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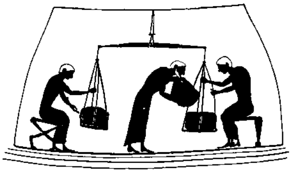

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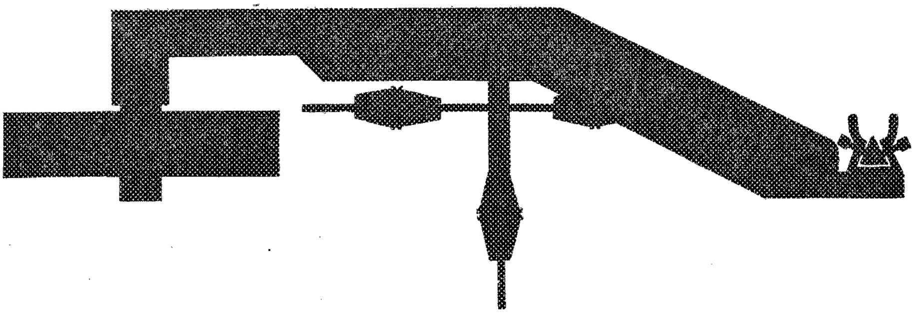

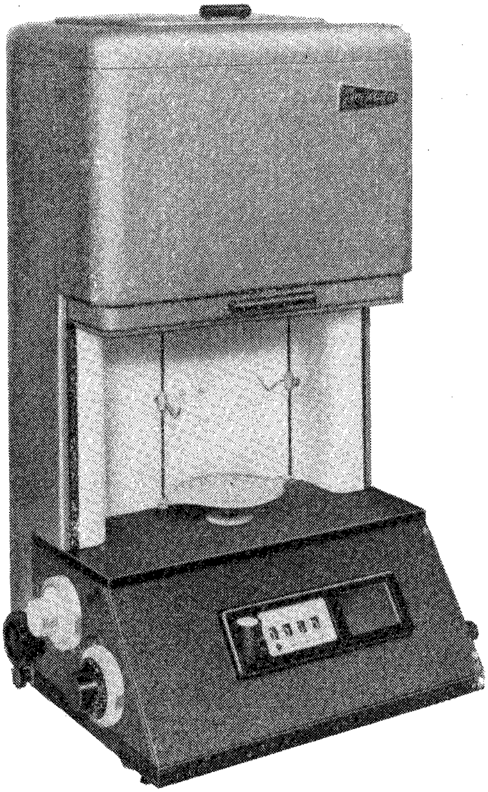

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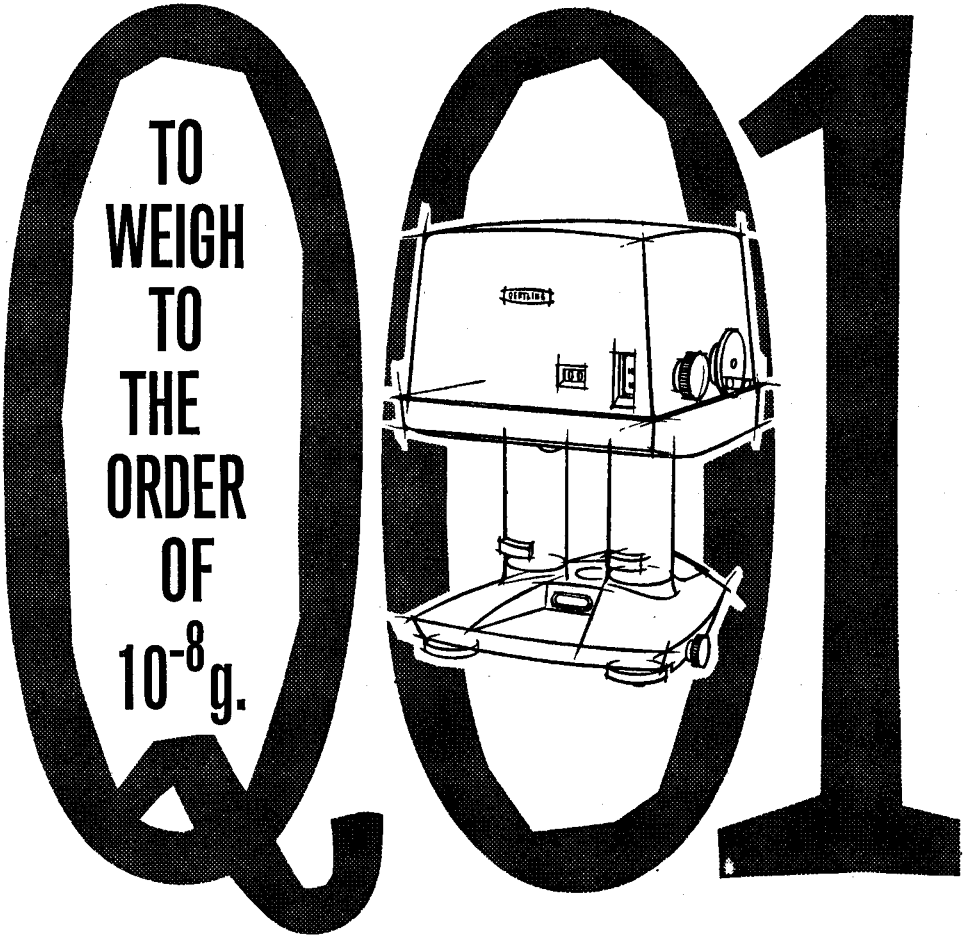
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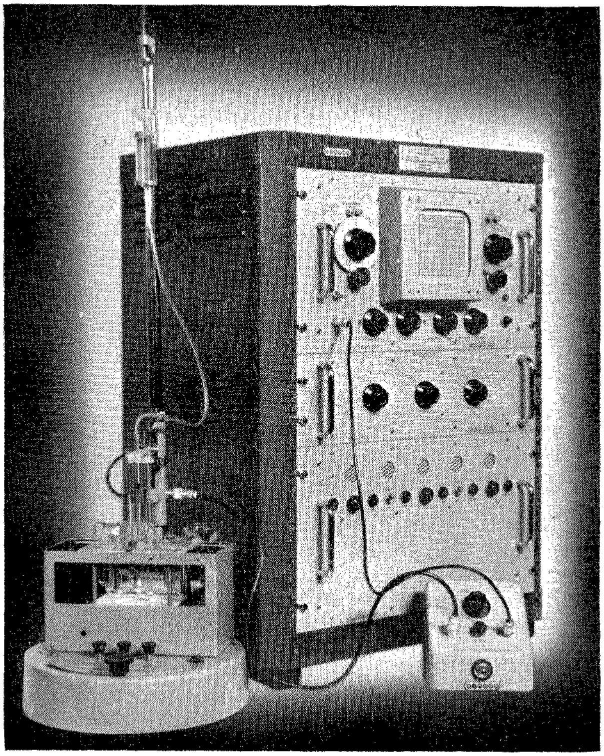

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A CRITICAL REVIEW OF METHODS OF ISOLATING AND SEPARATING THE SIX PLATINUM METALS

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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 foı 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.

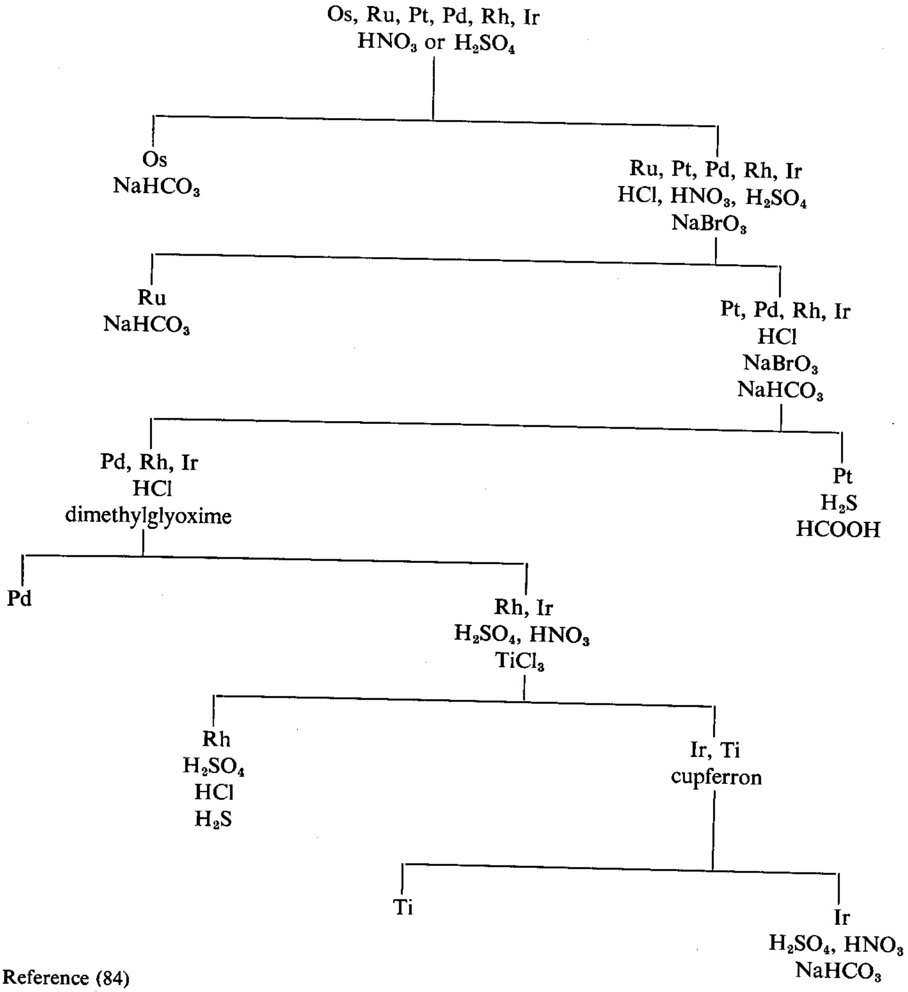
SEPARATIONS FROM AQUEOUS MEDIA

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

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

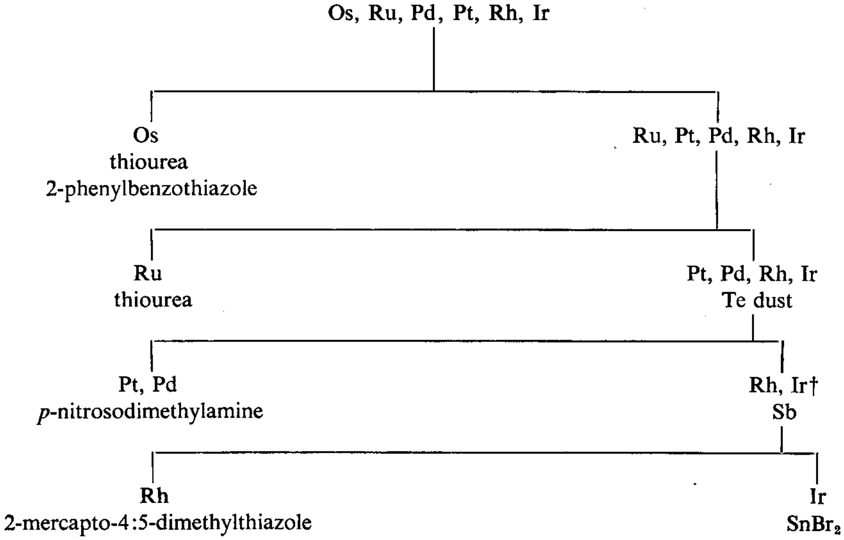


* Reference (84)

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 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 $6N$ 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 5–7*N* hydrochloric acid. Tetraphenylarsonium hexachlorosmate in 0·1–0·3*N* 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 1·0*N* 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 0·5M hydrochloric acid, then rhodium was eluted slowly with 2M hydrochloric acid, and finally iridium with 4–6M 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 6M 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 6M hydrochloric acid at 74°. The first colourless fraction of the effluent contained the iridium^{IV}-thiourea complex which was eluted with 3M 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:

$$G_I = I + C_I C + L_I L + K_I K + B_I \qquad (^{131}I) \tag{1}$$

$$G_C = I_C I + C + L_C L + K_C K + B_C \qquad (^{137}Cs) \tag{2}$$

$$G_L = I_L I + C_L C + L + K_L K + B_L \qquad (^{140}Ba\ ^{140}La) \tag{3}$$

$$G_K = L_K I + C_K C + L_K L + K + B_K \qquad (^{40}K) \tag{4}$$

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.

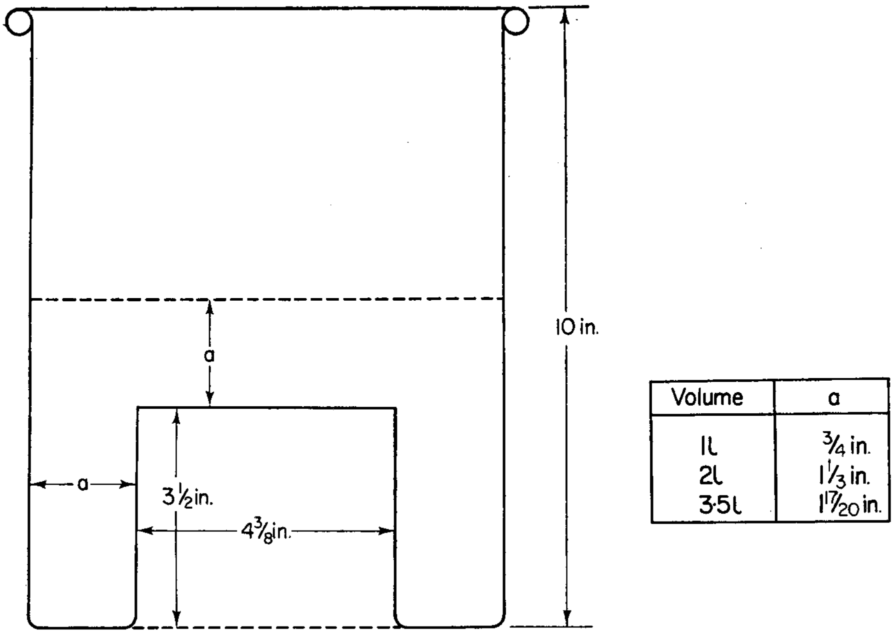
Since the geometry of the sample grossly affects the spectral shape obtained it was important to keep it constant in all work. Specially designed aluminium sample beakers (Fig. 1) surround the crystal for optimum and rigidly fixed geometry. A steel shelf supports the crystal and the sample.

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^{17}/$_{20}$ in.

FIG. 1—Specially designed sample beaker

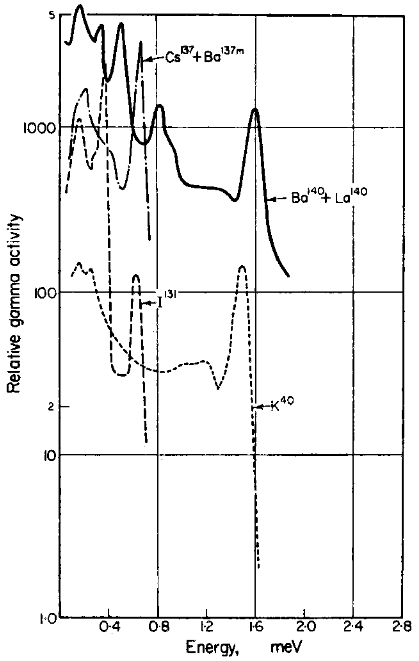


FIG. 2—Spectra of ^{131}I, Cs + ^{137m}Ba ^{140}Ba + ^{140}La and ^{40}K on low level gamma spectrometer

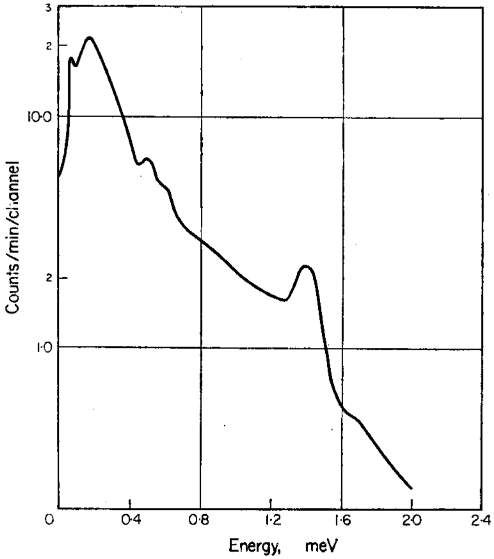


FIG. 3—Background spectrum on low level gamma spectrometer

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

A solution of 0·01M 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 abovementioned 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.

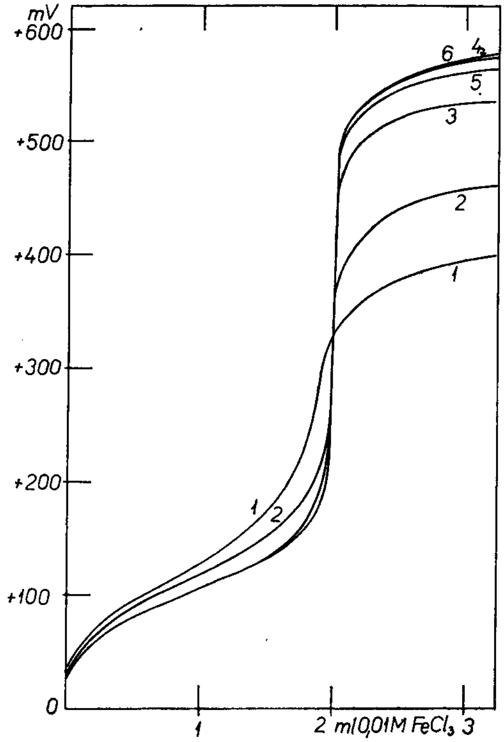


FIG. 1. Oxidation of Co^{II} with FeCl$_3$ solution. Effect of concentration of 1:10-phenanthroline. 2 ml of 0·01*M* Co(NO$_3$)$_2$, 25 ml of 1*M* buffer solution of pH 2·1 (monochloracetic acid–ammonia)—total volume of 50 ml—titrated with 0·01*M* FeCl$_3$. Pt-electrode vs. SCE. The curves were obtained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

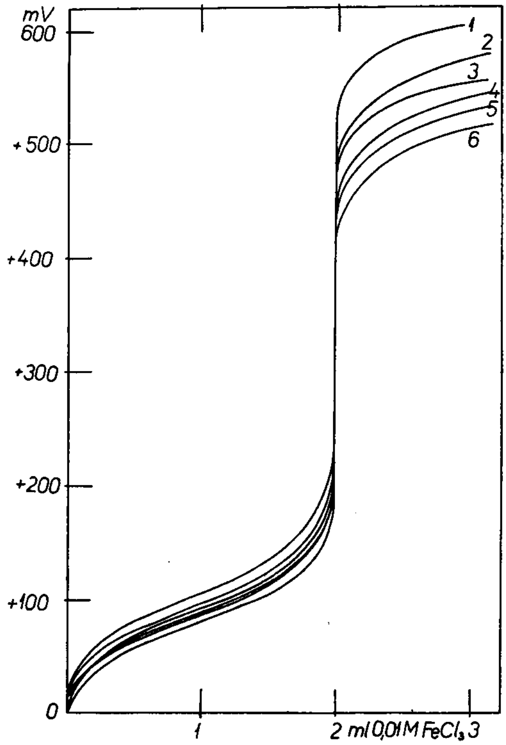


FIG. 2. Oxidation of Co^{II} with $FeCl_3$ solution. Effect of pH. 2 ml of 0·01*M* $Co(NO_3)_2$, 25 ml of 1*M* buffer solution (monochloracetic acid–ammonia) and 5 ml of 0·1*M* 1:10-phenanthroline—total volume of 50 ml—titrated with 0·01*M* $FeCl_3$. Pt-electrode vs. SCE.
1. pH 2·1, 2. pH 2·6, 3. pH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

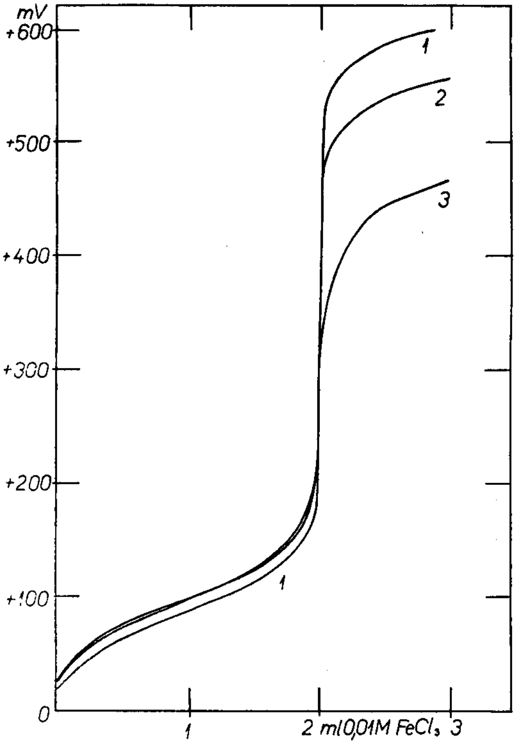
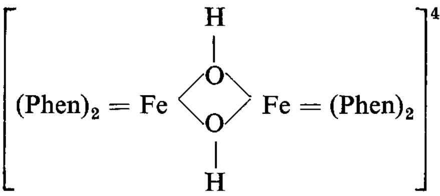


FIG. 3. Oxidation of Co^{II} with FeCl$_3$ solution. Effect of quality of pH-buffer. 2 ml of 0·01M Co(NO$_3$)$_2$, 5 ml of 0·1M 1:10-phenanthroline, pH adjusted with 25 ml of buffer solution with respect to a glass electrode—total volume of 50 ml—titrated with 0·01M FeCl$_3$. Pt-electrode vs. SCE. 1. 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 $8 \times 10^{-5}M$, 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.

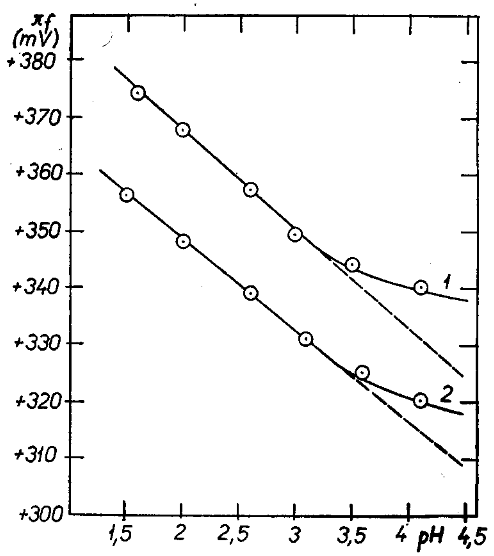


FIG. 4. Dependence on pH of formal redox-potential (π_f) of the system: $Co(Phen)_3^{2+} \rightleftharpoons Co(Phen)_3^{3+} + e$.
Values were plotted from the potentiometric titration curves under the different pH for the following ratios of Co : Phen:— 1. 1 : 3, 2. 1 : 25.

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

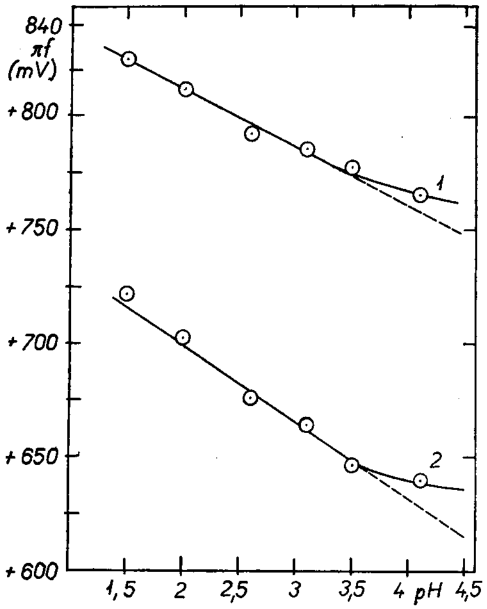


FIG. 5. Dependence on pH of the formal redox potential (π_f) of the system:

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

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.

(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, $pK_k = 21{\cdot}3$,[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.

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 $Co(Phen)_3^{3+}$.

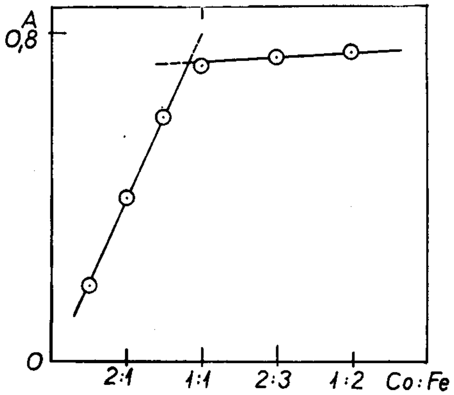

FIG. 6. Dependence of extinction of $Fe(Phen)_3^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of the ratio Co : Fe. 2 ml of 0·001M $Co(NO_3)_2$, 0·5–4 ml of 0·001M $FeCl_3$, 1 ml of 0·05M 1:10-phenanthroline, pH 3·5; total volume of 25 ml. The extinction was measured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

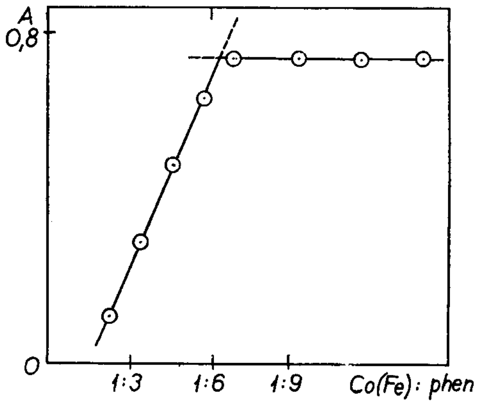

FIG. 7. Dependence of extinction of $Fe(Phen)_3^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of ratio (Co + Fe) : Phen. 2 ml of 0·001M $Co(NO_3)_2$, 0·5 ml of 0·05M $FeCl_3$, 1–5 ml of 0·005M 1:10-phenanthroline, pH 3·5, total volume of 25 ml. The extinction was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

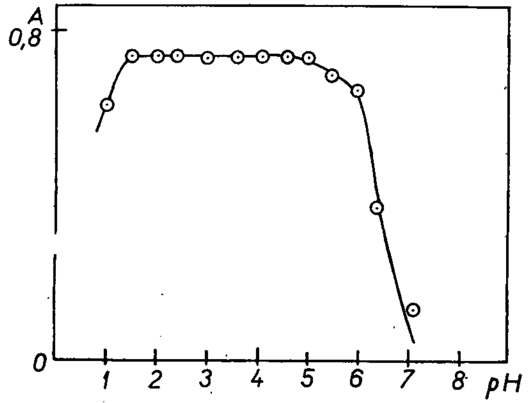

FIG. 8. Dependence of extinction of $Fe(Phen)_3^{2+}$ resulting from the oxidation of Co^{II} with $FeCl_3$ solution. Determination of pH-effect on reaction (1) 2 ml of 0·001M $Co(NO_3)_2$, 3 ml of 0·001M $FeCl_3$, pH adjusted with 0·1M HCl or 0·1M NaOH (glass electrode) and 5 ml of 0·05M 1:10-phenanthroline 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.

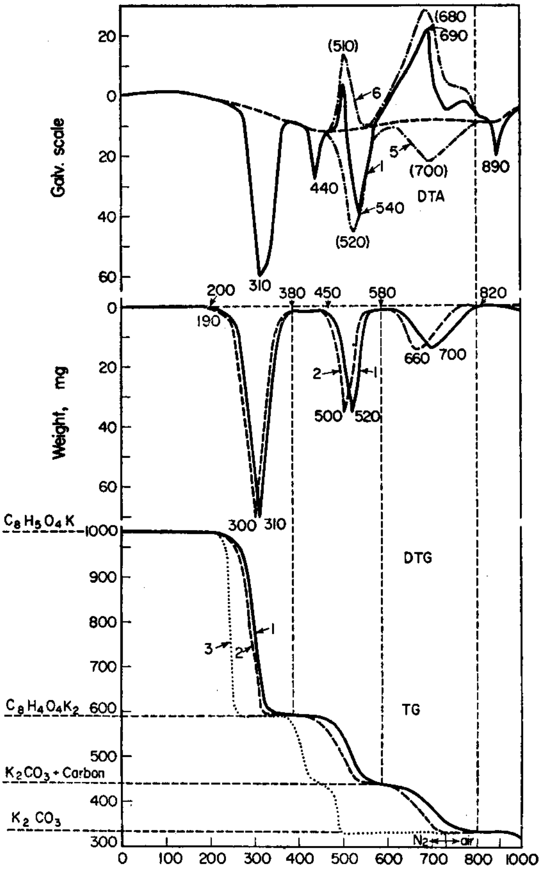

FIG. 1.

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°.

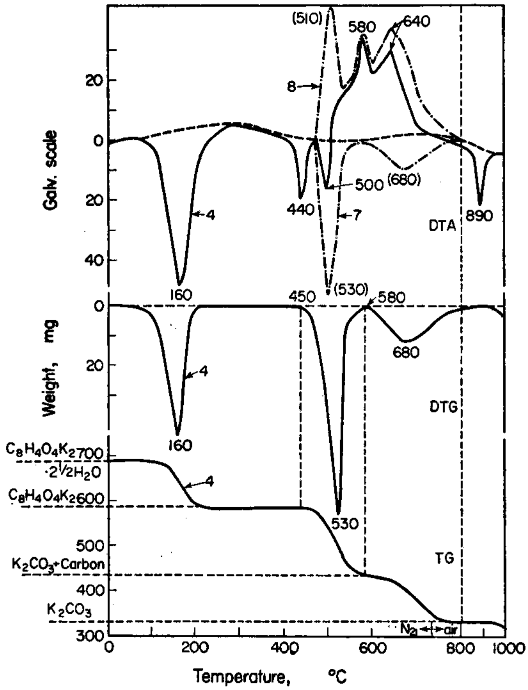

Fig. 2.

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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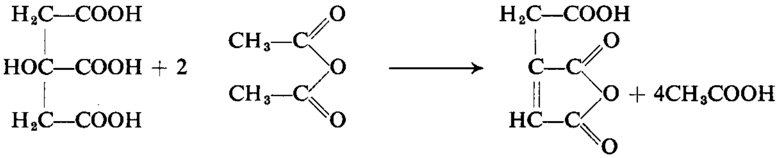
INTRODUCTION

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.

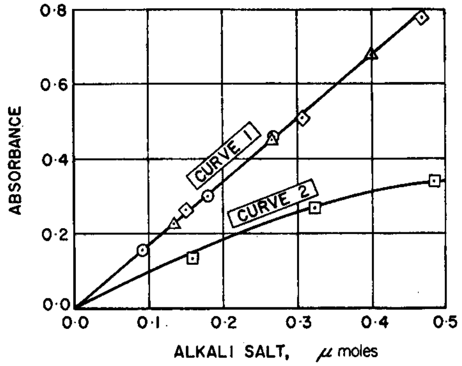


FIG. 1.—Calibration curves for the determination of alkali metal ions by reaction with citric acid.

⊙—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.

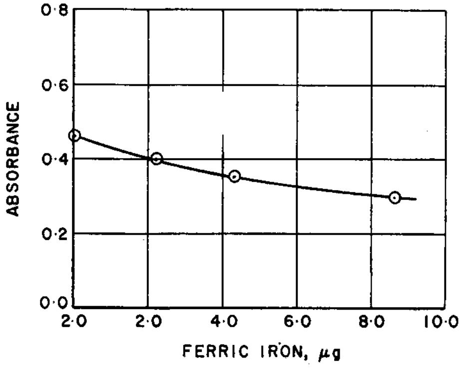


FIG. 2.—Effect of iron on the reaction of 35·2 μg of potassium chloride with citric acid.

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

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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

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
0·00025*M* thorium nitrate
8 mg/litre fluoride as sodium fluoride
0·3*N* chloracetic acid
0·15*N* sodium hydroxide
0·05*N* 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.

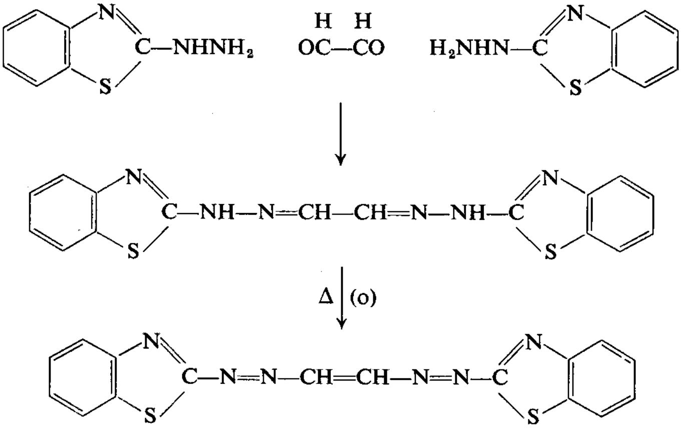
2:3-Diaminophenazine has been used to determine glyoxal.[4] However, this method requires several subsequent reactions to eliminate the interfering effect of excess reagent. Another disadvantage is that pyruvaldehyde also reacts with the reagent.

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

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 décelés avec le glyoxal comme réactif.

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[4] J. M. Dechary, E. Kun and H. C. Pilot, *Analyt. Chem.*, 1954, **26**, 449.
[5] H. W. Wanzlick and W. Löchel, *Ber.*, 1953, **86**, 1463.
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Talanta, 1960, Vol. 5, pp. 66 to 67. Pergamon Press Ltd. Printed in Northern Ireland

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.

The following meetings have been arranged

Friday 30 *September—Saturday* 1 *October* 1960: **Society for Analytical Chemistry,** North of England Section and Microchemistry Group and **Royal Institute of Chemistry,** North Wales Section: Joint Meeting. University College, Bangor, North Wales.

The following programme has been arranged:

Friday 30 *September*

6 p.m.—High tea, followed by Scientific Meeting on *Techniques and Scales of Analysis.* Speakers: Professor R. BELCHER and Professor C. L. WILSON.

Saturday 1 *October*

9.30 a.m.—Visit to Explosive Works, Penrhyndeudraeth. Lunch there, followed by afternoon coach tour.

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.

Talanta, 1960, Vol. 5, p. 68. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

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).

Ferrimetric determination of uranium^{IV} using Rhodamine-6G as fluorescent indicator. SEETARAMARAJU SAGI and G. GOPALA RAO. (6 *June* 1960).

The determination of gallium in rocks by neutron-activation analysis. D. F. C. MORRIS and Miss M. E. CHAMBERS. (6 *June* 1960).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution, II: Thorium. KAZUYOSHI TAKIYAMA, EUGENE D. SALESIN and LOUIS GORDON. (10 *June* 1960).

Photometric determination of tellurium with bismuthiol-II: JOSEF JANKOVSKY and OTAKAR KSIR. (14 *June* 1960).

The analysis of beryllium and beryllium oxide, IV: The determination of cobalt. A. F. ROSENBERG, J. O. HIBBITS and R. T. WILLIAMS. (16 *June* 1960).

PUBLICATIONS RECEIVED

Calculations of analytical chemistry. LEICESTER F. HAMILTON and STEPHEN G SIMPSON. Sixth edition. McGraw-Hill Book Company, New York: McGraw-Hill Publishing Company, London, 1960. Pp. xii + 334. 46s.

The radiochemistry of americium and curium. NAS-NS 3006. R. A. PENNEMAN and T. K. KEENAN. National Academy of Sciences, National Research Council, Washington, 1960. Pp. vi + 62. $0.75.

The radiochemistry of rhodium, NAS-NS 3008. G. R. CHOPPIN. National Academy of Sciences National Research Council, Washington, 1960. Pp. vi + 32. $0.50.

The radiochemistry of molybdenum, NAS-NS 3009. E. M. SCADDEN and N. E. BALLOU. National Academy of Sciences, National Research Council, Washington, 1960. Pp. vi + 38. $0.50.

Qualitative analysis and electrolytic solutions. EDWARD J. KING. Harcourt, Brace and Company Inc., New York, 1959. Pp. xxi + 641. $7.25.

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply).

3. The essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:

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5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

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CONTENTS

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