

A SYSTEM OF QUALITATIVE ANALYSIS FOR  
TELLURIUM, MOLYBDENUM, IRIDIUM, RHODIUM, AND  
THE COPPER GROUP ELEMENTS

Thesis

by

Robert H. Dalton

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CALIFORNIA INSTITUTE OF TECHNOLOGY

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## Introduction

The object of this work was the confirmation and rearrangement of the system of analysis worked out by G. V. Sammet, R. C. Robinson, and G. H. Buchanan to prepare it for incorporation in the scheme of qualitative analysis to be published by A. A. Noyes and W. C. Bray. A few new features have, however, been introduced. The work was carried out at the suggestion and under the supervision of Prof. Noyes and was aided financially by a grant made to him by the Carnegie Institution of Washington.

# ANALYSIS OF THE TELLURIUM AND COPPER GROUPS

WITH G. VICTOR SAMMET, [REDACTED], [REDACTED], [REDACTED],  
[REDACTED] AND ROBERT H. DALTON

## TABULAR OUTLINE VIII

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### GENERAL DISCUSSION

*D. 71. Elements Precipitated by Hydrogen Sulfide from the Acid Solution.*—The next step in the system of analysis is the precipitation of those elements which are thrown down from acid solution by hydrogen sulfide. The number of elements passing into this precipitate is greatly reduced by the fact that many that would otherwise be found here have been wholly or almost wholly removed by previous operations. Thus there has been eliminated substantially all of the selenium, arsenic, germanium, osmium, ruthenium, antimony, tin, mercury, gold, platinum, palladium, and silver. Moreover, any molybdenum in excess of 3 mg. (except when phosphate is also present), and any lead in excess of 20–30 mg. have been removed. Hence there will be found in the hydrogen sulfide precipitate only tellurium, molybdenum, iridium, and rhodium (constituting the *tellurium group*), and lead, bismuth, copper, and cadmium (constituting the *copper group*).

The fact that only this relatively small number of elements is precipitated by hydrogen sulfide has great advantages, first, in the respect that it much simplifies the (otherwise very complex) scheme of analysis for the precipitated elements; and secondly, in the respect that the separation of these from the elements that normally are not precipitated by hydrogen sulfide is on the average much more perfect. This last is especially important in view of the many cases<sup>1</sup> in which more soluble sulfides are carried down by less soluble ones. Moreover, the smaller number of elements to be detected makes it unnecessary to employ the very unsatisfactory separation with ammonium or sodium sulfide.

<sup>1</sup> See especially the recent paper by Feigl, *Z. anal. Chem.*, **65**, 25–46 (1924).

TABULAR OUTLINE VIII  
ANALYSIS OF TELLURIUM AND COPPER GROUPS

Precipitate, black; Te.	Filtrate. <i>Evaporate, add 6 n. HCl, shake with ether (P. 73).</i>		Filtrate: $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ , $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ . <i>Add HCl, evaporate, add <math>\text{Na}_2\text{CO}_3</math> and <math>\text{Br}_2</math> (P. 76).</i>	Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>	Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>	Solution: $\text{K}_2\text{Cu}(\text{CN})_2$ , $\text{K}_2\text{Cd}(\text{CN})_4$ . <i>Pass in <math>\text{H}_2\text{S}</math> (P. 85).</i>
	Ether layer. <i>Evaporate, add water, <math>\text{HC}_2\text{H}_3\text{O}_2</math>, <math>\text{NaNO}_2</math>, and <math>\text{NaOH}</math> (P. 75).</i>					
Residue, blue; $\text{MoO}_3$ , $x\text{MoO}_3$ . <i>Add HCl, KSCN, Zn.</i>	Filtrate: $\text{IrO}_2$ , $\text{RhO}_2$ . <i>Dissolve in <math>\text{HBr}</math>, evaporate with <math>\text{HCl}</math> and <math>\text{HNO}_3</math>, add water and <math>\text{NH}_4\text{Cl}</math> (P. 77).</i>		Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>	Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>	Solution: $\text{K}_2\text{Cu}(\text{CN})_2$ , $\text{K}_2\text{Cd}(\text{CN})_4$ . <i>Pass in <math>\text{H}_2\text{S}</math> (P. 85).</i>	
	Filtrate: $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ , $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ . <i>Add HCl, evaporate, add <math>\text{Na}_2\text{CO}_3</math> and <math>\text{Br}_2</math> (P. 76).</i>					
Red color: $\text{MoO}(\text{SCN})_3$ . <i>Pass in <math>\text{H}_2\text{S}</math>.</i>	Filtrate: $\text{IrO}_2$ , $\text{RhO}_2$ . <i>Dissolve in <math>\text{HBr}</math>, evaporate with <math>\text{HCl}</math> and <math>\text{HNO}_3</math>, add water and <math>\text{NH}_4\text{Cl}</math> (P. 77).</i>		Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>	Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>	Solution: $\text{K}_2\text{Cu}(\text{CN})_2$ , $\text{K}_2\text{Cd}(\text{CN})_4$ . <i>Pass in <math>\text{H}_2\text{S}</math> (P. 85).</i>	
	Filtrate: $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ , $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ . <i>Add HCl, evaporate, add <math>\text{Na}_2\text{CO}_3</math> and <math>\text{Br}_2</math> (P. 76).</i>					
Precipitate, brown; $\text{MoS}_2$ -3.	Filtrate: $\text{IrO}_2$ , $\text{RhO}_2$ . <i>Dissolve in <math>\text{HBr}</math>, evaporate with <math>\text{HCl}</math> and <math>\text{HNO}_3</math>, add water and <math>\text{NH}_4\text{Cl}</math> (P. 77).</i>		Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>	Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>	Solution: $\text{K}_2\text{Cu}(\text{CN})_2$ , $\text{K}_2\text{Cd}(\text{CN})_4$ . <i>Pass in <math>\text{H}_2\text{S}</math> (P. 85).</i>	
	Filtrate: $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ , $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ . <i>Add HCl, evaporate, add <math>\text{Na}_2\text{CO}_3</math> and <math>\text{Br}_2</math> (P. 76).</i>					
Precipitate, yellow; $\text{PbCrO}_4$ .		Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>		Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>		
Precipitate, red; $\text{Cu}_2\text{Fe}(\text{CN})_6$ ; white; $\text{Cd}_2\text{Fe}(\text{CN})_6$ .		Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , as sulfates. <i>Add <math>\text{NH}_4\text{OH}</math> (P. 82).</i>		Filtrate: $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (blue). <i>To a part add <math>\text{H}_2\text{SO}_4</math> (P. 85).</i>		

D. 72. *The Hydrogen Sulfide Precipitation (P. 70-71).*—The problem here presented consisted in determining the conditions under which the various elements of the tellurium and copper groups can be most rapidly and completely precipitated by hydrogen sulfide, while at the same time retaining in solution the elements of the later groups. The features not involved in common-element analysis are the difficulty of completely precipitating iridium, and in less degree much molybdenum, and the fact that indium is likely to be carried down in the hydrogen sulfide precipitate.

The process finally adopted consists: (1) in treating with hydrogen sulfide at 90–100° a solution which has a volume of 30 cc., an acid concentration of 1 normal, and contains chloride; (2) in diluting the solution to 100 cc., thereby making the acid 0.3 normal, and saturating it with hydrogen sulfide in the cold; and (3), in case iridium is to be tested for or molybdenum may be still unprecipitated, filtering the mixture, evaporating the filtrate to a small volume, making it strongly acid with hydrochloric acid, saturating it cold with hydrogen sulfide, and heating it at 100° in a pressure-bottle for half an hour (or longer if iridium is slowly precipitating). This process is convenient in execution; and it gives, so far as known, an entirely satisfactory separation, except in the one respect that, even after the heating under pressure, a small portion of the iridium may remain in solution.

The conditions prevailing in the first step of the process lead to a fairly complete precipitation of all the elements of the tellurium and copper groups (except iridium) from a solution which is still so acid that there is little tendency for other elements (such as indium, zinc, nickel, and cobalt) to be carried down with them. In the second step, in which the solution is cooled and diluted so that the acid becomes only 0.3 normal, the small proportions of lead, cadmium, and bismuth that may not have been previously precipitated are thrown down. As the complete precipitation of these elements and the non-precipitation of those of the following groups is dependent on a fairly close attainment of the acid concentration 0.3 normal, the acid-content of the solution is adjusted in advance with the aid of the indicator methyl violet by means of a simple procedure, which was worked out in detail. In the third step of the process (which has to be

resorted to only rarely), the addition to the solution of concentrated hydrochloric acid and the treatment with hydrogen sulfide at 100° under pressure greatly promote the separation of iridium, which from a perchloric acid solution or from a cold hydrochloric acid solution is only very slowly precipitated. The employment of the high temperature and of hydrogen sulfide under pressure also completes the precipitation of any molybdenum still remaining in solution.

*D. 73. Separation of Tellurium and Molybdenum from the Other Elements (P. 72-73).*—The solution of the sulfide precipitate is evaporated and made 3 normal in hydrochloric acid, and the tellurium is precipitated by saturating it with sulfur dioxide and heating. The only other element (aside from gold and palladium, which can not escape precipitation in the boiling with formic acid in P. 6) that would be thrown down under these conditions is selenium, and its presence is guarded against by previously passing sulfur dioxide into the solution while it is 12 normal in hydrochloric acid, whereby selenium, but not tellurium, is precipitated.

The molybdenum is then extracted with ether after reducing the volume and making the hydrochloric acid 6 normal. This method of separating molybdenum from other elements has been described by Blair.<sup>1</sup> It was found to be fairly effective, especially when, as in this case, the quantity to be removed is not large. Thus about 85 percent of the molybdenum passes into the ether layer when 15 cc. of this solvent are shaken with 5 cc. of the acid solution. The tellurium must be previously removed, as directed, since it also passes into ether in considerable quantity. Iridium, rhodium, and copper-group elements are not detectable in the ether layer after it has been washed with a little acid.

*D. 74. Separation of Iridium and Rhodium from the Copper Group and from Each Other (P. 75-77).*—The most difficult problem met with in developing the analysis of these groups was the separation of iridium and rhodium from the copper-group elements. This may be done by boiling the solution with formate, as described by Mylius and Dietz.<sup>2</sup> But the process requires many hours for its completion (see D. 18), and it yields the iridium

<sup>1</sup> Blair, *J. Am. Chem. Soc.*, **30**, 1229 (1908).

<sup>2</sup> Mylius and Dietz, *Ber. deutsch. chem. Ges.*, **31**, 3191 (1898).

and rhodium in the state of the metals, which can be brought into solution only by fusion. The most simple and effective method for this separation seems to be to convert these elements into their complex nitrites, as recommended by Leidié.<sup>1</sup> In this form they are not precipitated by sodium hydroxide, but this reagent precipitates the copper group. Even this process required investigation as to its details; but in the final form it gives a fairly sharp separation. The complex nitrites are first produced by making the solution slightly acid with acetic acid, adding sodium nitrite, and warming. The copper group is then precipitated with sodium hydroxide, and the precipitate is filtered out. Sodium hydrocarbonate is added to the filtrate, to destroy the excess of hydroxide, which may have caused a little lead to pass into solution.

The complex nitrites of iridium and rhodium are decomposed by evaporating the solution with hydrochloric acid; but this leaves them mixed with a large quantity of sodium salts, from which they must be removed before they can be satisfactorily separated from each other. For this purpose hydrogen sulfide was at first used; but this is unsuitable because of the extreme slowness with which iridium is precipitated even when heated with the gas under pressure. Recourse was therefore had to the hypobromite method of Mylius and Müzzucchelli,<sup>2</sup> consisting in precipitating the dioxides of iridium and rhodium, which has already been employed in the gold group for separating iridium from platinum (see D, 53). The two dioxides are thrown out merely by heating with sodium carbonate and bromine. The only defects in the process are that, when the elements are present in large quantity, the heating must be continued with occasional addition of bromine for about an hour, and that even then a small proportion of the iridium may escape precipitation.

The dioxides of iridium and rhodium are dissolved in hydrobromic acid, the bromine displaced by chlorine by evaporating with hydrochloric and nitric acids, and the iridium precipitated with ammonium chloride. In order to detect a small quantity of iridium, it was found that special precautions must be observed; but, when this is done, the test is a very delicate one.

<sup>1</sup> Leidié, *Bull. soc. chim.*, (3), 25, 10 (1901).

<sup>2</sup> Mylius and Müzzucchelli, *Z. anorg. Chem.*, 89, 14, 28 (1914).

The rhodium is found in the filtrate from the ammonium chloride precipitate. Its presence, when indicated by the red color of the solution, is confirmed by its conversion, through heating the solution with ammonium hydroxide, into the characteristic chlororhodium pentammine chloride, which separates from hydrochloric acid solution as a light-yellow crystalline precipitate.

*D. 75. Analysis of the Copper Group (P. 81-85).*—The analysis of the copper group needs little discussion. The process adopted is that given in A. A. Noyes' *Qualitative Analysis*, except that cadmium and copper are separated by precipitating the former with hydrogen sulfide from cyanide solution, instead of by using the longer process (advantageous in elementary instruction) of precipitating the copper by metallic iron and the cadmium in the filtrate by hydrogen sulfide.

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## ANALYSIS OF THE TELLURIUM AND COPPER GROUPS

### TABULAR OUTLINE VIII

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#### PROCEDURES AND NOTES

**Procedure 70.**—*Preparation of the Solution for the Hydrogen Sulfide Precipitation.*—Evaporate the filtrate from the HBr precipitate (P. 61) over a small flame until on removing the dish from the flame bubbles rapidly escape, but not until the  $\text{HClO}_4$  fumes strongly. Cool the mixture, measure the volume of the remaining liquid, and add to it 25 cc. of water.

In case the solution is colorless, light-blue, light-green, or yellow, determine its acid-content by proceeding as follows. Add from a pipette or graduated dropper into each of three small crucibles just 1 cc. of methyl violet reagent (see Note 5). From a dropper add to one crucible 5 drops (0.17 cc.), and to another crucible 7 drops, of exactly 1 n.  $\text{HClO}_4$  (see Note 6). Then to the third crucible add such a number of drops of the solution to be analyzed as will produce a color intermediate between that in the other two crucibles. (Take care, by using a suitable dropper and holding it always in the same position, that in all cases uniform drops are produced.) Calculate the acid-content of the whole solution, and the volume of 6 n. HCl (or 6 n.  $\text{NH}_4\text{OH}$ ) that must be added to it to make its acid-content 30 milli-equivalents; and add to it this calculated volume of HCl (or  $\text{NH}_4\text{OH}$ ).

In case the solution is red or dark-green, add enough 6 n. HCl (or 6 n.  $\text{NH}_4\text{OH}$ ) to bring the acid-content to 30 milli-equivalents, considering that 9 milli-equivalents of  $\text{HClO}_4$  are already present for each cubic centimeter of solution left after the evaporation.

*Notes.*—1. The solution from the HBr precipitation is evaporated to remove the HBr and  $\text{HCHO}_2$ . The escape of bubbles, which arise from decomposition of the remaining  $\text{HCHO}_2$ , fur-

nishes a good indication of the nearly complete removal of these acids, since this decomposition occurs only when the  $\text{HClO}_4$  has become concentrated. The heating is stopped before the  $\text{HClO}_4$  fumes strongly, so as to avoid reoxidation of iron, manganese, chromium, and vanadium to their higher valence states.

2. In order that the separation of the elements normally precipitated by  $\text{H}_2\text{S}$  from those not so precipitated may be sharp, it is essential that the acid concentration in the 100 cc. of solution in which the final precipitation is made (see P. 71) be in the neighborhood of 0.3 normal. It is most convenient to introduce the right quantity of acid at this point; and, when the solution does not have a color that interferes with the test, this quantity is conveniently determined with the aid of the indicator methyl violet, which in 25%  $\text{C}_2\text{H}_5\text{OH}$  undergoes a pronounced change of color from blue to green between the acid concentrations 0.15 and 0.18 normal.

3. When, because of color in the solution, this indicator cannot be employed, the acid-content has to be estimated, as well as may be, from the volume of the liquid left after the evaporation. This residual liquid may probably on an average be regarded as 9 n.  $\text{HClO}_4$ ; but its composition doubtless varies much with the nature of the elements (coming from the original material) that are in solution in the acid.

4. The only elements that seriously interfere with this indicator test are those which, like cobalt, give a reddish color, and those which, like chromium, give an intense green color to the solution. Iron, copper, nickel, and uranium, even when 500 mg. are present in the  $\text{HClO}_4$  solution, do not affect the color of the indicator so as to cause a change of more than one drop in the amount of 1 n.  $\text{HClO}_4$  that has to be added in the indicator test (provided in the case of iron not more than half of it is in the ferric state, as is ordinarily the case). Small quantities of  $\text{HBr}$  and of  $\text{HCHO}_2$ , such as might remain in the solution after the evaporation, do not affect the color.

5. The methyl violet reagent is made up by dissolving 1 mg. of the indicator in 25 cc. of 95%  $\text{C}_2\text{H}_5\text{OH}$  and 75 cc. of water. Less alcohol causes the methyl violet to be precipitated by the  $\text{HClO}_4$  contained in the solution to be tested. Much more alcohol makes it necessary to use a large amount of the tested solution.

6. The number of drops named in the Procedure are based on the use of an exactly 1 n.  $\text{HClO}_4$  (which should be kept as a standard solution in the laboratory), on the use of a dropper delivering 30 drops per cubic centimeter, and on a particular methyl

violet preparation. To meet possible variations in these conditions, the analyst should determine for himself the number of drops required to produce the most sensitive change in color; which number should be such that a difference of two drops causes a marked change in color from bluish-green to green. Since the color of the indicator in the presence of acid fades noticeably within 3 minutes, the tests must be quickly made.

**Procedure 71.**—*Precipitation with Hydrogen Sulfide*—Add to the solution \* prepared for the  $H_2S$  precipitation (P. 70) 4 cc. of 3 n.  $NH_4Cl$ , place it in a large test-tube set in boiling water, and pass through it a slow current of  $H_2S$  for 10 minutes. Cool the mixture, and saturate it with  $H_2S$ . Dilute it to 100 cc. with cold water, again saturate it with  $H_2S$ , and let it stand 15 minutes. (Precipitate, presence of TELLURIUM GROUP or COPPER GROUP.) Filter. Wash the precipitate with hot water.

In case iridium is to be tested for (see Note 7), or in case some molybdenum may still be unprecipitated (see Note 8), evaporate the filtrate to about 5 cc., and add to it (without filtering) just 10 cc. of 6 n.  $HCl$ . In case iridium is to be precipitated, boil the mixture with a return-cooler for 10 minutes. Cool the mixture, pour it into a 100-cc. pyrex bottle, add 5 cc. of water, and pass  $H_2S$  into it. While the bottle is filled with the gas, close it with a rubber stopper held securely in place by wiring it to the neck of the bottle, or by clamping the bottle in a pressure-bottle frame. Immerse the bottle in a vessel of water, and boil the water gently for half an hour. (If much dark precipitate separates, let the mixture cool, filter it, re-saturate the filtrate with  $H_2S$  in the pressure-bottle, and heat it in boiling water for half an hour, or longer if the precipitate is increasing.) Let the mixture cool, and filter it. Wash the precipitates with hot water, and unite them with the previous one. Add to the filtrate just 10 cc. of 6 n.  $NH_4OH$ , and dilute it to 100 cc.

Treat the precipitate by P. 72.

\* This solution should have a volume of about 30 cc. and be about 1 n. in  $HClO_4$  (or  $HCl$ ). Most reducible elements (except iron, when much is present) are in their lower valence-states.

Treat a part of the filtrate by P. 91, and the rest by P. 92.

*Notes.*—1. In order to secure by means of  $H_2S$  a good separation of the tellurium and copper groups from the elements of the following groups, careful attention must be given to the conditions of precipitation. The reasons for the operations prescribed in the first paragraph of the Procedure are given in Notes 2–6.

2.  $NH_4Cl$  is added before treating with  $H_2S$ , because zinc is less likely to be precipitated by  $H_2S$  from solutions containing chloride than from those in oxyacids alone, and because iridium, the most difficultly precipitated element of the tellurium group, is much more readily thrown down from chloride than from perchlorate solutions.

3.  $H_2S$  is passed into the solution when it is at nearly boiling temperature and when its volume is about 30 cc. and the free acid ( $HCl$  and  $HClO_4$ ) is about 1 normal: (1) because the precipitation of molybdenum, iridium, and rhodium is promoted by high temperature and large concentration of the element; and (2) because zinc and indium, which are likely to be carried down with copper-group sulfides, are not so carried down so long as the acid is as strong as 1 n. For this last reason also the solution is cooled and again saturated with  $H_2S$ , so as to precipitate the copper group as completely as possible before the solution is diluted.

4. The solution is then diluted to 100 cc., thereby reducing the acid concentration to 0.3 normal, since at higher hydrogen-ion concentrations lead, bismuth, and cadmium are not completely precipitated. On the other hand a much lower acid concentration can not be employed, since it would lead to the precipitation of zinc, indium, nickel, and cobalt, when much of them is present, even in the absence of copper-group elements.

5. Under the conditions discussed in the preceding Notes all the elements of the tellurium and copper groups are completely precipitated with the exceptions that most of the iridium may remain in solution, and that, when the solution contains a large quantity of molybdenum (owing to the simultaneous presence of phosphate), a considerable part (10–30% of 300 mg.) may remain dissolved, in which case it gives a deep-blue color to the solution.

6. Moreover, under these conditions, none of the elements of any of the following groups passes into the  $H_2S$  precipitate in considerable proportion (in relation to the total quantity of the element present). Thus even 500 mg. of zinc, iron, nickel, or cobalt, and 100 mg. of indium or gallium do not precipitate when present alone; and even 1 or 2 mg. of any of them, when present

with large quantities of copper-group elements, can be detected in the filtrate. Also under these conditions titanium remains in solution; though it would precipitate slowly as  $H_2TiO_3$  at 90–100° if the solution so heated were only 0.3 n. in acid.

7. Iridium and rhodium are very rarely found except in ores or alloys from special sources, and then they are almost always associated with some of the other platinum elements. It is therefore usually desirable to test for iridium and rhodium only when the source of the material makes their presence seem possible, and even then, only when some of the other platinum elements, osmium, ruthenium, platinum, and palladium, have been detected in the earlier stages of the analysis. Hence provision has to be made for ensuring more complete precipitation of iridium only in rare cases.

8. The case in which molybdenum is present with phosphate, and in which therefore molybdenum may be found in the filtrate from the  $H_2S$  treatments in an open vessel, is also a rare one. Moreover, it is indicated by the formation of a yellow precipitate of ammonium phosphomolybdate on the addition of  $NH_4Cl$  at the beginning of this Procedure, and by a blue coloration of the filtrate from the first  $H_2S$  treatments. It is therefore necessary to treat the filtrate by the supplementary process described in the second paragraph of the Procedure for the sake of ensuring complete precipitation of molybdenum only when these indications are obtained.

9. The supplementary process just mentioned is much more effective for precipitating iridium than the previous treatments, because after the heating with strong  $HClO_4$  the iridium is in the form of perchlorate, and from this it is much more slowly precipitated by  $H_2S$  than from the chloride, into which it is gradually converted by the boiling with strong  $HCl$ ; and because the solution is more concentrated both in  $H_2S$  and in the iridium in the treatment in the pressure-bottle than it is in the open vessel. Under the prescribed conditions about 90% of the iridium may be precipitated by one hour's heating under pressure.

10. The precipitation of the molybdenum is much more rapid in the pressure-bottle treatment mainly because of the higher concentration of the  $H_2S$  and of the molybdenum. When treated in the way described, some of the molybdenum precipitates during the evaporation of the solution, and the remainder usually comes down completely after a half-hour's heating in the pressure-bottle.

**11. When the pressure treatment is used a measured volume of**

HCl (10 cc. of 6 n.) is added; and at the end this is neutralized by adding an equal volume of 6 n.  $\text{NH}_4\text{OH}$ , in order that the concentration of free acid may be suitable for the subsequent treatment in P. 92. For the same reason the solution is finally diluted.

## TELLURIUM GROUP

**Procedure 72.**—*Dissolving of the Sulfides and Precipitation of Tellurium.*—Heat the  $\text{H}_2\text{S}$  precipitate (P. 71) in a casserole with 5–10 cc. of 12 n. HCl on a steam-bath for 5 minutes; add 1–2 cc. of 16 n.  $\text{HNO}_3$ , and heat the mixture to 60–70° till the residue dissolves or becomes light-colored. Evaporate the mixture just to dryness. Treat the residue with just 6 cc. of 12 n. HCl, and saturate the (cold) mixture with  $\text{SO}_2$  gas. Filter out and reject any residue. Transfer the solution to a large test-tube, add to it just 20 cc. of water, saturate it with  $\text{SO}_2$  gas, and heat it in boiling water for 15 minutes. (Black precipitate, presence of TELLURIUM.) Filter the hot mixture.

Treat the filtrate by P. 73.

Treat the precipitate no further.

*Notes.*—1. The  $\text{H}_2\text{S}$  precipitate is first heated with 12 n. HCl to dissolve the copper-group sulfides, all of which (except CuS) are readily acted upon by this solvent; thereby avoiding so far as possible liberation of sulfur in the subsequent treatment with  $\text{HNO}_3$ . Heating with the mixed acids is necessary, however, in order to dissolve the tellurium-group precipitate. In case of the sulfides of iridium and rhodium a fairly long treatment may be required. Heating on a steam-bath is preferable to boiling, as always in aqua-regia treatments, since boiling causes the two acids to destroy each other and the chlorine thereby produced to be expelled, before it has time to act upon the precipitate.

2. The solution is evaporated to destroy all the  $\text{HNO}_3$ , which otherwise would oxidize some of the  $\text{H}_2\text{SO}_3$  later added. The residue is treated with 12 n. HCl and the cold solution saturated with  $\text{SO}_2$ , in order to remove any selenium which might be present owing to its incomplete volatilization in the HBr distillation. Tellurium is not precipitated by  $\text{H}_2\text{SO}_3$  from a cold soluble in hot 3 n. HCl.

3. The solution is diluted so that the HCl becomes about 2.7 n.,

since at this concentration the tellurium is most rapidly precipitated by  $\text{H}_2\text{SO}_3$ . Under these conditions, after heating in boiling water for 15 minutes, 0.5 mg. of it gives a precipitate, and 100 mg. are completely precipitated. It separates as a black powder. With a small quantity the solution is only darkened at first, but a precipitate settles out on standing.

4. None of the other elements that can be present is reduced to the metallic state or precipitated as chloride under these conditions. Any quantity of lead that can be present (thus even 50 mg.) remains in solution, since  $\text{PbCl}_2$  and  $\text{PbSO}_4$  are fairly soluble in 12 n. HCl.

**Procedure 73.**—*Extraction of Molybdenum with Ether.*—

Evaporate the  $\text{H}_2\text{SO}_3$  solution (P. 72) almost to dryness. Add to the residue a few drops of 16 n.  $\text{HNO}_3$ , and evaporate the mixture to dryness on a steam-bath. Add 5 cc. of 6 n. HCl, and (without filtering out any residue) shake the solution for 2 or 3 minutes successively with two 15-cc. portions of ether in a short-stem separating-funnel (see Note 4, P. 51). Unite the ethereal extracts, wash them by shaking successively with two 2-cc. portions of 6 n. HCl, and reject the washings.

Treat the ethereal solution by P. 74.

Treat the aqueous solution by P. 75, in case iridium and rhodium are to be tested for. Treat it by P. 81, in case iridium and rhodium are not to be tested for.

*Notes.*—1. The filtrate from the  $\text{H}_2\text{SO}_3$  treatment is evaporated almost to dryness so as to enable the residue to be taken up in HCl of definite concentration. The residue is first heated with  $\text{HNO}_3$  to reoxidize any molybdenum that may have been reduced by the  $\text{H}_2\text{SO}_3$ . Lead will not be present in considerable quantity; but if any  $\text{PbCl}_2$  remains undissolved on adding the 5 cc. of 6 n. HCl, it need not be filtered off, since it does not interfere with the ether extraction.

2. In the extraction a small volume of the HCl is shaken with a larger volume of ether, since the distribution-ratio is not very favorable. Thus, under the specified conditions only about 85% of the molybdenum passes into the ether on the first shaking; but even so, only about 2-3% of it remains in the aqueous layer after the second shaking. This does not appreciably affect the estimate of the quantity of molybdenum present, nor does it interfere with

the subsequent analysis of the aqueous solution. The substance extracted by the ether is  $\text{MoO}_3 \cdot 2\text{HCl}$ . As the extraction of the various elements doubtless depends on the HCl concentration, the directions of the Procedure should be followed; thus 6 n. HCl and ether not previously shaken with it should be used.

3. The ether solution is washed with a little 6 n. HCl to remove from it small quantities of elements other than molybdenum. Thus copper and rhodium dissolve sufficiently to color the ether layer, and cadmium dissolves appreciably; but all these elements are removed by the washing with 6 n. HCl.

4. Not more than 2-3 mg. of molybdenum will ordinarily be found at this point, even when a large quantity was originally present; for nearly all of it remains with the tungsten and tantalum groups after the evaporation with  $\text{HClO}_4$ . Only when phosphate is also present will the molybdenum, owing to the formation of phosphomolybdic acid, pass largely or entirely into the  $\text{HClO}_4$  solution and therefore into the  $\text{H}_2\text{S}$  precipitate.

**Procedure 74.**—*Detection of Molybdenum.*—Evaporate the ethereal solution (P. 73) to dryness in a casserole on a steam-bath, and dry the residue completely by warming it over a small moving flame. (Dark-blue residue, presence of MOLYBDENUM.)

In case the residue is blue, add to it 2 cc. of 12 n. HCl and 0.5 cc. of 6 n.  $\text{HNO}_3$ , and evaporate again to dryness on a steam-bath. Dissolve the residue in 2 cc. of 6 n. HCl, and add 5 cc. of water and 5 cc. of 1 n. KSCN. (If there is a deep-red color, make the solution alkaline with 6 n. NaOH, heat it nearly to boiling, filter out the precipitate, neutralize the solution with 6 n. HCl, and add 2 cc. more.) Add about 0.1 cc. of finely granulated Zn. (Red color, increasing for some minutes, presence of MOLYBDENUM.) If an increasing red color results, decant the solution from the Zn into a test-tube, place the tube in boiling water, and pass a slow current of  $\text{H}_2\text{S}$  through it for 10 minutes. (Brown precipitate, presence of MOLYBDENUM.)

*Notes.*—1. The dark-blue color of the residue is an extremely delicate indication of molybdenum, even 0.1 mg. of it giving a distinct color; and when no color results, further testing for



molybdenum is unnecessary. In order that the conclusion may be reliable, however, the residue obtained on evaporating the ethereal solution must be dried completely by heating it gently over a small flame. The blue substance is probably "molybdenum blue," a molybdate of quinquivalent molybdenum (see Note 2, P. 36). It is produced by reduction of  $\text{MoO}_3 \cdot 2\text{HCl}$ , probably by organic substances coming from the ether.

2. As to the KSCN test for molybdenum and the need of guarding against the presence of iron, see Notes 1 and 2, P. 38.

3. The final precipitation with  $\text{H}_2\text{S}$  affords a further assurance that the red color produced by KSCN is not due to iron. It serves mainly, however, to make possible an estimate of the quantity present, which it is difficult to do by either of the color tests.

**Procedure 75.**—*Separation of the Copper Group from Iridium and Rhodium.*—Evaporate the aqueous solution from the ether extraction (P. 73) just to dryness. Add 1 cc. of 6 n.  $\text{HC}_2\text{H}_3\text{O}_2$ , 10 cc. of water, and 5 cc. of 3 n.  $\text{NaNO}_2$ ; and heat the mixture for 5 minutes at  $60\text{--}70^\circ$ . Cool; and, without filtering out any precipitate, add 6 n.  $\text{NaOH}$ , 0.5 cc. at a time, with vigorous stirring, till the solution turns litmus paper deep-blue, diluting with 10–20 cc. of water during the neutralization if a large precipitate separates. (Precipitate, presence of COPPER GROUP.) Filter the mixture. Wash the precipitate with hot water. To the filtrate add 5 cc. of 1 f.  $\text{NaHCO}_3$ ; and, if there is a precipitate, filter it off on a separate filter, wash it, and unite it with the previous one.

Dissolve the precipitate in 3–6 cc. of 6 n.  $\text{HNO}_3$ , and analyze the solution for the copper group by P. 81–85.

Treat the filtrate by P. 76.

*Notes.*—1. This separation depends on the facts that all the elements of the copper group (lead, bismuth, cadmium, and copper) are precipitated by  $\text{NaOH}$  in small excess; and that iridium and rhodium are not so precipitated, provided they have been converted by heating with  $\text{NaNO}_2$  into their complex nitrites,  $\text{Na}_3\text{Ir}(\text{NO}_2)_6$  (sodium iridonitrite) and  $\text{Na}_3\text{Rh}(\text{NO}_2)_6$  (sodium rhodonitrite).

2. A slight acidity promotes the reduction of iridium from the quadrivalent to the trivalent state and the complete conversion of it and of rhodium into the complex nitrite. The solution from

the ether extraction is therefore evaporated to dryness, and 1 cc. of 6 n.  $\text{HC}_2\text{H}_3\text{O}_2$  (rather than of a strong acid) is added, so as to produce only a small concentration of  $\text{H}^+$  and therefore of free  $\text{HNO}_2$ . Warming also promotes the formation of the complexes. Too great acidity or too much heating is unfavorable, since the free  $\text{HNO}_2$  is thereby rapidly decomposed. The complete conversion of these elements into their nitrites is shown by the production of a pure yellow solution; but this color may not be visible unless as much as 15–20 mg. is present.

3. In order to secure complete precipitation of lead, much excess of  $\text{NaOH}$  is avoided; and after filtering  $\text{NaHCO}_3$  is added, since under these nearly neutral conditions scarcely any of the slightly soluble  $\text{PbCO}_3$  is converted into soluble  $\text{NaHPbO}_2$ . The  $\text{NaHCO}_3$  is not added till after the mixture has been filtered, since otherwise much copper dissolves, forming a deep-blue solution, owing to production of a soluble complex salt, such as  $\text{NaHCu}(\text{CO}_3)_2$ , with the  $\text{NaHCO}_3$  in the solution. Some  $\text{Bi}(\text{OH})_3$  may precipitate, owing to hydrolysis of its salts in the  $\text{HC}_2\text{H}_3\text{O}_2$  solution, before the  $\text{NaOH}$  is added.

4. The separation is fairly satisfactory with respect to iridium and rhodium. Thus, when treated by the Procedure, 100 mg. of iridium or rhodium, when present alone, remain in solution (except that 1–2 mg. of rhodium may separate as a turbidity). And, when 1–2 mg. of iridium or rhodium are present even with a large quantity of copper-group elements (thus with 500 mg. of copper or with a mixture of 200 mg. each of bismuth, cadmium, and copper), more than half of the iridium and all of the rhodium pass into the filtrate. On the other hand, even though nitrite is present, 50 mg. of lead, and 500 mg. of other copper-group elements are completely precipitated; and even 1 mg. of any of them gives a precipitate.

**Procedure 76.—Precipitation of Iridium and Rhodium.—**

Add to the filtrate from the nitrite treatment (P. 75) 5 cc. of 12 n.  $\text{HCl}$ , and evaporate the solution just to dryness, taking care not to overheat the residue. Dissolve the residue in 15 cc. of water, and add to it 2 cc. of 3 n.  $\text{Na}_2\text{CO}_3$ . Heat the solution in a test-tube for 5 minutes in a boiling water-bath. Cool the mixture, add to it (without filtering) 2 cc. of 3 n.  $\text{Na}_2\text{CO}_3$  and 2 drops of liquid  $\text{Br}_2$ , and shake till the  $\text{Br}_2$  dissolves. If there is much precipitate, add 2–4 drops more of  $\text{Br}_2$ . Heat

the mixture in boiling water for 10 minutes, cool it, and add a drop of liquid  $\text{Br}_2$ . (Blue-black precipitate, presence of IRIDIUM; green precipitate, presence of RHODIUM.) Filter, and wash the precipitate thoroughly with hot water. If the filtrate is blue or green, heat it in a test-tube in boiling water for half an hour, cooling it from time to time and adding a drop of liquid  $\text{Br}_2$ . Filter out any precipitate, wash it, and unite it with the previous one.

Treat the precipitate by P. 77. Reject the filtrate.

*Notes.*—1. This Procedure serves to show at once whether iridium or rhodium is present, and to separate these elements, when present, from the large quantity of salt in the solution. The complex nitrites are first decomposed by boiling with  $\text{HCl}$ ; the  $\text{H}_3\text{IrCl}_6$  and  $\text{H}_3\text{RhCl}_6$  resulting are then converted, by heating with  $\text{Na}_2\text{CO}_3$ , into soluble  $\text{NaIrO}_2$  (sodium iridite) and into precipitated light-yellow  $\text{Rh}(\text{OH})_3$ ; and finally the trivalent iridium and rhodium are oxidized, by the  $\text{Br}_2$  added and the  $\text{NaBrO}$  thereby formed, to the insoluble hydrated dioxides,  $\text{IrO}_2$  and  $\text{RhO}_2$ , which are bluish-black and green respectively. Under the conditions of the Procedure 1 mg. of iridium or rhodium gives a precipitate.

2. To ensure decomposition of the complex nitrites, the solution is made strongly acid with  $\text{HCl}$  and boiled till it is all evaporated. This also removes the excess of acid, which otherwise would have to be neutralized; thereby avoiding the production of a large amount of salt which retards the precipitation of iridium and rhodium.

3. After addition of the  $\text{Na}_2\text{CO}_3$  the solution is heated; for otherwise, probably owing to incomplete decomposition of the chloroiridite and chlororhodite, rhodium is not precipitated as yellow  $\text{Rh}(\text{OH})_3$ , and iridium may not be precipitated on the later addition of  $\text{Br}_2$  when only a little is present. A large excess of  $\text{Br}_2$  decreases the delicacy of the rhodium precipitation; hence, unless much rhodium or iridium is present, only two drops of liquid  $\text{Br}_2$  are added. The subsequent heating serves to coagulate the precipitate. Prolonged heating may, however, cause the precipitate to redissolve, owing to decomposition of the  $\text{NaBrO}$ .

4. When much iridium or rhodium is present, a part of it remains unprecipitated and imparts a blue (or green) color to the

solution. Continued heating with occasional addition of  $\text{Br}_2$  may cause its coagulation, especially when only a small quantity is present. If after a half-hour's heating the liquid is still deeply colored, complete precipitation can best be secured by evaporating the mixture with  $\text{HCl}$ , to reconvert the iridium and rhodium into chlorides, and repeating the other operations of the Procedure. This is unnecessary, however, since by far the larger proportion of these elements is always precipitated, and since the filtrate is treated no further.

**Procedure 77.**—*Separation of Iridium from Rhodium.*—Heat the  $\text{NaBrO}$  precipitate (P. 75) in a small casserole with 1–3 cc. of 9 n.  $\text{HBr}$  on a steam-bath till it dissolves. Add 3 cc. of 12 n.  $\text{HCl}$  and 1 cc. of 16 n.  $\text{HNO}_3$ , and evaporate the solution just to dryness. To the residue add 1 cc. of 12 n.  $\text{HCl}$ , and evaporate again just to dryness. Add 2 drops of 6 n.  $\text{HCl}$ , and transfer the mixture to a weighing bottle with not more than 1–2 cc. of water. Saturate the solution with  $\text{Cl}_2$ , stopper the bottle, and heat it at about  $50^\circ$  for five minutes. Cool, add powdered  $\text{NH}_4\text{Cl}$  with constant agitation till no more of it dissolves, avoiding much excess. Heat the mixture on a steam-bath for 15 minutes. Cool it, saturate it with  $\text{Cl}_2$ , and let it stand 15 minutes. If no precipitate is visible, give the bottle a gentle rotary motion to cause any particles to gather in the center. (Dense black precipitate, presence of IRIDIUM; red solution, presence of RHODIUM.) If there is much precipitate, decant the liquid, heat it on a steam-bath for 15 minutes, cool it, saturate it with  $\text{Cl}_2$ , and let it stand 15 minutes, repeating these operations till no more precipitate separates. Filter the mixture through a very small filter; and wash the filter with 1 cc. of cold 3 n.  $\text{NH}_4\text{Cl}$ , adding the washings to the filtrate.

Treat the precipitate no further.

Treat the filtrate, if colored, by P. 78.

*Notes.*—1. The  $\text{NaBrO}$  precipitate (of  $\text{IrO}_2$  and  $\text{RhO}_2$ ) is heated with 9 n.  $\text{HBr}$ , since this acid, owing to its powerful reducing action, dissolves it more readily than  $\text{HCl}$  or  $\text{HNO}_3$ . The solution is evaporated with  $\text{HCl}$  and  $\text{HNO}_3$  to destroy the

bromide, and to oxidize the iridium to the quadrivalent state. It is then evaporated with HCl alone to ensure complete removal of the  $\text{HNO}_3$ .

2. The detailed operations of the Procedure serve to secure the precipitation of a small quantity of  $(\text{NH}_4)_2\text{IrCl}_6$ , which is somewhat soluble in water and tends to form supersaturated solutions. The residue after evaporation is dissolved in not more than 2 cc. of slightly acidified water. The solution is saturated with  $\text{Cl}_2$  and warmed to  $50^\circ$ , in order to ensure oxidation of the iridium to the quadrivalent state; a higher temperature being avoided, since the  $\text{Cl}_2$  is then more rapidly destroyed by action on the  $\text{NH}_4\text{Cl}$  (with formation of  $\text{N}_2$  and HCl). The solution is cooled and saturated with  $\text{NH}_4\text{Cl}$  to diminish the solubility of the complex salt (through the common-ion effect). The solution is finally warmed, since this has been found to promote the separation of the precipitate.

3. Under the conditions of the Procedure, when the final volume of the mixture is 2 cc., 0.2–0.4 mg. of iridium yields a precipitate. When a large quantity (50 mg. or more) is present, precipitation takes place slowly, and several hours are required to secure a fairly complete precipitation; even then some of it may remain in solution, but not enough to precipitate in the subsequent rhodium test. Even 100 mg. of rhodium remain in solution. Even 1 mg. of rhodium gives a pink color to 2 cc. of water saturated with  $\text{NH}_4\text{Cl}$ ; so that a colorless filtrate need not be further tested.

**Procedure 78.**—*Confirmation of Rhodium.*—To the filtrate from the  $\text{NH}_4\text{Cl}$  precipitate (P. 77) in a small casserole add 3 cc. of 15 n.  $\text{NH}_4\text{OH}$ , and evaporate the solution to dryness on a steam-bath. To the residue add 2–3 cc. of 6 n. HCl, bring the mixture to boiling, transfer it to a weighing bottle, and let it stand at least half an hour. If any  $\text{NH}_4\text{Cl}$  separates, add just enough cold water to dissolve it. (Light-yellow residue, presence of RHODIUM.)

*Notes.*—1.  $(\text{NH}_4^+)_3\text{RhCl}_6 \equiv$  (ammonium chloro<sup>rhodite</sup>iridite) is converted by heating with hot  $\text{NH}_4\text{OH}$  into  $\text{RhCl}(\text{NH}_3)_5^{++}\text{Cl}_2^-$  (chloropentammine rhodium chloride), which remains undissolved on adding cold 6 n. HCl. It is heated with this acid, which, when hot, dissolves it in moderate quantity, since it then separates on cooling as a fine yellowish-white crystalline powder. A precipi-

tate results even when only 0.5 mg. of rhodium is present in 2 cc. of solution. When a large quantity is present, a large bright-yellow precipitate forms, and the solution above it is deep-yellow, even though the precipitation be nearly complete. Iridium, at any rate in quantity up to 5 mg., remains in solution.

2. If only a small white precipitate separates, this may consist of silica introduced from the vessels or reagents. This is distinguished from a small quantity of the rhodium compound by its not dissolving on heating with HCl.

water and 1 n.  $\text{AgNO}_3$ , and the precipitate is removed by complete removal of the HBr.

P. 70, N. 2.—Use of Methyl Violet for Determining Rhodium Concentrations.—See Strupitz, *Qualitative Chemical Analysis*, p. 27, 6f, 10a (1926); Bray and Latimer, *Chemical Analysis*, 2 (1923).

Into each of several porcelain crucibles was introduced 1 cc. of a methyl violet reagent containing 1 mg. of crystalline methyl violet in 25 cc. of 95% C. H. OH and 75 cc. of water; and the volumes of 1.0 n. HClO<sub>4</sub>, shown below were added from a dropper. The colors produced were blue with 0.10 cc., light blue with 0.25 cc., blue-green with 0.50 cc., and with 0.75 cc., and green with 0.85 cc.

P. 70, N. 4.—Effect of Elements Forming Colored Salts on the Color of Methyl Violet.—To solutions, consisting of 1 cc. of methyl violet reagent and 6 drops of 1.0 n. HClO<sub>4</sub>, in porcelain crucibles were added such quantities of various elements as solutes as would correspond to the presence of 500 mg. of the elements in 25 cc. of solution (the volume prevailing in P. 70 when the solution is tested). The color of the resulting solutions with various elements added were as follows:

None added ... Blue-green.

Cobalt ... Lead-green.

Chromium ... Very dark-green.

Copper ... Blue-green.

Nickel ... Green (the blue caused by 3 drops more of 1 n. HClO<sub>4</sub>,

Uranium ... Green, like that caused by 27 drops more of 1 n. HClO<sub>4</sub>,

Ferric Iron ... Green, like that caused by 2 drops more of 1 n. HClO<sub>4</sub>,

Effect of Hydrobromic and Perchloric Acids on the Color of Methyl Violet.—1 cc. of methyl violet reagent was placed in each of two porcelain crucibles; to one were added 6 drops of pure 1 n. HClO<sub>4</sub>, and to the other 6 drops of 1 n. HClO<sub>4</sub>, which was also 1 n. in HClO<sub>4</sub>, and 0.1 n. in NH<sub>4</sub>Br; the color was the same in the two cases.

## ANALYSIS OF TELLURIUM AND COPPER GROUPS

## PRECIPITATION BY HYDROGEN SULFIDE

*P. 70, N. 1.—Removal of Formic and Hydrobromic Acids by Evaporation with Perchloric Acid to Slight Fuming.*—4.3 g. of 9 n.  $\text{HClO}_4$  were weighed out in a small dish, 10 cc. of 12 n.  $\text{HCHO}_2$  and 1 cc. of 9 n.  $\text{HBr}$  were added, the mixture was evaporated slowly over a small flame till, on removing the dish from the flame, there was rapid bubbling but only slight fumes of  $\text{HClO}_4$ , and the dish was reweighed: the residual liquid consisted of 4.0 g. (showing that the  $\text{HCHO}_2$  and  $\text{HBr}$  had been mostly or entirely expelled). To 0.1 cc. of this liquid, water and 1 n.  $\text{AgNO}_3$  were added: no precipitate formed (showing complete removal of the  $\text{HBr}$ ).

*P. 70, N. 2.—Use of Methyl Violet for Determining Hydrogen-Ion Concentrations.*—See Stieglitz, *Qualitative Chemical Analysis*, 2, 31, 61, 102 (1916); Bray and Latimer, *Course in General Chemistry*, 47 (1923).

Into each of several porcelain crucibles was measured 1 cc. of a methyl violet reagent containing 1 mg. of crystalline methyl violet in 25 cc. of 95%  $\text{C}_2\text{H}_5\text{OH}$  and 75 cc. of water; and the volumes of 1.0 n.  $\text{HClO}_4$  shown below were added from a dropper. The colors produced were: blue with 0.10 cc., light-blue with 0.13 cc., blue-green with 0.16 cc. and with 0.18 cc., and green with 0.21 cc.

*P. 70, N. 4.—Effect of Elements Forming Colored Salts on the Color of Methyl Violet.*—To solutions consisting of 1 cc. of methyl violet reagent and 6 drops of 1.0 n.  $\text{HClO}_4$  in porcelain crucibles were added such quantities of various elements as nitrates as would correspond to the presence of 500 mg. of the elements in 28 cc. of solution (the volume prevailing in P. 70 when the solution is tested). The colors of the resulting mixtures with various elements added were as follows:

None added... Blue-green.

Cobalt ..... Lead-grey.

Chromium ... Very dark-green.

Copper ..... Blue-green.

Nickel ..... Green, like that caused by 1 drop more of 1 n.  $\text{HClO}_4$ .

Uranium .... Green, like that caused by 0.7 drop more of 1 n.  $\text{HClO}_4$ .

Ferric Iron... Green, like that caused by 2 drops more of 1 n.  $\text{HClO}_4$ .

*Effect of Hydrobromic and Formic Acids on the Color of Methyl Violet.*—1 cc. of methyl violet reagent was placed in each of two porcelain crucibles; to one were added 6 drops of pure 1 n.  $\text{HClO}_4$ , and to the other 6 drops of 1 n.  $\text{HClO}_4$  which was also 1 n. in  $\text{HCHO}_2$  and 0.1 n. in  $\text{NH}_4\text{Br}$ : the color was the same in the two cases.

*P. 71, N. 2.—Effect of the Presence of Chloride on the Precipitation of Iridium by Hydrogen Sulfide.*—In C. E., P. 71, N. 5, 9, 10, contrast the slight precipitation of iridium from 1 n.  $\text{HClO}_4$  free from chloride with the more complete precipitation from HCl solution or from  $\text{HClO}_4$  solution in the presence of  $\text{NH}_4\text{Cl}$ .

*P. 71, N. 5.—Precipitation of Copper-Group Elements by Hydrogen Sulfide.*—See Noyes and Bray, *J. Am. Chem. Soc.*, 29, 188 (1907), many of whose results are reproduced here.

Various quantities of these elements in solutions of various HCl or  $\text{HNO}_3$  concentrations were treated with  $\text{H}_2\text{S}$  at  $20^\circ$  and allowed to stand 15 minutes with the results shown in the following table. (The experiments in  $\text{HNO}_3$  solution are reproduced from the article of Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 63. 1922.)

Element	Milligrams taken	Cc. of solution	Normality		Precipitate
			HCl	$\text{HNO}_3$	
Pb	10	100	0.45	—	Yes <sup>a</sup>
	1	100	0.3	—	Yes <sup>b</sup>
	2	50	0.6	—	No
	2	100	0.3	—	Yes
	300	50	—	0.6	Complete
	500	100	—	0.6	Complete
Cd	10	100	0.45	—	Yes <sup>a</sup>
	1	100	0.3	—	Yes
	2	16	1.8	—	No
	2	50	0.6	—	Yes
	300	50	—	0.6	Note <sup>c</sup>
	500	100	—	0.6	Note <sup>c</sup>
Bi	2	8	3.5	—	No
	2	16	1.8	—	Yes
	300	50	—	0.6	Complete
Cu	2	2	12	—	No
	2	4	7	—	Yes

<sup>a</sup> A precipitate appeared after 15 minutes, but was not visible at first.

<sup>b</sup> Scarcely visible till collected on a filter; filtrate with  $(\text{NH}_4)_2\text{S}$  showed only 0.1–0.2 mg. of Pb.

<sup>c</sup> The precipitation was not complete after 15 minutes, but became so on long standing.

The above-given experiments with 2 mg. of copper-group elements, and entirely similar ones with  $\text{As}^{\text{III}}$ ,  $\text{Hg}^{\text{II}}$ , Sb,  $\text{Sn}^{\text{II}}$ , and  $\text{Sn}^{\text{IV}}$ , are here presented in a different form. Starting with 2 mg. dissolved in 4 cc. of 7 n. HCl, precipitation occurred, upon saturating with  $\text{H}_2\text{S}$  at  $20^\circ$  for 15 minutes, only after adding the following quantities of water:

Water added in all . . . .	None	4 cc.	12 cc.	44 cc.	96 cc.
Elements precipitated . .	$\text{As}^{\text{III}}$ , $\text{Hg}^{\text{II}}$ , Cu	Sb	Bi, $\text{Sn}^{\text{IV}}$	Cd	Pb, $\text{Sn}^{\text{II}}$



P. 71, N. 5.—*Precipitation of Tellurium Sulfide by Hydrogen Sulfide, and its Decomposition into Tellurium and Sulfur.*—See C. E., P. 22, N. 4, and P. 32, N. 2, 6.

P. 71, N. 6.—*Behavior of Elements of the Aluminum, Nickel and Zirconium Groups with Hydrogen Sulfide.*—Various quantities of these elements in solutions of various HCl concentrations were treated with H<sub>2</sub>S with the results shown in the following table. The experiments with indium are taken from the publication of Wada and Ato (see C. E., P. 71, N. 5).

Element	Milli-grams taken	Cc. of solution	Normality in HCl	Saturation		Precipitate
				temp.	min.	
Zn	500	100	0.30	20	5	None
"	"	"	0.18	20	5	None
"	"	"	0.14	20	5	None
"	"	"	0.14	20	10	Yes
"	"	"	0.075	20	10	Yes
"	"	"	0.30	90	5	None
"	"	"	0.18	90	5	Slight
"	"	"	0.14	90	5	Large
"	50	"	0.15	20	10	None
"	"	"	0.075	20	10	Yes
Ni	500	"	0.075	20	10	None
Co	500	"	0.075	20	10	None
Fe <sup>II</sup>	500	"	0.075	20	10	None
Mn	500	"	0.075	20	10	None
{ Fe <sup>II</sup> Ni Co Mn	Mixture of 500 of each	"	0.03	20	10	1.2 mg. <sup>a</sup>
In	100	100	0.3	20	10	None
"	10	10	"	90	10	None
"	10	10	0.15	20	10	Nearly all
Ga	20	10	3.0	100 <sup>b</sup>	30	None
"	"	30	1.0	100 <sup>b</sup>	30	None
"	"	45	0.0 <sup>c</sup>	100 <sup>b</sup>	30	None
Zr	100	100	0.35	100 <sup>b</sup>	60	None
Ti	100	"	0.35	"	30	Large
"	"	"	0.70	"	30	None
"	"	"	0.70	"	60	Turbid
"	"	"	0.83	"	120	None

<sup>a</sup> Determined by igniting the dark precipitate (consisting mainly of sulfur) and weighing the residue.

<sup>b</sup> Saturated cold with H<sub>2</sub>S and heated under pressure in boiling water.

<sup>c</sup> 0.66 n. in H<sub>2</sub>C<sub>2</sub>O<sub>2</sub> and 0.33 n. in NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.

P. 71, N. 6.—*Co-Precipitation of Zinc, Manganese, Cobalt, Nickel, and Iron with Sulfides of the Copper Group.*—500 mg. of a copper-group element and 1 mg. (or more in a few cases) of an element of the

aluminum or nickel group were together dissolved in 100 cc. of 0.3 n. HCl, the solution was saturated with  $H_2S$  in the cold, the mixture filtered, and the filtrate made alkaline with  $NH_4OH$  and saturated with  $H_2S$ . The resulting precipitates were estimated by comparison with those obtained with known quantities. The quantities of the aluminum-group or nickel-group element that were thus found to have passed into the filtrate from the first  $H_2S$  precipitate are shown in the following table.

Copper-group element	Zinc		Manganese		Cobalt		Nickel		Ferrous iron	
	taken	found	taken	found	taken	found	taken	found	taken	found
500 Cu.....	1.0	1.0	1.0	1.0	1.0	0.5	1.0	0.5	1.0	1.0
500 Pb.....	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0
500 Cd...	1.0	0.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
" "	2.0	0.5	—	—	—	—	—	—	—	—
" "	3.0	1.0	—	—	—	—	—	—	—	—
" "	4.0	1.5	—	—	—	—	—	—	—	—

A mixture of 500 mg. of Cu with 1 mg. of Fe and 1 mg. of Ni, and a mixture of 500 mg. of Cu with 1 mg. of Co, in 40 cc. of 0.7 n. HCl, were treated with  $H_2S$  at  $80^\circ$  for 10 minutes, the solutions were cooled, diluted to 100 cc., treated with  $H_2S$  for 15–30 minutes, and filtered; and the filtrates were tested for iron, nickel, and cobalt: conclusive tests were obtained for all of them.

*Co-Precipitation of Gallium with Elements Precipitated by Hydrogen Sulfide.*—See de Boisbaudran, *Compt. rend.*, 1882, 1229, 1440, 1625.

To 25 mg. of Ga as  $GaCl_3$  in 30 cc. of a solution 1 n. in HCl and 0.3 n. in  $NH_4Cl$  were added in separate experiments 300 mg. of Cu, of Bi, and of Cd, as nitrates, and 300 mg. of As as  $NaAsO_2$ ; the solutions were saturated at  $90^\circ$  with  $H_2S$ , cooled, diluted to 100 cc., resaturated with  $H_2S$ , and filtered; and the precipitates were analyzed for gallium by dissolving them in  $HNO_3$ , evaporating, and precipitating the gallium by boiling with  $NH_4C_2H_3O_2$  and  $HC_2H_3O_2$  under proper conditions (see N. 3, P. 94): there was found no gallium in the cadmium or bismuth precipitate, 0.4 mg. in the copper precipitate, and 0.6 mg. in the arsenic precipitate.

These four experiments were repeated with 2 mg. of Ga, except that the filtrates, instead of the precipitates, were tested for gallium by boiling out the  $H_2S$ , neutralizing with KOH, adding 1 cc. of 6 n. HCl and 6 cc. of 3 n.  $NH_4C_2H_3O_2$ , and boiling two minutes: about 2 mg. of Ga were precipitated in each case. That these precipitates were gallium was confirmed by dissolving them in 5 cc. of 6 n. HCl and adding 5 cc. of 1 n.  $K_4Fe(CN)_6$ : the characteristic gallium precipitate formed.

These last experiments were repeated with 2 mg. of Ga, using in separate cases 300 mg. of Hg as  $\text{Hg}(\text{NO}_3)_2$ , of Sb as  $\text{SbCl}_3$ , and of Sn as  $\text{SnCl}_2$ , in place of the copper-group element: the whole of the gallium (about 2 mg.) was found in the  $\text{H}_2\text{S}$  filtrate in each case.

*Co-Precipitation of Indium with Elements Precipitated by Hydrogen Sulfide.*—For an extended series of careful experiments on this subject see Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 58, 64 (1922).—As the publication is not readily accessible, some of the more significant results are here tabulated. The mixtures were saturated with  $\text{H}_2\text{S}$  at  $20^\circ$ .

Milligrams taken		Cc. of solution	Normality in		Milligrams of indium in	
Indium	Other element		HCl	$\text{HNO}_3$	precipitate	filtrate
10	20 Cu	10	0.3	—	2	8
10	20 Cu	100	—	—	0.2	9.8
5	150 Pb	100	—	0.3	1.5	3.5
	150 Cd					
5	150 Pb	50	—	0.6	0.5	4.5
	150 Cd					
I	300 Pb	50	—	0.6	0.2	0.8
I	300 Cu	"	—	"	0.2	0.8
I	300 Cd	"	—	"	0.0	1.0
I	300 Bi	"	—	"	0.0	1.0
50	300 Pb	50	—	0.6	2	48
50	300 Cu	"	—	"	7	43
50	300 Cd	"	—	"	3	47
50	300 Bi	"	—	"	2	48

P. 71, N. 5, 9, 10.—*Precipitation of Molybdenum, Iridium, and Rhodium by Hydrogen Sulfide.*—Various quantities of these elements were treated with  $\text{H}_2\text{S}$  in the manner and with the results shown in the following table. In the experiments where  $\text{HClO}_4$  is present, a solution of the element in this acid (usually 5 cc. of 9 n.) was first fumed down to 3 cc.;  $\text{HNO}_3$  being also present in the two cases where no HCl or  $\text{NH}_4\text{Cl}$  was subsequently added. Saturation at  $90^\circ$  means that the solution was heated on a steam-bath or in boiling water and that a slow current of  $\text{H}_2\text{S}$  was passed through it for the time stated. In the "heating under pressure" the mixture was filtered after the saturation at  $90^\circ$  in an open vessel, saturated with  $\text{H}_2\text{S}$  in the cold, placed in a tightly closed bottle, and heated in boiling water for the time shown. Where two heatings are indicated, the mixture was filtered in between, and the filtrate resaturated in the cold with  $\text{H}_2\text{S}$  before reheating under pressure. The number of milligrams of iridium in the filtrate from the last precipitation was determined (except in the first experiment with 100 mg.) by evaporating it till the  $\text{HClO}_4$  fumed, diluting with 9 n.  $\text{HClO}_4$ , matching the purple color with standards prepared in the same way.

Element	Mgs. taken	Cc. of solution	Normal in HCl	Normal in other substances	Saturation		Precipitate	Heating under pressure				Mgs. in filtrate	
					temp.	min.		hours	ppt.	hours	ppt.		ppt.
Mo	100	100	0.3	—	20°	10	Small	—	—	—	—	—	
	100	100	0.3	—	90	10	Large	10	—	—	—	—	
	500	110	0.65	—	90	5	Large	Large	3	0	4	4	
	300	34	—	{ 1 n. in HClO <sub>4</sub> 0.4 n. in NH <sub>4</sub> Cl 0.15 f. in PO <sub>4</sub>	90	10	Large	—	—	—	—	—	Deep blue <sup>d</sup>
	50	100	0.3	—	20	—	< 1	—	—	—	—	—	—
Ir (as IrCl <sub>4</sub> )	50	100	0.3	—	90	—	Large	10	—	—	—	—	—
	50	100	0.3	—	90	5	Large	Large	3	0	>	2	—
	100	110	0.65	—	90	30	9	—	—	—	—	—	1
	10	10	2	—	90	30	9	—	—	—	—	—	1
	10	10	6	—	90	—	—	—	—	—	—	—	—
	50	30	—	{ 1 n. in HClO <sub>4</sub> 0.4 n. in NH <sub>4</sub> Cl	90	15	10	10	4 <sup>a</sup>	25	3	—	—
	10	10	4	{ 3 n. in HClO <sub>4</sub> 1.5 n. in HClO <sub>4</sub>	90	10	3	6	2	10	1	—	—
	50	18	4	{ 0.7 n. in NH <sub>4</sub> Cl 1 n. in HClO <sub>4</sub>	20	10	Note <sup>c</sup>	25	2	2 <sup>b</sup>	10	—	—
	100	30	0	—	20	10	Very small <sup>e</sup>	Medium	2	6 <sup>e</sup>	5	>	50
	100	30	0	{ 1 n. in HClO <sub>4</sub> 1 n. in HClO <sub>4</sub>	20	10	Large <sup>e</sup>	Large	1	—	0	—	—
Rh (as RhCl <sub>3</sub> )	50	34	—	{ 0.4 n. in NH <sub>4</sub> Cl	90	15	Large	—	—	—	—	—	0.5

<sup>a</sup> Before this treatment 20 cc. of 12 n. HCl were added.

<sup>b</sup> This was a further treatment, subsequent to the one recorded above it.

<sup>c</sup> Not filtered and not heated at 90° before the pressure-bottle treatment.

<sup>d</sup> On diluting this filtrate to 100 cc., saturating it cold with H<sub>2</sub>S, and letting it stand over night, 50 mg. of Mo more precipitated; on

boiling the filtrate from this down to 15 cc., 2 mg. more precipitated and the solution became colorless.

<sup>e</sup> Three 2-hour heatings with filtration and saturation in between.

A solution containing 50 mg. of Ir as  $\text{IrCl}_4$ , 4 cc. of 9 n.  $\text{HClO}_4$ , and 1 cc. of 16 n.  $\text{HNO}_3$  was heated to strong fuming: the resulting solution was deep-purple. It was refluxed for 15 minutes with 10 cc. of 12 n.  $\text{HCHO}_2$ : the color changed to green, but no metal separated. 2 cc. of 9 n.  $\text{HBr}$  were added, and the solution was evaporated on a water-bath till the  $\text{HClO}_4$  was almost fuming: the purple color reappeared. The solution was treated with 25 cc. of water and 4 cc. of 3 n.  $\text{NH}_4\text{Cl}$ , and was then treated with  $\text{H}_2\text{S}$  for 10 minutes in a testtube immersed in boiling water: the solution became colorless and a small brown precipitate containing 1-2 mg. of Ir resulted. The mixture was diluted to 100 cc., and saturated cold with  $\text{H}_2\text{S}$ : no more precipitate formed. The mixture was filtered, the filtrate was evaporated nearly to fuming, 6 cc. of 12 n.  $\text{HCl}$  added, and the resulting solution saturated with  $\text{H}_2\text{S}$  and heated 30 minutes in a pressure-bottle immersed in boiling water: a brown precipitate containing 12 mg. of Ir resulted. The mixture was filtered, resaturated with  $\text{H}_2\text{S}$  and heated as just stated: a precipitate containing 6 mg. of Ir separated. The filtrate was again saturated with  $\text{H}_2\text{S}$ , and heated as before for 4 hours: there was a precipitate containing 10 mg. of Ir. The filtrate was evaporated, and its purple color compared with standards: it was estimated to contain 20 mg. of Ir. (This color comparison was also used for estimating the iridium-content of the precipitates obtained previously in this experiment and of those obtained in the following experiment.)

A solution of 50 mg. of Ir as  $\text{IrCl}_4$  in 3.5 cc. of 9 n.  $\text{HClO}_4$  and 1 cc. of 16 n.  $\text{HNO}_3$  was heated till the mixture fumed strongly; 10 cc. of 12 n.  $\text{HCHO}_2$  were added, and the mixture was refluxed for 15 minutes: the solution became olive-green. It was then evaporated till the  $\text{HCHO}_2$  was entirely expelled: the solution was purple. To this were added 10 cc. of 6 n.  $\text{HCl}$ , and the mixture was refluxed for about 30 minutes: the color changed rapidly for 5 minutes, after which it had become a dark orange-red (dark-yellow in  $\frac{1}{2}$  cm. thickness, very dark-red in 3-4 cm. thickness). This solution was saturated with  $\text{H}_2\text{S}$  and heated  $1\frac{1}{4}$  hours in a pressure-bottle in boiling water: a large brown precipitate resulted. The mixture was filtered and the filtrate was examined for iridium: it contained only 5 mg. of Ir.

A mixture containing 300 mg. of Mo as  $(\text{NH}_4)_2\text{MoO}_4$ , 5 cc. of 9 n.  $\text{HClO}_4$ , 1 cc. of 16 n.  $\text{HNO}_3$ , and 400 mg. of  $\text{PO}_4$  as  $\text{H}_3\text{PO}_4$  was heated to fuming, treated with 25 cc. of water and 4 cc. of 3 n.  $\text{NH}_4\text{Cl}$ , placed in a testtube immersed in boiling water, and treated with  $\text{H}_2\text{S}$  for 10 minutes: a dark precipitate containing 130 mg. of Mo resulted. The mixture was filtered; and the (dark-blue) filtrate was diluted to

100 cc. and saturated cold with  $H_2S$ : a brown precipitate containing 100 mg. of Mo resulted. The mixture was filtered, and the (blue) filtrate was evaporated to 15 cc.: a brown precipitate containing 10 mg. of Mo formed. After filtering, the solution (now light-blue) was mixed with 5 cc. of 12 n. HCl, saturated cold with  $H_2S$ , and heated 30 minutes in a pressure-bottle in boiling water: a brown precipitate containing 30 mg. of Mo resulted. The mixture was filtered, and the (colorless) filtrate was again saturated with  $H_2S$ , and heated as just described: there was only a slight turbidity corresponding to 0.3 mg. of Mo. This experiment shows that, even in the presence of much phosphate, molybdenum is almost completely precipitated when the mixture is treated by the whole of P. 71, but not when the pressure-bottle treatment is omitted.

## TELLURIUM GROUP

*P. 72, N. 2.—Separation of Selenium from Tellurium by Sulfurous Acid in Concentrated Hydrochloric Acid.*—See Keller, *J. Am. Chem. Soc.*, **19**, 771 (1897); Noyes and Bray, *ibid.*, **29**, 202 (1907).

*P. 72, N. 3.—Precipitation of Tellurium by Sulfurous Acid.*—In eight separate testtubes 0.5 mg. of Te as  $\text{TeO}_2$  was added to 25 cc. of saturated  $\text{SO}_2$  solution and various quantities of 12 n. HCl. The mixtures were heated for 15 minutes in boiling water with the following results:

12 n. HCl added . . . . .	3 or 4 cc.	5 or 6 cc.	7 cc.	8 cc.	9 or 10 cc.
Precipitate formed . . . . .	slight	larger	maximum	large	smaller

The maximum effect, obtained with 7 or 8 cc. of 12 n. acid, corresponds to a HCl concentration of 2.6–2.9 n.

100 mg. of Te as  $\text{TeO}_2$  were dissolved in 60 cc. of 3 n. HCl and 2 cc. of 95%  $\text{H}_2\text{SO}_4$ , and the mixture was saturated with  $\text{SO}_2$  gas and heated 15 minutes on a steam-bath: a dense black precipitate formed. This was filtered out, the filtrate was evaporated to fuming, 40 cc. of 1.5 n. HCl were added, and the mixture was saturated with  $\text{H}_2\text{S}$ : only a white turbidity resulted.

*P. 72, N. 4.—Behavior of Lead, Copper, Molybdenum, Iridium, and Rhodium on Heating with Sulfurous Acid.*—Various quantities of these elements were in separate experiments dissolved in 30 cc. of 3 n. HCl, and the mixtures were saturated with  $\text{SO}_2$  gas and heated in boiling water for 15 minutes, with the following results:

Lead, 50 mg.: no precipitate or color.

Copper, 500 mg.: no precipitate; color becomes deep olive-green.

Molybdenum, 100 mg.: no color.

Iridium, 50 mg.: very dark color changes to very pale olive-green.

Rhodium, 100 mg.: deep-red color, undergoing no change with  $\text{SO}_2$ .

*P. 73, N. 2.—Extraction of Molybdenum with Ether.*—As to the preparation of  $\text{MoO}_3 \cdot 2\text{HCl}$ , see Pechar, *Compt. rend.*, **114**, 173 (1892); Smith and Oberholtzer, *Z. anorg. Chem.*, **4**, 236 (1893); Abegg-Auerbach, *Handbuch*, IV, 1, (2), 558 (1921).

As to its extraction by ether, see Pechar, *loc. cit.*; Blair, *J. Am. Chem. Soc.*, **30**, 1229 (1908); Swift, *ibid.*, **46**, 2378 (1924).

100 mg. of Mo as the c. p. ammonium molybdate of trade after the preliminary treatment shown in the table were dissolved in 5 cc. of 6 n. HCl, and shaken successively with two 15-cc. portions of ether. The amount of molybdenum was determined by precipitating it as sulfide and comparing with standards. The first two experiments were made with different samples of molybdate and with different reagents.

Preliminary treatment of molybdate	First ether extract	Second ether extract	Aqueous solution
None.....	—	—	6
None.....	—	—	6
Evaporated with HCl, then with HNO <sub>3</sub> .....	85	12	3
Heated 15 min. with 30 cc. of 3 n. HCl saturated with SO <sub>2</sub> , then evaporated.....	88	2	10

*P. 73, N. 3.—Behavior of Bismuth, Cadmium, Copper, Tellurium, Iridium, and Rhodium on Shaking Hydrochloric Acid Solutions with Ether.*—Various quantities of these elements were dissolved in 5 cc. of 6 n. HCl, and shaken with the volume of ether indicated below. The total amount extracted by the ether is shown in the next to last column, or in the last column in the cases where the ether extract was washed with 2 cc. of 6 n. HCl before determining its content.

Element	Milligrams taken	Ether used	Milligrams in ether extract	
			before washing	after washing
Bi.....	50	20	0	—
Cd.....	50	20	2-3	—
Cu.....	500	15	2	0
Te.....	50	20	10	—
Ir.....	50	15	—	0
Rh.....	100	15	2-3	0

*P. 74, N. 1.—Blue Color Test for Molybdenum.*—In separate experiments 0.1 mg., 0.5 mg., and 3 mg. of Mo as (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, dissolved in 5 cc. of 6 n. HCl, were shaken with 15 cc. of ether, and the ether solution was evaporated barely to dryness on a steam-bath in a small casserole: there was no blue color. The residue was dried by moving the dish several times through a gas flame: a deep-blue color developed, which covered more of the dish in the 3-mg. experiment.

300 mg. of Mo as (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> were evaporated with a mixture of 12 n. HCl and 16 n. HNO<sub>3</sub> to dryness on a steam-bath: the residue was blue, but not very dark. A few drops of 16 n. HNO<sub>3</sub> were added, and the mixture again evaporated to dryness: the residue was now yellow. This was treated with 5 cc. of 6 n. HCl: complete solution did not occur. A few drops of 16 n. HNO<sub>3</sub> were therefore added, and the solution was extracted with 15 cc. of specially purified alcohol-free ether: both layers assumed a deep-yellow color. The ether layer was heated at 50° till most of the ether was expelled: there remained a



small quantity of a yellow sirupy liquid and a light-yellow deposit on the sides of the casserole. The casserole was now placed on a steam-bath: there was a vigorous evolution of gas and a strong odor of aldehyde, and the liquid turned very dark-blue. This experiment shows that ether itself, even when pure, causes the molybdenum to be reduced to the blue compound.

*P. 74, N. 3.—Precipitation of Molybdenum by Hydrogen Sulfide after Treatment with Zinc and Thiocyanate.*—To 50 mg. of Mo as  $(\text{NH}_4)_2\text{MoO}_4$  were added 2 cc. of 6 n. HCl, 5 cc. of water, 5 cc. of 1 n. KSCN, and 0.1 cc. of granular Zn. After the solution had become deep-red, it was placed in a testtube immersed in boiling water and treated with  $\text{H}_2\text{S}$  for 10 minutes, and the large brown precipitate filtered off: the (light-green) filtrate contained 3–5 mg. of Mo.

The experiment was repeated, except that the solution was saturated with  $\text{H}_2\text{S}$  cold, instead of at  $100^\circ$ : the filtrate was much darker in color, showing that more molybdenum remained unprecipitated.

*P. 75, N. 2.—Behavior of Iridium and Rhodium on Heating the Solution with Nitrous Acid and Making Alkaline.*—Various quantities of these elements as chlorides were heated at various temperatures with 10 cc. of water, 5 cc. of 3 n.  $\text{NaNO}_2$  (or 10 cc. in the experiments where  $\text{HCHO}_2$  or no acid was added), and the acid shown in the table on the next page. The cold solutions were then treated with NaOH and  $\text{Na}_2\text{CO}_3$  as indicated. The results are shown in the last column.

The first experiment with iridium and that with rhodium show that 100 mg. of Ir remain completely in solution, and that 100 mg. of Rh give only a slight turbidity, when  $\text{HC}_2\text{H}_3\text{O}_2$  is used. The four iridium experiments show that its complete conversion into the complex nitrite occurred when the solution was acidified either with  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HCHO}_2$ , or HCl, but not when no acid was added. The rhodium experiments show that the conversion is more nearly complete with the weaker acids.

Element	Mgs. taken	Acid added	Heating		Alkali added	Result
			min.	temp.		
Ir	100	1 cc. of 6 n. $\text{HC}_2\text{H}_3\text{O}_2$	5	60-70°	NaOH till alkaline, 1 cc. 3 n. $\text{Na}_2\text{CO}_3$ .	Clear yellow solution.
	50	0.5 cc. of 6 n. HCl	5	70-80°	NaOH till alkaline.	Clear yellow solution.
	40	None	15	Boiling	None.	Small orange precipitate; yellow solution.
	40	3 cc. of 12 n. $\text{HCHO}_2$	1-2	70°	3 n. $\text{Na}_2\text{CO}_3$ till alkaline, 2 cc. more, then 1 cc. 6 n. NaOH.	Clear yellow solution.
Rh	100	1 cc. of 6 n. $\text{HC}_2\text{H}_3\text{O}_2$	5	60-70°	NaOH till alkaline, 1 cc. 3 n. $\text{Na}_2\text{CO}_3$ .	Yellow solution; slight turbidity not coagulated by heating.
	50	0.5 cc. of 6 n. HCl	5	60-70°	20 cc. $\text{H}_2\text{O}$ , then NaOH till alkaline.	Yellow solution; turbidity coagulated to yellow precipitate on heating.
	20	None	15	Boiling	1 cc. 3 n. $\text{Na}_2\text{CO}_3$ , 1 cc. 6 n. NaOH.	Pale yellow solution; no precipitate even on heating.
	40	3 cc. of 12 n. $\text{HCHO}_2$	1-2	70°	$\text{Na}_2\text{CO}_3$ till alkaline, 1 cc. 6 n. NaOH.	No precipitate even on heating.

P. 75, N. 3.—*Precipitation of Lead and Copper by Sodium Carbonate.*—To 1 mg. of Pb as  $\text{Pb}(\text{NO}_3)_2$  in 15 cc. of 1 n.  $\text{NaNO}_2$ , and 1 cc. of 6 n.  $\text{HC}_2\text{H}_3\text{O}_2$ , 6 n. NaOH was added till barely alkaline; then 0.5 cc. more and 1 cc. of 3 n.  $\text{Na}_2\text{CO}_3$  were added: there was no precipitate. Then 1 n.  $\text{NaHCO}_3$  was added, 1 cc. at a time, waiting 2 or 3 minutes after each addition: a precipitate appeared after 3 cc., and remained after 5 cc., were added.

A solution of 500 mg. of Cu in 15 cc. of 1 n.  $\text{NaNO}_2$  and 3 cc. of 12 n.  $\text{HCO}_2\text{H}$  was heated to 75°; then 3 n.  $\text{Na}_2\text{CO}_3$  was added till alkaline, and 2 cc. more; and the large precipitate was filtered out: the filtrate was deep-blue.

To 500 mg. of Cu in 15 cc. of 1 n.  $\text{NaNO}_2$  2 cc. of 6 n.  $\text{HC}_2\text{H}_3\text{O}_2$  were added, and the mixture was heated 2 minutes at 75°; 6 n. NaOH was added till alkaline, then 3 cc. of 3 n.  $\text{Na}_2\text{CO}_3$ ; and the precipitate was filtered out: the filtrate was colorless, and gave no precipitate with  $\text{H}_2\text{S}$ .

P. 75, N. 4.—*Separation of Iridium and Rhodium from Copper-Group Elements.*—Various quantities of the elements as chlorides were dissolved in 15 cc. of 1 n.  $\text{NaNO}_2$  and 1 cc. of 6 n.  $\text{HC}_2\text{H}_3\text{O}_2$ ; and the mixture was heated at 60–70° for 5 minutes; 6 n.  $\text{NaOH}$  was added till litmus was turned blue, then 1 cc. of 3 n.  $\text{Na}_2\text{CO}_3$ ; and the mixture was filtered. The results are shown in the table.

Element	Milligrams taken	Milligrams found in	
		precipitate	filtrate
Ir	100	Ir 0	—
Rh	100	Rh 1	—
{ Cu	500	—	Cu 0
{ Ir	2	—	Ir 2
{ Cu	500	—	Cu 0
{ Rh	1	—	Rh 1
{ Cu	200	—	Cu 0
{ Cd	200	—	—
{ Bi	200	—	—
{ Pb	1	Pb 1	—
{ Ir	2	—	Ir > 1
{ Rh	2	—	Rh 2

P. 76, N. 2–4.—*Decomposition of the Complex Nitrites of Iridium and Rhodium and their Precipitation with Sodium Hypobromite.*—As to the precipitation of iridium by  $\text{NaBrO}$  from its chloride, see C. E., P. 56, N. 2, 3.

1 mg. of Rh as  $\text{RhCl}_3$  was heated in a water-bath for 5 minutes with 30 cc. of water and 3 cc. of 3 n.  $\text{Na}_2\text{CO}_3$ ; a white precipitate separated. 3 drops of liquid  $\text{Br}_2$  were added and the solution warmed: the precipitate was blue at first, but became dark-green after it coagulated.

To 40 cc. of a solution containing 2 mg. of Ir as  $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ , 15 milliequivalents of  $\text{NaNO}_2$ , 6 milliequivalents of  $\text{NaC}_2\text{H}_3\text{O}_2$ , and 3 milliequivalents of  $\text{Na}_2\text{CO}_3$  there were added 25 milliequivalents of  $\text{HCl}$  (as 6 n.  $\text{HCl}$ ); and the mixture was boiled till the volume decreased to 10 cc.; 3 n.  $\text{Na}_2\text{CO}_3$  was added till the acid was neutralized, and then 1 cc. more; the solution was heated several minutes in a water-bath, cooled, treated with 2 drops of liquid  $\text{Br}_2$ , and warmed again; there was a blue-black precipitate corresponding to 2 mg. of Ir.

A solution of 1 mg. of Rh as  $\text{Na}_3\text{Rh}(\text{NO}_2)_6$  containing the same substances as in the preceding experiment was boiled down till the volume became 10 cc. To one half of this solution were added 5 cc. of water and 3 n.  $\text{Na}_2\text{CO}_3$  till the solution became neutral, then 1 cc. more; the solution was heated for 5 minutes in a water-bath: no white precipitate appeared. After cooling, 2 drops of liquid  $\text{Br}_2$  were added.

and the mixture again warmed: there was a green color, but no precipitate. The other half of the solution was evaporated with 2-3 cc. of 12 n. HCl till salts crystallized out, and it was then diluted to 10 cc., and treated like the first half: a blue-green precipitate resulted.

To 40 cc. of a solution containing 1 mg. of Rh as  $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ , 15 milliequivalents of  $\text{NaNO}_2$ , 6 milliequivalents of  $\text{NaC}_2\text{H}_3\text{O}_2$ , and 3 milliequivalents of  $\text{Na}_2\text{CO}_3$ , 5 cc. of 12 n. HCl were added, and the mixture was evaporated to dryness; the residue was dissolved in 15 cc. of water and 2 cc. of 3 n.  $\text{Na}_2\text{CO}_3$ , and the mixture was heated 5 minutes: there was a white precipitate. The mixture was cooled, treated with 2 drops of liquid  $\text{Br}_2$ , and heated: a bluish-green precipitate separated. Four more drops of liquid  $\text{Br}_2$  were added: the precipitate became lighter green, and some of it apparently dissolved.

The experiment was repeated with 100 mg. of Rh. After adding the  $\text{Na}_2\text{CO}_3$  and heating, a large yellow precipitate formed. After adding the  $\text{Br}_2$  and heating, the precipitate became dark-green. This was filtered off: the filtrate was green. It was heated an hour with occasional addition of a drop of  $\text{Br}_2$ : a green precipitate coagulated. The mixture was filtered: the filtrate was now colorless.

The experiment was repeated with 50 mg. of Ir as  $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ . After adding the  $\text{Na}_2\text{CO}_3$  and heating, a small light-yellow precipitate separated which contained 1 mg. of Ir and some rhodium (due to impurity in the sample). Upon adding the  $\text{Br}_2$ , a large black precipitate formed. The mixture was heated and filtered: the filtrate was a clear dark-blue. It was heated an hour with occasional addition of  $\text{Br}_2$ : some precipitate separated. The mixture was filtered: the solution was still dark-blue. 1 cc. of  $\text{C}_2\text{H}_5\text{OH}$  was added, and the mixture heated: no precipitate formed. It was shaken with filter-paper pulp and filtered: the pulp was colorless. The solution was saturated with  $\text{CO}_2$ : no precipitate separated. The solution was evaporated almost to dryness, and the residue treated anew with water,  $\text{Na}_2\text{CO}_3$ , and  $\text{Br}_2$  as at the beginning of the experiment: a black precipitate containing 5-8 mg. of Ir separated, and the filtrate was colorless.

70 mg. of Ir as  $\text{IrCl}_4$  were heated with 20 cc. of water and 2 cc. of 3 n.  $\text{Na}_2\text{CO}_3$  for 5 minutes on a steam-bath: a large light-colored precipitate separated. The mixture was cooled, and 6 drops of liquid  $\text{Br}_2$  were added: a large bluish-black precipitate separated. The mixture was heated for 10 minutes on a steam-bath and filtered; the filtrate was heated 5 minutes longer with 2 drops of liquid  $\text{Br}_2$ : there was a precipitate containing 15 mg. of Ir. The filtrate from this was heated 10 minutes with 3 drops of liquid  $\text{Br}_2$ : another precipitate containing about 5 mg. of Ir formed. The filtrate stood a week in

the cold: about 3 mg. of Ir more had separated, and the filtrate was only slightly bluish.

*P. 77, N. 1.—Dissolving of Iridium and Rhodium Dioxides in Acids.*  
—50 mg. of Ir as  $\text{IrO}_2$  (precipitated by  $\text{NaBrO}$ ) were heated for 5 minutes on a steam-bath with 8–10 cc. of 12 n.  $\text{HCl}$ : there was little action. 0.5 cc. of 16 n.  $\text{HNO}_3$  was added, and the heating continued: the precipitate had not entirely dissolved at the end of 30 minutes.

The experiment was repeated using  $\text{RhO}_2$  in place of  $\text{IrO}_2$ : the result was similar.

50 mg. of Rh as precipitated  $\text{RhO}_2$  were treated in the cold with 5 cc. of 9 n.  $\text{HBr}$ : in 5 minutes the  $\text{RhO}_2$  entirely dissolved, forming a dark-orange solution.

*P. 77, N. 2, 3.—Precipitation of Iridium by Ammonium Chloride.*  
In five experiments 0.1 mg. of Ir as  $\text{IrCl}_4$  was dissolved in 1 cc. of water, and the solution was saturated with  $\text{NH}_4\text{Cl}$  and treated as follows, with the results indicated:

- a*, let stand 12 hours: bluish-black flocculent precipitate (of  $\text{IrO}_2$ ).
- b*, 0.04 cc. of 12 n.  $\text{HCl}$  added, let stand 12 hours: no precipitate.
- c*, 0.04 cc. of 12 n.  $\text{HCl}$  added, saturated with  $\text{Cl}_2$ , let stand 12 hours: black precipitate.
- d*, 0.04 cc. of 12 n.  $\text{HCl}$  added, saturated with  $\text{Cl}_2$ , heated, let stand 12 hours: small black precipitate.
- e*, saturated with  $\text{Cl}_2$ , let stand 20 minutes, heated on steam-bath, cooled: black precipitate.

In three experiments 0.3 mg. of Ir as  $\text{IrCl}_4$  was dissolved in 1 cc. of 0.5 n.  $\text{HCl}$ . In the first one, the solution was saturated cold with  $\text{NH}_4\text{Cl}$  and  $\text{Cl}_2$ , and then let stand. In the second one it was so saturated, let stand 15 minutes, heated 15 minutes on a steam-bath, and cooled. In the third one, the solution was first saturated cold with  $\text{Cl}_2$ , heated to  $50^\circ$  for 2–3 minutes, cooled, saturated with  $\text{NH}_4\text{Cl}$ , heated 15 minutes on a steam-bath, and cooled. In the first case a precipitate formed only after 2 hours; in the second case it formed immediately; and in the third case, also immediately, but in larger quantity.

A solution of 0.5 mg. of Ir as  $\text{H}_2\text{IrCl}_6$  in 1 cc. of water was acidified with 2 drops of  $\text{HCl}$  and saturated with  $\text{NH}_4\text{Cl}$ : within half an hour a black precipitate had separated.

A solution of 50 mg. of Ir as  $\text{IrCl}_4$  in 2 cc. of water was saturated with  $\text{Cl}_2$ , heated 3 minutes at  $50^\circ$ , saturated with  $\text{NH}_4\text{Cl}$ , heated 15 minutes on a steam-bath, cooled, and allowed to stand 15 minutes: a black precipitate containing about 40 mg. of Ir formed. The solution was decanted and saturated with  $\text{Cl}_2$ : a small precipitate formed. The

mixture stood several hours: there was little increase in the precipitate. The mixture was heated 15 minutes on the steam-bath, cooled, and let stand 10 minutes: there was now a precipitate corresponding to 5-6 mg. of Ir; and the filtrate was still dark-yellow. The iridium in it was estimated by further treatment to be 2-3 mg.

*P. 77, N. 3.—Non-Precipitation of Rhodium by Ammonium Chloride.*—A solution of 100 mg. of Rh as  $\text{RhCl}_3$  in 2 cc. of water was saturated with  $\text{Cl}_2$ , heated, cooled, saturated with  $\text{NH}_4\text{Cl}$ , heated again, cooled, and allowed to stand several hours: no precipitate separated.

*P. 78, N. 1.—Precipitation of Rhodium as Chloropentamine Rhodium Chloride.*—1 mg. of Rh as  $\text{RhCl}_3$  in 2 cc. of saturated  $\text{NH}_4\text{Cl}$  and 3 cc. of 15 n.  $\text{NH}_4\text{OH}$  was evaporated to dryness, the residue dissolved in 2 cc. of hot 6 n.  $\text{HCl}$ , the mixture cooled, and let stand 15 minutes: a slightly yellow, crystalline powder separated.

The experiment was repeated with 0.5 mg. of Rh: there was a slight precipitate.

The experiment was repeated (with 1 mg. of Rh), except that the mixture was heated in a pressure-bottle 30 minutes before being evaporated: the result was the same.

The experiment was twice repeated with the change that the  $\text{NH}_4\text{Cl}$  solution was first evaporated to dryness and then heated 30 minutes in a pressure-bottle with 3 cc. of 15 n.  $\text{NH}_4\text{OH}$ ; in one case the residue after evaporation was heated with 2 cc. of 6 n.  $\text{HCl}$ , in the other with 2 cc. of 6 n.  $\text{NH}_4\text{OH}$ : in both cases a slightly yellow powder remained.

A solution of 100 mg. of Rh as  $\text{RhCl}_3$  in 2 cc. of saturated  $\text{NH}_4\text{Cl}$  and 3 cc. of 15 n.  $\text{NH}_4\text{OH}$  was evaporated to dryness, and the residue was heated with 2 cc. of 6 n.  $\text{HCl}$ : a large bright-yellow precipitate remained. The mixture was cooled and allowed to stand: the solution above the precipitate was deep-yellow. The solution was evaporated repeatedly with  $\text{HCl}$  and  $\text{HNO}_3$  (to destroy ammonium salts), the residue was dissolved in 10 cc. of water and a few drops of  $\text{HCl}$ , and saturated hot with  $\text{H}_2\text{S}$ : a black precipitate corresponding to 1 mg. of Rh separated.

*Non-Precipitation of Iridium by Digestion with Ammonium Hydroxide and Addition of Hydrochloric Acid.*—5 mg. of Ir as  $\text{IrCl}_3$  were heated in a pressure-bottle in boiling water with 1 cc. of saturated  $\text{NH}_4\text{Cl}$  and 3 cc. of 15 n.  $\text{NH}_4\text{OH}$  for 30 minutes; the solution was evaporated to a few drops, heated to boiling with 2 cc. of 6 n.  $\text{HCl}$ , filtered, and cooled: no precipitate separated.

#### COPPER GROUP

*P. 81-85.—Analysis of the Copper Group.*—See Noyes and Bray, *J. Am. Chem. Soc.*, 29, 196-199 (1907).