effect solution if necessary.

A 1·0-ml aliquot of the aqueous sample solution is pipetted into a 5-ml beaker and 0·04 ml of pure concentrated sulphuric acid is added with a graduated 1-ml pipette. Approximately 5–10 mg of chemically pure resorcinol is added, the mixture is thoroughly stirred to promote solution of the resorcinol, and the samples are placed in an oven (125°), for 1·5 hr. At the completion of this reaction period, the samples are removed from the oven and allowed to cool to room temperature. The reaction products in the beaker are taken up in distilled water and quantitatively transferred to a 200-ml volumetric flask. If a high concentration of *o*-phthalic acid is present in the sample, some difficulty may be encountered in dissolving the reaction products. However, addition of a small amount of dilute sodium hydroxide readily effects solution. Dilution to 200 ml is made with distilled water and a 10-ml aliquot portion of this solution is transferred to a 100-ml volumetric flask. Dilution to 100 ml is made with $2M$ sodium hydroxide. This solution is then used for the fluorescence intensity measurement. The double dilution is used to minimise blank fluorescence, which is significant in more concentrated solution.

To obtain the fluorescence intensity of the sample, the fluorometer is adjusted to give a zero reading with distilled water and the fluorescence intensity of the sample solution is read relative to this setting. If a null-point type instrument, such as the Lumetron model 402-EF, is used for the fluorescence intensity measurements, a standard solution must be used to obtain a 100% setting. A fluorescein solution, of appropriate concentration for the range being studied, is sufficiently stable for this purpose.

After the fluorescence intensity of the solution has been measured, the quantity of *o*-phthalic acid treated originally is found by comparison of the intensity value with a calibration curve.

No correction is applied for blank fluorescence because it is relatively constant and is incorporated in the calibration curve. However, it is wise to prepare a blank as a control for each group of samples determined.

The calibration curve is prepared by treating *o*-phthalic acid solutions of known concentrations as described above, and determining their fluorescence intensities. Primary standard grade potassium acid phthalate can conveniently be used to prepare standard solutions for preparation of the calibration curve.

DISCUSSION AND RESULTS

The optimum concentration range that can be covered by the method is 50–5000 μg of *o*-phthalic acid per 1-ml aliquot reacted. With samples containing less than 50 μg the contribution of the blank fluorescence becomes significant and poor reproducibility of sample fluorescence results. Above 5000 μg the linearity of the fluorescence versus concentration plot falls off rapidly and poor reproducibility again results.

The results obtained with some prepared unknowns are shown in Table II. The samples were in all cases aqueous solutions of *o*-phthalic acid, and where contaminants were added, the aqueous *o*-phthalic acid solution was saturated with the contaminant.

The contaminants selected are those which might be expected as by-products if *o*-phthalic acid were prepared by oxidation of impure *o*-xylene or naphthalene. The results indicate that none of the contaminants grossly affect the method. However, the presence of α-naphthoquinone causes an orange-red colour in the reaction solution

TABLE II

Contaminant	Taken, μg	Found. μg	% Error
None	140	139	−0·7
None	219	227	+3·6
None	579	585	+1·0
None	1080	1090	+0·9
m- and *p*-Phthalic acid	500	494	−1·2
Benzoic acid	1000	990	−1·0
α-Naphthoquinone	1000	975	−2·5
Benzoic acid and α-naphthoquinone	1000	950	−5·0

which is accompanied by a slight decrease in fluorescence intensity and leads to consistently low results. This effect is particularly noticeable in solutions saturated with both benzoic acid and α-naphthoquinone.

Zusammenfassung—Ein fluorimetrische Methode zur Bestimmung von o-Phthalsäure durch Überführung in Fluorescein wird beschrieben. Der optimale Mengenbereich ist 50–5000 μg. Die Bestimmung kann auf 5% genau ausgeführt werden, selbst wenn beträchtliche Mengen der in o-Phthalsäure überlicherweise anwesende Verunreingungen vorhanden sind.

Résumé—Les auteurs décrivent une méthode fluorométrique de dosage de l'acide o-phtalique par transformation en fluorescéine. La quantité optimum d'acide o-phtalique pour l'application de cette méthode est de 50–5000 μg. Le dosage peut être effectué avec une erreur relative de moins de 5 pour cent même quand des quantités importantes d'impuretés courantes de l'acide o-phtalique sont présentes.

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PRELIMINARY COMMUNICATION

Indirect neutron absorptiometry

(*Received* 4 *August* 1960)

It is possible to utilise the absorption of neutrons for analysis just as the absorption of electromagnetic radiation is used for other methods. In the past few years, some work of this type has been reported in the literature[1-6] but in general this method has had little acceptance except for the analysis of boron.

The tendency for an element to absorb thermal neutrons is indicated by a "thermal neutron absorption cross-section". Table I lists these cross-sections for the 20 elements which are the best neutron absorbers. It is interesting to note that most of these elements, particularly those with the highest cross-sections, are rather exotic elements not often encountered in the majority of analytical laboratories.

TABLE I. THERMAL NEUTRON ABSORPTION CROSS-SECTIONS[7]

Element	Cross-section, *barns*
Gadolinium	46,000
Samarium	5,500
Europium	4,600
Cadmium	2,550
Dysprosium	1,100
Boron	750
Iridium	430
Mercury	380
Indium	190
Rhodium	150
Thulium	118
Hafnium	105
Lutetium	108
Gold	98
Rhenium	84
Lithium	71
Holmium	64
Silver	62
Neodymium	46
Terbium	44

The application of neutron absorptiometry to the analysis of boron appears to have filled a need for a rapid, non-destructive, and on occasion "in-line"[8,9] method for macro amounts of this element. From Table I we see, however, that there are several elements for which the method would be much more sensitive and for which there would be less potential interference. Indeed, the element gadolinium would be some 60 times more sensitive than boron and almost 10 times better than any other element in the periodic system.

We are studying a technique for utilising this unique neutron absorption property in the analysis of common elements such as fluorine. This technique, which we call "Indirect Neutron Absorptiometry", is analogous to radiometric analysis in that neutron absorbing elements are utilised in the determination of elements which do not themselves absorb neutrons.

In a typical procedure, fluoride ions in solution are precipitated with an excess of gadolinium ions. Gadolinium ions adsorbed on the precipitate are washed off or eliminated by a dissolution and reprecipitation. Neutron absorption measurements are then made either on the dissolved precipitate or on the liquid residue. The neutron-absorbing gadolinium measured thus represents a stoichiometric amount of fluoride.

The sensitivity obtainable is quite dependent upon the geometry of the neutron source, sample container and neutron detector within the assembly. At present a modified Nuclear-Chicago Neutron Howitzer is being used with a 5-curie plutonium-beryllium source. This permits a bottled liquid sample to be placed between the source and the detector. We are, however, assembling a modified apparatus in which the sample solution is contained in a Marinelli-type beaker surrounding the small neutron detector tube. This should eliminate much of the scattered neutron radiation which now reaches the detector without "seeing" the sample. By improving the geometry we should also increase the sensitivity of the method.

Preliminary results indicate that the idea of indirect neutron absorptiometry is sound and that values reproducible to within a few per cent can be obtained rapidly by this technique. Even with relatively poor geometry it is possible to analyse for milligram amounts of fluoride and it should be possible to improve this sensitivity with the new apparatus being assembled. This method should also be applicable to the analysis of other ions which form insoluble compounds with gadolinium. It may even be possible to analyse for potassium as the tetraphenylborate by this technique.

Indirect neutron absorptiometry is a non-destructive method which utilises encapsulated sources only and does not require handling of radioactive solutions. In this respect it presents no more problems than the thousands of thickness, density and level gauges used routinely in industry at the present time. Furthermore, it utilises the same principles of absorptiometry already so familiar to the analytical chemist—only the type of radiation is different.

Work is continuing on this method to elaborate the areas of analysis in which it will be most useful. Detailed evaluation of procedures and equipment will establish limits of sensitivity, as well as point up problems of contamination, manipulation, and the like. It appears now, however, that this indirect approach to neutron absorption has considerable potential for the average analytical laboratory.

Acknowledgement—The author enjoyed many fruitful discussions with G. W. Leddicotte and J. E. Strain on the general topic of neutron absorption during a leave at Oak Ridge National Laboratory in the Spring of 1960. The work was partially supported by the U.S. Atomic Energy Commission.

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Summary—A preliminary account is given of the use of the neutron absorption of suitable elements (such as gadolinium) for the determination of non-absorbing elements (such as fluorine) by measuring the absorption of a dissolved precipitate (in the case quoted, gadolinium fluoride). This indirect determination by neutron absorption gives reproducible results rapidly and non-destructibly. The applications of the method are being studied.

Zusammenfassung—Eine Vorläufige Mitteilung über die Anwendung von Neutronenabsorbtion wird gegeben. Geeignete Elemente wie z.B. Gadolinium zönnen zur Bestimmung von nichtabsorbierenden Elementen z.B. Fluor herangezogen werden, indem die Absorbtion eines Niederschlages (im Beispielsfalle Gadoliniumfluorid) gemessen wird. Die Indirekte Bestimmung durch Neutronenabsorbtion gibt rasch reproduzierbare Resultate. Weitere Anwedungsmöglichkeiten der Methode werden studiert.

Résumé—L'auteur donne un compte-rendu préliminaire sur l'utilisation de l'absorption des neutrons par des éléments convenables (tels que le gadolinium) pour le dosage d'éléments non absorbants (tels

que le fluor) par la mesure de l'absorption d'un précipité convenable (dans le cas cité, fluorure de gadolinium). Le dosage indirect par absorption de neutrons donne rapidement des résultats reproductibles et n'altère pas l'échantillon. Les applications de cette méthode sont étudiées actuellement.

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SHORT COMMUNICATIONS

The application of the cathode ray polarograph to the analysis of explosives—III

Simultaneous determination of nitroglycerine and dinitroglycol

(*Received* 1 *February* 1960)

IN a previous paper[1], details are given of the determination of nitroglycerine (NG) in various explosive mixtures without explanation of the electrode process involved in its reduction. In the present paper, a polarographic technique is described for the determination of NG and dinitroglycol(EGDN) in mixtures containing both explosives. The mechanism of the reduction process for NG is discussed. The simplicity of the determination of NG described in the previous paper provided the basis for investigating a method for the determination of EGDN in presence of NG.

It has been found that in a base electrolyte consisting of aqueous KCl and NH_4Cl, EGDN is reduced with the formation of two waves. NG is also reducible, forming 3 waves, the first of which closely precedes both waves of EGDN and cannot be separated using direct current. The second and third waves of NG coincide with the waves of EGDN. Applying derivative current, the three waves are well separated, allowing the possibility of the determination of both compounds.

EXPERIMENTAL

0·1, 0·2, 0·3 and 0·4 Ml of a standard solution of EGDN in methanol (2 mg/ml) were introduced into 10-ml flasks, made up to the mark with a base electrolyte consisting of 10 ml of *N* KCl, 50 ml of 2*N* NH_4Cl, and 40 ml of water (pH 6) and shaken well. For measurement, 5 ml of solution was transferred to a polarographic cell. The polarograms were recorded with a starting potential of −0·2 V, after de-aerating with nitrogen. The diffusion currents of EGDN were observed at peak potentials −0·44 V and −0·62 V. Both waves are quantitative. Applying direct current, the total height of both waves can be used to estimate the concentration of EGDN (Fig. 1) and applying derivative current, either of the wave heights can be used (Fig. 2), measuring the left-hand side of the first wave and the right-hand side of the second. The results are tabulated below.

TABLE I.—WAVE HEIGHTS OF DINITROGLYCOL

Dinitroglycol, μg	Wave heights, *divisions*		
	Direct current	Derivative current	
	Total wave height	First wave	Second wave
100	12	7·5	3·5
200	22·5	15·5	7
300	33·5	22	9
400	44	29	13

The wave heights are measured in divisions of the graticule, where 9 cm are divided into 50 divisions. The scale factor on direct current was 6·0 and on derivative current 0·06. The mercury pool was used as the reference electrode throughout at a constant temperature of 25°.

The effect of the presence of NG on the reduction of EGDN was investigated. The addition of 100 μg of NG to the above samples (100–400 μg EGDN) increases the second EGDN wave by approximately 1% and depresses the first (Fig. 3).

Working with calibration graphs prepared from synthetic samples, with a selected range of concentration of both explosives, a simple and accurate determination of NG and EGDN can be achieved. In exceptional cases, where the determination of NG is required in a large excess of EGDN, it is only necessary to modify the method by the addition of pyridine to the base electrolyte. It has been found that EGDN is not reducible in the presence of pyridine, although the reduction of NG results in the formation of a single wave. Such a phenomenon is of great interest in the analysis of both compounds, since it allows the possibility of determining NG in the presence of a large excess of EGDN.

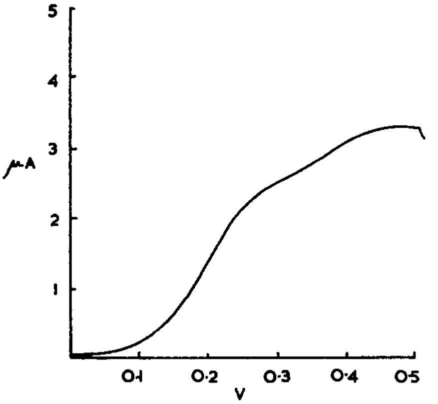


FIG. 1.—300 μg dinitroglycol. Direct current

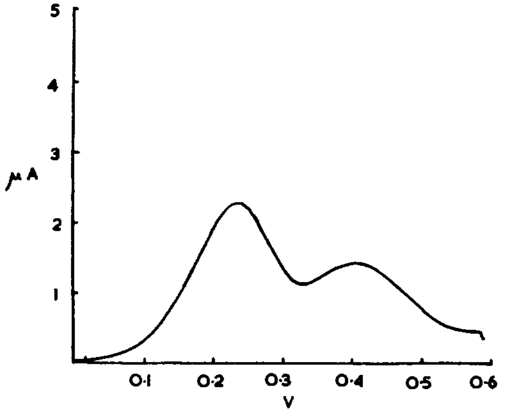


FIG. 2.—300 μg dinitroglycol. Derivative current

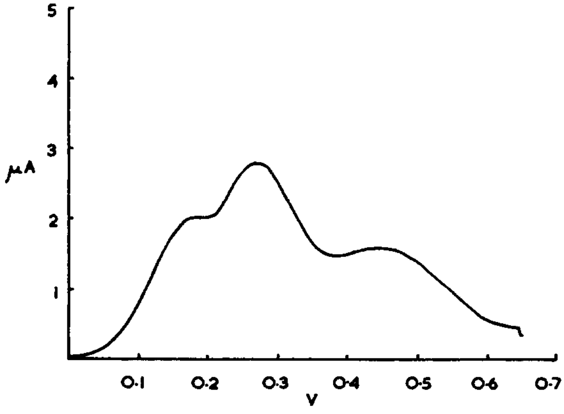


FIG. 3.—300 μg nitroglycerine, 300 μg dinitroglycol

Procedure

The main components of blasting explosives are ammonium nitrate (30–70%) and sodium chloride (10–40%). Introduce 0·5 g of sample into a 50-ml flask, shake with 25 ml of methanol, and make up to the mark with water. Transfer 1 ml to a 10-ml flask, make up to the mark with base electrolyte, and record the polarogram on a 5-ml aliquot, after de-aerating with nitrogen for 5 min. Record the NG wave and the first EGDN wave with a starting potential of −0·15 V, and the two EGDN waves with a starting potential of −0·3 V, using a scale factor of 0·06.

The concentrations of NG and EGDN given in Table II were obtained by comparison with a standard sample prepared in the following way. 300 mg of ammonium nitrate and 140 mg of sodium chloride were introduced into a 50-ml flask, 25 ml of a standard solution of NG in methanol (2 mg/ml) and 6·25 ml of the standard solution of EGDN were added, and made up to the mark with water, thus making the concentrations of NG and EGDN, 10% and 2·5% respectively; 1 ml was transferred into a 10-ml flask, made up to the mark with base electrolyte and the polarograms recorded as before.

TABLE II. NITROGLYCERINE AND DINITROGLYCOL IN BLASTING EXPLOSIVES.

	% in sample I		% in sample II	
	Actual*	By comparison	Actual*	By comparison
Nitroglycerine	9·4	9·6	11·3	11·6
Dinitroglycol	2·3	2·4	2·8	2·7

* Percentages as found at I.C.I. Laboratories, Nobel Division.

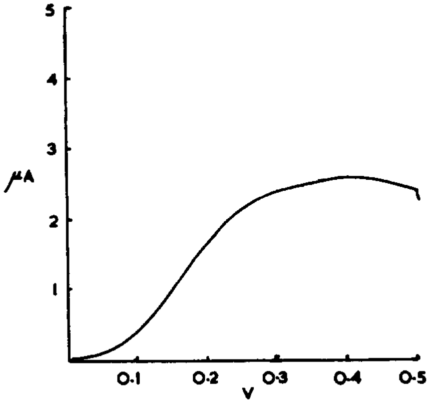


FIG. 4.—200 μg nitroglycerine. Direct current

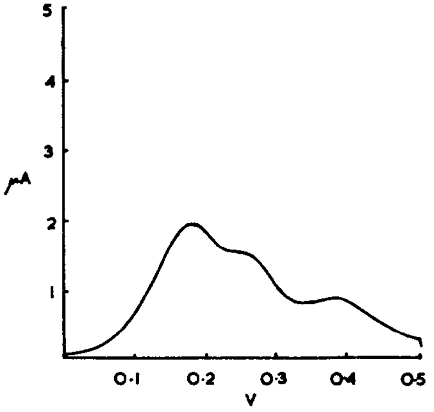


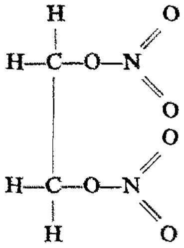
FIG. 5.—200 μg nitroglycerine. Derivative current

DISCUSSION

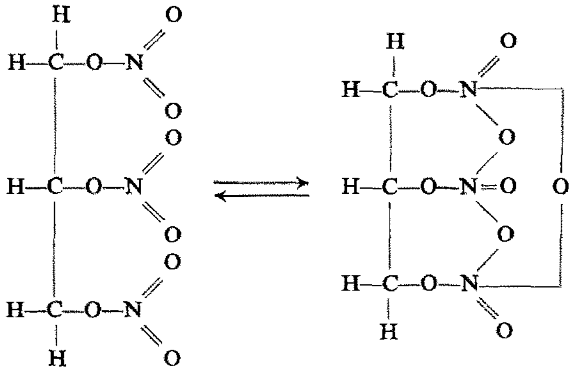
The mechanism of reduction of polynitrate esters has been investigated by Whitnack *et al*[2]. They show that the reduction is independent of pH, and that the number of electrons involved in the reduction is two for each $O—NO_2$ group in the molecule. In the base electrolyte used above, the reduction of EGDN results in the formation of two waves, as is expected, due to the presence of two $O—NO_2$ groups. The reduction of NG produces three clearly marked waves at peak potentials −0·35 V, −0·44 V, and −0·62 V (Figs. 4 and 5).

The addition of 0·5 ml of pyridine to 5 ml of base electrolyte containing NG changes the reaction mechanism, resulting in the formation of a single wave at peak potential −0·27 V. The addition of the same amount of pyridine to a solution containing EGDN completely removes both waves, indicating the irreducibility of EGDN under these conditions.

The addition of pyridine increases the pH of the solution from 6 to 7·3. Originally it was believed that the change in reaction mechanism was due to the change in pH. The effect of pH was further investigated. A water solution of 0·4M trihydroxymethyl-aminomethane was prepared and 0·1, 0·2 and 0·3 ml were added to 5 ml of base electrolyte containing both NG and EGDN, the resulting pH values were 7·4, 7·8, 8·0. No alteration of the reduction waves was observed, confirming the investigation of Whitnack. This behaviour may be explained by a consideration of the structures:



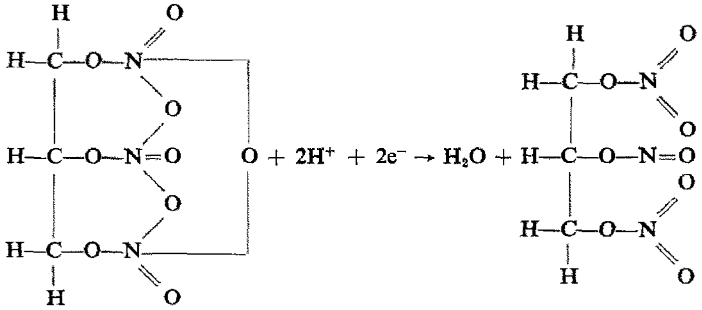
Dinitroglycol



(I) Stable (II) Labile

Nitroglycerine.

Assuming that the second tautomeric form[3,6] is stable in pyridine, it is possible that the oxygen link between the two external nitrogen atoms is more exposed to chemical reaction, involving a two-electron reduction, at the cost of the secondary O—NO_2 group



For EGDN, no configuration similar to that of NG is possible, and this could explain the irreducibility in the presence of pyridine. Work on the mechanism of the reaction, including the determination of the number of electrons taking place in the reduction of EGDN, is in progress and will be published in a future paper.

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Summary—A polarographic method for the determination of nitroglycerine and dinitroglycol in mixtures containing both of these substances is described. The nature of the reductions involved is discussed.

Zusammenfassung—Eine polarographische Methode zur Bestimmung von Nitroglyzerin und Dinitroglycol in Mischungen beider wird beschrieben. Die Reduktionsreaktionen werden diskutiert.

Résumé—Une méthode polarographique de dosage de la nitroglycérine et du dinitroglycol dan des mélanges contenant ces deux substances est décrite. La nature des réductions mises en jeu est discutée.

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Analytical applications of 3-acetyl-4-hydroxycoumarin—II*

Spectrophotometric determination of iron^{II}

(*Received* 18 *March* 1960)

BHAT and Jain[1] have recently used 3-acetyl-4-hydroxycoumarin for the determination of uranium and thorium and for their separation from each other as well as from rare earths. We have now found that this reagent may also be used successfully for the spectrophotometric determination of iron^{II}. Iron^{III} gives, with this reagent, a yellowish tinge which is too faint for spectrophotometric investigations. When an alcoholic solution of the coumarin is added to an aqueous solution of an iron^{II} salt, a deep orange-red complex, soluble in 50% (v/v) ethanol is obtained. The colour of the complex is stable for several days and is not affected by temperature variations between 5° and 40°. The complex obeys the Lambert-Beer law at 400 mμ in the concentration range 1·5–5·3 ppm of iron. The intensity of the colour does not vary between pH 2·8 and 4·3.

EXPERIMENTAL

Reagents

3-Acetyl-4-hydroxycoumarin: 3-Acetyl-4-hydroxycoumarin, prepared as outlined previously,[1] was purified to a colourless crystalline product by sublimation at 75–85° under reduced pressure. 204·2 Mg of this material were dissolved in about 200 ml of ethanol, then diluted to 500 ml. The strength of the solution so obtained was 2×10^{-3} g mole/litre.

Standard solution of iron^{II}: Prepared by dissolving 784·3 mg of iron^{II} ammonium sulphate (Pro Analysi E. Merck) in about 50 ml of 1% aqueous hydroquinone solution, then finally making

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* For Part I see reference 1.

determination of the number of electrons taking place in the reduction of EGDN, is in progress and will be published in a future paper.

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the volume to 1 litre with further hydroquinone solution of the same strength. The solution contained 2×10^{-3} g mole per litre of the iron$^{\text{II}}$ salt.

All other metal salts used were of either of A. R. quality or E. Merck Pro Analysi.

Apparatus

A Hilger U.V. spectrophotometer was employed for taking the absorption spectra of 3-acetyl-4-hydroxycoumarin and its iron$^{\text{II}}$ complex. The other spectrophotometric measurements were made with a Unicam Spectrophotometer S.P. 600.

The absorption cells had a light path of 10 mm. These cells could not be thermostated but all solutions were brought to a constant temperature of 30 ± 0·05° in a thermostat before measuring the optical density.

A Beckmann pH Meter Model H2 was used for measuring pH.

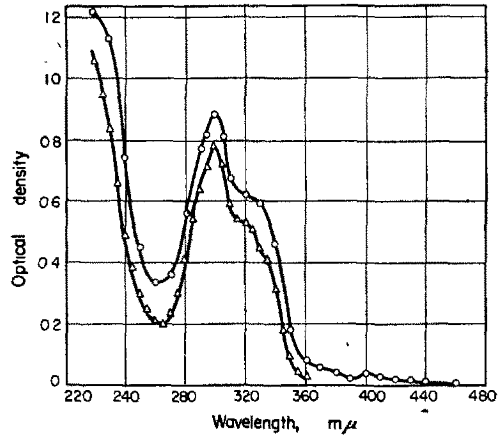

FIG. 1.—Δ-absorption spectrum of 3-acetyl-4-hydroxycoumarin. O-absorption spectrum of iron$^{\text{II}}$ 3-acetyl-4-hydroxycoumarin complex.

Absorption spectra

The absorption spectrum of 3-acetyl-4-hydroxycoumarin was taken in the ultraviolet region of the spectrum and the maximum absorption occurred at 300 mμ (Fig. 1). There was no absorption observed in the visible region.

The absorption spectrum of iron$^{\text{II}}$ 3-acetyl-4-hydroxycoumarin was taken in the ultraviolet as well as in the visible region of the spectrum. A maximum observed in the ultraviolet region at 300 mμ was obviously due to the reagent itself. At 400 mμ another maximum, though of low intensity, was also recorded (Fig. 1) even when the strength of the complex was extremely low as normally required for ultraviolet absorption studies. In the later part of the present investigations a strong absorption at 400 mμ was observed when adequate concentrations were employed, and thus the wavelength of 400 mμ was chosen for all spectrophotometric studies of the complex throughout this investigation.

Minimum amount of 3-*acetyl-4-hydroxycoumarin necessary for determination of iron*$^{\text{II}}$

The optical densities at 400 mμ of a series of solutions containing the coumarin and iron$^{\text{II}}$ in the mole ratio of 0·5:1 to 9:1 are plotted in Fig. 2; it is seen that the portion AB of the curve is a straight line up to the molar ratio of 5. For the determination of iron$^{\text{II}}$, however, the molar ratio of the coumarin to iron$^{\text{II}}$ was maintained at 8 in the subsequent studies. An excess of the reagent had no effect on the optical density of the complex.

Effect of pH on iron$^{\text{III}}$ 3-*acetyl-4-hydroxycoumarin complex*

The effect of pH on the complex was studied and it was found that the absorption by the complex remained the same in the pH range 2·8–4·3 (Fig. 3). The pH of the iron$^{\text{II}}$ solution was adjusted by the addition of 0·1*N* sodium hydroxide or 0·1*N* hydrochloric acid. The pH of each solution was determined with the Beckmann pH meter using a suitable glass electrode.

Stability of the colour

The formation of the complex was instantaneous and its colour was stable for more than 1 week. The effect of temperature on the colour of the complex was studied by placing the coloured complex in a thermostat for 0·5 hr at various temperatures between 15° and 40°. The effect of low temperature was studied by keeping the complex in a refrigerator. No change in the optical density of the complex could be observed in the temperature range 5–40°.

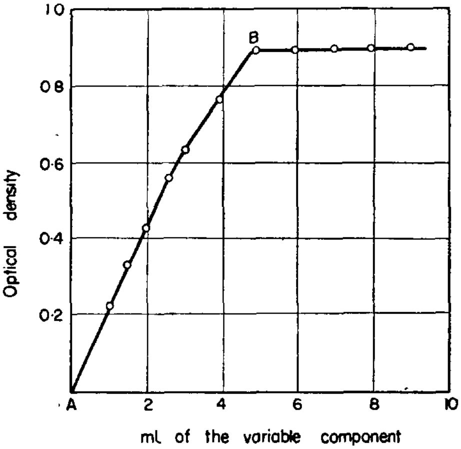

FIG. 2.—Minimum amount of 3-acetyl-4-hydroxycoumarin necessary for the determination of iron^{II}.

The complex was found to obey the Lambert-Beer law at 400 mμ for the concentration range of 1·3–5·5 ppm of iron.

Molar composition of the complex

The molar composition of the complex was determined by Job's[2] method of continuous variations as modified by Vosburgh and Cooper.[3] The optical densities at 400 mμ of the following two solutions, prepared by mixing (a) x ml of 2·0 × $10^{-3}M$ 3-acetyl-4-hydroxycoumarin solution with (10 − x) ml of 2·0 × $10^{-3}M$ iron^{II} solution and (b) x ml of 1·0 × $10^{-3}M$ coumarin solution with (10 − x) ml of iron^{II} solution (where x varied from 1 to 10), were determined employing alcohol as a reference solution. The absorption due to the iron^{II} solution and 3-acetyl-4-hydroxycoumarin solution is negligible at 400 mμ. Hence the function *Y*, defined as the difference between the optical density observed for a given mixture of the constituents and the corresponding optical densities of the respective components for no reaction, was taken in the present case as the observed optical density of the complex solution. The values of *Y* are plotted against x in each case in Fig. 4, in which the peaks occur when the molar ratio of the coumarin to iron^{II} ions is 7·5:2·5, *i.e.* 3:1 in each case. The complex, therefore, has the molar composition FeL_3 where *L* is an ion of the coumarin ligand.

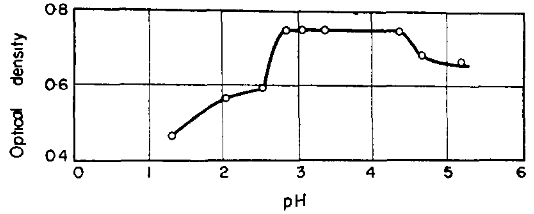

FIG. 3.—Effect of pH on the optical density of the iron^{II} complex.

The molar composition of the iron complex was also verified by the slope ratio method of Harvey and Manning.[4] For this purpose two series of solutions were prepared employing $2{\cdot}0 \times 10^{-3}M$ solutions of the coumarin and of iron^{II}. In one series the iron^{II} concentration was varied, maintaining the concentration of the coumarin constant and in a sufficient excess. In the other, the coumarin concentration was varied maintaining the iron^{II} concentration constant and in a sufficient excess. The optical densities of the solutions of both these series were determined at 400 mμ with alcohol as reference. The obtained values are plotted as the curves P and Q of Fig. 5. In the curves P and Q, only the straight line portions AB and CD, respectively, were taken into account to find out the slopes:

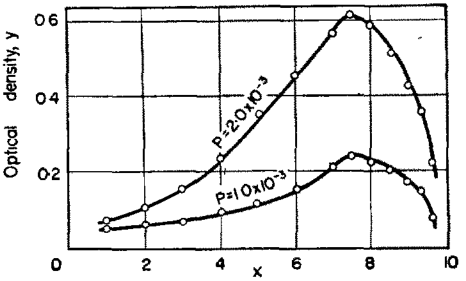

FIG. 4.—Determination of the molar composition of the iron^{II} complex by Job's method of continuous variations.
x ml of P-molar 3-acetyl-4-hydroxycoumarin solution added to (10 − x) ml of P-molar iron^{II} solution, and total volume made to 20 ml with alcohol.

$$\tan \theta_1 = \text{slope of the curve P(AB)} = 0{\cdot}59$$

$$\tan \theta_2 = \text{slope of the curve Q(CD)} = 0{\cdot}19$$

$$\text{Molar ratio of the complex} = \frac{0{\cdot}59}{0{\cdot}19} \simeq 3$$

Thus the slope ratio of the two curves indicates that the molar ratio of the coumarin to iron^{II} in the complex is 3, which confirms the results obtained by using Job's method.

Studies relating to the elucidation of the structure of the above complex are in progress.

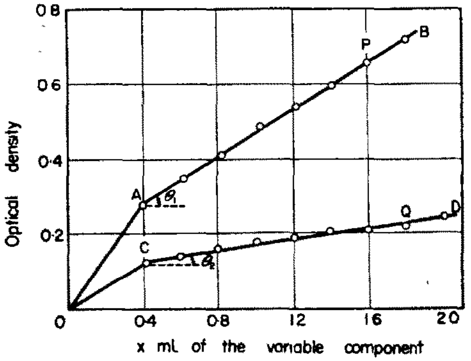

FIG. 5.—Determination of the molar composition of the iron^{II} complex by the slope ratio method.
Curve P: x ml of $2 \times 10^{-3}M$ iron^{II} solution added to 12 ml of $2 \times 10^{-3}M$ coumarin solution and the final volume made to 14 ml with alcohol.
Curve Q: x ml of $2 \times 10^{-3}M$ coumarin solution added to 5 ml of iron^{II} solution and the final volume made to 14 ml with alcohol.

Interference due to foreign ions

The interference due to various cations and anions in the determination of iron^{II} with the reagent was studied and it was found that copper^{II}, molybdate, tungstate and citrate interfered even when present in extremely small quantities. The limits of interference due to the following ions were determined: tartrate (200 ppm), oxalate (10 ppm), nickel^{II} (5·8 ppm), lead^{II} (115 ppm), manganese^{II} (15 ppm), magnesium (125 ppm) and beryllium (4·5 ppm). No interference was observed in the case of chloride, bromide, iodide, thiocyanate, sodium or potassium, even when these ions were present at 200 ppm per 2 ppm of iron.

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Summary—3-Acetyl-4-hydroxycoumarin has been used for the spectrophotometric determination of iron^{II}. With iron^{II} this reagent forms an orange-red complex soluble in 50% (v/v) ethanol. The characteristics of the complex have been studied spectrophotometrically, and its molar composition determined. The complex obeys the Lambert-Beer law at 400 mμ within the concentration range 1·5–5·3 ppm of iron in the reaction mixture. The molar composition of iron^{II}-3-acetyl-4-hydroxycoumarin shows that it contains iron and the coumarin in the molar ratio of 1:3. The limits of interference due to various cations and anions in the determination have been defined.

Zusammenfassung—3-Acetyl-4-oxycumarin wurde zur spectrophotometrischen Bestimmung von Eisen (II) verwendet. Der entstehende orangeröte complex ist in 50% igem (volum) Äthanol löslich. Die Eigenschaften des Komplexes wurden studiert und seine Zusammensetzung spektrophotometrisch ermittelt. Bei 400 mμ ist Beer's Gesetz in einem Konzentrationsbereich von 1·5–5·3 milligramm per Liter erfüllt. Die Zusammensetzung des Komplexes ist Fe:Cumarin 1:3. Störungen durch verschiedene Ionen wurden untersucht.

Résumé—La 3-acétyl-4-hydroxycoumarine a été utilisée pour le dosage spectrophotométrique du fer(II). Le réactif forme avec le fer(II) un complexe rouge orangé soluble dans l'éthanol à 50% (en volume).

Les caractéristiques du complexe ont été étudiées par spectrophotométrie, et sa composition molaire déterminée. Le complexe obéit à la loi de Beer à 400 mμ dans le domaine de concentration 1,5–5,3 p.p.m. de fer dans le mélange réactionnel. Il contient le fer et la coumarine dans le rapport molaire 1/3. Les limites d'interférence de divers cations et anions ont été déterminées.

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Determination of reducing sugars with 3:6-dinitrophthalic acid*

(*Received* 15 *March* 1960)

SEVERAL nitro compounds are now available with which reducing sugars can be determined spectrophotometrically in an alkaline medium. In the authors' laboratory, 3:6-dinitrophthalic acid proved to give the most sensitive and stable colour reaction.[1] This new reagent was successfully used in the

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* Organic Analysis—XXVI. For part XXV see *Chem. Pharm. Bull.* (*Tokyo*), 1960, in press.

present in extremely small quantities. The limits of interference due to the following ions were determined: tartrate (200 ppm), oxalate (10 ppm), nickel^{II} (5·8 ppm), lead^{II} (115 ppm), manganese^{II} (15 ppm), magnesium (125 ppm) and beryllium (4·5 ppm). No interference was observed in the case of chloride, bromide, iodide, thiocyanate, sodium or potassium, even when these ions were present at 200 ppm per 2 ppm of iron.

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determination of glucose in blood and urine by a simple procedure,[2] and also in the estimation of the sugar in the same sample with the naked eye.[3] This communication extends the use of the reagent to the determination of other reducing sugars.

EXPERIMENTAL

Sugars

These were recrystallised from dilute alcohol and dried at 100°, except for maltose and rhamnose which were weighed in the form of the monohydrate. The purity of the sugars was checked by means of melting point determinations.

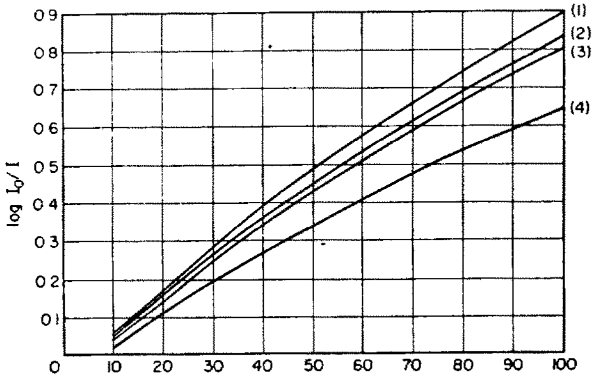

FIG. 1.—Calibration Curves: (1) Xylose and Arabinose, (2) Rhamnose, (3) Glucose, Fructose, and Galactose, and (4) Lactose and Maltose.

Inversion of sucrose

To 10 ml of a sucrose solution which contained 0·1 ~ 1% of the sugar, 3 ml of 0·1*N* hydrochloric acid was added, and heated under reflux in a boiling water bath for 30 min. After cooling, the mixture was neutralised with 3 ml of 0·1*N* sodium hydroxide, then diluted with water to measure 1000 ml.

Colour developing agents and procedure

These were as detailed previously.[2] Two ml of the sample solution, containing 10 ~ 100 μg/ml of reducing sugar, should be used.

TABLE I.—ABSORPTION INTENSITY OF THE DEVELOPED COLOUR OF PENTOSES. MOLECULAR WEIGHT OF XYLOSE/MOLECULAR WEIGHT OF RHAMNOSE = 0·915

Concentration, *μg/ml*		30	50	70	90
Sugar	Rhamnose	0·264	0·448	0·612	0·767
	Xylose	0·285	0·490	0·662	0·821
Ratio of absorption intensities		0·926	0·915	0·925	0·934

RESULTS AND DISCUSSION

The calibration curves for the studied reducing sugars are shown in Fig. 1. Of the pentoses, xylose and arabinose give the same calibration curve, but rhamnose (methylpentose) gives a slightly different curve which is in inverse proportion to the molecular weight (Table I). The calibration curves for glucose fructose, and galactose coincide with each other. Therefore, the configuration of hydroxyl groups of the sugars has no effect on the reducing power to the reagent. This fact is also shown in the case of the disaccharides, lactose and maltose giving the same curve.

It is important to note that fructose gives exactly the same calibration curve as glucose. This fact indicates that sucrose can be determined in the presence of glucose or fructose. In the determination of a mixture of glucose and sucrose, one portion of the mixture is developed for glucose, and another portion is inverted and developed for total invert sugar. The sucrose is calculated from the equation:

$$(\text{Total invert sugar} - \text{Free glucose}) \times 0{\cdot}95 = \text{Sucrose}.$$

The results obtained by this method are shown in Table II. The found values of glucose and sucrose coincide with the calculated ones within a maximum error of ±3% over a wide range of the quantity of glucose and sucrose.

TABLE II.—DETERMINATION OF A MIXTURE OF GLUCOSE AND SUCROSE

Amount calculated, *μg/ml*		Amount found, *μg/ml*		Error, %	
Glucose	Sucrose	Glucose	Sucrose	Glucose	Sucrose
15	30	15·4	30·0	+2·7	0
15	40	14·8	38·8	−1·3	−3·0
15	50	15·0	48·8	0	−2·4
15	60	15·0	60·3	0	+0·5
15	70	15·3	69·7	+2·0	−0·4
15	80	15·1	81·5	+0·7	+1·9
20	50	20·5	49·1	+2·5	−1·8
30	50	30·8	49·6	+2·7	−0·8
40	50	39·9	50·2	−0·3	+0·4

The 3:6-dinitrophthalic acid solution and the alkaline solution are sufficiently stable for long use. This is proved by the absorption intensity of the blank solution which remains about 0·020 ~ 0·025 for several weeks. The calibration curves are reproducible within a maximum deviation of about ±0·01 in the absorption intensity. This value is equivalent to a maximum error of about ±2·5% for monosaccharides and of about ±3% for disaccharides at a concentration level of 50 μg/ml.

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Summary—Reducing sugars are determined in the concentration range 10 ~ 100 μg/ml using 3:6-dinitrophthalic acid as a colour developing agent. Individual pentoses, hexoses, and disaccharides give the same calibration curves, respectively. Sucrose is also determined in the presence of glucose or fructose.

Zusammenfassung—Reduzierende Zucker können in Konzentrationen von 10–100 μg per ml bestimmt werden, wenn 3,6-dinitrophthalsäure als farbentwickelndes Reagens verwendet wird. Individuelle Pentosen, Hexosen und Disaccharide geben ähnliche Eichkurven. Sucrose kann in Gegenwart von Glucose und Fructose bestimmt werden.

Résumé—Les sucres réducteurs sont dosés à des concentrations de 10 à 100 μg/ml en utilisant l'acide 3-6 dinitrophtalique comme réactif coloré. Les pentoses, les hexoses et les disaccharides donnent individuellement des courbes d'étalonnage semblables. Le sucrose peut aussi être dosé en présence de glucose ou de fructose.

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Note on the titration of iodide by the Andrews method

(*Received* 28 *June* 1960)

INTRODUCTION

ANDREWS' method[1] for the determination of iodides involves two major stages:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (1)$$

$$IO_3^- + 2I_2 + 5Cl^- + 6H^+ \rightarrow 5ICl + 3H_2O \quad (2)$$

The second of these is usually said to require the presence of relatively concentrated hydrochloric acid (at least $3N$). Most standard text-books of titrimetric analysis, however, do not make it clear whether hydrochloric acid is specific, nor why it must be so concentrated.

Andrews realised that it was necessary to prevent the hydrolysis of iodine monochloride and the subsequent disproportionation of the hypoiodous so formed. He represented the hydrolysis in terms of a molecular equation:

$$ICl + H_2O \rightarrow HOI + HCl \quad (3)$$

It is now clear, however,[2] that the iodine monochloride is converted to the ion ICl_2^-. In the original form of the titration, it was necessary for this ion to be formed and retained in the aqueous layer so that the presence of iodine in the organic layer (chloroform or carbon tetrachloride) should not be masked by molecular iodine monochloride.

The position of the equilibrium:

$$ICl + Cl^- \rightleftarrows ICl_2^- \quad (4)$$

is, however, reported[3] to be substantially independent of the concentration of hydrochloric acid between $0{\cdot}2N$ and $10N$. Moreover, we have calculated from Faull's data[4] that in a titration of $0{\cdot}1N$ iodate against $0{\cdot}1N$ iodide, a final chloride ion concentration of only $0{\cdot}1N$ would reduce the concentration of free iodine monochloride below the level at which it could interfere with the end-point of the titration.

Once this minimum concentration of chloride ion has been reached, it is not clear why a much higher concentration of hydrochloric acid should be needed to achieve a satisfactory titration. Swift[5] has suggested that a high concentration of hydrogen ions is needed, not to suppress hydrolysis of iodine monochloride, but to increase the rate of reaction (2). The following results provide some experimental support for this suggestion, though the precise function of the hydrogen ion in this reaction is not yet clear.

EXPERIMENTAL

Titrations were carried out in which (a) the concentration of hydrochloric acid was varied, (b) the hydrochloric acid was replaced by combinations of other acids with potassium chloride to give varying concentrations of hydrogen and chloride ion. The results are shown in Table I.

The specific effects of hydrogen and chloride ion on reaction (2) were also investigated (Table II). The concentrations used were too low for satisfactory titration and the extent of oxidation of iodine was measured as a function of time. The effect of indifferent salts was also examined.

Reagents: The reagents used were of AnalaR grade, except for sulphuric acid and carbon tetrachloride. A sample of hydrochloric acid of "analytical reagent quality" liberated a small but significant quantity of iodine from potassium iodide. It probably contained free chlorine and was rejected as unsuitable for this work.

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TABLE I. OXIDATION OF I^- TO ICl_2^-

Series I	Concentration* of HCl, M		Nature of Reaction†
	4·68		A
	2·81		B
	0·93		C
	0·46		D
Series II	Concentration of KCl, M	Concentration of H_3PO_4, M	
	0·13	5·0	D
	0·63	5·0	D
	1·13	5·0	C
	3·00	5·0	A
Series III	Concentration of KCl, M	Concentration of HCl, M	
	3·0	0·0	no reaction
	3·0	0·2	D
	3·0	0·5	C
	3·0	1·0	B
	3·0	2·0	A-B
Series IV	Concentration of KCl, M	Concentration of H_2SO_4, M	
	0·2	2·5	D
	0·5	2·5	D-C
	1·0	2·5	C
	0·2	1·5	D
	0·5	1·5	D-C
	1·0	1·5	C
	0·2	0·5	D
	0·5	0·5	D
	1·0	0·5	D-C

* The concentrations are those obtaining at the end of each titration.

† A: the reaction proceeds at the optimum rate for titration,

B: the reaction is slower than in A, but fast enough for use in titrations,

C: the reaction is too slow for use in titration,

D: the reaction is slower than in C, taking up to 30 min for completion.

Procedure: The titrations (Table I) were carried out with standard solutions of approximately 0·1N potassium iodate (0·025M) and potassium iodide (0·05M). A standard volume, 5 ml, of carbon tetrachloride was used to indicate when the iodine liberated in the first stage had been completely removed. The volumes of solution used were arranged to give the quoted concentrations at the end of the titrations.

In the subsequent experiments (Table II), a standard solution of iodine in carbon tetrachloride was shaken with aqueous solutions of the remaining substances. For each point the carbon tetrachloride layer was separated from the aqueous layer at the stated time, washed quickly with a large volume of distilled water and separated again. The remaining iodine was then determined by titration with aqueous sodium thiosulphate.

The experiments were carried out at room temperature.

TABLE II. OXIDATION OF I_2 TO ICl_2^-

A. Effect of [Cl^-]

	Time, *min*	I_2, % oxidised
(i) 0·2*M* KCl 0·5*M* H_2SO_4	1	22
	2	32
	5	44
	10	50
(ii) 0·5*M* KCl 0·5*M* H_2SO_4	1	61
	2	71
	5	87
	10	89
(iii) 0·2*M* KCl 0·3*M* KNO_3 0·5*M* H_2SO_4	1	20
	2	28
	5	46
	10	52

B. Effect of [H^+]

	Time, *min*	I_2, % oxidised
(i) 0·5*M* H_2SO_4 0·2*M* NaCl	1	28
	2	32
	5	44
	10	52
(ii) 1·5*M* H_2SO_4 0·2*M* NaCl	1	47
	2	66
	5	77
	10	86
(iii) 0·5*M* H_2SO_4 1·0*M* Na_2SO_4 0·2*M* NaCl	1	10
	2	21
	5	24
	10	31

DISCUSSION

(*a*) *Concentration of hydrochloric acid*

From Table I it is clear that, for a satisfactory titration, the solution titrated should be no less than 3*N* in hydrochloric acid at the end of the reaction. Chloride ions must be present in a concentration greater than that required for substantially complete conversion of ICl to ICl_2^-.

Whereas some deficiency in hydrogen ions can be made up by excess of chloride ions (Series III), the reverse is not obviously the case (Series II*). Even in the former case, it appears that the ionic product, [H^+][Cl^-], must correspond to that in 3*M* hydrochloric acid.

(*b*) *Effect of indifferent ions*

From Table II it is clear that indifferent ions either do not seriously affect the rate of reaction (2), or reduce it, depending on the ionic strength of the solution.

This investigation clarifies the conditions needed for satisfactory titration of iodide by the Andrews

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* For this purpose, phosphoric acid is regarded as being, to a first approximation, a monobasic acid.

method. It is not yet clear, however, whether the dependence of the rate of the slow reaction on the concentrations of hydrogen ion and chloride ion is due to their presence as reactants or as catalysts.

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Summary—For a satisfactory determination of iodide by Andrews' method, the concentration of hydrochloric acid in the solution should not fall below 3*N*. A high concentration of each ion is required; that of chloride ion is much greater than is needed for conversion of ICl to ICl_2^-. The effects of varying the concentrations of H^+, Cl^- and indifferent ions on the rate of the slow stage (oxidation of I_2 to ICl) are demonstrated.

Zusammenfassung—Für eine zuverlässige Bestimmung von Jodid nach der Andrews Methode soll die Salzsäurekonzentration in der Lösung nicht unter 3 n absinken. Eine hohe Konzentration für jedes Ion ist nötig. Die Chloridkonzentration ist viel grösser als an sich für die Überführung von JCl in JCl_2^- stöchiometrisch nötig. Der Einfluss wechselnder Konzentrationen von H^+, Cl^- und indifferenten Ionen auf die Geschwindigkeit des langsamen Reaktionschrittes (Oxydation von J_2 zu JCl) wird demonstriert.

Résumé—Pour une estimation satisfaisante de l'iodure par la méthode d'Andrews, la concentration de l'acide chlorhydrique dans la solution ne devrait pas être inférieure à 3 N. Une forte concentration de chaque ion est nécessaire; celle de l'ion chlorure est beaucoup plus grande que cela n'est nécessaire pour la transformation de ICl en ICl_2^-. Les influences des variations des concentrations de H^+, Cl^- et des indifférents sur la vitesse du stade lent (oxydation de I_2 enICl) sont démontrées.

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Contribution to the basic problems of complexometry—III

Some advantages of acetate buffer

(*Received* 2 *May* 1960)

IT is well known, that some bivalent metals can be readily determined by EDTA titrations in a weak acid medium (pH 5–6). In addition, other indicators, Xylenol Orange[1] and Methyl Thymol Blue[2], have been recommended for these titrations because of their brilliant colour changes. Solutions are usually buffered with urotropine. Some cations having incomplete inner orbits, such as copper, nickel, cobalt etc. form substitution-stable complexes with these indicators, thus making direct complexometric titration impossible. It is not possible, for example, to titrate copper using Xylenol Orange or Methyl Thymol Blue, even at higher temperatures, but only copper solutions buffered with urotropine. We have found that by the use of acetate buffer it is possible to titrate copper directly at a temperature of about 70°, using either indicator, with the accuracy of the usual complexometric methods. Recently Přibil[3] discovered that in the direct titration of copper in the cold, after the addition of a small amount of *o*-phenanthroline, the colour change of Xylenol Orange was substantially improved. This phenomenon he explained on the basis of the formation of a substitution-labile copper complex with *o*-phenanthroline, which reacts with EDTA easily at the end-point.

In a detailed study it was found, that α:α'-bipyridyl*, cupferron, ethylendiamine, dicuprale,

* α:α-Bipyridyl at about pH 5·5 may be used like *o*-phenanthroline for masking most of bivalent metals.

method. It is not yet clear, however, whether the dependence of the rate of the slow reaction on the concentrations of hydrogen ion and chloride ion is due to their presence as reactants or as catalysts.

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Summary—For a satisfactory determination of iodide by Andrews' method, the concentration of hydrochloric acid in the solution should not fall below 3*N*. A high concentration of each ion is required; that of chloride ion is much greater than is needed for conversion of ICl to ICl_2^-. The effects of varying the concentrations of H^+, Cl^- and indifferent ions on the rate of the slow stage (oxidation of I_2 to ICl) are demonstrated.

Zusammenfassung—Für eine zuverlässige Bestimmung von Jodid nach der Andrews Methode soll die Salzsäurekonzentration in der Lösung nicht unter 3 n absinken. Eine hohe Konzentration für jedes Ion ist nötig. Die Chloridkonzentration ist viel grösser als an sich für die Überführung von JCl in JCl_2^- stöchiometrisch nötig. Der Einfluss wechselnder Konzentrationen von H^+, Cl^- und indifferenten Ionen auf die Geschwindigkeit des langsamen Reaktionschrittes (Oxydation von J_2 zu JCl) wird demonstriert.

Résumé—Pour une estimation satisfaisante de l'iodure par la méthode d'Andrews, la concentration de l'acide chlorhydrique dans la solution ne devrait pas être inférieure à 3 N. Une forte concentration de chaque ion est nécessaire; celle de l'ion chlorure est beaucoup plus grande que cela n'est nécessaire pour la transformation de ICl en ICl_2^-. Les influences des variations des concentrations de H^+, Cl^- et des indifférents sur la vitesse du stade lent (oxydation de I_2 enICl) sont démontrées.

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Contribution to the basic problems of complexometry—III

Some advantages of acetate buffer

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It is well known, that some bivalent metals can be readily determined by EDTA titrations in a weak acid medium (pH 5–6). In addition, other indicators, Xylenol Orange[1] and Methyl Thymol Blue[2], have been recommended for these titrations because of their brilliant colour changes. Solutions are usually buffered with urotropine. Some cations having incomplete inner orbits, such as copper, nickel, cobalt etc. form substitution-stable complexes with these indicators, thus making direct complexometric titration impossible. It is not possible, for example, to titrate copper using Xylenol Orange or Methyl Thymol Blue, even at higher temperatures, but only copper solutions buffered with urotropine. We have found that by the use of acetate buffer it is possible to titrate copper directly at a temperature of about 70°, using either indicator, with the accuracy of the usual complexometric methods. Recently Přibil[3] discovered that in the direct titration of copper in the cold, after the addition of a small amount of *o*-phenanthroline, the colour change of Xylenol Orange was substantially improved. This phenomenon he explained on the basis of the formation of a substitution-labile copper complex with *o*-phenanthroline, which reacts with EDTA easily at the end-point.

In a detailed study it was found, that α:α′-bipyridyl*, cupferron, ethylendiamine, dicuprale,

* α:α-Bipyridyl at about pH 5·5 may be used like *o*-phenanthroline for masking most of bivalent metals.

o-phenylenediamine and glycine behave in the same manner as *o*-phenanthroline. Only milligram amount of these substances are required in the direct titration of copper using either indicator, if the solutions are buffered with sodium acetate. For the copper titration, the addition of 1 mg of dicuprale, 2 mg of cupferron, 20 mg of *o*-phenylenediamine, 25 mg of ethylenediamine or 300 mg of glycine are sufficient. When solutions are buffered with urotropine, it is necessary to use a higher concentration of these substances to produce the same effect (0·2 g of *o*-phenylenediamine, 0·3 g of ethylenediamine or 1 g of glycine). In this case, also, the success of the titration depends on the order in which the substances are added. The favourable effect of the additives is manifested only when their addition takes place before the buffer solution is added.

Even gram amounts of these substances do not affect the titration of copper favourably at room temperature. Only *o*-phenanthroline or α:α′-bipyridyl (0·1 mg) are effective, without regard to the order of addition.

It is advantageous, for routine analysis, to use sodium acetate buffer solution with addition of one of the above-mentioned complex-forming substances.

This phenomenon is not only important for the direct determination of copper, but its consequence is general. Traces of copper do not influence the consumption of EDTA solution but substantially obscure the colour change of Xylenol Orange or Methyl Thymol Blue. When the acetate buffer is used this disturbing effect is completely eliminated.

The proper buffer solutions, with the addition of complex-forming substance can also be used for the determination of copper in the presence of other compex-forming substances. For such titrations a back-titration with lead nitrate against Xylenol Orange was previously proposed.[4] Correct buffering permits direct titration of the copper. As before, *o*-phenanthroline or α:α′-bipyridyl was found to be the best additive.

The reason for the different behaviour of urotropine and acetate buffers has not yet been satisfactorily solved. Electrometric control has proved that the pH of the solution is not a decisive agent in influencing the phenomenon. One possible explanation is that sodium acetate functions here as an "auxiliary complex-forming agent" as well as the *o*-phenanthroline or other additive. It is effective only in higher concentrations. This is in agreement with the relative stabilities of the *o*-phenanthroline and acetate complexes of bivalent copper. Formation of the urotropine complex with copper, which has a disturbing effect on the mechanism of the indicating reaction, is a possible clue to the explanation. This opinion is supported by the fact that such substances as, for example, triethanolamine, which also form complexes with copper but are not capable of functioning as auxiliary complex-forming substances, according to Přibil, prevent the titration of copper, even where the solution is buffered with sodium acetate and is titrated at higher temperature. The behaviour of triethanolamine is thus similar to that of urotropine; it disturbs the indication of the end-point even in the presence of complex-forming substances. A more precise explanation may be possible after detailed study.

Acknowledgement—It is our pleasant duty to thank Dr. Rudolf Přibil, Analytical Laboratory, Czechoslovak Academy of Sciences, for his active interest in this work.

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Summary—Acetate buffer, in conjunction with additives such as *o*-phenanthroline or α:α′-bipyridyl, permits the titration of metallic cations such as copper with EDTA in weakly acid medium, using Xylenol Orange of Methyl Thymol Blue as indicators. In this it is superior as a buffer to the more generally used urotropine. The nature of its action is discussed.

Zusammenfassung—Die Verwendung eines Acetatpuffers in Verbindung mit Zusätzen wie o-Phenanthrolin oder α,α-Dipyridyl gestattet die Titration von Metallionen wie Kupfer mit EDTA in schwach saurem Medium unter Verwendung von Xylenolorange oder Thymolblau als Indicatoren. Die Pufferkombination ist der üblichen Verwendung von Urotropin überlegen. Der Mechanismus der Reaktion in der Puffermischung wird diskutiert.

Résumé—Le tampon acétate, en liaison avec des additifs tels que l'o-phénanthroline ou l'α-α′-bipyridyle permet le titrage de cations métalliques comme le cuivre par l'EDTA en milieu faiblement acide, le xylenol orange ou le bleu de méthyl thymol étant utilisés comme indicateurs.

Pour ce titrage, ce tampon est supérieur à l'urotropine plus généralement utilisée. La nature de son action est discutée.

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Determination of oxygen in zirconium by the platinum flux technique

(*Received* 28 *June* 1960)

OXYGEN in zirconium is often determined by the Walter method[1] at 2100° or, on a microscale, by the platinum bath method.[2] The practical difficulties involved in the Walter method, particularly the use of graphite chips in the crucible, were examined in an earlier paper.[3] Bennett and Covington[4] reported that zirconium, when present as an alloying constituent in titanium, did not interfere with the oxygen determination by the platinum bath method at 1900°. Smiley[5] suggested and Hansen, Mallett and Trzeciak[6] developed the platinum flux technique for the analysis of titanium and enumerated the advantages of this over the platinum bath method. The present paper deals with the application of the platinum flux technique to the analysis of zirconium for its oxygen content.

EXPERIMENTAL

Apparatus

The vacuum fusion apparatus was described earlier.[7]

Standard sample

A known amount of gaseous oxygen was added to a rod of iodide-zirconium in a Sieverts apparatus. Then the rod was heated at 1000° for 5 hr to diffuse and level the oxygen content. Further homogenisation was effected by arc melting the metal twice in an argon atmosphere.

Effect of temperature and flux-to-sample ratio

When a platinum flux was used with titanium, a brilliant flash was observed after each sample was dropped into the crucible. Smiley reported that, with a platinum bath, only the first sample dropped produced a flash. This is probably due to the exothermic formation of a compound between titanium and platinum. Since a similar reaction was anticipated for zirconium, the literature on the binary compounds with platinum was reviewed to arrive at a suitable ratio for the initial experiments. The compound which contains the highest amount of platinum is $ZrPt_3$.[8] The weight ratio of platinum to zirconium in this compound is approximately 6:1. Allowing an excess for quantitative reaction, a ratio of 10:1 was fixed for the initial experiments. An extraction temperature of 2100° was arrived at from a consideration of the operating temperature employed in the application of the Walter method to the analysis of zirconium. As the extraction of oxygen from the synthetic standard under these conditions was apparently quantitative, further experiments were carried out at each of several successively lower temperatures varying the flux-to-sample ratio. The results are given in Table I.

The extraction of oxygen was complete at temperatures of 1850°–2100°, with flux-to-sample ratios ranging from 10:1 to as low as 4:1. The extraction period was 20 min in most cases. Conditions under which the extraction had to be continued 5–10 min longer for completion, included flux ratios above 8:1 at 2100°, and sometimes at ratios of 4·2:1 and below at 2000° and lower. At 1800° and 1700°, the recovery of oxygen was only about 95%. Hence, the final experimental conditions, considered best for the extraction of oxygen from about 0·10-g samples, were 1900°–1950°, 20 min extraction, and a ratio of flux to sample of about 5:1.

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Procedure

Samples weighing about 0·10 g were prepared in the normal way, cutting with a hacksaw, abrading the surfaces with a smooth flat file, degreasing with acetone (C.P.), and weighing. Approximately equal lengths of platinum wire of 1-mm diameter were cut, each length weighing about 0·5 ± 0·02 g. The samples were wrapped in the wire and loaded in the sample arm of the apparatus preceded by a 0·5-g sample of the platinum itself. The furnace assembly was prepared as described earlier.[3] The system was pumped down and degassed for 2 hr at about 2250°. By this time an outgassing rate lower than 0·05 ml STP for 5 min at 2250° was achieved. The temperature was then lowered to 1900°–1950° and maintained there throughout the run. The sample of platinum was dropped and gases were collected for 20 min. These gases constituted the blank for both the platinum flux and the furnace. The gases were passed over copper^{II} oxide at 325° and analysed by the fractional freezing method. The zirconium samples were dropped and analysed in the same manner as the flux. This procedure of analysing the flux gives the corrections due to the furnace blank and the gas content of the flux in a single step.

TABLE 1.—VARIATION OF PLATINUM FLUX-TO-SAMPLE RATIO AT DIFFERENT TEMPERATURES

Weight		Ratio of flux to sample	Extraction temperature, °*C*	Oxygen, *weight %*
Sample, *g*	Platinum flux, *g*			
0·1635	1·675	10·3	2100	0·132*
0·1580	1·616	10·2	2100	0·127*
0·2040	2·021	9·9	2100	0·127*
0·2960	2·963	10·0	2100	0·135*
				Average 0·130
0·1166	0·342	8·1	2100	0·131
0·1144	0·919	8·0	2100	0·132
				Average 0·132
0·0895	0·532	6·0	2100	0·132
0·1135	0·699	6·2	2100	0·130
				Average 0·131
0·1077	0·649	6·0	2000	0·134
0·1005	0·597	5·9	2000	0·132
				Average 0·133
0·0995	0·422	4·2	2000	0·127
0·1050	0·442	4·2	2000	0·138*
				Average 0·133
0·0955	0·484	5·1	1900	0·133
0·1090	0·457	4·2	1900	0·131*
				Average 0·132
0·1010	0·505	5·0	1850	0·133
0·1090	0·431	4·0	1850	0·138*
				Average 0·136
0·0990	0·501	5·1	1800	0·124
0·0343	0·418	4·4	1800	0·122
				Average 0·123
0·0950	0·470	4·9	1700	0·122
0·0870	0·391	4·5	1700	0·127
				Average 0·125

* Extraction of gases required 5 to 10 min longer than the usual 20 min.

RESULTS

Table II contains the analytical results for iodide-zirconium (the base material) and a synthetic standard sample. Standard deviations of 0·0023 and 0·0038 weight %, and coefficients of variance of 10% and 2·9%, were obtained, respectively, at the 0·023- and 0·131-weight % oxygen levels. Because of the excellent results obtained with the 0·10-g samples, no attempt was made to analyse samples of greater weight. Also, no significant gain in precision was expected, since an increase in sample size would necessitate an increase in blank correction for the gas content of the flux. With 0·5 g of platinum, a total blank for 20 min at 1900° was of the order of 0·05 ml STP.

After a run of 8 samples, the furnace was allowed to cool to room temperature in vacuum overnight. The next day, the crucible and contents were reheated and degassed at 1900°, and two more samples were analysed. The results for these are the last two listed for the synthetic standard in Table II. They show no difference from the first-day values listed immediately above them.

The first two values listed for the standard were obtained in series with the base analysis.

TABLE II.—ANALYSIS OF ZIRCONIUM SAMPLES BY THE PLATINUM FLUX TECHNIQUE AT 1900°

Sample	Weight		Ratio of flux to sample	Oxygen, *weight %*
	Sample, *g*	Platinum flux, *g*		
Iodide-zirconium (base)	0·1080	0·499	4·6	0·022
	0·1075	0·504	4·7	0·024
	0·1088	0·519	4·8	0·022
	0·1063	0·501	4·7	0·022
	0·1045	0·498	4·8	0·021
	0·1030	0·509	4·9	0·020
	0·1065	0·483	4·5	0·023
	0·1080	0·493	4·6	0·028
	0·1015	0·505	5·0	0·022
	0·0995	0·486	4·9	0·021
				Average 0·023 ± 0·002
Synthetic* sample	0·0923	0·394	4·3	0·134
	0·0760	0·338	4·5	0·136
	0·0945	0·466	4·9	0·132
	0·1045	0·512	4·9	0·124
	0·0980	0·475	4·8	0·131
	0·1020	0·485	4·8	0·133
	0·0893	0·460	5·2	0·135
	0·1014	0·484	4·8	0·127
	0·1044	0·510	4·9	0·128
	0·1020	0·490	4·8	0·129
	0·1037	0·495	4·8	0·136
	0·0910	0·465	5·1	0·132
				Average 0·131 ± 0·003

* 0·023 base value + 0·102 added oxygen = 0·125 weight % of oxygen expected. The slightly higher average value is probably due to pick-up of a small amount of oxygen during arc melting.

DISCUSSION

It is normally considered that a higher operating temperature is required for the extraction of the oxygen from zirconium than from titanium. This is because of the difference in the free energies of formation of their oxides. The results of this study showed, however, that the extraction of oxygen from zirconium was quantitative at the same temperature of 1850° as reported in the case of titanium analysis,[6] using the same platinum flux method. Similarly Bennett and Covington[4] observed that, with a platinum bath method at 1900°, zirconium did not interfere in the analysis of titanium-base alloys for their oxygen contents. This apparent anomaly may be due to the exothermic reactions involved. Successful platinum flux analyses of both titanium and zirconium are initiated by a bright flash shortly after the sample enters the crucible. Although reactions with both metals start at the same temperature, the actual temperature of the flash may be different in the two cases. During the flash, conditions are established for the completion of the extraction reaction at the set temperature of the furnace.

It may be mentioned in this context that Booth, Bryant, and Parker[2] worked with the platinum bath method on a microscale and recommended an optimum temperature of 1880° ± 20° for titanium, which is slightly higher than the optimum temperature of 1860° ± 20° employed by them for the zirconium analysis. But they, also, stated that the extraction of oxygen from zirconium was complete in a temperature range of 1700° to 1950° without explaining how a fluid bath was obtained at 1700° with platinum (melting point, 1774°). In the present study, the extraction of oxygen from a homogeneous sample was only of the order of 95% at 1700° and 1800°, as shown in Table I. Allowing a margin in the measurement and control of temperatures, 1900°–1950° was finally recommended.

The atomic ratio of zirconium to platinum, considered as optimum, corresponds approximately to 1:2. The atomic ratio of titanium to platinum employed[6] by Hansen *et al.*, also works out to be the same. This, again, points to the similarity in the nature of reactions taking place in both cases.

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Summary—The platinum flux technique, well established for the determination of oxygen in titanium, was successfully applied to the analysis of zirconium for its oxygen content after a systematic study of the optimum experimental conditions. The extraction of oxygen was complete in 20 min in the temperature range of 1850 to 2100° with a ratio of flux to sample of about 4·5:1 to 8:1. Statistical analysis of the results on a homogeneous sample gave a standard deviation of 0·0038 weight% and a coefficient of variance of 2·9% at a level of 0·131 weight % of oxygen in zirconium. The recommended experimental conditions are a 0·1-g sample, a 5:1 flux-to-sample ratio, and 20 min extraction at 1900°–1950°.

Zusammenfassung—Die gut arbeitende Platin-Schmelz-Methode zur Bestimmung von Sauerstoff in Titan wurde nach eingehender Studie der experimentellen Bedingungen erfogreich auf die Bestimmung des Sauerstoffgehaltes von Zirkonmetall angewendet. Die Extraktion des Sauerstoffes war nach 20 Minuten vollständig bei einer Temperatur von 1850–2100° und einem Verhältniss Flussmittel: Probe von etwa 4,5:1 bis 8:1. Statistische Auswertung der Resultate an homogenen Proben ergab eine Standardabweichung von 0,0038 Gewichts% und einen Variationskoeffizienten von 2,9% bei 0,131% Sauerstoff in Zirkon. Die empfohlenen experimentellen Bedingungen sind: 0,1 g Probe, 5:1 Verhältnis von Flussmittel zu Probe und 20 Minuten Extraktion bei 1900–1950°.

Résumé—La technique du fondant au platine, bien connue pour le dosage de l'oxygène dans le titane, a été appliquée avec succès à l'analyse de la teneur en oxygène du zirconium après une étude systématique des conditions expérimentales les meilleures. L'extraction de l'oxygène était complète en 20 minutes dans le domaine de température 1850–2100° avec un rapport du fondant à l'échantillon d'environ 4,5/1 à 8/1. L'analyse statistique des résultats sur un échantillon homogène donnait un écart standard de 0,0038 pour cent en poids et un coefficient de variance de 2,9 pour cent pour une teneur en oxygène du zirconium de 0,131 pour cent en poids. Les conditions expérimentales recommandées sont: un échantillon de 0,1 g, un rapport du fondant à l'échantillon de 5/1 et 20 minutes d'extraction à 1900–1950°.

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LETTERS TO THE EDITOR

SIR:

I read in the May issue of *Talanta* the letters of F. Solymosi[1] and of B. R. Sant and S. B. Sant[2] regarding their discussion on quantitative oxidations by potassium ferricyanide. I personally do not know any of the authors, and have never done similar investigations; therefore, I think that I can consider myself impartial.

I really do not know who is right in the discussion, whether B. R. Sant and S. B. Sant gave enough credit to F. Solymosi in their paper,[3] and I do not want to deal with this question. Unfortunately, however, each letter contained one remark which, I think, does not fit in a scientific communication. Please let me discuss this question very briefly.

F. Solymosi when dealing with the paper of S. B. Sant[4] raised the question in his letter[1] "whether slight changes in a procedure warrant a fresh scientific publication". In my opinion, the editor of a scientific journal and his editorial board have the exclusive right to decide whether a paper should or should not be published in that journal. Naturally everybody has the right to criticise the *contents* of the paper but not the fact whether its publication was justified or not.

B. R. Sant and S. B. Sant when answering[3] Solymosi's criticism, are not satisfied with a scientific answer ("In our opinion . . . any titration is . . . more convenient . . . if it can be performed at room temperature") but go further and mention, as a final thrust, that the "question arises . . . whether the same work by the same author need be published in two different journals".[5,6]

This statement raises the feeling that the authors were not sure that their scientific answer was strong enough, and wanted, therefore, to add a subjective remark to it. Besides the fact that there should be no place for such malicious remarks in a scientific communication, the statement by B. R. Sant and S. B. Sant demonstrates that they did not inform themselves.

It is well known that smaller countries, whose language is not understood in other countries, are accustomed to publishing scientific journals in the accepted international scientific languages (English, French, German) which contain, in addition to original publications, the text of some papers already published in a journal in the regional language. Such a journal, is, as you know, for example, the Collection of Czechoslovak Academy of Sciences.

In addition to this, it should not be forgotten that particularly in the Eastern-European countries, the Academy of Sciences is the highest scientific board and it is an honour for somebody who is not a member of the Academy to have the opportunity for a member to present his paper before a meeting of a section of the Academy. In practice, works are mostly presented "officially" which have already been published elsewhere. On the other hand, the papers which are presented in such a manner are then published automatically in one of the journals of the Academy. I think that this is the custom, for example, at the French Academy of Sciences (and the papers are then published in the Comptes Rendus des Scéances de l'Académie des Sciences); and the Hungarian Academy of Sciences works similarly, publishing the presented papers in one of its journals such as the Acta Chimica Academiae Scientiarum Hungaricae.

In Solymosi's case, it is quite natural that he should ask to present his work, which was already published in a Hungarian-language scientific journal (Magyar Kémiai Folyóirat, which is the journal of the Hungarian Chemical Society), before the chemical group of the Academy. This then resulted later (it is a two-year-difference in the two publications!) in the publication in the Acta Chimica.

I would like to repeat my statement at the beginning of my letter: I have no relation with any of the authors, and I am not working in their field. I felt, however, that for the case of scientific objectivity, the above mentioned facts should be mentioned.

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23 *August* 1960

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SIR:

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Israel Atomic Energy
Commission Laboratories, Rehovoth
21 September 1960.

Y. MARCUS

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[1] F. Habashi, *Talanta*, 1959, **2**, 380.
[2] C. E. Crouthamel and C. E. Johnson, *Analyt. Chem.*, 1952, **24**, 1780.
[3] Y. Marcus, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, United Nations, Geneva, 1958, Vol. 3, Processing of Raw Materials, p. 465.

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[1] F. Solymosi, *Talanta*, 1960, **4,** 211.
[2] B. R. Sant and S. B. Sant, *ibid.*, 212.
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[5] F. Solymosi, *Magyar Kém. Foly.*, 1956, **62,** 318.
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Talanta, 1960, Vol. 5, pp. 290 to 292. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Oxidation-Reduction Potentials of Organic Systems. W. Mansfield Clark. The Williams and Wilkins Company, Baltimore, 1960. pp. xi + 584. $13.50

The present reviewer has frequently had the opportunity to refer people studying the oxidation-reduction behaviour of organic compounds to the magnificent series of fundamental studies on that subject, which were made by W. Mansfield Clark and his co-workers during the period of 1923 to 1931, and which were published as Hygienic Laboratory Bulletins and Supplements to the Public Health Reports under the general title of "Studies of Oxidation-Reduction." Consequently, the reviewer welcomed with keen anticipation the appearance of the present volume by Dr. Clark, to whom contemporary chemists and biochemists, indeed all scientists and technologists, owe a great debt not only for his labours in the area indicated by the title of the volume, but also because of his pioneering work on pH. Those of us who started in chemistry during the nineteen twenties and thirties appreciate the impressive contribution to experimental and theoretical chemistry made by Dr. Clark's classic monograph, *The Determination of Hydrogen Ions* (first edition, 1920; third edition, 1928).

The present volume is an individualistically designed work which must be judged in its own terms. As one might expect, it is lucidly written; an added pleasure is the witty presentation (when will editors and authors again realise that scientific literature need not be necessarily poorly, or at least dully, written).

The first three chapters (106 pages) review the historical development of the general area of oxidation-reduction, relevant areas of thermodynamics, and the often confusing conventions and definitions which have accumulated in electrochemistry, including the omnipresent question of the signs to be used on potentials. Chapter 4 (42 pages) indicates how the relation between a cell reaction and the measured electromotive force of the cell has been formulated, the role of pH, and the reporting and interpretation of data. Chapter 5 (11 pages) deals with the rectification of experimental redox titration curves by the method of Reed and Berkson, which utilises the "ideal" portion of the curve. Chapters 6 to 8 (74 pages) consider some of the complications which are introduced by the nature of the chemical species involved in the cell reactions, specifically with the modifications which need to be made in the primary equations to account for the formation of dimers, semiquinones (intermediate free radicals), and co-ordination compounds.

Chapters 9 to 11 (87 pages) deal with experimental factors, including the effects of liquid junction potentials, the experimental standardisation of potential and pH scales, and the general techniques used in precise potentiometric measurement.

Chapter 12 (9 pages) on criteria for evaluating the reliability of oxidation-reduction potential data is followed by a chapter (26 pages) on miscellaneous topics (polarography, kinetics, oxidation-reduction in living cells). These serve to introduce Chapter 14 (162 pages) which is a massive and amazing compilation of data on what must be every reversible organic oxidation-reduction system for which adequate data are available, ranging from quinone-hydroquinone to systems that can be equilibrated with the DPN and TPN systems. The hundred tables of data in the latter chapter are supplemented by the text of the chapter, which lucidly and helpfully guides the reader in the evaluation and interpretation of the data given.

The text abounds in illustrative examples and critical analyses of perhaps overly complacently accepted scientific conceptions. The bibliography is delightfully convenient in including the titles of all of the papers listed.

The reviewer was much impressed by this synoptic picture of an area which is of such fundamental importance in the understanding not only of many chemical processes, but also in the elucidation of the oxidation-reduction processes which are so basic in biological systems. One might pick many things in the volume with which to disagree. One might argue about some of the specific interpretations made by the author in respect to thermodynamic and electrochemical conventions.

The reviewer would have liked a more extensive consideration of the problem of the deviation of organic oxidation-reduction systems from reversibility. However, the present volume should be judged not for what it is not, but for what it is; taken as a whole, the volume is a major contribution which can be strongly recommended to all concerned with the oxidation-reduction behaviour of organic systems both for a review of the fundamentals in the area and for stimulation in the furtherance of one's own specific research interests.

Dr. Clark has further put scientists in debt to him for this stimulating volume.

PHILIP J. ELVING

Électrochimie Theorique. EUGÈNE DARMOIS et GENÈVIEVE DARMOIS. Masson et Cie., Paris 1960. Pp. vi + 239.

THIS small book, in the French language, is concerned entirely with the fundamentals and basic theory of electrochemistry in a broad sense of the term. The treatment commences with a brief historical introduction, followed by a discussion of the ionic theory and Faraday's laws. This leads into a discussion of equivalent conductivity, transport numbers and the mobility of ions, together with the effects of hydration and viscosity. Throughout the book thermodynamic aspects are simply and clearly outlined and the more important equations are given.

A comparatively large space is devoted to the properties and anomalies of strong electrolytes and ionic interactions. The Debye-Hückel theory and more recent studies are adequately described. Galvanic cells of all types are given a comprehensive treatment with which is associated hydrogen ion concentration, pH, overvoltage and modern theories of acids and bases. The logical sequence of the book would have been improved if this large section had followed directly after the Chapter on E.M.F. and activity coefficient. Instead, these are separated by the Chapters on strong electrolytes and those dealing with the optical properties of electrolyte solutions and fused salt melts.

The wide coverage of the book is shown by the fact that it includes, in addition to the above, Chapters on colloidal electrolytes, polarisation and polarography, double-layer capacity phenomena and electrocapillarity, electro-osmosis and electrophoresis, electropolishing and solid electrolytes and semiconductors. The electrochemistry of gases is discussed in detail, including discharge phenomena and electrochemical reactions and products in the gas phases. Short Chapters at the end of the book give brief notes on various analytical applications and electrodeposition.

The inclusion of so great a volume of material on so many diverse topics in so small a book has been achieved by keeping the written text to an absolute minimum and relying on simple diagrams and equations. For this reason it is easy to read. It should prove attractive to the student and to those who require to make reference of the principles of the subject. Very little of a practical nature is included and the Chapter on analytical applications is too short and lacking in detail to be of real value.

The binding is flimsy and the type too small for comfort, but it is otherwise an excellent and up-to-date book which is welcomed and can be recommended.

G. F. REYNOLDS

Deutsche Einheitsverfahren zur Wasser Untersuchung. Fachgruppe Wasserchemie, Gesellschaft Deutscher Chemiker. Third Edition. Verlag Chemie, Weinheim, 1960. Pp. 88 in Ring Binder. DM 20.—.

THIS is the first part of the third edition of standard physical, chemical and bacteriological methods for the examination of water, sewage, sewage sludge and boiler water, prepared by a group of chemists of the German Chemical Society. It is well produced in loose-leaf form to enable improved methods of analysis to replace existing procedures without the need to await revision of the whole book.

In the physical section methods for measuring turbidity, temperature, reaction, β-radiation are described. Spectrographic, flame photometric and absorption spectroscopic methods are referred

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to briefly. Determinations of sulphite, sulphide, cyanide, thiosulphate and thiocyanate in water are described in adequate detail. The section on the determination in the ionic form of those heavy metals, zinc, nickel and copper found in water or polluted waters is the best in the collection of methods described, and is equalled only by the authoritative description of methods for determining phenols.

A useful feature of the book is the brief account of the theoretical basis of each method, with mention of interfering substances and an indication of the range of concentrations for which the method is suitable. References to the literature are either sparingly given or omitted altogether. The book is a collection of practical, well tried methods of analysis.

S. H. JENKINS

Talanta, 1960, Vol. 5, p. 293. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The B.S.I. News announces the following new British Standards:

B.S. 1748: *Methods for the analysis of copper alloys*: *Part* 6: 1960. *Tin (nickel coil reduction method).* This specifies reagents required, recommended methods of sampling, and test procedure for the determination of tin in alloys having a tin content between 1·0 and 14·0%. The method is applicable to phosphor bronze and gun metals. (Price 3s.)

Part 7: 1960. *Silicon (photometric method).* This specifies reagents required, recommended methods of sampling, and test procedure for the determination of silicon in alloys having a silicon content between 0·005 and 0·2%. The method is applicable to phosphor bronze and gun metals. (Price 3s.)

Part 8: 1960. *Phosphorus (photometric method).* This specifies reagents of phosphorus in alloys having a phosphorus content up to 1·20%. The method is applicable to all types of copper alloys provided a suitable compensating solution is used when elements are present which would otherwise interfere in the optical density determination. (Price 3s.)

B.S. 1121: *Methods for the analysis of iron and steel: Part* 41: 1960. *Lead in carbon and low alloy steel.* This specifies a gravimetric method applicable to carbon steels and low alloy steels containing chromium, copper, molybdenum and nickel and with lead contents up to 0·05%. Tin up to 0·25% and tungsten up to 2·0% do not interfere. (Price 3s.)

This method supersedes B.S. 1121: Part 1C.

The following amendment slips to British Standards are also given:

B.S. 604: 1952. *Graduated measuring cylinders. Amendment No.* 4: *PD* 3783. (Gratis).
B.S. 733: 1952. *Density bottles. Amendment No.* 2: *PD* 3763. (Gratis).
B.S. 1017: *Part* 1: 1960. *Sampling of coal. Amendment No.* 1: *PD* 3796. (Gratis).
B.S. 1797: 1952. *Tables for use in the calibration of volumetric glassware. Amendment No.* 2: *PD* 3766. (Gratis).

Talanta, 1960, Vol. 5, p. 294. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric determination of manganese^{II} with benzohydroxamic acid: DWIGHT O. MILLER and JOHN H. YOE. (15 *July* 1960).

The fluorometric determination of *o*-phthalic acid: GLEN A. THOMMES and ELMER LEININGER. (15 *July* 1960).

Analytical applications of 3-acetyl-4-hydroxycoumarin—III: Gravimetric determination of zirconium and titanium; A. N. BHAT and B. D. JAIN. (26 *July* 1960).

The rapid determination of water in magnesium perchlorate desiccant. G. FREDERICK SMITH. (26 *July* 1960).

Effect of chloride ions on nitrate determinations by Leithe's method: CARLA HEITNER-WIRGUIN and DEBORA FRIEDMAN. (30 *July* 1960).

Deuterium analysis by infrared spectrophotometry. (MRS) M. A. MACKENZIE and R. NORMAN JONES. (1 *August* 1960).

The co-crystallisation of ultramicro quantities of molybdenum with α-benzoinoxime: Determination of molybdenum in sea water. HERBERT V. WEISS and MING GON LAI. (3 *August* 1960).

Indirect neutron absorption. W. WAYNE MEINKE. (4 *August* 1960).

Tetracyanoethylene chemistry. Indirect photometric determination of anthracene in naphthalene. GEORGE H. SCHENK and MARA OZOLINE. (5 *August* 1960).

Applications of infrared spectroscopy, III: The simultaneous determination of methoxyl and ethoxyl groups. D. M. W. ANDERSON and J. L. DUNCAN. (10 *August* 1960).

Applications of complementary tri-stimulus colorimetry: II; A least squares method applicable to multicomponent systems. HERMANN FLASCHKA. (12 *August* 1960).

Investigations with iridium-192 of separations of platinum and rhodium from iridium, I: K. W. LLOYD and D. F. C. MORRIS. (12 *August* 1960).

Investigations with iridium-192 of separations of platinum and rhodium from iridium, II: K. W. LLOYD and D. F. C. MORRIS. (12 *August* 1960).

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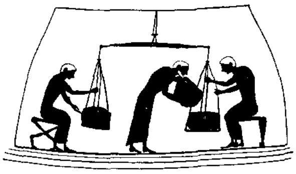

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(*Names of authors of books reviewed are in italics*)