

## TALANTA REVIEW\*

### A CRITICAL EVALUATION OF COLORIMETRIC METHODS FOR DETERMINATION OF THE NOBLE METALS—III†‡

#### PALLADIUM AND PLATINUM

F. E. BEAMISH

Department of Chemistry, University of Toronto, Toronto 5, Canada

(Received 3 December 1964. Accepted 17 May 1965)

**Summary**—Spectrophotometric methods for palladium and platinum recorded subsequent to 1958 are critically reviewed. Associated with the descriptions of each metal there is included a table which identifies reagents recorded before 1958 together with pertinent references.

#### INTRODUCTION

THE number of spectrophotometric methods for the noble metals published during the past two decades probably exceeds the total number of all other reported quantitative methods for these metals. Simultaneously, new systems of analysis for alloys, solutions, ores, *etc.*, which contain traces of noble metals have been reported. Many of these analytical systems involve separational techniques, such as chromatography, ion exchange and extraction with immiscible solvents, which processes lend themselves especially to final spectrophotometric determinations. Arising out of these areas of research there has been developed a variety of methods for the determination of even fractions of micrograms of noble metals in kilogram amounts of sample. Systems for which no analytical methods were previously available may now be treated with simplicity and accuracy. A case in point is the separation and determination of microgram amounts of rhodium and iridium.

Ironically, this surplus of methods has created the usual problems associated with superabundance. Thus, the choice of method has now become a difficulty and this, in turn, has created a more critical attitude towards the content of pertinent publications. In general, the spectrophotometric methods are concisely and effectively recorded. However, there remain difficulties of interpretation and application and it is with a hope for the extended usefulness of spectrophotometric methods that the author, who has struggled under, and contributed to these difficulties, offers the following comments.

Practically all of the spectrophotometric methods for the determination of the noble metals deal with the problem of interfering constituents. Indeed, many authors justify their contributions with the claim for an improved degree of selectivity. In general, the technique used to ascertain the toleration for impurities is based on a prescribed small percentage departure from a specific absorbance resulting from a measured addition of the interfering constituents being tested. Thus, it is assumed that the identity of the dissolved constituent is fixed and permanent and irresponsive

\* For reprints of this Review see Publisher's Announcement at the end of this issue.

† Part II: see reference 11.

‡ Part III: to be continued.

to the influences of dissolution processes, variations in acidities, age of solutions and air oxidation, *etc.*

It is clearly evident that too little attention has been given to the effect on the colour-forming capacity of noble metal solutions resulting from aging. It may be noted that a determination of the effects of aging require simultaneous variations in acidity, temperature, salt content, *etc.* In general, aging effects are not made evident by determining separately the effect of changes of temperature, of acidity, *etc.*

Among the noble metals there is no more striking example of the effect of long standing on solution composition than that visibly evident when an iridium metal or salts are fused with sodium peroxide and subsequently acidified with hydrochloric acid. Recently, Ryan<sup>1</sup> noted the effect of long standing on the chloroform-extraction properties of an iridium solution treated with 4,5-dimethyl-2-mercaptothiazole. As early as 1924 Ardagh *et al.*<sup>2</sup> recorded that aged solutions of chloroplatinate developed a colour with potassium iodide more rapidly than freshly prepared solutions. Recently, it has been shown that the cation isolation of ruthenium from base metals by Dowex 50  $\times$  8 is adversely affected if the solution is allowed to age.<sup>3</sup>

Perhaps one of the most enlightening examples of the influence of long standing or aging on the colour-forming capacity is found with the osmium-thiourea reaction. Solutions of osmium made by distilling octavalent oxide into sulphur dioxide-hydrochloric acid yield an immediate pink on the addition of thiourea. With continued standing a solution, similarly prepared, may fail to produce a colour. This failure which has been erroneously ascribed to losses of osmium is, in fact, the result of changes in dissolved osmium constituents.

Recently, Némec, Berka and Zýka<sup>3a</sup> recorded a titrimetric method for ruthenium which involves a titration of  $\text{Ru}^{4+}$  or  $[\text{RuCl}_6]^{2-}$  with lead tetra-acetate. The authors state,

"In order to achieve a satisfactory course of the titration it is, however, necessary that the solutions of tetravalent ruthenium in dilute HCl which are titrated should be older than 14 days (from the day of their preparation).

The colour of tetravalent ruthenium stock solutions in dilute HCl (0.7N) changes after some time from the red-brown colour of freshly prepared solutions to a dark-brown to violet-brown color. Only sufficiently old solutions of the latter color can be used for the oxidation with  $\text{PbAc}_4$  to be described."

Examples of the deleterious influence on solution composition of a previous fuming with sulphuric acid as opposed to the direct addition of a sulphate are numerous. It has been stated that large amounts of added sulphate can be tolerated in the spectrophotometric determination of platinum by 5-(*p*-dimethylaminobenzylidene)-rhodanine while a previous fuming cannot be tolerated.<sup>4</sup> The classical precipitation of rhodium by hydrogen sulphide requires a treatment with hydrochloric acid in those instances where rhodium solutions have been subjected to a period of fuming with sulphuric acid. Furthermore, the latter process applied to solutions of platinum chloride prevents the quantitative oxidation of platinum to the quadrivalent state which is required for hydrolytic separation from the remaining noble metals.<sup>5</sup> In these instances and others the direct addition of comparable amounts of sulphate ion provides relatively little interference with subsequent spectrophotometric and other determinations.

From these data, together with the voluminous literature dealing with the

complexities of solution compositions of the noble metals, it would appear reasonable that consideration should be given to the interrelated effects of dissolution techniques, acidities, ion concentrations, period of aging, *etc.*, in the determination of the optimum conditions for the colour formation of reagent-noble metal constituents. This necessity may be further emphasised by a consideration of the unpredictable behaviour of hydrochloric acid solutions of iridium, which metal can be separated from other noble metal constituents by reductants from whose potentials one would predict a complete precipitation of iridium. The explanation for this anomaly may lie, not in incorrect potentials, but in a lack of information concerning the solution composition of the simple iridium solution.

Despite these instances of environmental difficulties, the tolerances for potentially interfering cations and anions determined by mixing the required solutions will in some cases prove to be acceptable data. This is particularly true when the investigator has made some effort to duplicate the character of the dissolved constituents, perhaps only by using salts whose oxidation states would correspond to those obtained by dissolution processes involving the commonly used oxidants such as nitric acid.<sup>6</sup> Furthermore, one cannot expect investigators to provide interference data derived from the many and various methods of dissolution. However, in those instances where dissolution may be accomplished by a simple treatment with *aqua regia* or with fuming sulphuric acid, some effort should be made to subject the mixed solution to a comparable procedure, and in any case careful consideration should always be given to the character of the noble metal salts used and the data should be accompanied by clearly defined descriptions of the environment used for colour development. Perhaps it should be stressed that the analytical chemist who is concerned about interference from specific constituents should, when it is practicable, determine for himself the tolerances applicable to his own techniques.

Here, perhaps one may suggest also that researchers in the field of spectrophotometric methods for noble metals have been traditionally and sometimes unduly preoccupied with immiscible solvent extractions as a means of accomplishing selectivity and eliminating interferences; relatively little attention has been given to the use of ion-exchange techniques as part of a colorimetric procedure. Contrary to the opinion that these techniques involve the treatment of large volumes of solutions, one may, by applying the full capacity of an exchanger, accomplish excellent separations with volumes at least comparable to those involving solvent extractions. In the areas of noble-metal determination, one may collectively separate large proportions of many associated base metals with an efficiency exceeding that often accomplished by the use of immiscible solvents. There is here a potentially useful adjunct to trace methods of analysis.

A clear recognition of the effect on colour formation of environmental influences may dictate favourable procedural techniques.

Colour reagents which require media of low acidity usually offer some difficulty. The fact that, with the exception of quadrivalent platinum, these metals are quantitatively precipitated as hydrated oxides at a pH approaching neutrality will sometimes dictate a specific order of reagent addition and heating techniques. In general, when a pH of about 2–7 is required, the reagent, *etc.*, should be added before an adjustment to the required acidity and before any required heating period. These procedures may avoid low values resulting from the appearance of colloidal hydrated oxides

which are usually insensitive to the colour reagent. Examples of this difficulty are found in the determination of ruthenium by acetylacetone,<sup>7</sup> in which case the pink complex is formed most rapidly at pH 5-6, and in the determination of osmium with anthranilic acid which requires a pH of 5.5-6.5 for colour development.<sup>8</sup>

Spectrophotometric procedures which belong to this category may prove discouraging to the practising analyst who wishes to achieve a good degree of precision and accuracy.

Almost invariably, published reports of new spectrophotometric procedures contain some expression of reaction sensitivity. The confusion concerning a precise meaning of sensitivity, evident in the early literature which deals with qualitative detection, has been removed largely by the work of Feigl who distinguished between quantity sensitivity and concentration sensitivity.<sup>9</sup> To express the former Feigl used the term identification limit, which is the mass limit of the constituent, usually expressed in micrograms, which can be detected. The limiting value to which this identification limit may be diluted is expressed as the "limiting concentration", "dilution limit" or "concentration limit".

Obviously, spectrophotometric techniques as they are presently described do not allow the use of the term identification limit. However, it is encouraging to note in a few recent reports the inclusion of data describing dilution limits for those reactions which produce visible colour changes. These data may well provide useful procedures for the detection of noble metals, particularly for the much needed field tests.

An approach to the use of dilution limits for spectrophotometric determinations was recommended by Sandell,<sup>10</sup> who defined sensitivity as "the number of micrograms of element, converted to the coloured product, which in a column of solution having a cross section of 1 cm<sup>2</sup> shows an absorbance of 0.001". "Sensitivity", thus defined, assumes that the Beer-Lambert Law holds to infinite dilution and thus cannot be applied to those methods which require working curves. Recently, various authors have expressed sensitivities in terms of absorbances greater than 0.001, *e.g.*, 0.01, and in addition have provided data concerning concentration sensitivity as expressed by Feigl.

The greater number of recently recorded spectrophotometric methods include data denoting the optimum range of concentrations. Presumably, the most favoured methods are those with a wide range of applicable concentrations and exceptionally high sensitivities. Perhaps too little attention has been given to those methods which apply only to concentrations which fall within the range of classical methods. Not infrequently, such methods are of considerable value in industrial laboratories when large numbers of samples must be analysed and rapidity of determination is of primary importance and high accuracy only of secondary importance.

Reports of procedures involving new reagents generally include data dealing with accuracy and precision. In common with all analytical methods, any expression of these terms for spectrophotometric methods must involve the efficient functioning of some mechanical equipment as well as the efficiency with which the unit is operated and with which the associated techniques are manipulated. An adequate recognition of the variability in human frailties requires acceptance with reservations of data concerning accuracy and precision. Thus, in some instances an experienced operator may increase the accuracy of a spectrophotometric method beyond that designated by the author or there may be failure to achieve this limit. Generally, one may hope

to reach an accuracy of about  $\pm 1$  to 3% from most direct spectrophotometric methods. Very few if any of these methods applied to the determination of noble metals achieve an accuracy in excess of 1%, which is also the approximate limit for such competitive methods as optical and X-ray spectrographic analysis. In general, the authors determine the accuracy of their method over a quoted optimum range of concentrations. Because of the relatively low accuracy as compared with many classical analytical methods, the problem of achieving high precision is of less importance. However, one must hope that newly proposed methods will contain some expression of precision and preferably these expressions should be confined to those commonly recognised and perhaps confined to those generally useful in the ranges of concentration to which spectrophotometric procedures apply. In the present author's opinion, few, if any, of the recorded spectrophotometric methods for noble metals, except perhaps in certain restricted areas of routine practice, provide an accuracy which could justify the inclusion of complete statistical expressions. Perhaps an adequate description of precision would be achieved by recording the number of determinations, the arithmetical mean and the average deviation. The more statistically useful "standard deviation" is seldom required and such terms as relative analytical error, *etc.*, often add to confusion and uncertainty of meaning. In any case, uniformity in expressions of accuracy and precision would add to the clarity achieved by the recent improvements in the symbology of expression for the Beer-Lambert Law.

With respect to the numbers of spectrophotometric methods now available, one may note the deficiency of methods for iridium and ruthenium and the relative abundance of methods for palladium. This situation exists also in all classical methods. One could hope that the efforts expended in the development of methods for palladium might be applied to the discovery of methods for the remaining platinum metals for most of which there is some deficiency of reagents. In defence of the rapidly accumulating methods for palladium it has been stated that a newly proposed method, despite any lack of obvious advantages, may supply a special need in some unforeseen application. In the case of palladium the present author entertains reservations concerning this opinion and, in any case, perhaps here and in related situations one may conserve printed space through limiting the content of such reports to the degree that a record of the new reagent will not be lost.

The present review deals with the spectrophotometric methods recorded subsequent to the author's second review.<sup>11</sup> The seven tables, one for each noble metal, contain a complete list of reagents, including those discussed in the first and second reviews, together with the recommended range of concentration for each method and the reference to the pertinent publication. In general, these ranges are expressed as optimum ranges and in those instances in which the range is an expression only as that over which the Lambert-Beer Law applies, it is so indicated by the symbol B.L. In a very approximate way the reagents are listed in the order of an increasing lower limit of the concentration range. In some instances this arrangement is ignored; in general, this discontinuity is infrequent and appears especially in instances when there is a very close similarity of reagent structure.

Even a casual examination of the tables will reveal the superfluity of palladium reagents and a more detailed examination of the recorded descriptions of each palladium method may well serve to discourage a researcher who wishes to publish a new method for palladium and who seeks to find some justification for its publication.

On the other hand, the tables indicate a deficiency of methods for the remaining noble metals and strangely, this is the case with even the more common of the noble metals, *e.g.*, gold and platinum. Because spectrophotometric methods are generally applied subsequent to some method of concentration and because the concentration frequently involves the use of fusion mixtures, chlorination and mixtures of mineral acids, such as *aqua regia*, perchloric acid, fuming sulphuric acid, *etc.*, the spectrophotometric methods which may be integrated with these dissolution processes are especially useful. These preliminary processes invariably involve the necessity of transferring and washing and there are, therefore, difficulties in maintaining small volumes. Methods which allow colour development in volumes of noble metal solutions of the order of 10 ml or more are advantageous.

Much of the present author's research over the past three decades has included the application of spectrophotometric determinations subsequent to the use of the above dissolution and concentrating techniques. Initially, each researcher is required to make a choice of methods appropriate to his problem. It may be of interest to note that, despite the wide variety of preliminary treatments to secure the noble metal solution, and the variety of sensitivities and ranges involved, the following selection of methods is almost invariably made:

for platinum and palladium—tin(II) chloride and <i>p</i> -nitrosodimethylamine,	
for rhodium	—tin(II) bromide or tin(II) chloride,
for iridium	—tin(II) bromide,
for osmium and ruthenium	—thiourea.

#### PALLADIUM

Palladium has been determined by an extraction with ethylene chloride of a complex formed by mixing with palladium chloride solution, first a potassium iodide solution, then tetra-ethyleneglycoldimethyl ether to form the tetra-iodopalladate(II) salt.<sup>12</sup> The palladium solution was evaporated to remove nitric acid and adjusted to 3% in hydrochloric acid. Subsequent to the addition of the iodide and reagent solution, three to four extractions were made with ethylene chloride. The organic phase was filtered into a volumetric flask, made to volume with the organic extractant and the absorbance measured at 340 m $\mu$ . Large proportions of rhodium, nickel and cobalt are tolerated, but there is interference from copper(II), gold(III), iron(III), and platinum(IV) chloride.

Beer's Law applied over the range of 0–6 ppm of palladium with a sensitivity of about 0.2  $\mu\text{g}/\text{cm}^2$ .<sup>\*</sup> Better methods are available from the point of view of tolerance and of freedom from cumbersome techniques. Exposure of the organic extract to sunlight or extended exposure to daylight must be avoided. The required time of extraction is stated as 10 min.

*N,N'*-Bis-(2-sulphethyldithio-oxamide) was used by Goeminne *et al.*<sup>13</sup> to produce two complexes with palladium. With at least a four-fold excess the complex has a mole ratio of platinum to reagent of 1:2. With a deficiency of reagent the mole ratio is 1:1. The former is the more stable and is formed in 5–6*M* hydrochloric acid solutions. Maximum absorbance, measured at 425 m $\mu$ , was reached in 30 min and remained constant for 30 min. The applicable range of concentration is 0.02–0.2

<sup>\*</sup> The expression for sensitivity used throughout this review is that proposed by Sandell and described above.

ppm of solution. The sensitivity is  $0.0083 \mu\text{g}/\text{cm}^2$ ; the molar extinction coefficient is 12,860. There is interference from relatively small proportions of copper, iron, gold, platinum and ruthenium, less interference from rhodium and iridium, and relatively little interference from nickel and cobalt. Buffered solutions (pH 3–8) may also be used for the determination. The absorbance is then measured at  $392 \text{ m}\mu$ . Tolerance for associated base and platinum metals is less than that for the determination in acid solutions.

A spectrophotometric method less susceptible to interferences from associated metals was described by Gustin and Sweet.<sup>14</sup> The method was used over the range of  $2\text{--}150 \mu\text{g}/50 \text{ ml}$  of the sample, which volume is recommended in the procedure. Thus the sensitivity on this basis is  $0.04 \text{ ppm}$  of solution. The reagent, 8-aminoquinoline, reacts with palladium at an acidity of pH 2.5 or less to form an insoluble yellow chloride complex with bivalent palladium with a mole ratio of palladium to reagent of 1:2. The precipitate is converted to a violet, insoluble complex at pH 10.2 or higher. This complex is extracted by chloroform to form a violet solution with an optimum absorbance at  $590 \text{ m}\mu$ , which absorbance must be measured within 1 hr. Applied to synthetic samples containing the associated platinum metals with copper, iron, chromium(III), nickel, *etc.*, the results obtained indicated appreciable freedom from interferences. Iridium interferes in relatively small proportions. However, the proposed method requires the use of EDTA. The effect of gold was not determined.

One of the most effective methods of determining traces of palladium in the presence of the base metals frequently associated in such natural occurrences as ores, concentrates and alloys involves the selective isolation of palladium by coprecipitation with tellurium by tin(II) chloride. This method, applied to sulphide minerals, meteorites, *etc.*, was described by Sandell.<sup>10</sup> The method was modified by Marhenke and Sandell<sup>15</sup> to the extent that the precipitate of tellurium-palladium is treated to allow for an extraction by diethyl oxalate, which is preferred to the usual extractants, such as isopropyl ether and *n*-butanol, because of its lesser volatility, its density of 1.05 and its greater insolubility in water. Separation from water is clean and the palladium-*p*-nitrosodiphenylamine complex is stable in the extractant. The absorbance is measured at  $525 \text{ m}\mu$ . Over the range  $0.2\text{--}0.5 \mu\text{g}$  of palladium the recovery is 90% or greater. Presumably, the slightly low results arise from adsorption of palladium by coprecipitated metastannic acid.

The procedure requires a treatment of the sample with nitric and hydrochloric acids, removal of nitric oxides, addition of tellurium solution to the  $3M$  hydrochloric acid solution, and finally addition of tin(II) chloride solution to precipitate the tellurium along with the palladium. The mixed precipitate is converted to a chloride solution,  $0.01M$  in hydrochloric acid, treated with the reagent and then extracted with diethyl oxalate. As one would expect, the reduction procedure would ensure simultaneous precipitation of gold and silver. Treatment of the mixed precipitate would result in the formation of silver chloride which has a marked tendency to adsorb palladium. Thus, the amount of silver in the sample should not exceed  $0.1 \text{ mg}$ . In the case of gold, dissolution of the mixed precipitate would result in an association of gold with the palladium, the former causing high results by giving a colour with the reagent. The ratio of gold to palladium should not, therefore, exceed ten if the error in palladium is to be kept below 10%. Undoubtedly, an extraction of gold chloride following dissolution of the mixed tellurium precipitate would serve to

remove this interference. There is practical value in the fact that the method tolerates as much as 100  $\mu\text{g}$  of the associated platinum metals as well as large proportions of the base metals, iron, copper, nickel, cobalt, lead and chromium. The amount of selenium should not exceed 100  $\mu\text{g}$ .

The authors predict a successful application of the method to meteorites, dunites, *etc.* It may be noted that a comparable separation of gold from a specific ore by McBryde and Yoe<sup>16</sup> yielded promising results. However, predictions of this nature should be accepted with some reservations. The complexities of the compositions of rocks, ores and natural alloys, along with the variations in solution composition resulting from even presumably consistent techniques of dissolution, will, not infrequently, render inapplicable a procedure which has proved eminently satisfactory when applied to synthetic materials.

8-Mercaptoquinoline (thio-oxine) was used by Bankovskii and Ievin'sh<sup>17</sup> to form a red chelate,  $\text{Pd}(\text{C}_9\text{H}_6\text{NS})_2 \cdot \text{H}_2\text{O}$ , insoluble in water and extractable with chloroform, chlorobenzene and bromobenzene. In these solvents the colour is an intense orange or rose. Extractions are made from 4–6*M* hydrochloric acid and with chloroform the three absorption maxima are 272, 286 and 485  $\text{m}\mu$ . The corresponding sensitivities are 0.024, 0.003 and 0.14  $\mu\text{g}/\text{cm}^2$  of palladium. Beer's Law applies up to 27  $\mu\text{g}/\text{ml}$  in 6*M* hydrochloric acid; 2  $\mu\text{g}/25 \text{ ml}$  can be determined quantitatively. As much as 20 mg of platinum and 1–2 mg of osmium and ruthenium can be masked by thiourea. Iridium and rhodium do not react with thio-oxine in the strongly acid solution. Tervalent iron does not interfere in amounts up to 80 mg; larger amounts can be complexed by sodium hypophosphite. Copper, silver, gold and mercury react with thio-oxine and while the salts are not soluble in chloroform, they interfere, and to avoid this, thiourea is added to the mixtures of immiscible solvents subsequent to an initial shaking to remove the palladium complex. Molybdenum interferes and a modification of the method is required in its presence. Oxidising reagents must be absent.

In a later paper<sup>18</sup> these authors discussed the analytical applications of 8-mercaptoquinoline with the platinum metals. A significant feature of these reactions is that the complexes with platinum and palladium are salts of the type  $\text{MeR}_2$ , and with iridium, rhodium, osmium and ruthenium, of the type  $\text{MeR}_3$ . In the case of the platinum and palladium complexes, prepared in a pyridine medium, there is some coprecipitation of the oxidation product, thio-oxine-8,8'-diquinolylsulphide. The thio-oxinates of the remaining platinum metals do not coprecipitate with the oxidation product.

Xavier<sup>19</sup> used 2-mercaptoquinoline, whose sensitivity limit for palladium is 0.05 ppm. Colour development occurred at pH 1.4–2.8 and the absorbance was measured at 450  $\text{m}\mu$ . There was interference from associated base and noble metals.

Potassium thiocyanate in 100-fold excess can be used to form  $\text{Pd}(\text{SCN})_4^{2-}$ , whose maximum absorbance in solution occurs at 310  $\text{m}\mu$ .<sup>20</sup> From 0.1 to 2  $\mu\text{g}$  of palladium can be determined in the presence of a 300-fold amount of iron(III). Moderate amounts of platinum, iridium and rhodium may be tolerated if the absorbance is measured immediately. Thiocyanate was previously used by Przheva'shiĭ *et al.*<sup>21</sup> to produce a red complex,  $[\text{Pd}(\text{SCN})_4]_2^{2-}$ , extractable with isoamyl alcohol or with butyl alcohol at a pH below 5. There was no interference from platinum(IV). Excess of thiocyanate ion prevented interference from iridium. Iron was complexed with disodium hydrogen phosphate.

Two of the most promising spectrophotometric reagents for palladium were



proposed by Busev and Naku.<sup>22</sup> 1-Mercaptopropionic-*p*-aniside and the corresponding *p*-toluidide produced yellow precipitates in an acidic medium with relatively high concentrations of palladium and a yellow colour with low concentrations. The yellow constituents were extractable by chloroform and benzene to give yellow solutions. The mole composition of the yellow constituent is 1:2 for palladium to the reagent. The absorption maximum in chloroform or benzene was 410 m $\mu$  for both reagents. Beer's Law applied over the range 0.2–12  $\mu$ g of palladium/ml. The procedure for colour development required the use of 2–140  $\mu$ g of palladium in 10–15 ml of solution. In chloroform the molar extinction coefficient for the aniside reagent was 15,700 with a sensitivity of 0.14  $\mu$ g/cm<sup>2</sup>. These data were comparable for the toluidide reagent and for benzene solvents. Optimum absorbance was attained over the range 0.1–3*M* hydrochloric acid. There was a slight decrease in absorbance at higher acidities. At least a 6-fold excess of reagent was necessary for the chloroform extracts of the palladium complexes of both reagents; with a sufficient excess in 1*M* hydrochloric acid the colour of the complex reached a maximum value after 30 min and remained constant for 24 hr. Before extracting, the reaction mixture required shaking for a few seconds and standing for 5–10 min. A single extraction with chloroform, made over a period of 2 min, was sufficient for quantitative recovery. Absorbance was measured 30 min after extraction.

With the described procedure there was no interference from the associated platinum metals, platinum(IV), rhodium(III), iridium(IV) and osmium(IV), in proportions of 1000:1. In weakly acidic solutions these metals produce precipitates, which are, however, insoluble in chloroform or benzene. Cobalt and nickel form grey-black precipitates at pH 6–8 only; they do not interfere in the prescribed procedure. Molybdenum (MoO<sub>4</sub><sup>2-</sup>) interferes but can be masked by tartaric acid, the latter also masking interference from iron(III), bismuth(III), zinc(II), lead(II) and tin(II).

The single difficulty with the proposed method seems to be the interference from copper, which metal is often associated with the platinum metals. The experimental data recorded by the authors, all of it in the microgram range, indicates very satisfactory recoveries and it may be hoped that the method will receive further attention.

Chrome Azurol S (Colour Index No. 43825; trisodium salt of 3"-sulpho-2",6"-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid) was used by Sangal and Dey<sup>23</sup> to produce at pH 4 a violet chelate whose composition indicated a mole ratio of palladium to reagent of 1:1. The maximum colour was developed in 5 min and remained insensitive to temperatures of 5° to 95°. The colour conformed to Beer's Law over the range 0.33–7.3 ppm. The sensitivity was 0.04  $\mu$ g/cm<sup>2</sup>; for an absorbance of 0.01 the sensitivity was 0.4  $\mu$ g/cm<sup>2</sup>. Absorbance was measured at 580 m $\mu$ . Interferences were determined by the direct addition of cation and anion constituents. In general, associated base and noble metals interfered.

Sangal and Dey<sup>24</sup> have added 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulphonate (Thoron) to their list of new reagents for the colorimetric determination of palladium. The reddish-violet 1:1 complex has a maximum absorbance at 525 m $\mu$ , a sensitivity of 0.0106  $\mu$ g/cm<sup>2</sup> and an applicable range of 0.35–25.4 ppm of palladium. Colour formation is instantaneous over the optimum pH range of 2.0–10.0 and it is insensitive to a wide range of temperatures. A large number of cations and ions interfere.

2-Mercaptobenzimidazole and 2-mercaptobenzothiazole were used for the

spectrophotometric determination of palladium by Majumdar and Chakrabartty.<sup>25</sup> These reagents and their red coloured complexes with palladium show high absorbance in the ultraviolet region and less high in the visible, where there are no sharp absorbance peaks. Absorbance measurements must be made from a rather limited wavelength region where there is minimum absorbance by reagent and maximum absorbance by the coloured palladium complex. These reagents offer such advantages as the stability of reagent and of the coloured complex, the wide optimum pH range and the useful range of palladium concentrations. However, they are not especially selective.

2-Mercaptobenzimidazole was also used by Xavier<sup>26</sup> who preferred a pH range of 1.0–2.6. Absorbance measurements were made at 380 m $\mu$ , 10 min after adding the reagent. There is interference from gold, platinum, silver and iron. Iron(III) is complexed with phosphate. Small amounts of cobalt, nickel, copper and iron(II) are tolerated. The sensitivity is recorded as 0.04 ppm of palladium.

Quinoxaline-2,3-dithiol was used by Ayres and Janota<sup>27</sup> for the range 0.4 to 3 ppm of palladium. The reagent is insoluble in water, chloroform, benzene, *etc.* It was used as a 0.1 % solution in dimethylformamide, but to ensure stability protection from light was necessary. Measurements with the red complex were made at 548 m $\mu$ ; a yellow complex was also detected with a maximum absorbance at 466 m $\mu$ . The colour develops rapidly and is reasonably stable. There is interference from platinum, iron, cobalt and nickel. The reagent has also been applied for the simultaneous determination of palladium and platinum.<sup>28</sup> Palladium concentrations from 0.40 to 2.80 ppm, and platinum concentrations from 1.03 to 7.18 ppm, and concentration ratios of palladium:platinum varying from 0.056:2.8 were applicable. The most suitable wavelengths were 624 and 548 m $\mu$ , slightly less precision being obtained at 624 and 517 m $\mu$ .

The reagent in dimethylformamide produces a red complex with palladium and a blue complex with platinum. The required bivalency for platinum is achieved by tin(II) chloride and the formation of insoluble complexes is avoided by the addition of *N,N*-dimethylformamide. In a previous report Ayres and Janota<sup>27</sup> indicated that platinum, osmium, nickel, cobalt and iron(III) interfered seriously. In a recent report on the successful use of the reagent for the spectrophotometric determination of platinum, Ayres and McCrory<sup>29</sup> found interference from copper, cobalt, nickel and rhodium. With both determinations the data obtained indicated relatively little interference from sulphate and a variety of other anions, frequently used for the purpose of dissolution and separation of the noble metals. It should be noted that these conclusions were based on the direct addition of the anion or cation to a solution of the platinum or palladium. Therefore, one must not conclude that similar results will obtain when the foreign ions are associated with the noble metal throughout the processes of dissolution or of any prior separations.

5-(*p*-Dimethylaminobenzylidene)-rhodanine in ethyl alcohol reacts with palladium in neutral or slightly acid solutions to form a violet precipitate.<sup>30,31</sup> Relatively stable solutions of the palladium complex are formed in formic or propionic acid solutions. With the former solvent the absorbance maximum is 515 m $\mu$  and with the latter, 530 m $\mu$ . In hydrochloric acid the maximum absorbance occurs at 515 m $\mu$ . Different lots of the reagent give slight differences of absorbance maxima and recalibration is necessary for each new lot of reagent. Absorbance increases slightly with excesses of reagent. The optimum range is about 0.4–2.5 ppm of palladium. In propionic acid,

maximum colour is attained at room temperature in 10–15 min, and is stable for more than 2 hr. There is interference from platinum, ruthenium, iridium, iron, chromium, copper and gold.

Other reagents for the lower range limit of about 0.4 ppm of palladium contain 5-membered rings with nitrogen and sulphur and the reactive mercapto group. Among these are derivatives of thiodiazoles, benzimidazole and benzothiazole. The first of these derivatives applied to the colorimetric determination of palladium was 2-mercapto-4,5-dimethylthiazole. Ryan<sup>32</sup> used this reagent for the range 0.5–8 ppm. As would be expected with this type of reagent, precipitates are formed with palladium and amounts of the latter beyond the recommended range may produce a turbidity. Beer's Law is not obeyed over the optimum range.

However, the method is not sensitive to variations in acidity or salt content and only platinum interferes. To separate the latter the usual hydrolytic separation may be used. If necessary, palladium can be isolated by an ethyl acetate extraction of the palladium-diphenylamine complex. Subsequently, the organic matter is destroyed before treatment with the dimethylthiazole reagent. This separation is unnecessarily cumbersome. Although the method has the advantage that comparable concentrations of gold do not interfere, the obvious disadvantage is the interference of platinum which is the almost constant associate of palladium. The effective concentration range allows for some application to the analysis of assay beads. It should be noted, however, that when sulphuric acid is used as a parting acid the hydrolytic separation from platinum is only applicable after a fuming and ashing process.

An examination of 2-mercapto-4,5-dimethylthiazole as a reagent for palladium was also made by Radford.<sup>33</sup> It was found that, when the absorbance was measured in the ultraviolet region using a mercury-vapour lamp and Wood's glass filters, there was an increase of 160% in sensitivity and that the coloured constituents obeyed Beer's Law. Increases in the concentration of hydrochloric acid caused slightly higher absorbance values, and the acidity must, therefore, be controlled. It was also found that the addition of ethanol to prevent turbidity was unnecessary.

The data described above for rhodanine apply also to the thiosalicylic-acid method recorded by Dema and Voicu.<sup>34</sup> The range for this reagent is 0.5–2.6 ppm of palladium and the acidity for colour development is pH 2–4 in an acetone medium. There is here, an advantage in the non-interference of gold, copper, iron and nickel. This advantage is to a degree vitiated by the interference from both platinum(II) and platinum(IV). Rhodium also interferes.

Ayres and Alsop<sup>35</sup> recorded two procedures for the determination of palladium by tin(II) salts. For the range 0.5–2.5 ppm tin(II) phosphate was used in a medium of phosphoric and perchloric acids; for the range 8–32 ppm in 1-cm cells tin(II) chloride was used in a hydrochloric and perchloric acid medium. For the latter reagent the absorbance peak occurs at 635 m $\mu$ . The green colour reaches maximum intensity in about 20 min at room temperatures and remains stable for about 30 min. The applicable range of acidity for colour development is 1.5–2.1*M* and the optimum perchloric acid concentration is 0.5*M*, and the maximum concentration for phosphoric acid is 2*M*. Beyond these proportions an unstable colour is developed. Tin(II) chloride concentrations in the final solution should be 0.02–0.04*M*. The presence of chloride ion is essential and should not fall below 0.92*M*. Lower concentrations result in low absorbance values. The order of addition of reagents should be palladium solution,

dilute mixed acids and finally the reagent tin(II) chloride. The total volume of solution is somewhat critical. For a final volume of 25 ml the addition of tin(II) chloride reagent to 17 ml or less of palladium and acid mixture, gives reproducible absorbancies. The rate of addition of reagent and temperature variations are not critical. There are objectionable interferences from all of the noble metals, but relatively large amounts of iron and cobalt can be tolerated. Nitrate and sulphate ions do not interfere. No method of colour extraction has yet been recorded.

The palladium-tin(II) phosphate system produces a red-violet colour in the absence of chloride ion and the presence of perchlorate ion. The narrow absorbance band has its maximum at  $487\text{ m}\mu$  and the colour system obeys Beer's Law. Maximum colour develops within 10 min at room temperature and is stable for 1.5 hr. The absorbance for a fixed amount of palladium is dependent upon the concentrations of perchloric and phosphoric acid. The identity of the coloured tin(II) complex is not known.

Useful reagents applicable to about the same range of palladium concentration as the tin(II) method are found with the naphthol derivatives. Some of these are discussed in previous reviews.<sup>11,36</sup>

A variety of thio-organic compounds was examined by Burke and Yoe<sup>37</sup> with a view to their use as spectrophotometric reagents for palladium. Each of five reagents provided absorption curves of approximately the same general shape with absorption maxima at  $270\text{ m}\mu$ , and with about the same sensitivity of  $0.01\text{ }\mu\text{g}$  of palladium/ $\text{cm}^2$ . The spot plate sensitivity was  $0.5\text{ }\mu\text{g}/0.05\text{ ml}$  and the limit of dilution was 1 in 5.

1-Thioglycerol was selected from the five reagents for detailed study. The identity of the yellow constituent was not determined and it was concluded that the complex was ionic and unstable. Beer's Law was obeyed over the range 0.5–9 ppm. The colour was insensitive to pH, the absorbance remaining constant over the pH range 2–7, and while buffers could be used if desired, in their presence the order of addition of reagents became an important factor; a 5% decrease in absorbance was observed if the buffer was added after colour development. Variations in room temperature did not effect the absorbance values. The degree of interference from associated base and noble metals was determined by direct addition of the constituents before colour development. Within this limitation only nickel of the associated metals could be tolerated in reasonable proportions. The reported non-interference of sulphate and nitrate ions is acceptable only with the reservations discussed previously in this paper. This spectrophotometric method will have only very restricted applications. The absorbance is measured in the ultraviolet range, the sensitivity and the applicable concentration range offer little or no advantages compared to other recorded reagents and the high degree of interferences will in general require a previous isolation of palladium.

Diethyldithiophosphate has been used for spectrophotometric, titrimetric and gravimetric determinations of palladium. Busev and Ivanyutin<sup>38</sup> provided a detailed description of the various applications of the reagent, which was used as the nickel salt dissolved in carbon tetrachloride. The yellow complex of 1 atomic weight of palladium to 2 moles of reagent has a maximum absorbance at  $295\text{ m}\mu$ , and a sensitivity of  $0.0034\text{ }\mu\text{g}/\text{cm}^2$ . Beer's Law holds over the range of 0.6 to about 4 ppm for a 1-cm cell. For the range of about 6 to 40 ppm measured at  $340\text{ m}\mu$ , visual colorimetry can be employed. The method involves the formation of the insoluble palladium complex, acidification and extraction with carbon tetrachloride and subsequent

washings with water and sodium hydroxide solution to remove excess reagent. Associated base and platinum metals interfere; to a limited degree interference from copper, iron, platinum, gold, *etc.*, can be eliminated by previous precipitations and selective solvent extractions. The method was used to determine palladium in the presence of lead and this application is worthy of further examination, because with some modification, it may thus be used to determine palladium in assay alloys.

2-Nitroso-1-naphthol-4-sulphonic acid<sup>39</sup> reacts with palladium to form a red complex whose composition is 1 atomic weight of palladium to 2 moles of the reagent. The complex can be extracted by isoamyl alcohol from solutions of nitric or sulphuric acids. Beer's Law is followed for 0.6–18.7  $\mu\text{g}$  of palladium/ml. The optimum wavelength is 525  $\text{m}\mu$ , measured in 7*M* acetic acid solution. There is interference from associated base and platinum metals.

Chromotrope 2 R (disodium 2-phenylazo-1,8-dihydroxynaphthalene-3,6-disulphonate) reacts with palladium to form a complex whose mole ratio is 1 to 1.<sup>40</sup> Maximum absorbance was obtained at pH 2.1–5.1 and measured at 574  $\text{m}\mu$ . Beer's Law holds over the range 0.6–12.3 ppm of palladium.

Xylenol Orange has been used for the spectrophotometric determination of palladium to form an orange complex with an absorption maximum at 518  $\text{m}\mu$ . The reported molar absorptivity of 26,000 indicates a sensitivity of 0.004  $\mu\text{g}/\text{cm}^2$ . The composition of the complex is 2 moles of reagent to 1 of palladium. Beer's Law applies over the range 0.2–4.0 ppm of palladium with an optimum range of 0.8–3.2 ppm of palladium. Because of the interference of chloride ion and in order to increase selectivity, Otomo<sup>41</sup> used a concentrated perchloric acid medium for the reaction with maximum and constant absorbance at a concentration range of 1.1–1.7*M*. An excess of reagent was required and a short period of boiling was necessary. No conclusive statement was made concerning the influence of associated base and noble metals. Distinct advantages of the method are the solubility in water of the orange palladium complex and the high sensitivity. One may hope that efforts will be made to apply the method to natural and artificial products containing palladium.

Other reagents for palladium containing the mercapto group are 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol-I) and 5-mercapto-3-phenyl-2-thio-1,3,4-thiadiazole-2-one (Bismuthiol-II). Majumdar and Chakrabarty<sup>42</sup> used Bismuthiol-I over the range of 0.8–8.0 ppm at wavelengths between 400 and 410  $\text{m}\mu$ . There are no sharp absorbance peaks. The colour develops instantaneously, is independent of pH and is acceptably stable under the conditions recommended. The palladium complex is fairly soluble in water. Bismuthiol-II was used by Majumdar and Chakrabarty<sup>42</sup> for the range 0.4–8 ppm of palladium. At a wavelength between 410 and 430  $\text{m}\mu$  the colour intensity is relatively insensitive to pH change, remaining stable between pH 3 and 10. The red coloured constituent forms immediately and because of its insolubility in water the addition of acetone or methyl cellosolve is required. The claim for a sensitivity greater than the *p*-nitrosodiphenylamine reagent is incorrect. Furthermore, the latter reagent has a lower limit of both detectability and sensitivity expressed as an absorbance-weight response. The extent of interference and the range of applicability of Bismuthiol-II is comparable to the mercaptans included above and none of these has advantages superior to the more established reagents.

Kodama<sup>43</sup> used *o*-nitrosoresorcinolmonomethyl ether for the range 0.8–2 ppm of palladium. The procedure involves a fuming period with perchloric or sulphuric acid

which allows adaptations to various stages of fire assay techniques, *e.g.*, parting of the silver bead. The fumed solution is mixed with coniferin and chloroform in a separatory funnel and the chloroform extract treated with sodium carbonate solution. The absorbance is measured at 420  $m\mu$ .

An interesting spectrophotometric method, used by Komatsu and Taki<sup>44</sup> for the range 1–30 ppm of palladium, involves the use of a large excess of the reagent 1-phenylthiosemicarbazide, which redissolves the initial orange-brown precipitate to form an orange-yellow solution. The wavelength used is 372  $m\mu$  and the optimum acidity is 3*M* in acetic acid. As would be expected, there is interference from associated base metals and some of the noble elements. Platinum forms an insoluble green precipitate. EDTA is used to remove interference from copper and silver and sodium fluoride is used for iron. Gold is removed by solvent extraction with ether.

2-Nitroso-1-naphthol has been used to determine palladium in uranium fission alloys.<sup>45</sup> There is no interference from uranium, ruthenium, zirconium and rhodium. The method is a combination of that proposed by Alvarez<sup>46</sup> and Cheng.<sup>47</sup> Palladium is quantitatively extracted by toluene along with excess reagent in the pH range 1.0–2.0; EDTA serves as a buffer and masking reagent. The excess reagent is scrubbed from the organic phase with dilute sodium hydroxide solution. Initial pH adjustments are made with aqueous ammonia rather than with sodium hydroxide solution because the latter produces low and erratic results. However, sodium hydroxide as the scrub solution, produces improved precision.

A second paper was recorded by Larsen and Ross.<sup>48</sup> Palladium was determined as its complex with 2-nitroso-1-naphthol after separation by the extraction of the complex in toluene; ruthenium was separated by distillation of its octavalent oxide, collection in a caustic solution of sodium hypochlorite and a subsequent spectrophotometric determination.

1,2-Nitrosonaphthol and the 2,1-derivative were used by Kodama<sup>49</sup> in perchloric or sulphuric acid solution and the resulting palladium complex was then extracted with chloroform. For the 1,2-complex the absorbance was measured at 298  $m\mu$  or at 441  $m\mu$ ; for the 2,1-derivative, 308, 376 or 385  $m\mu$  could be used. The most sensitive wavelength is 308  $m\mu$ .

A method which is useful for the simultaneous determination of platinum and palladium was recorded by Pyle and Jacobs.<sup>50</sup> The reagent, dibenzylthio-oxamide, produces a yellow palladium complex and with platinum a rose-coloured complex, both insoluble in aqueous media but extractable with chloroform. The absorption maxima are, respectively, 450 and 520  $m\mu$ . The applicable range of concentration is approximately 1–4 ppm or to 5 ppm in the case of platinum. The complexes contain a ratio of 1 mole of bivalent metal to 2 moles of reagent. The sensitivities are 0.0055  $\mu\text{g}/\text{cm}^2$  for palladium and 0.0075  $\mu\text{g}/\text{cm}^2$  for platinum. Colour development is optimum in hydrochloric acid solutions of a molarity of 8 or greater, with an immediate development in the case of palladium and with platinum, for which a sodium sulphite reduction is recommended, the optimum colour development requires 30 min. Two chloroform extractions remove the complexes and the colour remains stable for a least 48 hr. The recommended ratio of added reagent:metal is 31:1 for palladium and 76:1 for platinum. For the simultaneous determination the reagent:metal ratio is that used for platinum. The method is surprisingly free from interferences from associated noble and base metals. In the case of palladium, with

iron, nickel, cobalt, copper, chromium, the permitted proportions are about 1  $\mu\text{g}$  of palladium to 5000  $\mu\text{g}$  of the base metals. Gold interferes, except in the presence of sodium sulphite, which probably produces metallic gold. With the obvious exception of platinum the interference from the remaining noble metals is not excessive; in the case of osmium it may be noted that the use of osmium(VI) for determining the degree of interference does not necessarily duplicate the dissolved osmium constituent which would result from the author's preparation of the platinum-palladium solution. However, in any case, interference from osmium is readily removed by previous oxidation. In the case of platinum the interferences from similar associated metals was invariably greater than for palladium. Indeed, for most practical purposes any claim for freedom from interference is invalid, *e.g.*, the deleterious effects of copper, nickel and, of course, palladium reduces the value of the method. Any interference from gold is eliminated by reduction with the added sulphite.

Jacobs *et al.*<sup>51</sup> applied the didodecyl derivative of dithio-oxamide for the determination of palladium to produce a yellow water-insoluble complex in hydrochloric acid solutions of about 7.5M. The optimum concentration range is about 1–4  $\mu\text{g}$  of palladium/ml of solution. The sensitivity is 0.005  $\mu\text{g}/\text{cm}^2$ ; the colour is stable for at least 48 hr and its development requires about 15 min. The required ratio of reagent to palladium is at least 4 moles to 1 formula weight of palladium; larger ratios are recommended. This method will prove useful for the determination of palladium in the presence of platinum(IV). The permitted ratio is about 1 to 160, respectively. Gold interferes, except in the presence of sodium sulphite, which reagent disallows the presence of platinum and increases the tolerance for iron. The tolerance indicated for sulphate should not be interpreted to indicate the tolerance for sulphate solutions prepared, as they usually are in practice, to include a fuming process. The high tolerance for rhodium and iridium will have value only in relatively few analytical processes.

With palladium, tartrazine forms a stable orange complex which may be used for determinations in the range 1.23–9.83 ppm of palladium in the presence of 150-fold amounts of platinum(IV). The colour is developed in a sodium acetate solution at pH 5.5–5.75 and the absorbance is measured at 496 m $\mu$ .<sup>52</sup>

The spectrophotometric determination of palladium by sodium 1-nitroso-2-naphthol-3,6-disulphonate (Nitroso-R salt)<sup>53</sup> provides some advantages as compared to other nitrosonaphthols. The red complex is soluble in water and no extraction is required; the colour reaction is rapid, Beer's Law is obeyed, and the colour intensity is constant when measured 15 min after preparation and remains stable up to 24 hr. Furthermore, the reagent solution is stable for several months. While the maximum absorbance occurs at 430 m $\mu$ , there is some significant absorbance of the reagent at this wavelength and the plateau at 500–510 m $\mu$  is more suitable for measurements. The most sensitive range of concentration is 1.28–4.27 ppm of palladium. There is no interference from platinum, rhodium, osmium and gold, although in the presence of  $\text{HAuCl}_4$  the colour changes slowly and the absorbance measurements should be made within 1 hr after colour development. The best results are obtained at an acetic acid concentration of 0.2M and at a pH of about 2.6. Hydrochloric acid solutions at a pH of about 2 can also be used. It is desirable to use an excess of reagent because the absorbance is thereby somewhat increased.

The application of nitroso-R salt was also discussed by Garcia and Garride,<sup>54</sup> who

found that Beer's Law was obeyed over the range 5–13 ppm. The absorbance was measured at 520–560 m $\mu$ . The suitable pH range for colour formation was reported as 3.25–6.85. An excess of reagent was required and the colour reaction was insensitive to temperature changes.

Quinoline-2-aldoxime was used by Oi<sup>55</sup> to produce a yellow palladium complex at pH 5, which could be extracted by chloroform. Beer's Law applies over the range 1.5–70  $\mu\text{g/ml}$ . Interference from copper or platinum is avoided by the use of EDTA.

Phenyl-1-pyridyl ketoxime is a useful reagent for the spectrophotometric determination of palladium. Sen<sup>56</sup> included a recipe for preparation of the reagent but it has recently been made available commercially.\* This ketoxime forms a yellow, water-insoluble compound containing 1 mole of palladium to 2 moles of ketoxime. The chloroform extract exhibits absorbance peaks at 410 and 340 m $\mu$ . Beer's Law applies over the range 0.5–14 ppm of palladium with a 1-cm light path. The optimum range at 340 m $\mu$  is 1.5–8 ppm and at 410 m $\mu$  it is 2–10 ppm of palladium. The corresponding sensitivities are 0.0021  $\mu\text{g/cm}^2$  and 0.0036  $\mu\text{g/cm}^2$ .

Because there is some absorbance by the reagent at 340 m $\mu$ , the maximum at 410 m $\mu$  is recommended when excesses of reagent are unavoidable. The most favourable acidity for formation and extraction of the palladium chelate is between pH 8.5 and 10. Maximum colour development is instantaneous and the colour remains stable for at least 2 weeks. Temperature variations between 0° and 45° are without significance. The reagent forms coloured complexes with iron(II), cobalt, nickel and copper, which are simultaneously extractable. These interferences are avoided by the addition of EDTA which does not interfere when the absorbance is measured at 410 m $\mu$ . At 340 m $\mu$  EDTA must be included in the blank. Of the noble metals, only gold interferes. The complexes of the platinum metals, lead and iron(III) are not extracted by chloroform.

Jacobs<sup>57</sup> used *N,N'*-bis-(3-dimethylaminopropyl)-dithio-oxamide to produce a yellow, water-soluble chelate containing 1 mole of palladium and 2 moles of reagent. Beer's Law was followed over the range 0.20–8.0 ppm of palladium with the optimum range 1.6–5.7 ppm. The sensitivity of the reaction is 0.008  $\mu\text{g/cm}^2$ ; the absorbance maximum is at 427 m $\mu$ . Colour develops immediately at room temperatures and is independent of temperatures over the range 15–45° and stable for at least 4 hr. With a 7.5-fold or greater excess of reagent the absorbance remains constant. For maximum sensitivity the molarity of hydrochloric acid should be above approximately 3.4. Compared to most colorimetric methods for palladium there is relatively little interference from the platinum group, gold and nickel. Interference from osmium and ruthenium is of little consequence because these metals are readily removed and, particularly in this case, because nitrate and sulphate may be tolerated. In the presence of platinum the absorbance of the palladium complex is measured within 10–15 min because platinum slowly produces a rose colour. Copper and iron interfere.

The above reagent is also used for platinum<sup>58</sup> and for the simultaneous determination of palladium through a calculation involving the known molar absorbitivities of the two complexes. With platinum the rose coloured complex contains a ratio of reagent to platinum of 2:1. The sensitivity is 0.009  $\mu\text{g/cm}^2$ , which is considerably higher than the tin(II) chloride method but less than the *p*-nitrosodimethylaniline method. Absorbance is measured at 515 m $\mu$ . The optimum range is 1.8–6.5 ppm.

\* From G. Frederick Smith Co., Columbus, Ohio, U.S.A.



As in the case of palladium, the acid strength is adjusted to 4.8*M*. The colour is developed, subsequent to reduction of platinum by sodium sulphite, and a 10-min development period is required. An 18-fold or greater excess of reagent is required.

Because the absorbances of the complexes of both platinum and palladium are additive, and Beer's Law is obeyed at both 427 and 515  $m\mu$ , a simultaneous determination of platinum and palladium may be achieved. A technique such as this encourages applications for routine determinations. However, in those instances where there is a great difference in the proportions of the two constituents, the errors associated with the determinations of the constituent present in large proportions may become additive to the errors incident to the determination of the second constituent.

The method applied to platinum alone does not tolerate large proportions of associated noble or base metals. Gold, iridium, ruthenium, nickel and iron are tolerated in proportions of about 15 parts to one of platinum. Toleration of palladium, ruthenium, osmium, rhodium and copper is low.

5-Amino-2-benzimidazolethiol in excess produces an orange coloured complex with a ratio of 1 atomic weight of metal to 2 formula weight of reagent.<sup>59</sup> Maximum absorbance occurs at 390  $m\mu$  and the solution obeys Beer's Law between 1 and 8 ppm with an optimum range of 2–7 ppm. The sensitivity is 0.008  $\mu\text{g}/\text{cm}^2$ . Colour is developed at room temperature, remaining constant at a pH between 2 and 4 for 24 hr. Platinum and osmium interfere and must be separated. The claim for no interferences from other associated platinum and base metals is based on a permitted ratio of 4 ppm of palladium to about 8 ppm of foreign metal. In general, there is some increase in tolerance in the presence of EDTA.

Thiomalic acid, used by Wagner and Yoe<sup>60</sup> as a spectrophotometric reagent, provides the advantages that it is water soluble and commercially available, and reacts instantaneously with palladium over a wide acidity range, although maximum absorbance is obtained over a pH range of 1.1 to 2.6. Maximum absorbance of the yellow complex occurs at 350  $m\mu$ . The reagent does not absorb above 290  $m\mu$  and a water blank is satisfactory. The complex obeys Beer's Law over the range 0.4–10 ppm and it is stable for several days. Temperature variations over the range 15–35° are without significant effect.

The practical sensitivity of the reaction is about 0.05 ppm and the optimum range of concentration is 2–7 ppm of palladium. Although the reagent is unstable, solutions may be used over a period of 24 hr. While the order of addition of reagents is not critical, if the absorbance is to be measured immediately, the buffer must be added last, otherwise 1 hr is required for the colour reaction to reach a maximum intensity. The absorbance remains constant for at least 3 days. An excess of reagent is desirable because the absorbance of the complex is thus somewhat increased and the tolerance to several interferences is also increased. The reagent presumably forms two compounds, one of which is a stable complex consisting of 2 molecules of thiomalic acid to 1 formula weight of palladium and a lesser stable complex with a 1:1 ratio which absorbs to a lesser extent. Because the usual organic solvents fail to extract the yellow complex it is assumed to be ionic in aqueous solution. This extraction failure is unfortunate because, in spite of a claim for unusual specificity, there is interference from most of the noble metals, copper and iron(III). There is a large tolerance for nickel, cobalt, sulphate and nitrate.

1-(2-Pyridylazo)-2-naphthol, previously used for rhodium and iridium by Stokely

and Jacobs,<sup>61</sup> has been applied by Hayashi<sup>62</sup> for the determination of palladium. The green 1:1 mole-ratio complex, soluble in chloroform and isoamyl alcohol, forms in weakly acid solution. In chloroform the absorbance is measured at 678 m $\mu$ . Beer's Law applies over the range 1–20 ppm of palladium. Colour is developed by heating for a few minutes on a water bath. There is no interference from moderate amounts of rhodium, platinum, gold, silver and mercury. This reagent was also applied to determine traces of palladium and platinum in high-purity gold. Subsequent to the dissolution of the sample, gold was extracted with isopropyl ether and then palladium dimethylglyoxime with chloroform. The palladium was next converted to the above naphthol derivative (at a pH of 1.5–3.5). Platinum in the aqueous phase was reduced by tin(II) chloride, extracted with dithizone in carbon tetrachloride and the absorbance measured at 730 m $\mu$ ; 0.2 ppm of palladium or platinum could be determined.

Busev and Kiseleva<sup>63</sup> used a 1% solution of 1-(2-pyridylazo)-2-naphthol in methyl alcohol for a chloroform extraction at pH 2.5 and for a range of 6–14 ppm of palladium. The extract has absorbance maxima at 620 and 675 m $\mu$ ; the latter wavelength is preferable when the proportion of platinum is high. The method is reasonably free from noble metal interferences. Cobalt behaves similarly to palladium. The associated base metals can be extracted with isoamyl alcohol.

This naphthol derivative was also used by Sawada and Kato<sup>64</sup> for the determination of palladium in titanium alloys. Colour was developed at pH 3.0–3.5 and heating at 100°. The sensitivity was recorded as 0.006  $\mu\text{g}/\text{cm}^2$ .

Two new reagents containing the *o*-hydroxyazo group have been used for the determination of palladium(II). Sodium 1-azophenyl-2-hydroxy-6,8-naphthalene disulphonate at pH 6.5–6.8 was used to determine 1.04–14 ppm of palladium; sodium 1-phenyl-3-methyl-5-hydroxy-4-(*p*-sulphophenyl)-pyrazole reacts at pH 1 to determine palladium over the range of 12.61–189.22 ppm. It is stated that these reagents may be used for determinations in ores and that platinum, gold, nickel and mercury do not interfere.<sup>65</sup>

Among the numerous thiol reagents for the determination of platinum metals, 2-mercaptobenzoxazole was selected by Arita and Yoe<sup>66</sup> to produce an orange-yellow complex, with a mole ratio of reagent to metal of 1:1. The complex is soluble in a mixture of cyclohexanone and dioxan. Absorbance measurements are made at 375 m $\mu$ , the optimum concentration range is 15–30 ppm and Beer's Law applies over the range 2–40 ppm. The sensitivity for an absorbance of 0.001 is 0.08  $\mu\text{g}/\text{cm}^2$ ; for an absorbance of 0.005 the sensitivity is 0.4 ppm; the spot plate sensitivity is 0.05  $\mu\text{g}/0.05\text{ ml}$ .

The colour reaction is instantaneous but the complex is somewhat unstable, the intensity decreasing 1% in 10 min. There is also a decrease in stability with increasing basicity although this is accompanied by an increase in colour intensity. The addition of buffers encourages precipitation and measurements are, therefore, made in dilute hydrochloric acid solutions. Absorbance is measured at 375 m $\mu$  and is independent of the normal laboratory temperature changes and of the order of addition of reagents. The degree of interference from associated noble and base metals was determined by direct addition of the constituents before colour development. Except for cobalt, and to a lesser degree for nickel, there was interference from small proportions of associated metals, *e.g.*, 3 ppm of platinum salt added to 20 ppm of palladium produced an error of  $\pm 2\%$ .

Nitrilotri-acetic acid has been used for the spectrophotometric determination of palladium.<sup>67</sup> Except perhaps for very specific purposes the method will have little application. The optimum range of concentration is 20–220 ppm. Measurements are made at 330 m $\mu$ , and there is interference from the remaining platinum metals. No data were provided to indicate the effects of gold or associated base metals. In the presence of platinum metals, palladium is first removed by precipitation with dimethylglyoxime. The method offers no advantage over the many useful alternative methods.

Bis-(allylthiocarbamyl)-hydrazine (Dalzin) was used by Dutt and Sarma<sup>68a</sup> to produce an orange, insoluble complex with a 1:1 mole ratio of metal to reagent. The optimum acidity is pH 1.2–1.3. The chloroform extract shows a maximum absorbance at 365 m $\mu$ . In a later paper<sup>68b</sup> the authors recommended a pH of 3–6 and extracted the complex in the presence of EDTA. Beer's Law applied over the range of 1–20 ppm. The complex was found stable for several hours at 25–40°. Associated base metals, silver and mercury(I) did not interfere.

Nioxime was used by Pshenitsyn and Ivonina,<sup>69</sup> who added an aqueous solution of the reagent to the palladium solution adjusted to pH 1. After 10–15 min the complex palladium salt was extracted by chloroform.

Derivatives of nioxime are finding increasing use as analytical reagents for palladium. Banks and Smith<sup>70</sup> used 4-methyl-1,2-cyclohexanedione dioxime for palladium contents of 2.5–250  $\mu$ g. The solution is adjusted to pH 2 by a hydrochloric acid-potassium chloride buffer and allowed to stand for 1 hr. The insoluble complex is extracted by chloroform and the absorbance measured at 280 m $\mu$  using 1-cm cells. Interference from copper, cobalt and iron can be avoided by masking reagents but ruthenium must be removed. One should note that the working range of palladium concentration in a method such as this one is determined partly by the efficiency of the initial precipitation, together with the completeness of the complex formation, and not by the sensitivity in the organic extract which, in the case of this 4-methylnioxime reagent is 0.07  $\mu$ g of palladium/cm<sup>2</sup>.

Benzildioxime was also used<sup>69</sup> with palladium solutions at pH 2 and the absorbance of the chloroform extract is measured at 280 m $\mu$ .

Dimethylglyoxime, perhaps the most generally useful reagent for the gravimetric determination of palladium, was used by Kodama<sup>49</sup> for the spectrophotometric determination of palladium in preference to 1,2-nitrosophthalene when one must avoid interference from chloride.

The determination of palladium as its iodide compounds in nickel plating solution was studied by Frantsevich-Zabludovskaya, Kalimanova and Sharafan.<sup>71</sup> This is an interesting and useful examination of the palladium iodide reactions. It was found that the optimum absorbance of the brown solution reaches a maximum at a molar ratio of potassium iodide to palladium of 2:1, and subsequently remains constant up to a 50:1 ratio. The absorbance then decreases in the presence of a larger excess of potassium iodide, finally increasing again and at a 200-fold excess of the potassium iodide it remains constant, the solution now being coloured red. This dissolved constituent is K<sub>2</sub>(PdI)<sub>4</sub>; the maximum absorbance at a ratio of 2:1 presumably resulting from a colloidal suspension. The red constituent had previously been used by Fraser *et al.*<sup>72</sup> for the spectrophotometric determination of palladium. Frantsevich-Zabludovskaya applied this method successfully to the determination of palladium in

activating solutions contaminated with detergent. It was found that the absorbance was constant over the potassium iodide:palladium molar range from 200:1 to complete saturation of the solution of potassium iodide; it remained constant for 6 hr, decreasing after 24 hr and it was unaffected by acidity over the pH range 2.5–10. Maximum absorbance of the red complex reported by Fraser *et al.*<sup>72</sup> occurs at 410 m $\mu$ . Frantsevich-Zabludovskaya *et al.* used a blue filter of the FEK-M photoelectric colorimeter.

In the case of the brown solutions resulting from low ratios of potassium iodide:palladium, the authors<sup>71</sup> were unable to identify the coloured constituent. However, it was noted that the absorbance was constant with time; the solution conformed to Beer's Law and the molar extinction coefficient, albeit regarded as arbitrary, was calculated as  $4.3 \times 10^3$ . While the brown solution examined by an ultramicroscope failed to reveal colloidal particles, the dialysis data clearly indicated a colloidal suspension. It should be noted here that the present author<sup>73</sup> used potassium iodide for the gravimetric determination of palladium. An excess of at least 10 times the calculated weight of the iodide could be used and PdI<sub>2</sub> was applied successfully as the weighing form.

In a previous publication the present author expressed the opinion that the palladium iodide spectrophotometric method, because of its sensitivity to oxidising and cation interferences would find little practical application. Clearly this was an erroneous prediction.

1-Benzoyl-2-methylglyoxal dioxime was used by Schekochikhina, Peshkova and Shlenskaya<sup>74</sup> to react with palladium at pH 1.25–3.60, forming a yellow crystalline salt, soluble in alkaline solution. A chloroform extract eliminated interferences and the complex showed a maximum absorbance at 280 m $\mu$ .

2-Chloropyridine was used by Egli<sup>75</sup> to separate and to determine palladium and platinum. The separation was made in a special flask constructed from an Erlenmeyer flask in which the sample was weighed, reduced in hydrogen, dissolved in mixed acids and the solutions evaporated to form chloride solutions. The latter solution was then treated with 40% sodium nitrate solution followed by the 2-chloropyridine which must be pyridine free. Immediately after the addition of the chloropyridine, the solution was mixed, the layers were allowed to separate and the strongly acid aqueous layer, which contained most of the impurities, was drained off. The organic layer was washed with a solution of 40% sodium nitrate and nitric acid and the washings discarded. There was then added consecutively a 1:1 solution of acetic acid and butanol, an aqueous solution of anhydrous sodium acetate and sodium toluene sulphonate. The chloropyridine layer containing the palladium was drawn off into a 100-ml flask containing 50 ml of dimethylformamide.

The upper layer was similarly extracted with a solution of 2-chloropyridine, butanol and acetic acid, adding the extract to a calibrated cylinder. The aqueous layer with the platinum was treated immediately with 20% hydrochloric acid, a solution of tin(II) chloride and pure hydroquinone. The technique of the above extraction must be applied with precision. Variations in time, after the addition of the chloropyridine, will alter the distribution of the platinum in the two phases because of the dissociation of the platinum-chloropyridine complex. On standing there was a decrease in the amount of platinum in the aqueous layer and, furthermore, the complex may partially precipitate.

For the colorimetric determination of palladium the extract was now diluted to volume with dimethylformamide. A measured volume of this solution was transferred to a measuring flask and diluted with dimethylformamide, then solutions of acetic acid and sodium hydroxide were added. This was followed by a solution of potassium iodide and the volume was made up to the mark with dimethylformamide and allowed to stand in the dark overnight at 20°. The absorbance of the red colour was measured at 525 m $\mu$ .

For platinum the yellow tin(II) complex was extracted with acetic ester within a 24-hr period, the extracts were made up to volume and the absorbance was measured at 401 m $\mu$  against a blank containing acetic ester and hydroquinone. Correction factors were proposed to compensate for losses of platinum resulting from a variety of compositions and extraction conditions. Small errors of palladium may occur with high ratios of palladium to platinum. However, only traces of palladium should appear in the platinum phase. The use of a glass stirring rod rather than the Teflon protective rod, induced crystallisation of the platinum-palladium complexes. The claim by the author of an accuracy of palladium determination greater than that obtained from the iodide method is unsubstantiated. Maximum intensity of colour was achieved after 15 hr. The platinum-tin(II) method was modified by the use of hydroquinone rather than by resorcinol. Presumably, iridium interfered with the platinum determination and gold with the palladium determination. Quantities of the associated base metals, copper, iron, nickel, cobalt, chromium, lead, *etc.*, comparable to the amounts of platinum and palladium, introduce interference of less than 0.5%.

No data were provided to indicate the accuracy which can be achieved and it would seem that in the development of the equipment and of the technique of dissolution, some effort was made to add to the complexity and the difficulty of what is normally a relatively simple operation. Compared to the ease of application of a standard rose crucible the use of a specially constructed flask of 100-ml capacity, with the associated difficulty of weighing milligram amounts of metal by difference, is an unnecessary complication.

Although thionalide is a general precipitant for heavy metal cations it may be used for the spectrophotometric determination of palladium.<sup>76</sup> The complex has a mole ratio of metal to reagent of 1:2 and is extracted from 2-3*M* hydrochloric acid by a 2:1 chloroform-isoamyl alcohol mixture. Absorbance at 375 m $\mu$  is measured 10-15 min after a single extraction. Beer's Law is obeyed over the range of 0.4-12  $\mu\text{g/ml}$  and the sensitivity is 0.2  $\mu\text{g/ml}$ . The claim is made that palladium can be determined in the presence of 1000 times its amount of platinum, rhodium, iridium, osmium, cobalt and nickel. Tartaric acid is used to mask the presence of molybdate, iron(III), bismuth(III), zinc, lead(II) and tin(IV). Presumably, the degree of interferences was determined by the addition of constituents. An accuracy of  $\pm 5\%$  is claimed.

The related reagent thioglycollic acid has been used for the determination of palladium in titanium ores.<sup>77</sup> In the presence of tartaric acid the reaction produces a stable yellow colour. Maximum absorbance occurs at 371 m $\mu$  and the colour developed at pH 4 can be extracted by butyl alcohol. Copper, iron and molybdenum interfere; platinum does not.

4-(2-Thiazolylazo)-1-naphthol<sup>78</sup> produces a blue-green chelate with a mole ratio

of reagent to metal of 1:1 and a purple chelate with a 1:2 ratio. The former is obtained with a large amount of palladium and the latter with an excess of reagent.

TABLE I.—SPECTROPHOTOMETRIC METHODS FOR PALLADIUM

No.	Reagent	Range of concentration, ppm
1.	Tetra-ethyleneglycoldimethyl ether + potassium iodide <sup>12</sup>	0-6 B.L.
2.	<i>N,N'</i> -Bis-(2-Sulphethyldithio-oxamide) <sup>13</sup>	0.02-0.2
3.	8-Aminoquinoline <sup>14</sup>	0.04-30
4.	<i>p</i> -Nitrosodiphenylamine <sup>10, 15, 79-82</sup>	0.05-0.3
5.	<i>p</i> -Nitrosodimethylaniline <sup>79, 10</sup>	0.25-1
6.	3-Hydroxy-1-( <i>p</i> -sulphonatophenyl)-3-phenyltriazine <sup>297</sup>	0.2-6
7.	8-Mercaptoquinoline (thio-oxine) <sup>17-19</sup>	0.2-10 0-27 B.L.
8.	Thiocyanate <sup>20, 21</sup>	0.2-9
9.	1-Mercaptopropionic- <i>p</i> -aniside <sup>22</sup>	0.2-12 B.L.
10.	Chrome Azurol S (Trisodium salt of 3''-sulpho-2'',6''-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid) <sup>23</sup>	0.33-7.3 B.L.
11.	1-( <i>o</i> -Arsonophenylazo)-2-naphthol-3,6-disulphonate (Thoron) <sup>24</sup>	0.35-25.4
12.	5-Mercapto-3-phenyl-2-thiol-1,3,4-thiodiazole-2-one [Bismuthiol-I] <sup>43</sup>	0.4-8
13.	2-Mercaptobenzothiazole and 2-mercaptobenzimidazole <sup>25, 26</sup>	0.4-6 1.0-2.6
14.	Quinoxaline-2,3-dithiol <sup>27-29</sup>	0.4-3 0.4-2.8
15.	5-( <i>p</i> -Dimethylaminobenzylidene)-rhodanine <sup>30, 31</sup>	0.4-2.5
16.	Thionalide <sup>76</sup>	0.4-12
17.	2-Mercapto-4,5-dimethylthiazole <sup>22, 33</sup>	0.5-8
18.	Thiosalicylic acid <sup>34</sup>	0.5-2.6
19.	Tin(II) phosphate <sup>35</sup>	0.5-2.5
20.	1-Nitroso-2-naphthol <sup>11, 36</sup>	0.5-5
21.	1-Thioglycerol <sup>37</sup>	0.5-9 B.L.
22.	Diethyldithiophosphate <sup>38</sup>	0.6-4 B.L. 6-40 visual
23.	2-Nitroso-1-naphthol-4-sulphonic acid <sup>39</sup>	0.6-18.7 B.L.
24.	Chromotrope 2R (disodium 2-phenylazo-1,8-dihydroxynaphthalene-3,6-disulphonate) <sup>40</sup>	0.6-12.3 B.L.
25.	Xylenol Orange [3,3'-bis- <i>N,N</i> -di(carboxymethyl)-aminomethyl- <i>o</i> -cresolsulphonaphthalein] <sup>41</sup>	0.8-3.2
26.	Thiourea <sup>42</sup>	0.8-24
27.	2,5-Dimercapto-1,3,4-thiodiazole (Bismuthiol-I) <sup>43</sup>	0.8-8.0
28.	<i>o</i> -Nitrosoresorcinolmonomethyl ether <sup>43</sup>	0.8-2
29.	Tin(II) bromide <sup>44</sup>	1-10 B.L.
30.	1-Phenylthiosemicarbazide <sup>44</sup>	1-30
31.	$\alpha$ -Furildioxime <sup>45</sup>	1-5
32.	2-Nitroso-1-naphthol <sup>45-49, 56</sup>	1-5
33.	Dibenzylidithio-oxamide <sup>50</sup>	1-4
34.	Didodecyldithio-oxamide <sup>51</sup>	1-4
35.	Tartrazine <sup>52</sup>	1.23-9.83
36.	Sodium 1-nitroso-2-naphthol-3,6-disulphonate (Nitroso-R salt) <sup>53, 54</sup>	1.28-4.27 5-13 B.L.
37.	Quinoline-2-aldoxime <sup>55</sup>	1.5-70 B.L.
38.	Phenyl-1-pyridyl ketoxime <sup>56</sup>	1.5-8(340 m $\mu$ ) 2-10 410 m $\mu$ )
39.	<i>N,N'</i> -Bis-(3-dimethylaminopropyl)-dithio-oxamide <sup>57, 58</sup>	1.6-5.7
40.	5-Amino-2-benzimidazoethiol <sup>59</sup>	2-7
41.	Thiomalic acid <sup>60</sup>	2-7

TABLE I.—SPECTROPHOTOMETRIC METHODS FOR PALLADIUM (*continued*)

No.	Reagent	Range of concentration, ppm
42.	$\beta$ -Furaldioxime <sup>87, 88</sup>	2.4–6
43.	<i>N,N'</i> -Ethylene-bis-(4-methoxy-1,2-benzo-quinone-1-oxime-2-imine) <sup>89</sup>	4–100
44.	Catalytic with molybdenum blue <sup>91</sup>	4–11
45.	EDTA <sup>90</sup>	5–200 B.L.
46.	1-(2-Pyridylazo)-2-naphthol <sup>91–94</sup>	6–14
47.	Sodium 1-azophenyl-2-hydroxy-6,8-naphthalene disulphonate; <sup>95</sup> Sodium 1-phenyl-3-methyl-5-hydroxy-4-( <i>p</i> -sulphophenyl)pyrazole <sup>96</sup>	1.04–14 12.61–189.22
48.	Tin(II) chloride <sup>92, 93</sup>	8–32
49.	2-Mercaptobenzoxazole <sup>96</sup>	15–30
50.	Nitrilotri-acetic Acid <sup>97</sup>	20–220
51.	Bromide ion <sup>94</sup>	37–360
52.	Dimethylglyoxime and salicylaldoxime <sup>95</sup>	
53.	2-Mercaptoquinoline <sup>19</sup>	
54.	Bis-(allylthiocarbamyl)-hydrazine (Dalzin) <sup>98</sup>	
55.	Dithio-oxamide (Rubeanic acid) <sup>98</sup>	
56.	Nioxime <sup>99</sup>	
57.	4-Methyl-1,2-cyclohexanedione dioxime <sup>70</sup>	
58.	Benzildioxime <sup>69</sup>	
59.	Dimethylglyoxime <sup>49</sup>	
60.	Potassium iodide <sup>71–73</sup>	
61.	1-Benzoyl-2-methylglyoxal dioxime <sup>74</sup>	
62.	2-Chloropyridine <sup>75</sup>	
63.	Thionalide <sup>76</sup>	
64.	Thioglycollic acid <sup>77</sup>	
65.	4-(Thiazolylazo)-1-naphthol <sup>78</sup>	

The purple complex has a sensitivity of 0.006  $\mu\text{g}/\text{cm}^2$  and can be extracted with isoamyl alcohol.

#### PLATINUM

Tin(II) chloride remains one of the most useful and generally applicable spectrophotometric reagents for platinum. Recently, it has been used for the determination of trace amounts of platinum dissolved from platinum anodes during the electrolysis of sodium chlorate.<sup>97</sup>

Platinum was separated from interfering constituents by coprecipitation with copper sulphide. One milligram of copper was sufficient for the collection of microgram quantities of platinum from a 3*M* hydrochloric acid solution. The mixed sulphide precipitate was collected, treated with *aqua regia* and converted to chloride. The chloride solution was treated with tin(II) chloride reagent and the platinum complex extracted with ethyl acetate. Absorbance was measured at 420 *mμ*. The deleterious effect of chromium was eliminated by the ethyl acetate extraction. Gold did not interfere. No data were included to indicate interferences from copper, nickel or the associated base metal. However, the method was designed for, and applied successfully to solutions of sodium chloride, sodium chlorate and sodium bichromate. Following reduction of the oxidants by careful addition of concentrated hydrochloric acid, the platinum-copper sulphide precipitation was completed. For the range of 0.0–0.02 ppm of platinum an accuracy of 5–10% was obtained.

Berman and Goodhue<sup>98</sup> introduced a variation in the tin(II) method to achieve a sensitivity five times greater than that realised by the method proposed by Ayres and Meyer.<sup>92</sup> This was accomplished primarily by a larger reduction in the amount of tin(II) chloride and the addition of sulphuric and perchloric acids to stabilise the coloured constituent and to effect a hypsochromic shift in the absorption band from the tin(II) reagent.

In the absence of perchloric acid there is a marked fading caused, at least partially, by light. In the presence of 5 ml of concentrated perchloric acid the yellow colour develops within a few minutes and remains stable for at least 4 hr. The amounts of sulphuric acid are not critical but fuming should be avoided. If this inadvertently takes place, addition of several millilitres of hydrochloric acid and boiling to remove the volatile acid restores the colour systems. Too little sulphuric acid produces low results. The absorbance is measured at 310  $m\mu$  and the recommended range is 0.4–6 ppm with 1-cm cells, and 0.08–1.2 ppm with 5-cm cells. Quartz cells are used because 310  $m\mu$  is beyond the limit of 320  $m\mu$ , recommended for Corex glass cells. However, to avoid the necessity of ultraviolet accessories the authors determined that a tungsten lamp source and Corex glass cells could be used with a 3-fold increase in slit width. The method is particularly suitable for solutions containing nitric acid because the procedure accomplishes its removal. Interferences from associated metals have been properly examined by carrying the constituents through the complete treatment before measurements. In general, the platinum metals interfere, with iridium providing the least effect. Of the associated base metals, chromium, iron and copper provide the least interference. It is recommended that here, as with most other spectrophotometric methods for platinum, a previous separation of the latter be effected.

The stability of the tin(II)-platinum complex is not critically affected by the proportions of the reagent although minimum amounts are recommended. For the applicable range of platinum, 2 ml of the freshly prepared reagent is the optimum amount.

Tin(II) chloride in solutions of sulphuric and perchloric acids was used by Pilipenko and Sereda<sup>99</sup> for the simultaneous determination of platinum and palladium. Samples containing 0.4–10  $\mu\text{g}$  of the metals/ml were heated with concentrated sulphuric acid. Perchloric acid was added and the absorbance of the tin(II) chloride colour for palladium was measured at 630  $m\mu$ . The absorbance at 310  $m\mu$ , less that calculated from the palladium concentration, was used to determine platinum. There was little or no interference with the palladium determination from osmium, rhodium and iridium. Iridium, rhodium and ruthenium interfered with the platinum determination.

Tin(II) chloride was also used by Mizuike and Ujihira<sup>100</sup> to determine traces of platinum in chlorate cell liquor. Mercury and the tin(II) chloride solution were mixed. The mercury alloy of platinum was isolated followed by volatilisation of the mercury at 350° in a nitrogen stream. The platinum residue was then prepared for the tin(II) spectrophotometric method with the absorbance being measured at 420  $m\mu$ .

Faye and Inman introduced a useful variation in the tin(II) method.<sup>101</sup> The procedure followed a separation of platinum from palladium by an anion-exchange column, then stripping by perchloric acid and subsequent fuming with sulphuric acid. Following treatment in the presence of hydrochloric acid, the platinum was extracted



by a solution of tin(II) chloride and tributyl phosphate-hexane. The organic phase was centrifuged and the absorbance was measured in a 1-cm Corex cell.

It should be noted that the efficiency of the tin(II) method for platinum subsequent to stripping from an exchanger may be vitiated by the presence of organic matter. Coburn *et al.*<sup>102</sup> have recorded that nitric-sulphuric mixtures failed to destroy the organic matter but mixtures of perchloric and nitric acids were effective.

The tin(II) method was applied to binary alloys containing uranium and less than 5% of platinum. Larger proportions were determined gravimetrically. Wagner<sup>103</sup> and Shmulyakovskii<sup>104</sup> used the tin(II) method for platinum in catalysts and a procedure for determining platinum in cathode slimes with and without extraction was recorded by Struszynski and Chwastowska.<sup>105</sup>

5-(*p*-Dimethylaminobenzylidene)-rhodanine, previously used for the spectrophotometric determination of palladium over the range of 0.4–2.5 ppm,<sup>30,31</sup> has been applied by Piercy and Ryan to the determination of platinum over the range of 0.5–6 ppm.<sup>4</sup> While maximum absorbance occurs at 545 m $\mu$ , the appreciable absorbance of reagent required the use of 590 m $\mu$ , at which wavelength the reagent showed 100% transmittance. The procedure required reduction to platinum(II) by ascorbic acid although the mole ratio of metal to reagent proved to be 1:3. The dark red complex is developed at a pH between 2 and 4 and heating at 65–75° for 5 min. An extraction is made with propionic acid in which the red colour remains stable for 1 hr. There is interference from silver, copper, gold, rhodium and palladium. Interference from palladium can be reduced somewhat by the addition of dimethylglyoxime; 25 ppm of palladium to 2 ppm of platinum can be tolerated.

2,3-Quinoxalinedithiol (QDT), used by Ayres and Janota<sup>27</sup> for palladium was also applied for the spectrophotometric determination of platinum.<sup>29</sup> The method is applicable over the range 1.4–5 ppm. The procedure requires the use of *N,N*-dimethylformamide as a solvent and previous treatment with tin(II) chloride solution. With freshly prepared reagents full colour was developed within 50 min with constant absorbance up to 50 hr. Aged reagents decreased the period of stability. The tin reagent could be used for about 2 weeks and the QDT reagent in the dimethylformamide for about 4 days. The method was not sensitive to excess reagent or to acid content, but large proportions of tin(II) chloride resulted in a lack of precision. Associated base and platinum metals interfered and a previous separation of platinum is required. Although the authors failed to suggest a method of separation, a series of hydrolytic separations, both in the presence and in the absence of nitrite, ought to be effective. Convincing evidence was provided by the authors to indicate a platinum to reagent mole ratio of 1:2, providing a blue dissolved constituent with maximum absorbance occurring at 624 and 585 m $\mu$  and an intermediate minimum at 599 m $\mu$ . Each of these wavelengths was equally suitable for platinum determinations.

Potassium iodide was used by Karpova and Gut'ko<sup>106</sup> to determine rhodium, iridium and platinum in mixed solutions. Beer's Law was obeyed over the respective ranges of 30–3500, 1.6–160 and 0.4–64  $\mu\text{g/ml}$ , the respective maximum absorbances being 502, 488 and 494 m $\mu$ .

A potentially useful method for a range of platinum of 10–100 ppm in the presence of copper, selenium, and tellurium was described by Ginzburg and Sal'skaya.<sup>107</sup> Absorbance measurements could be made at 370–450 m $\mu$ . Beer's Law was obeyed

over the range 5–120  $\mu\text{g/ml}$ . The procedure required a conversion of the platinum salts by perchloric acid to hexabromoplatinic acid. During the fuming process the solution may become turbid if the larger amounts of platinum are present but dissolution is accomplished upon the required addition of hydrobromic acid. The method has been applied successfully to industrial products containing high proportions of copper, selenium and tellurium. The unsubstantiated claim is made that the method tolerates approximately equal amounts of platinum, selenium and iron, 4-fold proportions of tellurium and copper and 17-fold amounts of nickel. Before this work, hexachloroplatinate(IV) had been applied by Kirkland and Yoe<sup>108</sup> for the range of 3–11 ppm and with measurements made at 262  $\text{m}\mu$ . As in the proposed method, the platinum metals interfered.

TABLE II.—SPECTROPHOTOMETRIC METHODS FOR PLATINUM

No.	Reagents	Range of concentration, ppm
1.	Tin(II) salt <sup>82, 97–105, 115, 121</sup>	0.4–6 0.5–2 3–25
2.	5-( <i>p</i> -Dimethylaminobenzylidene)-rhodanine <sup>4, 80, 81</sup>	0.5–6
3.	<i>p</i> -Nitrosodimethylaniline <sup>122, 123</sup>	0.7–2.4
4.	Dibenzylthio-oxamide <sup>50</sup>	1–5 (see Palladium Table No. 33)
5.	2,3-Quinoxalinedithiol <sup>29</sup>	1.4–5
6.	Potassium iodide <sup>106, 123, 210</sup>	1.8–5
7.	<i>N,N'</i> -Bis-(3-dimethylaminopropyl)-dithio-oxamide <sup>37, 58</sup>	(see Palladium Table No. 39)
8.	Hexachloroplatinate(IV) <sup>108</sup> and hexabromoplatinate(IV) <sup>107</sup>	3–11 5–120 B.L. 10–100
9.	<i>o</i> -Phenylenediamine <sup>109</sup>	4–12
10.	Thiosemicarbazide <sup>110, 124, 125</sup>	10–90
11.	Anthranilic acid <sup>111, 112</sup>	16–48
12.	<i>o</i> -Aminophenol- <i>p</i> -sulphonic acid <sup>111</sup>	8–24
13.	Diacetoimidoplatinum <sup>124</sup>	250–900
14.	Dithizone <sup>113, 114</sup>	
15.	Phenylthiosemicarbazide <sup>126</sup>	
16.	Alkali fluoroplatinate <sup>127</sup>	
17.	2-Chloropyridine <sup>75</sup>	(See Table I, No. 62)

*o*-Phenylenediamine forms an orange solution with platinum(IV).<sup>109</sup> The optimum range is 4–12 ppm and the optimum wavelength is 450  $\text{m}\mu$ ; the sensitivity is 0.003  $\mu\text{g/cm}^2$ . The complex is formed in 25 min at pH 3–4 and remains stable for 1 hr. Absorbance increases up to pH 3 and decreases beyond pH 4.0. The complex contains a mole ratio of platinum to reagent of 1:2. There is interference from associated base and platinum metals.

Thiosemicarbazide was used by Barkovskii<sup>110</sup> to determine platinum in silver alloys without the removal of silver. The alloy was dissolved in nitric and hydrochloric acids and the silver chloride was dissolved by ammonium thiocyanate; then ammonia and sodium acetate were added. To an aliquot of the resulting liquid were added, in order, ammonium thiocyanate, gelatin, an aqueous solution of the thiosemicarbazide, sodium acetate and the absorbance was measured in a 3-ml cell with a green filter.

Anthranilic acid<sup>111</sup> produces a reddish-violet complex with a mole ratio of platinum(IV) to reagent of 1:1 and a maximum absorption at 500 m $\mu$ . The optimum concentration range is 16–48 ppm of platinum. The sensitivity is 0.068  $\mu\text{g}/\text{cm}^2$ . Beer's Law is obeyed over the range of 4–64 ppm of platinum. Unfortunately, there are insufficient data included in the published report to make clear the effects of acidity, salt content, *etc.* However, the data in the original thesis<sup>112</sup> indicate that the optimum pH is 5 with a tolerance of  $\pm 0.5$  unit. An increase of 4 ml of reagent solution above the recommended 3 ml is also without effect. Larger amounts result in a decrease of absorbance. The rate of colour formation is slow but the maximum colour intensity can be achieved by heating on a steam bath for 15–20 min; longer periods reduce the absorbance. As might be expected, the reagent is far from specific; copper, nickel, iron, rhodium and ruthenium interfere. Palladium and iridium can be tolerated up to ratios of 1:1. Nitric acid is removed by conventional methods.

It was found<sup>111</sup> that *o*-aminophenol-*p*-sulphonic acid also forms a coloured complex with platinum(IV) which showed a maximum absorption at 420 m $\mu$  and a sensitivity of 0.025  $\mu\text{g}/\text{cm}^2$ . The conditions for colour reactions were 1 ml of 1% reagent, a pH range of 5–6 and a reaction period of about 2 hr for maximum colour development. The optimum concentration was 8–24 ppm and Beer's Law was obeyed over the range 1–26 ppm. This reagent is a useful alternative to the more established reagents.

Dithizone in benzene has been used for the extraction of platinum(II) from sulphuric acid solutions of iron, nickel and chromium. Interfering elements can be removed by washing the extract with hydrochloric acid or by treating the sample solution with concentrated dithizone in benzene before the reduction of platinum with tin(II) chloride. Absorbance could be measured at either 490 or 720 m $\mu$ .<sup>113</sup>

The acidities required for the benzene-dithizonate extractions were also recorded by Kawahata, Mochizuki and Misaki.<sup>114</sup> These were for palladium, <15*N* and <pH 5, for platinum(II), 1.0–10.5*N*, for gold > 7*N*. The molar absorptivities were respectively,  $3.8 \times 10^4$  at 450 m $\mu$  and  $3.2 \times 10^4$  at 640 m $\mu$ ;  $4.1 \times 10^4$  at 490 m $\mu$ , and  $3.8 \times 10^4$  at 720 m $\mu$ ,  $2.6 \times 10^4$  at 450 m $\mu$ .

**Zusammenfassung**—Es wird eine kritische Übersicht über die nach 1958 veröffentlichten spektralphotometrischen Bestimmungsmethoden für Palladium und Platin gegeben. Zusammen mit den Beschreibungen des Verhaltens der Metalle wird eine Tabelle vorgelegt, die vor 1958 beschriebene Reagentien mit den einschlägigen Literaturzitaten registriert.

**Résumé**—On passe en revue, de façon critique, les méthodes spectro-photométriques de dosage du palladium et du platine publiées postérieurement à 1958. A la description de chaque métal est joint un tableau identifiant les réactifs mentionnés avant 1958 avec les références correspondantes.

#### REFERENCES

- <sup>1</sup> D. E. Ryan, *Canad. J. Res.*, 1961, **39**, 2389.
- <sup>2</sup> E. G. R. Ardagh, F. S. Seaborne and N. S. Grant, *Canad. Chem. Met.*, 1924, **8**, 117, 140, 3.
- <sup>3</sup> H. Zachariasen and F. E. Beamish, *Analyt. Chem.*, 1962, **34**, 964.
- <sup>3a</sup> I. Némec, J. Berka and J. Zkya, *Microchem. J.*, 1962, **6**, 525.
- <sup>4</sup> F. E. Piercy and D. E. Ryan, *Canad. J. Chem.*, 1963, **3**, 41, 667.
- <sup>5</sup> F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal.*, 1937, **9**, 460.
- <sup>6</sup> J. W. Murphy and H. E. Affsprung, *Analyt. Chem.*, 1961, **33**, 1658.

- <sup>7</sup> J. Brandstêtr and J. Vrestál, *Coll. Czech. Chem. Comm.*, 1961, **26**, 392.
- <sup>8</sup> A. K. Majumdar and J. G. Sen Gupta, *Analyt. Chim. Acta*, 1959, **20**, 532.
- <sup>9</sup> F. Feigl, *Laboratory Manual of Spot Tests*. Academic Press Inc., New York, 1943.
- <sup>10</sup> E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, Inc., New York, 3rd Ed., 1959.
- <sup>11</sup> F. E. Beamish and W. A. E. McBryde, *Analyt. Chim. Acta*, 1958, **18**, 551.
- <sup>12</sup> M. Ziegler and G. Pape, *Z. analyt. Chem.*, 1963, **3**, 197, 354.
- <sup>13</sup> A. Goeminne, M. Herman and Z. Eeckhaut, *Analyt. Chem. Acta*, 1963, **28**, 512.
- <sup>14</sup> V. K. Gustin and T. R. Sweet, *Analyt. Chem.*, 1963, **35**, 44.
- <sup>15</sup> E. R. R. Marhenke and E. B. Sandell, *Analyt. Chim. Acta*, 1963, **28**, 259.
- <sup>16</sup> W. A. E. McBryde and J. H. Yoe, *Analyt. Chem.*, 1948, **20**, 1094.
- <sup>17</sup> Y. U. A. Bankovskii and A. F. Ievin'sh, *Zhur. analit. Khim.*, 1958, **13**, 507.
- <sup>18</sup> Y. A. Bankovskii, G. P. Mezharauks and A. F. Ievin'sh, *ibid.*, 1962, **17**, 714.
- <sup>19</sup> J. Xavier, *Z. analyt. Chem.*, 1958, **163**, 182.
- <sup>20</sup> V. I. Shlenskaya, V. P. Khvostove and V. M. Peshkova, *Zhur. analit. Khim.*, 1962, **17**, 508.
- <sup>21</sup> E. S. Przheva'skii, V. I. Shlenskaya and L. F. Maternykh, *Ser. Fiz. Mat. i. Estetven Nauk*, 1954, **4**, 71.
- <sup>22</sup> A. I. Busev and A. Naku, *Zhur. analit. Khim.*, 1963, **18**, 500.
- <sup>23</sup> S. P. Sangal and A. K. Dey, *Mikrochim. Ichnoanalyt. Acta*, 1963, **5**.
- <sup>24</sup> *Idem*, *Microchem. J.*, 1963, **7**, 257.
- <sup>25</sup> A. K. Majumdar and M. M. Chakrabartty, *Naturwiss.*, 1957, **44**, 511; *Z. analyt. Chem.*, 1958, **162**, 96; *ibid.*, 1959, **20**, 379.
- <sup>26</sup> J. Xavier, *Z. analyt. Chem.*, 1958, **164**, 250.
- <sup>27</sup> G. H. Ayres and H. F. Janota, *Analyt. Chem.*, 1959, **31**, 1958.
- <sup>28</sup> *Idem*, *ibid.*, 1964, **36**, 138.
- <sup>29</sup> G. H. Ayres and R. W. McCrory, *ibid.*, 1964, **36**, 133.
- <sup>30</sup> G. H. Ayres and B. D. Narang, *Analyt. Chim. Acta*, 1961, **24**, 241.
- <sup>31</sup> F. Pantani, *Gazzetta*, 1960, **90**, 999.
- <sup>32</sup> D. E. Ryan, *Analyst*, 1951, **76**, 310.
- <sup>33</sup> A. J. Radford, *ibid.*, 1960, **85**, 445.
- <sup>34</sup> I. Dema and V. Voicu, *Acad. Rep. Populare Romine, Studii Cercetări Chim.* 1960, **8**, 173.
- <sup>35</sup> G. H. Ayres and J. H. Alsop, *Analyt. Chem.*, 1959, **31**, 1135.
- <sup>36</sup> F. E. Beamish and W. A. E. McBryde, *Analyt. Chim. Acta*, 1953, **9**, 349.
- <sup>37</sup> R. W. Burke and J. H. Yoe, *Talanta*, 1963, **10**, 1267.
- <sup>38</sup> A. I. Busev and M. I. Ivanyutin, *Zhur. analit. Khim.*, 1958, **13**, 18.
- <sup>39</sup> S. Komatsu and S. Kamiyama, *J. Chem. Soc. Japan*, 1960, **81**, 1034.
- <sup>40</sup> G. Popa, I. Panulescu and G. Baiulescu, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, 1961, **9**, 85.
- <sup>41</sup> M. Otomo, *Bull. Chem. Soc. Japan*, 1963, **36**, 889.
- <sup>42</sup> A. K. Majumdar and M. M. Chakrabartty, *Analyt. Chim. Acta*, 1958, **19**, 372; *Science and Culture*, 1957, **23**, 46.
- <sup>43</sup> K. Kodama, *Nagoyashi Kôgyô Kenkyûsho Kenkyû Hôkoku*, 1958, **19**, 1.
- <sup>44</sup> S. Komatsu and K. Taki, *J. Chem. Soc. Japan*, 1959, **80**, 397.
- <sup>45</sup> L. E. Ross, G. Kesser and E. T. Kucera, *Analyt. Chem.*, 1960, **32**, 1367.
- <sup>46</sup> E. R. Alvarez, *An. Direc. Gen. Ofic. Quim. Nac.*, B. Aires, 1949, **2**, 88.
- <sup>47</sup> K. L. Cheng, *Analyt. Chem.*, 1954, **26**, 1894.
- <sup>48</sup> R. P. Larsen and L. E. Ross, *U.S. At. Energy Comm.*, 1958, TID 7568, Pt. 1, 9.
- <sup>49</sup> K. Kodama, *Nagoyashi Kôgyô Kenkyûsho Kenkyû Hôkoku*, 1958, **19**, 4.
- <sup>50</sup> J. T. Pyle and W. D. Jacobs, *Talanta*, 1962, **9**, 761.
- <sup>51</sup> W. D. Jacobs, C. M. Wheeler and W. H. Waggoner, *ibid.*, 1962, **9**, 243.
- <sup>52</sup> G. H. Baiulescu and M. Papagheroghe, *Rev. Chim. (Bucharest)*, 1959, **10**, 710.
- <sup>53</sup> J. Shamir and A. Schwartz, *Talanta*, 1961, **8**, 330.
- <sup>54</sup> F. C. Garcia and M. L. Garrido, *Anales. Teal Soc. españ. Fis. Quim.*, 1962, **58B**, 397.
- <sup>55</sup> N. Oi, *J. Chem. Soc. Japan*, 1959, **80**, 1151.
- <sup>56</sup> B. Sen, *Analyt. Chem.*, 1959, **31**, 881.
- <sup>57</sup> W. D. Jacobs, *ibid.*, 1960, **32**, 512.
- <sup>58</sup> *Idem*, *ibid.*, 1961, **33**, 1279.
- <sup>59</sup> J. G. Sen Gupta, *Talanta*, 1961, **8**, 729.
- <sup>60</sup> V. L. Wagner and J. H. Yoe, *ibid.*, 1959, **2**, 239.
- <sup>61</sup> J. R. Stokely and W. D. Jacobs, *Analyt. Chem.*, 1963, **35**, 149.
- <sup>62</sup> M. Hayashi, *J. Chem. Soc. Japan*, 1960, **81**, 1703.
- <sup>63</sup> A. I. Busev and L. V. Kiseleva, *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz. Khim.*, 1958, **13**, 179.

- <sup>64</sup> T. Sawada and S. Kato, *Japan Analyst*, 1962, **11**, 544.
- <sup>65</sup> Gr. Popa, V. Croitoru and El. G. Radulescu, *Analele Univ. "C. I. Parhon" Bucuresti, Ser. Stiint. Nat.*, 1961, **10**, 197.
- <sup>66</sup> T. Arita and J. Yoe, *Analyt. Chim. Acta*, 1963, **29**, 500.
- <sup>67</sup> P. G. Desideri and F. Pantani, *Talanta*, 1961, **8**, 235.
- <sup>68a</sup> N. K. Dutt and K. P. Sarma, *Science and Culture*, 1957, **23**, 249.
- <sup>68b</sup> *Idem*, *J. Indian Chem. Soc.*, 1962, **39** 20.
- <sup>69</sup> N. K. Pshenitsyn and O. Ivonina, *Zavodskaya Lab.*, 1958, **24**, 1185.
- <sup>70</sup> C. V. Banks and R. V. Smith, *Analyt. Chim. Acta*, 1959, **21**, 308.
- <sup>71</sup> T. F. Frantsevich-Zabludovskaya, L. P. Kalimanova and G. I. Sharafan, *Zhur. analit. Khim.*, 1963, **18**, 1083.
- <sup>72</sup> J. G. Fraser, F. E. Beamish and W. A. E. McBryde, *Analyt. Chem.*, 1954, **26**, 495.
- <sup>73</sup> F. E. Beamish and J. Dale, *Ind. Eng. Chem., Analyt.*, 1938, **10**, 697.
- <sup>74</sup> R. L. Schekochikhina, V. M. Peshkova and V. I. Shlenskaya, *Vestn. Mosk. Univ., Ser.-1, Khim.*, 1961, **17**, 38.
- <sup>75</sup> R. A. Egli, *Z. analyt. Chem.*, 1963, **194**, 401.
- <sup>76</sup> A. I. Busev and A. Naku, *Zhur. analit. Khim.*, 1963, **18**, 1479.
- <sup>77</sup> V. Widtman, *Chem. Listy*, 1964, **58**, 211.
- <sup>78</sup> A. Kawase, *Japan Analyst*, 1963, **12**, 714.
- <sup>79</sup> J. H. Yoe and L. G. Overholser, *J. Amer. Chem. Soc.*, 1939, **61**, 2061; 1941, **63**, 3224.
- <sup>80</sup> J. H. Yoe and J. J. Kirkland, *Analyt. Chem.*, 1954, **26**, 1335.
- <sup>81</sup> D. E. Ryan, *Analyst*, 1951, **76**, 167.
- <sup>82</sup> E. S. Przheval'skii, V. I. Shlenskaya and I. S. Razina, *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron Fiz Khim.*, 1957, **12**, 111.
- <sup>83</sup> W. Nielsch, *Mikrochim. Acta*, 1954, 532.
- <sup>84</sup> F. Pantani and G. Piccardi, *Analyt. Chim. Acta*, 1960, **22**, 231.
- <sup>85</sup> O. Menis and T. C. Rains, *Analyt. Chem.*, 1955, **27**, 1932.
- <sup>86</sup> V. M. Peshkora, V. I. Shlenskaya and A. I. Rashevskaya, *Izv. Sektora Platiny i Drug. Blagorodn. Metal., Inst. Obshchei i Neorgan. Khim., Akad. Nauk S.S.S.R.*, 1955, **32**, 611.
- <sup>87</sup> E. W. Rice, *Analyt. Chem.*, 1952, **24**, 1995.
- <sup>88</sup> D. T. Hooker and C. V. Banks, U.S. Atomic Energy Comm., 1955, 1 SC-597, 113.p.p.
- <sup>89</sup> M. Mashima, *J. Chem. Soc. Japan*, 1959, **80**, 1260.
- <sup>90</sup> W. M. MacNevin and O. H. Kriege, *Analyt. Chem.*, 1954, **26**, 1768.
- <sup>91</sup> T. Shiokawa, T. Kambara and M. Yagi, *Japan Analyst*, 1955, **4**, 224, 227.
- <sup>92</sup> G. H. Ayres and A. S. Meyer, *Analyt. Chem.*, 1951, **23**, 299.
- <sup>93</sup> G. V. Knyazheva, *Izv. Sektora Platiny i Drug. Blagorodn. Metal., Inst. Obshchei i Neorgan. Khim., Akad. Nauk. U.S.S.R.*, 1948, **22**, 129.
- <sup>94</sup> G. H. Ayres and B. L. Tuffly, *Analyt. Chem.*, 1952, **24**, 949.
- <sup>95</sup> V. M. Peshkova, V. I. Shlenskaya and A. I. Rashevskaya, *Vestn. Mosk. Univ. 9, No. 5, Ser. Fiz Met. i Estestven Nauk.*, 1954, **3**, 83.
- <sup>96</sup> J. Xavier and P. Ray, *Science and Culture*, 1955, **20**, 609; 1955, **29**, 455.
- <sup>97</sup> Y. Ujihira and S. Hirano, *Bull. Chem. Soc. Japan*, 1964, **37**, 66.
- <sup>98</sup> S. S. Berman and E. C. Goodhue, *Canad. J. Chem.*, 1959, **37**, 370.
- <sup>99</sup> A. T. Pilipenko and I. P. Sereda, *Ukrain. Khim. Zhur.*, 1961, **27**, 524.
- <sup>100</sup> A. Mizuike and Y. Ujihira, *Japan Analyst*, 1963, **12**, 748.
- <sup>101</sup> G. H. Faye and W. R. Inman, *Analyt. Chem.*, 1961, **33**, 278.
- <sup>102</sup> H. G. Coburn, F. E. Beamish and C. L. Lewis, *ibid.*, 1956, **28**, 1297.
- <sup>103</sup> E. Wagner, *Z. analyt. Chem.*, 1955, **147**, 10.
- <sup>104</sup> Y. E. Shmulyakovskii, *Khim. i Tekhnol. Topliv i Masel* 1958, **3**, 56.
- <sup>105</sup> M. Struszyński and J. Chwastowska, *Chem. Analit.*, 1958, **3**, 949.
- <sup>106</sup> L. V. Karpova and A. D. Gut'ko, *Nikolorye Vopr. Emission i Molekul Spektroskop, Krasnoyarsk. Sb.*, 1960, 220.
- <sup>107</sup> S. I. Ginzburg and L. G. Sal'skaya, *Zhur. analit. Khim.*, 1962, **97**, 492.
- <sup>108</sup> J. J. Kirkland and J. H. Yoe, *Analyt. Chim. Acta*, 1953, **9**, 441.
- <sup>109</sup> J. G. Sen Gupta, *ibid.*, 1960, **23**, 462.
- <sup>110</sup> V. F. Barkovskii, *Izvest. Vysshykh Ucheb. Zavedenii, Khim. i Khim. Technol*, 1958, **3**, 52.
- <sup>111</sup> A. K. Majumdar and J. G. Sen Gupta, *Z. analyt. Chem.*, 1960, **177**, 265.
- <sup>112</sup> J. G. Sen Gupta, Ph.D., Thesis Jadavpur University, 1959.
- <sup>113</sup> M. Kawahata, H. Mochizuki and T. Misaki, *Japan Analyst*, 1962, **11**, 7.
- <sup>114</sup> *Idem, ibid.*, 1962, **11**, 819.
- <sup>115</sup> N. A. Figuorvski, *Ann. Sect. Plat. U.S.S.R.*, 1938, **15**, 129.
- <sup>116</sup> N. S. Polvektov and F. G. Spivak, *Zavodskaya Lab.*, 1945, **11**, 398.
- <sup>117</sup> B. G. Karpov and G. S. Savcemko, *Ann. Sect. Plat. U.S.S.R.*, 1938, **15**, 125.

- <sup>118</sup> O. I. Milner and G. F. Shipman, *Analyt. Chem.*, 1955, **27**, 1476.  
<sup>119</sup> C. W. Davies, *U.S. Bureau of Mines, Tech. Paper*, 1921, 270.  
<sup>120</sup> G. H. Ayres, *Analyt. Chem.*, 1953, **25**, 1622.  
<sup>121</sup> A. S. Meyer and G. H. Ayres, *J. Amer. Chem. Soc.*, 1955, **77**, 2671.  
<sup>122</sup> J. J. Kirkland and Y. H. Yoe, *Analyt. Chem.*, 1954, **26**, 1340.  
<sup>123</sup> J. C. H. Mingaye, *Records. Geol. Surv. New South Wales*, 1909, **8**, 284.  
<sup>124</sup> V. F. Barcovskii and L. M. Kulberg, *Izv. Sektora Platiny i Drug. Blagorodn. Metal. Inst. Obshchei i Neorgan. Khim., Akad. Nauk S.S.S.R.*, 1955, **29**, 141, 149.  
<sup>125</sup> W. B. Pollard, *Analyst*, 1942, **67**, 184.  
<sup>126</sup> S. Komutsu and K. Oonishi, *J. Chem. Soc. Japan*, 1955, **76**, 661.  
<sup>127</sup> T. E. Wheeler, T. P. Perros and C. R. Naeser, *J. Amer. Chem. Soc.*, 1955, **77**, 3488.