

is to devise methods for determining, at least approximately, the intermediate energy levels for sulfates, chlorates, perchlorates, etc. It should be clear that the difficulties that we have with these electrolytes are similar in principle to the difficulties that we have with organic compounds. Most of the passive resistances to change will prove to be energy humps.

Summary

The general results of this paper are:

1. The oxidation of dilute aqueous sulfurous acid or sodium sulfite is an irreversible reaction because, for reduction to take place, the system must pass through an energy level or energy hump which is higher than the energy level for nascent hydrogen as obtained by electrolysis.
2. With sulfuric acid solutions, and presumably with all other solutions, the energy hump decreases with increasing concentration, rising temperature and activating adsorption.

3. The stabilities of sodium chlorate and sodium perchlorate relatively to sodium hypochlorite are due to the intermediate energy levels which must be surmounted if reduction is to take place.

4. Sodium chlorate is adsorbed and activated so much by pulverulent copper that it can then be reduced by hydrazine.

5. An irreversible reaction may give a definite electromotive force. The limiting, ideal equation for the irreversible sulfite-sulfate electrode at constant pH is $nFE = RT \ln P' \times p_{SO_2}$.

6. All of Conant's work on irreversible reduction falls into line if one rejects the two assumptions of a reversible electrolytic step and a practically irreversible, non-electrolytic step. There is no experimental evidence for either, and both are superfluous. There is no reason at present for making any fundamental distinction between hydrogenation and reduction.

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A Procedure for the Separation of the Six Platinum Metals from One Another and for their Gravimetric Determination^{1,2}

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In a paper³ from this Laboratory, presented at the Ninth International Congress of Pure and Applied Chemistry in Madrid, April, 1934, a group of reactions was described which can be used for the quantitative separation of the six platinum metals from one another, and for their determination. The paper likewise contained a discussion of the analytical methods most generally used, and of certain others of special interest.

In this new system of analysis, the detailed procedure of which is given in the present paper, precipitation with ammonium chloride, fusion with pyrosulfate and extraction of metallic residues with acids are avoided entirely. The separation of platinum from palladium, rhodium and iridium is accomplished by controlled hydrolytic

precipitation. When a boiling solution containing these four metals as chlorides, and in addition sodium bromate, is neutralized to approximately pH 7, the hydrated dioxides of palladium, rhodium and iridium precipitate quantitatively, leaving platinum in solution. A second precipitation of the dioxides suffices to effect complete removal of platinum. This method is applicable not only to the joint separation of palladium, rhodium and iridium from platinum, but also to the individual separation of these metals from platinum. It has a very great advantage over the older method by which platinum is separated from palladium, rhodium and iridium by precipitation with ammonium chloride. The hydrolytic method effects a clean separation of the platinum, whereas that in which the platinum is precipitated as ammonium chloroplatinate involves at least two inherent types of error. One type of error results from the persistent contamination of the platinum salt by rhodium and iridium (even though tervalent) and, to a less extent, by palladium. The other error occurs be-

(1) Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

(2) Presented at the Meeting of the American Chemical Society in New York, April 25, 1935.

(3) R. Gilchrist and E. Wichers, "A New System of Analytical Chemistry for the Platinum Metals." Paper No. 178 of the Scientific Program of the Ninth International Congress of Pure and Applied Chemistry. As the proceedings of the Congress have not been published, reprints of this paper are not yet available.

cause ammonium chloroplatinate is appreciably soluble. It is true that the solubility of the platinum salt can be reduced to an amount which may be negligible in some analytical procedures by adding a large excess of ammonium chloride and digesting the solution. These conditions, however, greatly increase the contamination of the salt by other platinum metals. The same criticism applies to the separation of quadrivalent iridium from rhodium and palladium, by means of ammonium chloride. A full discussion of the shortcomings of the traditional methods of separating the platinum metals from one another cannot be given in this paper, but will be found in detail in the paper presented at the International Congress.

Palladium is readily and completely separated from rhodium and iridium, in chloride solution, by precipitation with dimethylglyoxime, a single precipitation being sufficient.

Rhodium is separated from iridium by reducing it to metal with titanous chloride in a boiling solution of the sulfates in diluted sulfuric acid. The metallic rhodium is dissolved in hot sulfuric acid and precipitated a second time, to remove iridium completely.

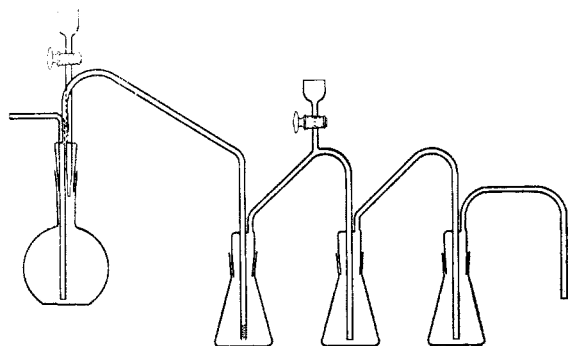


Fig. 1.—Distilling flask with train.

When this new procedure is applied to the separation of all six of the platinum metals from one another, osmium is the first metal which is isolated. This is accomplished by distilling its volatile tetroxide from a nitric acid solution. Ruthenium is next isolated by distilling its tetroxide from a solution of the sulfates in diluted sulfuric acid to which sodium bromate is added. A very suitable reagent for the absorption of osmium tetroxide, and also of ruthenium tetroxide, is 6 *N* hydrochloric acid saturated with sulfur dioxide.

In the recovery and determination of each of the six metals, the new features of the procedure

consist in the precipitation of osmium, of ruthenium and of iridium, as hydrated oxides, with final ignition to metal. Rhodium, and also platinum, are recovered as sulfides, and ignited to metal. Palladium is recovered as the glyoxime compound, in which form it may be weighed, or it may be determined as metal, after ignition of the glyoxime precipitate.

The accuracy of this new method is comparable to that of the best analytical procedures for the common metals. The reagents used are generally available, and no special equipment is required. While the operations must be performed carefully, they do not involve technique unfamiliar to a trained analyst.

The individual procedures upon which the general scheme for the group as a whole is based are to be found in the papers to which the references in this paper are given. These papers also contain a detailed account of the experimental work upon which the individual procedures were developed. They should be consulted for details which obviously cannot be included in the present paper. The general procedure, as given in this paper, was tested by analyzing solutions containing, simultaneously, known quantities of the six pure metals. The procedure is designed for the analysis of the platinum group, in the absence of other metals.

Consideration of the elements occurring in crude platiniferous materials will be taken into account in the extension of this scheme to their analysis.

Procedure Recommended for the Analysis of the Platinum Group

I. Separation and Determination of Osmium⁴

1. **Distilling Apparatus.**—The distilling apparatus, which is shown in Fig. 1, consists of three main parts, namely, a 700-ml. distilling flask, a set of three 300-ml. absorbing flasks and a train of inlet and delivery tubes which are sealed into one piece. The thistle tube, closed by a stopcock and placed between the first and second absorbing flasks, serves to replenish the absorbing solution with sulfurous acid if an unusual amount of nitric acid is distilled and also, at the end of the operation, to rinse the tube connecting the two flasks. The entire apparatus is constructed of Pyrex glass. The joints must be very carefully ground, and it is advantageous if they are made so that the flasks are interchangeable. It is important to note that these joints are sealed with a film of water only and not with lubricating grease, because the latter would cause reduction of some osmium tetroxide to dioxide

(4) R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931); RP 286.

which cannot be readily recovered. It was found necessary to grease the stopcock in the tube used for the introduction of nitric acid into the distilling flask, but this constitutes the only exception. During distillation, this delivery tube is frequently flushed with water in order to remove any osmium tetroxide which may have diffused into the column of water held in it. Three absorbing flasks are used, but the absorption of osmium tetroxide is practically complete in the first flask, and no osmium has been found to escape the second flask.

2. Separation of Osmium by Distillation as Osmium Tetroxide.—Place 150 ml. of diluted hydrochloric acid (1 + 1),⁵ which has been freshly saturated with sulfur dioxide, in the first absorbing flask and 50 ml. of the same reagent in each of the other two flasks. Place the solution containing the platinum metals in the distilling flask and make sure that the separate parts of the entire apparatus are properly connected. If necessary, dilute the solution in the distilling flask to about 100 ml. with water, and add through the inlet tube 40 ml. of diluted nitric acid (1 + 1). Flush the thistle tube and stopcock with 10 ml. of water. Pass a slow current of air through the apparatus and heat the solution in the distilling flask to boiling. Continue the distillation for one hour. This length of time should be sufficient to ensure complete elimination of osmium from solutions in which it was originally present as an alkaline osmate or bromosmate. If, however, the osmium is present as chlorosmate, the time required will be from seven to eight hours. In this case, it is preferable to distil from concentrated sulfuric acid, thereby greatly reducing the time required, or, if ruthenium is known to be absent, from concentrated sulfuric acid to which a few milliliters of nitric acid is added.

3. Recovery of Osmium by Precipitation as the Hydrated Dioxide.—Unite the portions of the absorbing solution and evaporate as far as possible on the steam-bath in a clean, unetched beaker. It is important, in precipitating the platinum metals hydrolytically, that the beakers used do not have an etched surface. An etched beaker often becomes stained with the precipitate, and this stain cannot always be removed readily. Digest the residue with 10 ml. of hydrochloric acid for fifteen minutes, and evaporate a second time. Repeat the digestion with hydrochloric acid and the evaporation three times more. This is done to ensure complete decomposition of any sulfite compounds of osmium. Dissolve the residue from the last evaporation in 150 ml. of water. Heat the resulting solution to boiling, and add to it a filtered 10% solution of sodium bicarbonate until a precipitate appears and suddenly coagulates. Add a few drops of brom phenol blue indicator solution (0.04%) to the hot solution. This indicator changes from yellow to blue at pH 4. Add the bicarbonate solution dropwise until the indicator assumes a faint bluish color. Finally, boil the solution for five to six minutes to ensure complete precipitation of the hydrated osmium dioxide.

(5) Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; sulfuric acid, the concentrated acid of specific gravity 1.84. Diluted acids will be designated as follows: for example, diluted hydrochloric acid (1 + 1) will mean one volume of the concentrated acid of specific gravity 1.18 diluted with one volume of water.

4. Determination of Osmium as Metal.—Filter the solution through a Munroe platinum crucible,⁶ carefully pouring the supernatant liquid through first. Transfer the precipitate, and wipe the inner walls of the beaker and also the glass rod with a rubber policeman which has been thoroughly wetted so that the precipitate will not cling to it. It should be borne in mind that filter paper must not be used to wipe the beaker, although it is used when handling precipitates of any of the other five platinum metals. Wash the precipitate thoroughly with a hot 1% solution of ammonium chloride, and then cover it with solid ammonium chloride. Moisten the ammonium chloride with a few drops of the wash solution and saturate the precipitate by applying suction. If desired, a saturated solution of ammonium chloride may be used to impregnate the precipitate. Continue the suction until the bottom of the crucible is coated with solidified ammonium chloride. Wipe off this coating of salt and place the platinum cap on the bottom of the crucible.

Cover the crucible with a Rose lid, preferably of quartz. Ignite a stream of hydrogen from a Rose delivery tube, likewise of quartz, and regulate the stream so that a very small flame is produced. Then insert the tube through the opening in the lid. The hydrogen flame will probably become extinguished by this operation and must be re-ignited. This is done by momentarily placing a burner flame under the crucible. The hydrogen will now burn as it emerges from under the lid at the edge of the crucible. The ignited hydrogen generates the requisite amount of heat to dehydrate the osmium compound without causing deflagration. After five minutes, gradually heat the crucible with the burner flame until all of the ammonium chloride is expelled. Ignite the osmium residue strongly in hydrogen for ten minutes. Remove the burner and allow the crucible to cool somewhat. Extinguish the hydrogen flame by momentarily breaking the current of hydrogen, and allow the crucible to cool to room temperature. Finally, displace the hydrogen with a current of carbon dioxide without even momentary access of air. If the hydrogen is not displaced by an inert gas, such as carbon dioxide, the reduced metal will be rapidly attacked when first exposed to the air, with significant loss of osmium. Weigh the residue as metallic osmium.

II. Separation and Determination of Ruthenium^{7,8}

1. Preparation of the Solution.—Evaporate to dryness on the steam-bath the solution which remains in the distilling flask after the elimination of osmium. Add 5 to 10 ml. of hydrochloric acid and again evaporate. Repeat the evaporation with hydrochloric acid until oxides of nitrogen are no longer evolved. Dissolve the residue from the last evaporation in about 20 to 30 ml. of water. Add 10 ml. of sulfuric acid and evaporate the resulting solution carefully until vapors of sulfuric acid are evolved. Trans-

(6) The chief disadvantage in the use of a Gooch crucible with an asbestos pad is the difficulty encountered during the ignition of the dioxide to metal. Even when the Gooch crucible is protected from the burner flame by setting it in a circle of asbestos board in a larger porcelain crucible, one is not always able to extinguish the hydrogen flame readily. Another disadvantage is the inadequate protection of the reduced metal from attack by air diffusing through the holes in the bottom of the crucible.

(7) Gilchrist, *Bur. Standards J. Research*, **3**, 993 (1929); RP 125.

(8) Gilchrist, *ibid.*, **12**, 283 (1934); RP 654.

fer the solution, and any residue of platinum which may have separated, to the distilling flask that was used for the distillation of osmium tetroxide. Dilute the solution in the distilling flask to 100 ml. with water.

2. Separation of Ruthenium by Distillation as Ruthenium Tetroxide.—Place 150 ml. of diluted hydrochloric acid (1 + 1), freshly saturated with sulfur dioxide, in the first receiving flask and 50 ml. of the same reagent in each of the other two flasks. Add 100 ml. of a filtered 10% solution of sodium bromate through the thistle tube to the distilling flask. This tube should be flushed with water occasionally in order to remove any ruthenium tetroxide which dissolves in the column of liquid held in the tube. In order to maintain an excess of sulfur dioxide in the absorbing solution, a saturated solution of sulfur dioxide in water should be added from time to time through the thistle tube situated between the first and second receiving flasks. Pass a gentle current of air through the apparatus, and heat the solution in the distilling flask to boiling. Distil⁹ in this fashion for one and one-half hours. Add 25 ml. of the bromate solution, and continue to distil for an additional hour.

3. Recovery of Ruthenium by Precipitation as a Hydrated Oxide.—Combine the portions of the absorbing solution and evaporate to a moist residue on the steam-bath. Add 10 ml. of hydrochloric acid and digest the solution, in a covered beaker, on the steam-bath for one-half hour. Add 50 ml. of water and heat the solution to boiling in order to dissolve completely the somewhat difficultly soluble ruthenium compound formed on evaporation. When the ruthenium compound is completely dissolved, filter the solution and wash the filter with diluted hydrochloric acid (1 + 99). Filtering ensures the elimination of a small amount of silica which may be present. Dilute the ruthenium solution to 200 ml., heat it to boiling and add a filtered 10% solution of sodium bicarbonate until a precipitate begins to form. Add 3 or 4 drops of brom cresol purple indicator solution (0.04%). Continue neutralization of excess acid by adding the bicarbonate solution dropwise until the indicator changes from yellow to blue. Boil the solution for five to six minutes to coagulate the precipitate.

(9) See original paper for a discussion of various solutions from which to distil ruthenium. The usual way is to distil from an alkaline solution which is saturated with chlorine. If this procedure is used, one can never be sure that the elimination of ruthenium is complete, even though additional alkali is added and the distilling process repeated, owing to the precipitation, near the neutral point, of iridium hydroxide which carries with it some ruthenium. It is necessary, therefore, in order to prevent the precipitation of iridium, to distil from an acid solution. The distillation of ruthenium tetroxide may be made immediately after the elimination of osmium, without removing the contents of the distilling flask, by adding a solution of sodium bromate. From 5 to 10 ml. of nitric acid should be added to increase the acid concentration of the solution. The minimum time required for complete removal of ruthenium from a boiling solution is about three and one-half hours. Although the solution requires some preparation, distillation from a solution of ruthenium sulfate in diluted sulfuric acid, as given in the procedure, is preferable. The elimination of ruthenium tetroxide from such a solution is much more rapid than from a solution containing the ruthenium as chlororuthenate. A further advantage is gained by being able to conduct the entire distillation at the boiling temperature without danger of depositing ruthenium dioxide on the walls of the flask and delivery tube, since the cause of such deposition, namely, hydrochloric or hydrobromic acid, is removed during the preparation of the solution for distillation.

The precipitate which is formed is a hydrated oxide of ruthenium, probably of tervalent ruthenium. In general appearance, it resembles other hydrated oxides of tervalent platinum metals. It does not settle as quickly nor appear as compact as the precipitate formed on the hydrolysis of compounds of quadrivalent ruthenium. However, it is quantitatively precipitated, and no difficulty is encountered in handling it.

4. Determination of Ruthenium as Metal.—Filter the solution and wipe the inner walls of the beaker and also the glass rod with a small piece of ashless filter paper. Wash the filter and the precipitate thoroughly with a hot 1% solution of ammonium sulfate. Finally, wash three or four times with a cold (room temperature) 2.5% solution of ammonium sulfate.

Place the filter and precipitate in a porcelain crucible, dry them and char the filter slowly. The dried filter will usually char completely when once it begins to smoke. This operation should be done carefully in order to prevent loss of ruthenium by deflagration. Ignite the residue strongly in air and then in hydrogen. The ignition in hydrogen is made in a manner similar to that described for the determination of osmium. Cool the resulting metal in hydrogen and leach it well with hot water. This is done to ensure the removal of traces of soluble salts. It is well to leach the residue in the crucible first and then to transfer it to a filter. Ignite the filter and metal sponge in air and in hydrogen. Cool the residue in hydrogen and weigh it as metallic ruthenium.

III. Separation and Determination of Platinum¹⁰

The solution which remains in the distilling flask after the elimination of ruthenium contains the four metals, platinum, palladium, rhodium and iridium, together with sulfuric acid, sodium sulfate or acid sulfate, bromine and undecomposed bromate. Experience shows that the platinum, rendered partly insoluble in the preparation of the solution for the distillation of ruthenium, is entirely dissolved during the distilling operation. A trace of iridium sometimes separates as the dioxide toward the end of the distilling period.

1. Preparation of the Solution

a. Treatment of the Solution from the Distilling Flask.—In order to prepare the solution for subsequent operations, transfer the contents of the distilling flask to a liter beaker. Cautiously decompose the remaining bromate with hydrochloric acid. Unless precaution is taken in this treatment, mechanical loss may occur owing to the vigorous evolution of gas. Evaporate the solution when it has become quiescent. Make certain that any bromate remaining is decomposed, by evaporating with hydrochloric acid. Occasionally, the distilling flask is found to be slightly stained with iridium dioxide near where the level of the solution has stood. It is well, therefore, always to clean the flask with 5 to 10 ml. of aqua regia, which then must be evaporated with hydrochloric acid to decompose nitroso compounds before it is added to the main solution. Finally, evaporate the solution as far as possible on the steam-bath, and then dilute it to 200 ml. with water.

(10) Gilchrist, *Bur. Standards J. Research*, **12**, 291 (1934); RP 655.

b. **Treatment of a Solution which has not Contained Osmium or Ruthenium.**—If the solution being analyzed is known not to contain either osmium or ruthenium and the parts of the general procedure referring to these metals have not been followed, evaporate it to a moist residue on the steam-bath. If the solution has contained nitric acid, add 5 ml. of hydrochloric acid and again evaporate, repeating this operation to ensure the decomposition of nitroso compounds. Add 2 g. of sodium chloride and 5 ml. of hydrochloric acid and evaporate this time to dryness on the steam-bath. Add 2 ml. of hydrochloric acid and dilute the solution to 300 ml. with water.

2. **Separation of Platinum by Joint Precipitation of Palladium, Rhodium and Iridium as Hydrated Dioxides.**—Heat the solution containing platinum, palladium, rhodium, and iridium to boiling, and add to it 20 ml. of a filtered 10% solution of sodium bromate. Carefully add a filtered 10% solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the hot solution from time to time by allowing a drop of brom cresol purple indicator solution (0.01%) to run down the stirring rod into the drop which clings to it as it is lifted from the solution. Enough bicarbonate has been added when the color of the indicator changes from yellow to blue. At this stage, add 10 ml. more of the bromate reagent and boil the solution for five minutes. Increase¹¹ the pH of the solution slightly by carefully adding dropwise bicarbonate solution until a faint pink color is produced in the test drop by a drop of cresol red indicator solution (0.01%). Again add 10 ml. of the bromate reagent and boil for fifteen minutes.

On removing the beaker from the source of the heat, the mixed precipitate will settle quickly, leaving a mother liquor containing the platinum. Filter the solution by suction, using a porcelain filtering crucible¹² having solid walls and a porous base.

(11) Since previous publication on this subject [*Bur. Standards J. Research*, 12, 291 (1934); RP 655], it has been found that, whereas a pH of 6 ensures complete precipitation of rhodium and of iridium, this acidity is on the borderline with respect to the precipitation of palladium. In the procedure as finally recommended, hydrolytic precipitation is made, during the first boiling period, at a pH value (approximately pH 6) corresponding to the change in color of brom cresol purple (0.01%) when a drop of the indicator solution is allowed to react with a drop of the boiling solution. A second boiling period, at a pH value (approximately pH 8) corresponding to the change in color of cresol red (0.01%), ensures quantitative precipitation of palladium. It is preferable to perform the precipitation in two stages in order to be able to observe the faint pink color of cresol red in the test drop. It was determined experimentally, with solutions made to contain the same quantity of acid and salts as do those which result from the removal of osmium and ruthenium by distillation, that no interference is encountered in the precipitation of palladium, rhodium and iridium. It was further observed that rhodium and iridium are quantitatively precipitated under the conditions specified for precipitating palladium, and that platinum does not contaminate the precipitated dioxides to any greater extent than when the hydrolytic operation is conducted at pH 6 alone. In the absence of palladium, it is recommended that the hydrolytic precipitation be made at the color change of brom cresol purple (pH 6).

(12) This type of crucible is manufactured by the State Porcelain Works, Berlin, Germany. A crucible of convenient size is one having a height of 45 mm., a diameter at the top of 40 mm. and a capacity of 30 ml. The crucible designated by the mark "A1" filters rapidly and allows no trace of the precipitate to escape. Crucibles marked "A2," but somewhat smaller in size, were found to be perfectly satisfactory. No doubt glass crucibles of suitable porosity could also be used.

It is highly desirable to avoid the use of filter paper when repeated precipitations are to be made. The material of which the paper is composed undoubtedly reacts with acids and probably forms small quantities of organic compounds with the platinum metals which are not easily hydrolyzed. Iridium dioxide, which dissolves much less readily than either palladium or rhodium dioxide, tends to stain paper pulp. The stain cannot always be removed by washing. These difficulties are avoided if the porcelain filtering crucible is used. Furthermore, such crucibles have the advantage that concentrated hydrochloric acid can be used to dissolve the hydrated dioxides, and considerable time is saved in preparing the solution for subsequent treatment.

Pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker and wash the precipitate with a hot 1% solution of sodium chloride, the acidity of which has been adjusted to between pH 6 and 7. Place the crucible with the precipitate, and also the stirring rod, in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker during filtration. It is preferable to do this with moistened crystals of sodium chloride, on the finger, rather than to use paper or a rubber policeman. Replace the watch glass and add from 10 to 20 ml. of hydrochloric acid, pouring most of it into the crucible. Place the covered beaker on the steam-bath. The rhodium and palladium compounds will dissolve quickly, the iridium dioxide much more slowly. Carefully lift the crucible with the stirring rod, wash it with water and place it in a 250-ml. beaker. Pour 5 ml. of hydrochloric acid into the crucible. Cover the beaker with a watch glass and set it on the steam-bath. This treatment will usually leach out the small quantity of metal chlorides in the porous bottom. This operation should be repeated with fresh acid to ensure complete removal. Combine the leachings with the main portion of the dissolved precipitate, add 2 g. of sodium chloride, and evaporate to dryness on the steam-bath. Add 2 ml. of hydrochloric acid, dilute the solution to 300 ml. with water, and repeat the precipitation of the hydrated dioxides. Two such precipitations are sufficient ordinarily to effect the complete separation of platinum from palladium, rhodium and iridium.

3. **Recovery of Platinum by Precipitation with Hydrogen Sulfide.**—Add 20 ml. of hydrochloric acid to each of the filtrates obtained from the hydrolytic precipitation of the dioxides of palladium, rhodium and iridium. Carefully warm the solutions until they become quiescent. Partially concentrate the filtrates, combine them and then evaporate to dryness. Make certain that all of the bromate is destroyed, by evaporation with hydrochloric acid. Dilute the yellow platinum solution somewhat and filter it. Wash the filter with diluted hydrochloric acid (1 + 99). Dilute the filtered solution to about 400 ml. with water and have it contain 5 ml. of hydrochloric acid in each 100 ml. volume.

Precipitate the platinum, in a hot solution, with hydrogen sulfide, using a rapid stream. Continue the passage of hydrogen sulfide as the solution cools somewhat, to ensure complete precipitation.

4. **Determination of Platinum as Metal.**—Filter the solution and wash the precipitate with diluted hydro-

chloric acid (1 + 99). Ignite the dried filter and precipitate in a porcelain crucible. Leach the metal residue with diluted hydrochloric acid, transfer it to a filter and wash it thoroughly with hot water. Ignite the filter and metal again strongly in air. Weigh the residue as metallic platinum. The metal so obtained will usually contain a small but significant amount of sulfur¹³ which cannot be eliminated by ignition in either air or hydrogen.

If the highest accuracy is desired, dissolve the metallic platinum, obtained by ignition of the sulfide, in aqua regia. Destroy nitroso compounds by evaporation with hydrochloric acid. Filter the solution into a clean, unetched beaker. Wash the filter with diluted hydrochloric acid (1 + 99). Dilute the solution to 100 ml., heat it to boiling and add to it a solution containing 3 g. of sodium acetate and 1 ml. of formic acid for each 0.25 g. of platinum. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1% solution of ammonium chloride. Place the filter and the spongy metal in a porcelain crucible and ignite them strongly in the air. Leach and wash the ignited metal as previously directed. This precaution is taken to ensure the removal of soluble salts. Finally ignite the platinum in air again. Weigh the residue as metallic platinum, which will now be free from sulfur.

It is far better to precipitate the platinum first by hydrogen sulfide, and then to reprecipitate it by formic acid in a buffered solution, than it is to attempt to precipitate the platinum directly by formic acid. The precipitation with hydrogen sulfide eliminates the relatively large amount of sodium salts which cause trouble in the formic acid reduction.

IV. Separation and Determination of Palladium¹⁰

1. **Separation of Palladium by Precipitation with Dimethylglyoxime.**—Dissolve the precipitate of the hydrated dioxides of palladium, rhodium and iridium in hydrochloric acid as previously directed. Filter the solution and dilute it to a volume of about 400 ml. Add a sufficient volume of a 1% solution of dimethylglyoxime in 95% ethyl alcohol to precipitate all of the palladium (2.2 g. of the solid reagent is required for 1 g. of palladium). An excess of the reagent amounting to 10% should be added to ensure complete precipitation. Let the solution stand for one hour and then filter it. The manner of filtration will depend upon the form in which the palladium is to be determined. Wash the precipitate with diluted hydrochloric acid (1 + 99), and finally with hot water. The precipitate can be washed with a considerable volume of water without a trace of it dissolving. A single precipitation of the palladium is sufficient to separate it completely from rhodium and iridium.¹⁴

(13) In 17 experiments, the weights of platinum (0.25-g. portions) recovered by ignition of the sulfide in air exceeded those taken by amounts which ranged from 0.0 to 1.0 mg., and averaged 0.5 mg. The retention of sulfur by palladium is very marked, and the sulfide may even fuse into globules which cannot be completely decomposed by ignition. Therefore, palladium must not be determined by ignition of its sulfide. No significant amount of sulfur is retained when rhodium sulfide is ignited.

(14) If, for any reason, it is desired to reprecipitate the palladium, catch the precipitate on paper. Transfer the washed filter and precipitate to an Erlenmeyer flask, closed with a short-stemmed funnel

2. Determination of Palladium

a. **As Palladium Dimethylglyoxime.**—Palladium dimethylglyoxime is sufficiently stable and constant in composition to be dried and weighed. If the determination is to be made in this manner, catch the precipitate in a porcelain or glass filtering crucible, using suction. Wash the precipitate as previously directed and dry it at 110° for one hour. Calculate the quantity of palladium, using the theoretical factor, 0.3167.

b. **As Metal.**—If the palladium is to be determined as metal, which in certain cases may be more convenient, catch the precipitate on an ashless filter. Wipe the inner walls of the beaker and also the glass rod with a small piece of ashless paper. Wrap the filter and precipitate in a second filter and place them in a porcelain crucible. Dry them, and ignite them carefully in the air. Only sufficient heat should be supplied to keep the papers smoking gently. Ignite the charred residue strongly in air, and then in hydrogen. Ignite the metallic palladium in carbon dioxide¹⁵ for two minutes and cool it in carbon dioxide. Weigh the residue as metallic palladium.

V. Separation and Determination of Rhodium^{10,16}

1. **Preparation of the Solution.**—Place the solution containing the rhodium and iridium as chlorides, together with the excess of dimethylglyoxime remaining from the precipitation of palladium, in a 500-ml. Erlenmeyer flask. Place a short-stemmed funnel in the mouth of the flask. Add 10 ml. of sulfuric acid and 2 to 3 ml. of nitric acid, and evaporate until heavy vapors of sulfuric acid are evolved. To ensure complete destruction of organic matter, add a small quantity of nitric acid from time to time and continue to heat over a free flame, keeping the solution in constant motion. Dilute the cooled solution with 20 ml. of water and again evaporate it until vapors of sulfuric acid appear. This is done to destroy nitroso compounds which may interfere in the precipitation of rhodium by titanous chloride.

2. **Separation of Rhodium by Precipitation with Titanous Chloride.**—Transfer the sulfate solution to a clean, unetched beaker, dilute it to 200 ml. and heat it to boiling. Add dropwise a solution of titanous chloride (a 20% solution of this reagent may be purchased) until the supernatant liquid appears slightly purple. If the solution is placed over a 100-watt light and stirred, observation of the end-point is greatly facilitated. The metallic rhodium which is precipitated quickly coagulates into a spongy mass. If much iridium is present, the end-point can be determined by the lack of formation of any further precipitate and the appearance of an orange color in the solution. Boil the solution for two minutes and filter it.

and decompose them in a mixture of sulfuric and nitric acids. Heat the solution until vapors of sulfuric acid are evolved, dilute it somewhat and filter it. Precipitate the palladium from the diluted solution of its sulfate with dimethylglyoxime.

(15) Palladium possesses the property of absorbing a considerable quantity of hydrogen, so that it is difficult to obtain constant weight. If the absorbed hydrogen is eliminated by igniting the metal so obtained in an inert gas, no difficulty is encountered. Strong ignition in air is sufficient to decompose all oxides of palladium, without resort to hydrogen, but the gray metal tarnishes as it cools unless an inert gas protects it. The error involved, however, amounts to only 0.1 mg. with quantities of palladium weighing 100 mg.

(16) Gilchrist, *Bur. Standards J. Research*, **9**, 547 (1932); RP 489.

Wipe the walls of the beaker and also the stirring rod with a piece of ashless filter paper. Wash the filter and precipitated metal thoroughly with cold (room temperature) diluted sulfuric acid (2.5 + 97.5).

Place the filter with its contents in a 500-ml. Erlenmeyer flask, add 10 ml. of sulfuric acid, char gently, add 5 ml. of nitric acid and digest the solution on a hot plate. Usually, the rhodium dissolves fairly readily. Complete the solution of the rhodium by heating the flask over a free flame, keeping the contents of the flask in constant motion. Ensure the destruction of organic matter and the elimination of nitroso compounds. If some black specks remain, dilute the solution, filter it and return the filter to the flask. Wipe down the walls of the flask with a piece of ashless filter paper. Add 5 ml. of sulfuric acid, char the paper, and destroy all organic matter with nitric acid. Heat the solution until heavy vapors of sulfuric acid are evolved. This treatment will dissolve any remaining metal and will leave only a slight deposit of colorless silica.

Precipitate the rhodium a second time in the manner described above. Redissolve the rhodium as before, dilute the sulfuric acid solution with 20 ml. of water and 10 ml. of hydrochloric acid and boil the resulting solution for fifteen minutes. This treatment is necessary to convert the rhodium into a form which will allow complete precipitation by hydrogen sulfide. During this treatment, the color of the solution will change from yellow to rose. Filter the solution and wash the filter with diluted hydrochloric acid (1 + 99). Finally, dilute the solution to a volume of from 400 to 500 ml.

3. Recovery of Rhodium by Precipitation with Hydrogen Sulfide.—Precipitate the rhodium as sulfide from a solution, kept just at the boiling point, by passing a rapid stream of hydrogen sulfide through it. Allow the solution to cool somewhat, with the hydrogen sulfide still passing through it.

4. Determination of Rhodium as Metal.—Filter the solution and wash the precipitate with diluted sulfuric acid (2.5 + 97.5), and finally with diluted hydrochloric acid (1 + 99). Place the filter with the sulfide precipitate in a porcelain crucible. Ignite the dried precipitate carefully in air. Finally, ignite the oxidized residue in hydrogen, cool the resulting metal in hydrogen and weigh it as metallic rhodium.

VI. Recovery and Determination of Iridium^{10,16}

Iridium may be determined in either of two ways. If the solution containing both rhodium and iridium can be divided conveniently into aliquot parts, the determination of iridium is greatly simplified and the precipitations of titanium by cupferron avoided. The rhodium and iridium in one portion of the solution can be recovered by hydrolytic precipitation as described in the procedure for the separation of platinum. If this is done, the mixed precipitate of rhodium and iridium dioxides is washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (pH 7), instead of with a solution of sodium chloride. The dried filter and precipitate are impregnated with a few drops of a saturated solution of ammonium chloride, in order to prevent deflagration, and carefully ignited to a mixture of the anhydrous oxides. The oxidized residue is ignited and cooled in hydrogen, and weighed as a mixture of metallic rhodium

and metallic iridium. In order to calculate the quantity of iridium, it is necessary, in addition, to determine rhodium as previously described in a separate portion of the solution.

If the iridium cannot be determined in this way, it is necessary to recover it from the filtrates resulting from the precipitation of rhodium by titanous chloride.

1. Elimination of Titanium by Precipitation with Cupferron.—Dilute the combined filtrates from the precipitation of rhodium by titanous chloride to 800 ml. Cool the solution by placing the beaker in crushed ice. Add a chilled, filtered, freshly prepared 6% solution of cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$) in slight excess. Filter the solution and wash the titanium precipitate with chilled diluted sulfuric acid (2.5 + 97.5) containing some cupferron. The cupferron precipitate is usually slightly contaminated by iridium, but the amount does not exceed 1 mg. when about 0.2 g. of iridium is being handled. Return the filter and precipitate to the beaker, add 20 ml. of nitric acid, and heat until the precipitate is mostly decomposed. Add 20 ml. of sulfuric acid and heat the solution until vapors of sulfuric acid appear. Destroy the remaining organic matter by adding nitric acid, and heating. Dilute the resulting solution to 800 ml. and repeat the precipitation of the titanium. Unite the filtrates from the cupferron precipitations and evaporate until approximately 10 ml. of sulfuric acid remains. Ensure the destruction of all organic matter. Dilute the solution somewhat and filter it.

2. Recovery of Iridium by Precipitation as the Hydrated Dioxide.—Dilute the solution to 200 ml. with water and neutralize most of the acid contained in it with a filtered solution of sodium bicarbonate. Heat the solution to boiling and complete its neutralization with bicarbonate to the end-point of brom cresol purple, as described in the procedure for the separation of platinum. Add 20 ml. of a filtered 10% solution of sodium bromate, and boil the solution for twenty to twenty-five minutes. Be sure that sufficient bromate is present to oxidize all of the iridium to the quadrivalent state. Filter the solution and wash the precipitate thoroughly with a hot 1% solution of ammonium chloride.

3. Determination of Iridium as Metal.—Place the filter and precipitate in a porcelain crucible. Dry them somewhat and then moisten them with a few drops of a saturated solution of ammonium chloride. Ignite the filter and precipitate carefully in the air and then in hydrogen. Leach the metallic residue with diluted hydrochloric acid, then transfer it to a filter, and wash it with hot water. Ignite the filter and metallic residue in air. Finally, ignite the resulting oxidized metal in hydrogen, cool it in hydrogen and weigh it as metallic iridium.

The procedure as herein written is designed for the highest degree of accuracy. If, however, one is not interested in such accuracy, the procedure may be shortened in a number of places. For instance, some of the reprecipitations which are recommended may be omitted. Time can be saved by making only one hydrolytic precipitation of palladium, rhodium and iridium, in separating them from platinum, and by determining platinum by simply igniting its sulfide. The second reduction with titanous

chloride might be dispensed with, and also the precipitations with cupferron can be avoided by determining rhodium and iridium together in aliquot portions of the solution at this stage. It must be remembered, however, that in so doing errors of varying magnitude will be introduced, depending upon the relative proportions of the metals present.

Accuracy of the Proposed Method

The accuracy which can be attained with the procedure described in this paper is best illustrated by means of data which have been taken from the publications cited and compiled in the accompanying table. In addition, the results of the complete analysis of three solutions, to which all six of the metals were added, are included.

In the development of the various parts of the general procedure, given in detail in the original papers cited, it was found by chemical means that no ruthenium, platinum, palladium, rhodium or iridium appeared in the absorbing solutions under the conditions established for distilling osmium

tetroxide. In the separation of platinum from rhodium, no platinum was detected by means of ammonium chloride in the solutions of the second hydrolytic precipitate of rhodium, whereas, in solutions of known platinum content, 0.1 mg. of platinum was readily detected, and a precipitate was formed with 0.05 mg. of platinum. Rhodium was detected in only one of the five residues of platinum, obtained in the same experiments, by a test which is capable of detecting an extremely small amount of rhodium, namely, the greenish discoloration of the small amount of ammonium chloroplatinate which remains in solution when the bulk of the redissolved platinum is precipitated by ammonium chloride. In the separation of platinum from palladium, no palladium was detected with dimethylglyoxime in the dissolved platinum residues, nor was any platinum found, by means of ammonium chloride, in the filtrates from the precipitation of the palladium with dimethylglyoxime. In the separation of plati-

TABLE I

RESULTS WHICH ILLUSTRATE THE ACCURACY OF THE PROCEDURE

No.	Osmium, g.		Ruthenium, g.		Platinum, g.		Palladium, g.		Rhodium, g.		Iridium, g.	
	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered
1	0.1608	0.1606	0.075	0.100	0.020	0.016	0.200
2	.1390	.1388	.075100020016200
3	.1548	.1546	.075100020016200
41090	0.1091093
51564	.15651426	0.1427
61556	.15561605	.1603
71243	.12442125
81153	.1152	.2739108400761955
90451	0.0451	.0735
101355	.1354	.1103
111442	.1442	.1413	.1412
121216	.1215	.1624	.1622
130840	.0838	.1320	.1320
142848	0.2849	.1044	0.1043
152793	.2794	.1243	.1243
162469	.24690291	.0291
172479	.24790244	.0243
182617	.26180295	.0296
192359	.23581944	.1945
202692	.26942039	.2040
212501	.25012455	.2456
2226420465	.0464	.1385
230342	.0342	.01772300
240333	.0333	.01122154
25	.1155	.1153	.11171141101311451194
26	.1507	.1505	.11951008110911091159
27	.1623	.1622	.1323	.1321	.1341	.1342	.1301	.1299	.0905	.0904	.1042	.1042
28	.1882	.1880	.1399	.1397	.1104	.1102	.1278	.1277	.0922	.0922	.1416	.1414
29	.1602	.1600	.0999	.0994	.1123	.1124	.1184	.1183	.0967	.0968	.1145	.1145
301234	.1234	.1194	.1195	.10081083	.2090 ^a
311340	.1339	.0875	.0875	.12631092	.2355 ^a

^a This figure is that of the combined determination of rhodium and iridium.

num from iridium, a quantity of iridium less than 0.1 mg. was detected, in one experiment, in the filtrates obtained from the precipitation of platinum, first by hydrogen sulfide and then by formic acid, whereas no iridium was detected in the two other experiments.

In order to ascertain, in the separation of ruthenium by the recommended procedure, whether any of the other platinum metals reached the absorbing solutions, the ruthenium recovered from each of the three complete analyses was examined spectrochemically by Bourdon F. Scribner for osmium, platinum, palladium, rhodium and iridium, but no trace of these metals was detected.

The results of 31 experiments are given in Table I. Those reported in Nos. 1 to 24, inclusive, are taken from previous publications cited in this paper. Experiments Nos. 25 to 29, inclusive, were conducted according to the recommended procedure, except that brom cresol purple was used to determine the end-point for the hydrolytic precipitation. In these experiments some palladium escaped precipitation and was subsequently separated from the platinum by means of dimethylglyoxime. The results in Nos. 30 and 31 were obtained by following the procedure as herein written. Although osmium and ruthenium were not included, the solutions were, nevertheless, subjected to the same treatment as if

they had been present, except that the distilling operations were omitted, in order to duplicate conditions which normally obtain at the end of the ruthenium distillation. In these two experiments, rhodium and iridium were not separated from each other but were recovered together by hydrolytic precipitation. The mixed precipitate was washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (pH 7), and ignited to a mixture of metallic rhodium and iridium. The final filtrates obtained in these two experiments were found to be free from the four metals concerned.

The quantities of metal listed in the table can be conveniently handled, analytically. In the case of platinum, 2 g. of this metal is easily handled, and 5 g. should introduce no difficulties.

Summary

1. A new and reliable procedure is described for the separation, recovery and determination of each of the six platinum metals.

2. The accuracy of this new method is comparable to that of the best analytical procedures for the common metals. No special equipment or reagents are necessary and the operations do not involve technique unfamiliar to a trained analyst.

WASHINGTON, D. C.

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Structural Changes Taking Place upon Aging of Freshly Prepared Crystalline Precipitates. V. The Thermal Aging of Freshly Prepared Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In papers III and IV of this series¹ it has been shown that the rapid internal perfection of the crystalline particles of freshly precipitated lead sulfate on aging in the supernatant mother liquor at room temperature is to be attributed to a rapid recrystallization process by way of the solution² and not to a free mobility of the lead ions in the amicronic particles within the microcrystals as originally concluded from the results reported in papers I and II.³ Aside from the aging in liquid media it appears reasonable to expect that aging

will occur in the dry state as well, provided that the fresh precipitate is heated to temperatures high enough to increase the thermal energy of the ions at the active surface. The results of this study are reported in this paper.

We may distinguish between two principal types of thermal aging.

1. **Microscopic Aging.**—At the higher temperatures a *sintering* of the microscopic particles may occur, resulting in a decrease of the external surface. The magnitude of this surface can be determined from the dimensions of the particles as seen with a microscope. Since the precipitates used in these studies were highly heterodisperse,

(1) THIS JOURNAL, **57**, 597, 607 (1935).

(2) This matter will be dealt with in detail in a subsequent paper of this series.

(3) THIS JOURNAL, **56**, 1264, 1658 (1934).