mole of hydrazine. With constant large excess of ferric salt it varies with the acid concentration, and passes through a minimum in the neighborhood of 2 *N* acid. With constant acid concentration the value decreases with decreasing excess of the ferric salt. The results obtained and the analogy with the manganic-hydrazine reaction indicate that the limiting reaction is $N_2H_5^+ + Fe^{+++} = NH_4^+ + {}^1/_2N_2 + H^+ + Fe^{++}$.

The conclusion that this type of reaction is not likely to occur in alkaline solution is supported by the fact that the amount of ferric salt required increases with decreasing acid concentration, and by the behavior of hydrazine in alkaline solution towards ferricyanide and other oxidizing agents.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS]

INVESTIGATIONS ON THE PLATINUM METALS. V THE ANALYTICAL SEPARATION OF COPPER FROM THE PLATINUM METALS[1]

BY WM. H. SWANGER[2] AND EDWARD WICHERS[3]

RECEIVED MAY 13, 1924 PUBLISHED AUGUST 5, 1924

The various methods that have been proposed for the analysis of crude platinum and of platinum alloys containing copper usually provide for the determination of copper in the solutions from which silver and gold and the bulk of the platinum metals have been previously removed.

From such solutions copper is precipitated by hydrogen sulfide together with all of the remaining quantity of the platinum metals. The precipitate usually includes most of the rhodium that was in the sample. This mixture of sulfides is ignited strongly in air and then leached with nitric acid. It is the supposition that copper dissolves completely while the platinum metals remain as the undissolved residue.

It has been the experience in this Laboratory that nitric acid does not separate the copper completely from such an ignited mixture, leaving as a residue all of the platinum, iridium and rhodium. The following experiments were made in order to determine to what extent this separation may be in error.

Extraction with Nitric Acid.—Solutions were prepared containing approximately 50 mg. of copper with the amount of noble metal indicated in Col. 2 of Table I. The metals were precipitated by hydrogen sulfide. The mixed sulfides were ignited strongly in air and then leached with 20 cc. of nitric acid (1 volume of nitric acid, d. 1.42, diluted with 1 volume of

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water) for two hours on the steam-bath. The weights of the undissolved residue after ignition and reduction in hydrogen are given in Col. 3.

TABLE I

EXTRACTION OF IGNITED SULFIDES WITH NITRIC ACID

Solution	Wt. of noble metal G.	Wt. of residue G.	Solution	Wt. of noble metal G.	Wt. of residue G.
1	0.0500 Au	0.0512	6	0.0496 Ir	0.0493
2	.0500 Au	.0519	7	.0532 Rh	.0785
3	.0500 Pt	.0524	8	.0532 Rh	.0781
4	.0500 Pt	.0519	9	.0266 Rh	.0422
5	.0496 Ir	.0496	10	.0266 Rh	.0429

In Solutions 5 and 6 no copper was detected in the residues of iridium. In all of the other residues the presence of copper was detected when they were further leached with concd. nitric acid. The residues from the mixtures of copper and rhodium contained a greater amount of copper than did the others. Similar results were obtained with a mixture of copper and rhodium by using hydrochloric acid, instead of nitric acid, to leach the ignited sulfides. Small amounts of platinum and of rhodium were dissolved by the nitric acid but no gold or iridium was found with the copper from Solutions 1 and 2, and 5 and 6.

Extraction of Un-ignited Sulfides.—Attempts were made to separate copper from the platinum metals by treating the un-ignited sulfides with hydrogen peroxide. Un-ignited copper sulfide was found to be readily dissolved by hydrogen peroxide, while the sulfides of platinum, palladium and rhodium were not appreciably attacked by a 3% solution of hydrogen peroxide. The sulfides obtained when iridium was precipitated by hydrogen sulfide were almost completely dissolved. However, when copper was precipitated in the presence of platinum metals and the resulting mixture of sulfides was treated with a 3% solution of hydrogen peroxide, the copper sulfide was not completely dissolved. The copper solution contained iridium, with only a very small amount of any of the other platinum metals. Similar experiments with nitric acid and with bromine water gave less satisfactory results than did those with hydrogen peroxide. Copper was always found with the residue and the solution always contained platinum metals.

Precipitation with Ammonium Thiocyanate.—The precipitation of copper as cuprous thiocyanate, first proposed by Rivot and further investigated by Parr, Van Name and Demorest,[4] was at one time extensively used to separate copper from iron, nickel, zinc, cadmium, etc. The solutions containing copper are saturated with sulfur dioxide; ammonium thiocyanate is added in moderate excess, and the precipitated cuprous thiocyanate filtered off. Copper can then be determined in any one of several

[4] Rivot, *Compt. rend.*, **38**, 868 (1854). Parr, THIS JOURNAL, **22**, 685 (1900). Van Name, *Z. anorg. Chem.*, **26**, 230 (1901). Demorest, *J. Ind. Eng. Chem.*, **5**, 215 (1913).

ways. If certain precautions are taken, the procedure given by these investigators can also be used to precipitate copper in the presence of platinum, palladium, iridium and rhodium.

Solutions of the platinum metals, in the form of chlorides, when boiled with a soluble thiocyanate form complex thiocyanates of the platinum metals. According to Iwanoff[5] these compounds can be used for the quantitative determination of platinum, palladium, or rhodium. However, in solutions that are saturated with sulfur dioxide, the platinum metals are probably in the form of sulfites or of double sulfites and do not seem to react with the thiocyanate.

Cuprous thiocyanate, when precipitated in the presence of relatively large amounts of platinum metals, is nearly always contaminated and must be reprecipitated. The second precipitation, which is made in the presence of a much smaller amount of platinum metals, usually yields a precipitate free from contamination.

Recommended Procedure.—The following procedure was found to give the best results. The volume of the solution should be from 150 cc. to 250 cc. and should contain not more than 100 mg. of copper, because of the bulkiness of the subsequently precipitated cuprous thiocyanate. It may contain as much as several grams of the platinum metals. The solution is first treated with sulfur dioxide. This is best done by adding a saturated solution of sulfur dioxide in 20cc. portions until, after digesting for one-half hour on the steam-bath, the solution still smells strongly of sulfur dioxide and is a pale yellow. The solution is then cooled and most of the free acid is neutralized by adding sodium hydroxide solution until a precipitate just begins to form. Concd. hydrochloric acid, 6 to 10 drops, is then added. A large excess of free acid may cause incomplete precipitation of the copper, while in neutral or nearly neutral solutions, containing alkali sulfites, rhodium may precipitate as a double sulfite.

A solution of ammonium thiocyanate, containing 2 g. of the salt in 100 cc. of saturated sulfur dioxide solution, is used as the precipitant. For every 50 mg. of copper present, 10 cc. of this solution is added drop by drop to the cold solution, which is stirred vigorously meanwhile. Since most of the sulfur dioxide present in the solution has been neutralized by the sodium hydroxide, the presence of sulfur dioxide in the reagent solution insures a slight excess at all times.

In order to allow the precipitate to settle, the cold solution is set aside for several hours. However, to insure complete precipitation, it should be allowed to remain overnight. The precipitate is filtered on a tight paper, washed with cold water containing a small quantity of sodium chloride and, with the paper, is returned to the beaker. Nitric acid (1 volume of nitric acid, d. 1.42, diluted with 3 volumes of water), sufficient to dis-

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[5] Iwanoff, *Chem.-Ztg.*, **47**, 209 (1923).

solve the precipitate, is added and the beaker set on the steam-bath for one-half hour. The resulting solution is filtered from the paper pulp and the copper is precipitated again in the manner described above.

The greater portion of the platinum metals which contaminated the first precipitate remains with the paper pulp from the nitric acid treatment. This is recovered by digesting the pulp with aqua regia and adding the solution to the original filtrate. The filtrate from the second precipitation of the copper also contains a small amount of platinum metals, and is added to the first filtrate.

The final precipitate of cuprous thiocyanate, which is white if pure, is filtered off and washed with cold water containing a small amount of ammonium chloride or sulfate until free from alkali salts. Copper may then be determined in a variety of ways. It is probably simplest to convert the precipitate into metallic copper. The paper with the precipitate is first charred in an atmosphere of hydrogen, in a porcelain crucible, and then ignited in air. The residue is reduced in hydrogen and weighed as metallic copper.

Table II gives the results of analyses made according to the procedure described above.

Table II

Precipitation of Copper as Cuprous Thiocyanate

Each solution contained G.	Wt. of copper recovered G.	Each solution contained G.	Wt. of copper recovered G.
0.0266 Rh	(1) 0.0496	0.0500 Cu	(1) 0.0493
.0500 Cu	(2) .0496	.0500 Rh	(2) .0491
	(3) .0495	.0250 Pt	(3) .0502
	(4) .0495	.0250 Pd	(4) .0505
	——	.0250 Ir	(5) .0503
	Av. .0496		——
			Av. .0499

In all of the above analyses the copper was obtained as a bright spongy mass that showed no contamination with platinum metals. The presence of a significant amount of platinum metals can be detected by the discoloration of the reduced copper sponge.

Two samples, each containing 1.000 g. of palladium and 0.0250 g. of copper, were analyzed for copper. The first precipitate of cuprous thiocyanate was white, and it was not reprecipitated. The weights of copper obtained were 0.0246 g. and 0.0247 g. The copper sponge was not discolored, and no palladium was detected by dissolving the copper in nitric acid and testing the solution with dimethylglyoxime.

Summary

1. Extraction of an ignited mixture of the sulfides of copper and of the platinum metals with nitric acid does not effect a quantitative separation of the copper.

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.

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[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS]

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

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RECEIVED MAY 13, 1924 PUBLISHED AUGUST 5, 1924

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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