2. Extraction of the un-ignited sulfides with nitric acid or with bromine water is even less satisfactory. A rough separation of copper from the platinum metals can be made by extracting the un-ignited sulfides with a 3% solution of hydrogen peroxide.

3. The familiar precipitation of copper as cuprous thiocyanate will separate it quantitatively from platinum, palladium, iridium and rhodium if sufficient sulfur dioxide is present to prevent the platinum metals from forming thiocyanates, and if the solution is just acid enough so that the double sulfite of rhodium does not precipitate.

WASHINGTON, D. C.

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INVESTIGATIONS ON THE PLATINUM METALS. VI THE ANALYTICAL SEPARATION OF RHODIUM FROM PLATINUM[1]

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Introduction

In the literature on analytical methods for the platinum metals there are very few methods which attempt to provide for the isolation of rhodium. Of the compounds of rhodium which have been used to separate this metal from others in the group few, if any, have a solubility low enough to be suitable for analytical purposes. Up to the present time the determination of rhodium has not been included in the commercial evaluation of crude platinum, quite possibly because of the lack of an adequate method. It is to be noted that the value of this constituent may exceed that of the gold or palladium present, both of which are usually determined.

The purpose of this paper is to describe a method for isolating rhodium from a mixture of platinum and rhodium when the two metals are in solution as chlorides. This method is based on the hydrolysis of rhodium chloride in nearly neutral solution, to form an insoluble compound, whereas the hydrolysis of chloroplatinates proceeds very slowly at the neutral point, and apparently without the formation of insoluble compounds in the first stages of the reaction.

Previous Analytical Practice

Separation by Ammonium Chloride.—When the determination of rhodium was occasionally required, analysts usually directed their efforts toward removing the other platinum metals from solution and concentrating

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[1] Published by permission of the Director of the Bureau of Standards, United States Department of Commerce.

[2] Chemist, Bureau of Standards.

rhodium in the mother liquors, from which it was finally precipitated by hydrogen sulfide or by a reducing agent, along with variable amounts of the other metals which had escaped the earlier separations.

The means usually adopted for thus concentrating rhodium is the precipitation of platinum with ammonium chloride; iridium and palladium are either precipitated with the platinum or removed separately by appropriate methods. This method was used by Deville and Debray and by Deville and Stas in their very extensive work on the analysis of crude platinum and platinum alloys, specifically in the analysis of the platinum-iridium alloys used for the international standards of length and mass.[3] These authors knew, however, that this separation was incomplete, in that the precipitation of platinum was by no means quantitative, and that the platinum precipitate was always contaminated with rhodium. They regarded the separation simply as one which yielded two fractions, one rich and the other poor in rhodium. Both fractions were subjected to painstaking repeated extractions with fused potassium pyrosulfate, which removed nearly all of the rhodium together with a small amount of platinum.

In practice this method becomes exceedingly tedious if the necessary corrections are made. In an analysis, made by the author, of commercial platinum containing about 1% of rhodium, 17 fusions with potassium pyrosulfate were required to obtain a fairly correct value for rhodium. Probably because of the excessive time taken by such corrections, there has been an unfortunate tendency to omit them entirely and to regard the simple separation with ammonium chloride as sufficient. For reasons already given this method cannot give an accurate value for rhodium except by an accidental compensation of errors. It is to be noted also that when conditions are arranged to make the precipitation of platinum as nearly complete as possible, the contamination of this precipitate with rhodium is correspondingly increased. The following data, obtained in the refining of platinum-rhodium scrap, illustrate the tenacity with which rhodium clings to platinum in the separation by ammonium chloride, even when conditions are arranged to insure minimum contamination with rhodium rather than maximum precipitation of platinum. The material, estimated by thermo-electric measurement to contain 0.7% of rhodium, yielded a first precipitate of ammonium chloroplatinate which contained about 0.2% of rhodium. On reprecipitation the platinum contained about 0.04% of rhodium, and after five more precipitations a minute amount of rhodium could still be detected in the mother liquor from a quantity of ammonium chloroplatinate equivalent to about 450 g. of platinum.

Similarly, in the analysis of an alloy containing 9% of rhodium and 91%

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[3] "Procès Verbaux Comité International des Poids et Mesures," **1877**, p. 151.

of platinum, the ammonium chloroplatinate, precipitated in the manner prescribed by Deville and Stas to insure minimum contamination with rhodium, contained 85.4% of the sample, of which about 0.5% was rhodium. The remainder of the rhodium, together with about 6% of the platinum, was in the filtrate.

Distillation of Platinum in a Stream of Carbon Monoxide and Chlorine

The work of Mylius and Foerster[4] on the detection of small quantities of impurities in platinum by volatilizing most of the platinum in a current of carbon monoxide and chlorine at about 240° pointed out a better way to concentrate rhodium. Although two fractions are still obtained, one is apparently entirely free from rhodium. The other fraction, rich in rhodium, may be extracted as before with fused pyrosulfate. Materials rich in rhodium are best subjected to a preliminary separation with ammonium chloride, after which the fraction rich in platinum is distilled as described and the residue united with the rhodium-rich fraction. Somewhat unusual equipment is required for the distillation, and the tedious and really inadequate extractions with fused pyrosulfate cannot be avoided.

Behavior of Rhodium and Platinum toward Hydrolysis

Rhodium.—The precipitation of rhodium hydroxide by alkalies and alkali carbonates is well known, but no use seems to have been made of this reaction in the analytical separation of rhodium. The observation of Claus[5] that the hydrolysis of rhodium chloride by milk of lime and by borax is not complete, seems not to have been disputed. The collective precipitation of impurities from a solution of platinum by means of milk of lime was proposed by Doebereiner and for a time was extensively used in the refining of platinum. Claus[5] pointed out that the elimination of impurities by this method was never complete. More recently Mylius and Mazzucchelli[6] proposed a similar collective precipitation of impurities for use in the approximate analysis of commercial platinum. In their method, sodium hypobromite is added to a neutral or faintly alkaline chloride solution. The reaction is essentially one of hydrolysis, such metals as may be oxidized separating as hydroxides of the higher valence. The authors do not claim a strictly quantitative separation of all impurities and do not give data on the behavior of individual elements.

It seemed advisable to determine whether the known hydrolysis of rhodium might be made quantitative and under conditions which would not involve excessive co-precipitation of platinum.

It was found that rhodium could be precipitated over a wide range of alkalinity. However, precipitation apparently never was quite complete

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[4] Mylius and Foerster, *Ber.*, **25,** 665 (1892).

[5] Claus, *Bull. acad. sci.*, St. Petersburg, **3,** 38 (1845).

[6] Mylius and Mazzucchelli, *Z. anorg. Chem.*, **89,** 1 (1914).

from solutions which were slightly on the acid side of the neutral point, say with hydrogen-ion concentration of 10^{-5}, that is, *P*H 5.[7] Also, solutions which were strongly alkaline, some of them with approximately normal sodium hydroxide content, seemed to retain small amounts of rhodium. In the latter case the data collected were not sufficient to prove this with entire satisfaction, as the use of strongly alkaline solutions was abandoned for other reasons. More platinum was carried down with the rhodium than was the case in approximately neutral solutions and the glass vessels were excessively attacked. From solutions which were kept faintly alkaline, rhodium could be quantitatively precipitated.

In order to determine approximately the point at which the larger part of the rhodium in a chloride solution precipitates by hydrolysis, a solution of rhodium chloride, containing about 0.4 mg. of rhodium per cc. together with some free hydrochloric acid and a little sodium chloride, was treated with sodium hydroxide, at room temperature, until the solution was faintly alkaline to cresol red (about *P*H 8.5). The solution was then boiled for 30 minutes, after which it was filtered from the precipitated rhodium hydroxide and diluted with an approximately equal volume of the wash solution, which was neutral and contained 2% of sodium chloride. This filtrate was estimated, by indicator methods, to have an acidity corresponding to *P*H 5.0 to 5.1.

As a fair proportion, but not nearly all, of the rhodium was precipitated, the acidity mentioned may be regarded as a point somewhere in the large middle portion of the hydrolysis curve of a rhodium chloride solution. It should be expected that an hydroxyl-ion concentration of one hundredfold that represented by *P*H 5, namely *P*H 7 (the neutral point of pure water), would make hydrolysis sufficiently complete for analytical purposes, provided that the product of hydrolysis is practically insoluble. The latter was demonstrated by the fact that no rhodium was precipitated by means of hydrogen sulfide from rhodium solutions which had been subjected to hydrolysis at *P*H 7 to 7.5.

Platinum.—Without attempting to discuss here the complex problem of the behavior of chloroplatinates with respect to hydrolysis, a few observations should be noted which bear on the rhodium separation. It was found that solutions containing platinum alone, as chloroplatinate, could be kept at the boiling point for long periods without appreciable precipitation, either when they were approximately neutral, or when they were made very strongly alkaline by caustic alkalies. In the latter case hydrolysis was probably completed with the formation of soluble platinates.[8]

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[7] For the significance of the symbol *P*H, and for the preparation and use of indicators see Clark, "The Determination of Hydrogen Ions," second edition, published by Williams and Wilkins Co., Baltimore.

[8] For the purposes of this discussion a "neutral solution of chloroplatinate" means a solution of chloroplatinic acid to which alkali is added at room temperature until the

When sodium hydroxide was added in small portions to a hot neutral solution of a chloroplatinate, variable amounts of alkali were consumed with very little precipitation until digestion had been much prolonged. Under these conditions the acidity of the platinum solution tended to revert to a point estimated by the use of indicators as between *P*H 4 and 5. Under certain conditions considerable precipitation of platinum compounds occurred. This was observed when a moderately dilute solution of chloroplatinate was digested with an excess of sodium carbonate, and also when a more concentrated solution was treated with insufficient sodium hydroxide to complete the conversion to soluble platinate. The latter took place during the purification of a quantity of platinum by von Schneider's method.[9] The solution approached neutrality with the formation of a copious precipitate which dissolved readily when a further quantity of sodium hydroxide was added.

Precipitation of Rhodium by Sodium Hypobromite

When rhodium is precipitated by a hydrolytic agent which has no oxidizing power, the precipitate has a bright orange-yellow color and is presumably tervalent rhodium hydroxide, $Rh(OH)_3$. If chlorine or bromine is present when the alkali is added, or if an oxidizing alkali such as a hypochlorite or hypobromite is used, the precipitate is greenish-black and probably consists of hydrated rhodium dioxide, the formula for which may be written $Rh(OH)_4$. The earlier discussion of the completeness of the precipitation of rhodium by hydrolysis refers to the tervalent hydroxide, but the quadrivalent hydroxide also precipitates quantitatively from faintly alkaline solutions.

The quadrivalent compound has certain characteristics which are advantageous in analytical work. Its dark color aids in the detection of small quantities of rhodium. Both the tervalent and quadrivalent hydroxides coagulate well on boiling for a short period, but on prolonged boiling the former becomes more finely divided and consequently more difficult to filter. On the other hand, the hydrated dioxide is not so affected. In the early experiments it was supposed that prolonged boiling was necessary to complete the precipitation of rhodium and for this reason a solution of sodium bicarbonate in saturated bromine water was used as the reagent. This reagent is really a solution of sodium hypobromite which may or may not contain unused bicarbonate, depending upon the amount of the latter added to the bromine solution. Mylius and Mazzuc-

solution reacts just alkaline to an indicator such as cresol red. This reaction is presumed to neutralize the replaceable hydrogen atoms of chloroplatinic acid, H_2PtCl_6, resulting in a salt such as sodium chloroplatinate, Na_2PtCl_6. By a platinate is meant a salt of an oxygen acid of platinum, which may have some such formula as Na_2PtO_3 or $Na_2Pt(OH)_6$.

[9] von Schneider, *Ann.*, **5** (suppl.) 261 (1867).

chelli used a 4% solution of sodium bicarbonate in bromine water in the collective separation of impurities from platinum previously referred to. These authors did not usually boil the solutions but digested them on the steam-bath for a short time. The hydrolysis of rhodium chloride proceeds relatively slowly and is not completed at the usual temperature of the steam-bath (about 85°) unless digestion is prolonged for several hours.

The authors mentioned above removed excess acid from their solutions and neutralized the chloroplatinic acid, before adding sodium hypobromite, by adding sodium chloride, evaporating to dryness, and baking at 120° for an hour; after this the water solution of the residue was heated with a small amount of sodium bicarbonate. In their procedure the baking served the added purpose of making most of the gold insoluble. In the work herein described the preliminary neutralization was accomplished by adding sodium hydroxide to the solution at room temperature, either to the predetermined color of a suitable indicator or until initial precipitation of rhodium occurred. The latter takes place in cold solutions unless the proportion of rhodium present is relatively small. After the mixed solutions of platinum and rhodium had been thus neutralized, freshly made sodium hypobromite solution was added and the solutions were boiled for periods of 15 to 60 minutes.

In the experiments to be discussed in the following paragraphs many of the details of procedure were uniform and may be described here. The platinum and rhodium were of the same quality as the specially purified materials used at the Bureau of Standards for making thermocouples. The solution of chloroplatinic acid, prepared in the usual way, contained approximately 50 mg. of platinum per cc. and some excess of hydrochloric acid. The solution of rhodium was prepared from sodium rhodium chloride and was intended to contain 2.000 mg. of rhodium per cc. It contained some excess of sodium chloride and was practically neutral. The calculated rhodium content was verified by precipitating rhodium sulfide[10] from two 50cc. portions, igniting the precipitated sulfide in air, reducing in hydrogen and weighing the metal after cooling in hydrogen.

Unless otherwise mentioned the total metal content of the mixtures of platinum and rhodium was 2.00 g., the platinum content being only approximately known, while the rhodium content was fixed to a small fraction of a milligram. Precipitation was usually made in a volume of 200–250 cc. Filter paper of close texture (as S. and S. No. 589, blue ribbon)

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[10] To insure complete precipitation of rhodium, the temperature of the solution should be maintained practically at the boiling point during the treatment with hydrogen sulfide. If the solution is hot before hydrogen sulfide is introduced, the precipitate is less likely to adhere to the glass. Precipitation is usually complete in 30 minutes but it is well to test the filtrates by further treatment with hydrogen sulfide. A suitable acid concentration is 3 to 5% by volume of sulfuric acid (d., 1.84) or hydrochloric acid (d., 1.18).

was used throughout. The hot wash solution contained 2% of sodium chloride. The precipitate and papers were returned to the beakers and digested with 25 cc. of hydrochloric acid (1 volume of acid of d. 1.18 and 3 or 4 volumes of water) until the hydroxides were dissolved. After filtering from the paper pulp, the solutions were made ready for reprecipitation. Three precipitations of the hydroxide were usually made, after which the rhodium was precipitated as sulfide and determined in the manner described in the preceding paragraph.

The metals contained in the filtrates from the second and third precipitations as hydroxide were always recovered, in order to determine the extent to which the previous precipitate of rhodium hydroxide had been contaminated with platinum and the extent to which rhodium had escaped complete precipitation. This recovery was made by means of hydrogen sulfide after the solutions had been acidified with hydrochloric acid, evaporated to dryness and filtered from insoluble matter. The ignited sulfides failed to dissolve completely in aqua regia except when only a very small proportion of rhodium was present. In the latter case the aqua regia solution was examined for rhodium by evaporating with a small amount of ammonium chloride after nitric acid had been expelled. Upon adding just enough water to dissolve the excess of ammonium chloride, as little as a few hundredths of a milligram of rhodium could be detected either by the rose color of the solution or the greenish color of the ammonium chloroplatinate precipitate. When the platinum sponge failed to dissolve completely in aqua regia, the presence of a larger proportion of rhodium was indicated, the magnitude of which could be roughly estimated from the depth of color obtained by fusing with potassium pyrosulfate.

When desired the final rhodium solution could be readily examined for platinum. A small fraction of a milligram of platinum could be detected as ammonium chloroplatinate, in the presence of 200 mg. of rhodium, by evaporating the whole chloride solution to dryness with ammonium chloride and then redissolving the ammonium rhodium chloride and the excess of ammonium chloride in a little water. On whirling the solution in the beaker, even a minute amount of the platinum salt could be collected. There was no attempt to obtain quantitative results from these tests.

Data on the Separation of Rhodium from Platinum by Sodium Hypobromite

Series 8.—The reagent was 100 cc. of 2% solution of sodium bicarbonate in saturated bromine water. The solutions were boiled for 30 minutes; 0.2000 g. of rhodium was added.

Sample	Rh recovered G.	Pt in 2d filtrate G.	Pt in 3d filtrate G.
A	0.1982	0.0057	0.0016
B	.1986	.0042	.0008
C	.1989	.0042	.0007

Remarks.—In every case the platinum recovered after the second and third precipitations was contaminated with a quantity of rhodium of the order of 0.5 mg. As so little platinum was recovered from the third precipitation the final rhodium solution was not examined for platinum.

Series 9.—50 cc. of 4% solution of sodium bicarbonate in saturated bromine water, 30 minutes' boiling; 0.2000 g. of rhodium was added.

Sample	Rh recovered G.	Pt in 2d filtrate G.	Pt in 3d filtrate G.
A	0.2032	0.0198	0.0057
B	.2023	.0175	.0049
C	....	.0152	.0045

Remarks.—The rhodium from Sample C was examined for platinum and an appreciable amount was detected. No rhodium was found with the platinum from the second and third precipitations except a doubtful trace in one case. In every case the solutions were alkaline to litmus paper after boiling for 30 minutes.

Series 11.—80 cc. of 2.5% solution of sodium bicarbonate in saturated bromine water, 30 minutes' boiling; 0.2000 g. of rhodium was added.

Sample	Rh recovered G.	Pt in 2d filtrate G.	Pt in 3d filtrate G.
A	0.1987	0.0049	0.0023
B	.1978	.0056	.0018
C	....	.0064	.0022

Remarks.—The rhodium from Sample C showed a doubtful trace of platinum. In every case the platinum recovered was contaminated with rhodium. The amount was probably from 0.5 to 1.0 mg. All of the solutions were neutral or slightly acid to litmus after boiling for 30 minutes.

From the foregoing experiments and from other work it became evident that it would be difficult to establish and maintain the desired degree of alkalinity. It should be noted, however, that the results given are for analyses in which boiling was continued for 30 minutes. It is possible that with a shorter period of boiling, which was later found to be adequate, less difficulty would be experienced. Furthermore, if the average rhodium values obtained in the three series are calculated in percentage of the sample, the result in Series 9 is 10.14%, and in Series 8 and 11, 9.93% and 9.92%, respectively, as compared with the true value of 10.00%. In Series 9 the result could have been improved by a fourth precipitation. Any of the results might be considered sufficiently accurate for many purposes, particularly if a more exact method of separation were lacking.

Precipitation of Rhodium by Sodium Hydroxide.—An attempt was made to effect the hydrolysis by adding sodium hydroxide gradually to the boiling chloride solution of rhodium and platinum to a fixed end-point determined by an indicator, as is done in the precipitation of aluminum by ammonium hydroxide according to Blum's[11] method. This was unsatisfactory because the platinum reacted too rapidly with sodium hydroxide to keep the solution neutral or faintly alkaline long enough to

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[11] Blum, This Journal, **38**, 1282 (1916).

insure complete precipitation of rhodium. Furthermore, the orange-red color of chloroplatinate solution and the yellow color of rhodium hydroxide mask the color of many indicators. It is possible that conditions could be established for the satisfactory use of this method.

Precipitation by Barium or Calcium Carbonate.—Finally, the very slightly soluble barium and calcium carbonates were used. These reagents were freshly prepared by mixing a solution of sodium carbonate with an equal volume of a solution of barium or calcium chloride of such concentration that there was always a slight excess of chloride. Of the two, barium carbonate is the more satisfactory because it precipitates in a gelatinous form which is not much changed on prolonged boiling. Because of its greater surface it appears to act more rapidly as a source of hydroxyl ions than does calcium carbonate, which rapidly changes to a dense granular precipitate, especially on heating. Both were found to have nearly the same alkalinity in suspension in the solution from which they were precipitated. The $P_{\rm H}$ for barium carbonate was estimated by indicator methods to be 7.25, that for calcium carbonate 7.4. In a preliminary experiment with barium carbonate on two solutions containing rhodium alone, the hydroxide was completely precipitated after boiling for five minutes.

In Series 14 the first precipitation was made by means of calcium carbonate. After two minutes' boiling precipitation was judged incomplete in two out of three samples. A supplementary precipitation was then made by boiling for a few minutes with an additional small quantity of calcium carbonate. This appeared to complete the precipitation, but the solutions were given a final treatment with a little barium carbonate to make sure that all of the rhodium was separated. These three fractions were united and dissolved in hydrochloric acid. Two reprecipitations were made with barium carbonate.

In Series 15 and 16 barium carbonate was used throughout. The reagent was prepared by mixing equal volumes of two solutions containing 90 g. of barium chloride dihydrate and 36 g. of anhydrous sodium carbonate per liter, respectively. During 10 minutes' boiling, a neutral chloroplatinate solution containing about 2 g. of platinum in 200 cc. dissolved the barium carbonate obtained by mixing 2cc. portions of the two solutions. During the boiling the red color of cresol red was observed until nearly all of the barium carbonate dissolved. In the analysis, 1 cc. of each solution was used for each 10 mg. of rhodium present, but in no case was the total amount used less than 5 cc. of each. In all cases some excess of barium carbonate remained when boiling was completed. Most of the remaining details of procedure were the same as those given for the experiments with sodium hypobromite.

To determine whether rhodium could be precipitated with hydrogen sulfide in the presence of barium chloride without significant contamination, four solutions of rhodium chloride containing 100 mg. of rhodium were prepared. *A* and *B* contained no barium chloride, while *C* and *D* each contained 1.80 g. of crystallized barium chloride. The total volume was about 200 cc. and all of the solutions contained 10 cc. of hydrochloric acid (d., 1.18). Rhodium was determined as previously described, with the following results: *A*, 0.1002; *B*, 0.0999; *C*, 0.1000; *D*, 0.0996. There was apparently no serious contamination. It was observed, however, that when the filtrates from the sulfides were given a prolonged treatment with hydrogen sulfide a small amount of white precipitate was formed, which was evidently barium sulfate. For this reason the treatment with hydrogen sulfide in the presence of barium should not be prolonged more than 30 to 60 minutes and the precipitate should be filtered off at once. If desired, barium may be removed as sulfate before the precipitation of rhodium.

Data on Separations with Barium Carbonate

Series 14.—Mixtures of 90% of Platinum and 10% of Rhodium.—Calcium carbonate was used for the first precipitation, as noted. For the second and third precipitations barium carbonate was used and the solutions were boiled for 2 minutes in each case; 0.2000 g. of rhodium was present.

Sample	Rh recovered G.	Pt in Filtrate II G.	Pt in Filtrate III G.
A	0.2003	0.0167	0.0022
B	.1995	.0141	.0019
C	.2001	.0161	.0017

REMARKS.—In every case the platinum contained a small amount of rhodium, in all but "II B" and "III C" not over 0.1 mg. The solutions probably should have been boiled a little longer.

Series 15.—Mixtures Containing 2.50%, 5.00% and 10.00% of Rhodium.—The solutions were boiled for 2 minutes for the first precipitation and 3 minutes each for the second and third.

Sample	Rh present G.	Rh recovered G.	Pt in Filtrate II G.	Pt in Filtrate III G.
A	0.0500	0.0511	0.0103	0.0017
B	.1000	.1004	.0107	.0012
C	.2000	.2005	.0189	.0017

The platinum recovered contained no rhodium in any case except "III C," which contained a little.

Series 16.—Mixtures Containing 1.00% and 0.10% of Rhodium in a Total of 2.00 g. of Metal.—For the first precipitation 5 cc. of each of the reagent solutions was used and 2 cc. of each for the second and for the third. For the first precipitation of Samples A and B the end-point of the preliminary neutralization with sodium hydroxide was determined by the initial precipitation of rhodium hydroxide. For Samples C and D an indicator was required and cresol red was used. In the second and third precipitations, the indicator was used in all of the solutions so as to avoid any possibility of adding too much sodium hydroxide. The solutions were boiled for 2 minutes for the first treatment and for 3 minutes each for the second and third.

Sample	Rh present G.	Rh recovered G.	Pt in 2d filtrate G.	Pt in 3d filtrate G.
A	0.0200	0.0206	0.0089	0.0005
B	.0200	.0204	.0100	.0004
C	.0020	.0021	.0044	.0002
D	.0020	.0021	.0047	.0001

REMARKS.—No rhodium was found in the platinum recovered in any case. With Samples C and D the precipitation of rhodium sulfide was not complete in 30 minutes from solutions containing 4 to 5% by volume of hydrochloric acid (d., 1.18). On diluting to about half this concentration of acid the remainder of the rhodium was precipitated.

Discussion of Results.—The data obtained from the experiments with barium carbonate show that rhodium can be quantitatively separated from platinum in solutions with a rhodium content of 0.1 to 10% of the total metal. That it can be separated as well from mixtures in which rhodium is predominant is shown in effect by the behavior of the two metals in the second and third precipitations. In these series it was considered unnecessary to examine the final rhodium solution for platinum because earlier work with other reagents had shown the elimination of platinum to be progressive. The recovery of relatively small quantities of platinum after the third precipitation was found to indicate that the rhodium no longer contained any appreciable amount of platinum. While the weights of rhodium recovered, in all cases but one, were high by 0.1 to 1.1 mg., with an average of 0.36 mg., it is believed that this represents contamination with other impurities such as silica or barium compounds, rather than with platinum.

The results also show that two precipitations of rhodium hydroxide would be sufficient for many purposes, especially when dealing with mixtures containing a relatively small proportion of rhodium. The following table shows the error which would be involved in accepting the rhodium value after two precipitations instead of three, assuming the same degree of contamination with ordinary impurities.

Series	True Rh value %	Value after 3d precipitation %	Value after 2d precipitation %
14	10.00	10.00 (av. of three)	10.10
15	2.50	2.56	2.64
	5.00	5.02	5.07
	10.00	10.03	10.11
16	1.00	1.03 (av. of two)	1.05
	0.10	0.11 (av. of two)	0.11

Behavior of Other Metals with Respect to Hydrolysis

A few experiments were made to determine the behavior of the other platinum metals as well as gold under the conditions prescribed for the precipitation of rhodium by hydrolysis. These experiments may be summarized as follows. The period of boiling was three minutes in all cases. All of the solutions were made with very pure metals.

Palladium.—A solution of palladous chloride, containing very little palladic chloride, if any, showed initial precipitation when neutralized with sodium hydroxide at room temperature. Precipitation was complete after boiling with barium carbonate. The color of the precipitate was reddish-brown. In considering the color of this and other precipitates it should be remembered that a variable excess of barium carbonate was present in all cases.

Iridium.—A solution of tervalent iridium chloride showed not more than a trace of turbidity when neutralized with sodium hydroxide. The precipitate with barium carbonate was nearly white. The filtrate showed a small amount of precipitate when treated with hydrogen sulfide in a pressure bottle.

A solution of quadrivalent iridium chloride changed in color from deep red to orange-yellow, with no turbidity, when neutralized with sodium hydroxide. Boiling with barium carbonate produced a blue precipitate, probably the well-known hydrated dioxide. The filtrate yielded not more than a trace of iridium sulfide.

Osmium.—A solution of quadrivalent osmium bromide (or bromo-osmic acid) showed a precipitate when neutralized with sodium hydroxide. Precipitation with barium carbonate was complete, the color of the precipitate being blue-black.

Bivalent Platinum.—A solution of potassium chloroplatinite was prepared from the chloroplatinate by prolonged boiling with the calculated quantity of potassium oxalate as directed by Vèzes.[12] It may have contained a small proportion of unreduced chloroplatinate. It was neutralized with sodium hydroxide without precipitation or change of color. Boiling with barium carbonate produced a very dark precipitate. The filtrate yielded a slight precipitate of sulfide.

Ruthenium.—This solution was prepared by decomposing ammonium nitrosochlororuthenate, $(NH_4)_2RuNOCl_5$, with aqua regia and evaporating several times with hydrochloric acid. The solution showed a precipitate on preliminary neutralization. The precipitate with barium carbonate was dark and the filtrate was yellow. The filtrate assumed the characteristic color of ruthenium nitrosochloride on digestion with hydrochloric acid, and evidently contained quite a little ruthenium. Subsequent tests showed that the solution as prepared was a mixture of ruthenium trichloride, $RuCl_3$, and ruthenium nitrosochloride, $RuNOCl_3$. The former compound appears to be hydrolyzed by barium carbonate with complete precipitation, whereas a dilute solution of the latter yields very little precipitate when thus treated, by far the greater portion of the ruthenium appearing in the filtrate.

Gold.—A solution of chloro-auric acid, $HAuCl_4$, containing 0.025 g. of gold in about 100 cc. became practically colorless when neutralized with sodium hydroxide but showed no precipitate. After boiling with barium carbonate the residue was white and the filtrate was colorless. A small amount of gold was present in the residue but most of it was in the filtrate.

Base Metals.—No study was made of the behavior of base metals but it is well known that those which are likely to be encountered in the analysis of platinum metal alloys or mixtures, notably iron and copper, can be completely precipitated by hydrolysis from faintly alkaline solutions.

Discussion.—The experiments just described were intended to be qualitative only and no use should be made of them in quantitative pro-

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[12] Vèzes, *Bull. soc. chim.*, [3] **19**, 879 (1898).

cedures without additional work. However, the results indicate that the precipitate of rhodium obtained by hydrolysis will be contaminated to a greater or less degree if any of the metals named is present. As stated in an earlier paragraph, most analytical procedures for this group of metals leave the separation of rhodium and platinum until other metals, with the possible exception of copper, have been removed. A suitable separation of rhodium from copper is described in another paper from this Laboratory.[13] Bivalent platinum is seldom encountered and may be readily oxidized to the quadrivalent condition before the separation of rhodium.

There is undoubtedly opportunity to use hydrolysis more extensively in analytical methods for the platinum group than has been done in the past. It is intended to develop certain of these applications in subsequent papers, both with regard to specific separations and as used in complete procedures. No attempt is made in this paper to apply the suggested separation of rhodium from platinum to any particular scheme of analysis. The particulars of its application may be modified according to the previous treatment of the solution at hand.

Effect of Certain Other Reagents

Although the hydrolysis of rhodium can undoubtedly be effected by a variety of reagents, some of those which are often used for other metals are not suitable. Ammonium hydroxide cannot be used because it reacts with the platinum metals to form ammines, rather than hydroxides. All of these ammines are more or less soluble. Furthermore, in the case of several of the metals, the complex ammine group does not yield enough metal ions to exhibit the usual properties of the element.[14]

Alkali nitrites, which are sometimes used as hydrolytic agents, cannot be used for rhodium because of the formation of very stable double nitrites. In general no reagent should be used which is known to form a double salt with rhodium.

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[13] Swanger and Wichers, This Journal, 46, 1814 (1924).

[14] Ammonium hydroxide should never be added to solutions of platinum metals except when the formation of ammines is the specific object. An important example is the reduction of platinum from solution by means of formic acid. In many references to this operation it is directed that the solution be nearly neutralized with ammonium hydroxide before adding the reducing agent. If this is done and the solution becomes even momentarily alkaline so that free ammonia is present, part of the platinum will be converted to an ammine, which can be reduced to metal only with the greatest difficulty. In this Laboratory it was once found necessary to evaporate such a solution to dryness and to ignite the salts in order to recover the platinum. For this reason the necessary neutralization of excess acid should be effected by some other alkali or by means of sodium or ammonium acetate.

Obviously, this precaution applies not only to reductions but to any reactions in which an appreciable concentration of the metal ion is required. It is to be noted also that as solutions of the platinum metal ammines are not deeply colored, considerable quantities of the metals may escape detection in an apparently colorless solution.

Ammonium salts must be absent if rhodium is to be precipitated by hydrolysis, because they will consume whatever alkali is used, with the liberation of ammonia. When barium carbonate is used, alkali sulfates should be absent because they react to form barium sulfate and an alkali carbonate, resulting in a solution which is too strongly alkaline. It is believed that acetates also are likely to interfere. Soluble chlorides do not interfere and it is believed that incidental amounts of nitrates have no effect.

Recommended Procedure

The following procedure is recommended for the separation of rhodium from platinum in chloride solutions from which other heavy metals have been removed and which do not contain the undesirable salts mentioned in the preceding paragraph.

A solution of sodium hydroxide is added at room temperature until yellow rhodium hydroxide begins to precipitate. When the concentration of rhodium is thought to be less than 10 mg. per 100 cc., it will be better to add 2 or 3 drops of 0.4% solution of cresol red per 100 cc. and to add sodium hydroxide until the alkaline color appears. The color need not persist more than a few seconds. When the original solution is very acid it may be partially neutralized with a strong solution of the alkali. A solution containing from 30 to 40 g. of sodium hydroxide per liter is suitable to complete the neutralization and is best added quite rapidly.

After the preliminary neutralization the volume of the solution should be so adjusted that the estimated total content of platinum and rhodium does not exceed 1 g. per 100 cc. A mixture of equal volumes of solutions containing 90 g. of crystallized barium chloride and 36 g. of anhydrous sodium carbonate per liter, respectively, is added. This mixture will contain a small excess of barium chloride. One cc. of each solution should be used for every 10 mg. of rhodium estimated to be present, but the total amount used should not be less than 2 cc. for each gram of platinum. In any case the minimum amount to be taken for the first precipitation is 5 cc. of each solution. After the suspension of barium carbonate is added the solution is rapidly heated to boiling and boiled for two minutes. The residue is filtered off and washed several times with a hot 2% solution of sodium chloride, after which it is returned, with the filter paper, to the original beaker and digested with 25 cc. of hydrochloric acid (1 volume of acid, d. 1.18, diluted with 4 volumes of water) until solution is complete. The presence of barium carbonate with the rhodium hydroxide may be noted by the evolution of carbon dioxide when the acid is added. If no barium carbonate is present the platinum solution should be given a second treatment. If the reagent is again consumed, the condition of the platinum solution is at fault and should be corrected before assuming that all of the rhodium is removed. If the first precipitate contains barium carbonate the platinum solution may be acidified with hydrochloric acid and set aside for the subsequent recovery of platinum.

After the mixture of barium carbonate and rhodium hydroxide has dissolved in the hydrochloric acid, the solution is diluted somewhat and filtered from the paper pulp. The solution is now treated exactly as before except that the volume need not exceed 200 cc. in any case and the amount of barium carbonate to be added may be computed from the estimated rhodium content alone. Care should be taken not to add an excess of sodium hydroxide in the preliminary neutralization. If the amount of rhodium present is very small, it is better to leave the solution slightly acid before adding barium carbonate. The period of boiling should be extended to three minutes. The precipitate is handled as before and a third precipitation made if desired. For mixtures containing 1% or less of rhodium, two precipitations should be sufficient, unless the first precipitate was for some reason unduly contaminated with platinum. After some experience is gained, the amount of platinum in the filtrate from the second precipitation may be estimated from the color after acidifying, unless an indicator is present.

The final solution of rhodium chloride and barium chloride, containing nearly 25 cc. of hydrochloric acid (1:4 by volume), is diluted to 100–150 cc. In case the estimated rhodium content exceeds 100 mg., the solution is made up to a larger volume with the same relative concentration of hydrochloric acid. It is heated to incipient boiling, and kept at this temperature for 30–45 minutes while a current of hydrogen sulfide is passed in. After the precipitation the rhodium sulfide is filtered off at once, washed with water containing a little ammonium chloride, and ignited in a weighed porcelain crucible. The ignited sulfide is finally reduced in a current of hydrogen and cooled in hydrogen.[15] This is best done by using a Rose cover and delivery tube. The current of hydrogen should be continued until the crucible is nearly at room temperature. The rhodium sponge should have a clean, light gray color. General experience in this Laboratory shows that it is not necessary to displace hydrogen with nitrogen or carbon dioxide to secure results of sufficient accuracy for the usual analytical work. Rhodium is weighed as metal after the crucible has been brought to room temperature in a desiccator.

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[15] When rhodium sulfide is ignited in air it is presumably converted into an oxide or a mixture of oxides. With such material ignited in an open porcelain crucible over a Tirrill burner, the loss in weight on reduction in hydrogen was found in several observations to be somewhat less than that calculated from the reaction $Rh_2O_3 + 3H_2 = 2Rh + 3H_2O$, assuming that Rh = 102.9.

suggestions. The last named made the indicator measurements of acidity which are referred to in the paper.

Summary

1. The customary separation of rhodium from platinum by means of ammonium chloride is unsatisfactory unless regarded merely as a preliminary fractionation.

2. Rhodium can be separated from quadrivalent platinum by hydrolysis in faintly alkaline chloride solutions.

3. Data are given for the separation of rhodium by means of sodium hypobromite and by means of barium carbonate. The latter is the more satisfactory reagent, particularly because it readily maintains the desired alkalinity. Two precipitations are sufficient for most purposes, but a third should be made when high accuracy is desired.

4. Experiments were made to determine the behavior of bivalent platinum chloride, as well as of the other platinum metals and gold, with respect to hydrolysis.

5. A procedure is recommended for the separation of rhodium from platinum in the absence of other platinum metals and of certain undesirable salts.

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NOTES

The Atomic Weight of Zirconium.—Results of our investigation of the atomic weight of zirconium were published in THIS JOURNAL in 1917.[1] The compound selected for analysis was zirconium tetrachloride. Determinations of zirconium as the oxide gave an average of 92.1 and those of the chlorine an average of 91.76 for the atomic weight of zirconium. The divergences in the individual determinations were too large for atomic weight work. At the time we could offer no explanation for these divergences, though the suggestion was made that in the case of the weighings of zirconia they might be due to the retention of chlorine even after 50 to 60 hours of heating at about 1000°. We were at quite a loss to explain those found in the chlorine determinations.

The war interrupted our work. Later, various methods of removing the chlorine supposed to be present yielded no results. The discovery of hafnium by Hevesy and the proof that it accompanied zirconium in all of its minerals has at last revealed the cause of our difficulties. Dr. Hevesy has very kindly examined three mixed samples of the zirconia from bulbs such as were used by us and has reported the amount of hafnium oxide present in each. In No. 1 he found 1% of hafnium dioxide, HfO_2; in No. 2, 0.95%; in No. 3, 0.7%. He states that by his method it is scarcely

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[1] THIS JOURNAL, **39**, 1598 (1917).