

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SEPARATION AND DETERMINATION OF COBALT. I. THE SEPARATION OF COBALT BY MEANS OF PHENYL-THIOHYDANTOIC ACID¹

BY H. H. WILLARD AND DOROTHY HALL

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Part I. Separation of Cobalt from Other Metals

Introduction

The present methods for the separation and determination of cobalt leave much to be desired in respect to accuracy and rapidity. Especially is there need of some reagent which will separate it from a large number of other metals. Nitroso- β -naphthol is widely used for this purpose, but it also precipitates iron, one of the metals most commonly associated with cobalt. Pozzi-Escot² suggested as a qualitative test for cobalt its precipitation from ammoniacal solution by the monosubstitution products of the thiohydantoic acids, particularly phenyl- or β -naphthyl-hydantoic acid; cobalt gives a purplish-red precipitate and nickel a brown one, the latter being soluble in concentrated ammonia, thus making possible the detection of cobalt in the presence of nickel. As a qualitative reagent phenyl-thiohydantoic acid was introduced into this laboratory some years ago. It seemed desirable, therefore, to study its use as a quantitative reagent, and since the precipitate thus obtained cannot be weighed directly it was necessary to investigate the gravimetric and volumetric methods of determining cobalt, the report of which will appear in subsequent papers.

Phenyl-thiohydantoic acid precipitates cobalt quantitatively in slightly ammoniacal solution. The compound varies somewhat in color; it is usually brownish- or purplish-red and is readily filtered and washed, especially when hot. The precipitate contains a large amount of water and shrinks enormously in volume when dried. By means of this reagent, cobalt may be completely separated from aluminum, chromium, vanadium, uranium, tungsten, molybdenum, arsenic, titanium, zinc, manganese, calcium and magnesium, while iron is carried down only to a very slight extent. Nickel is partially precipitated and the precipitate is soluble in concentrated ammonia. It is, however, impossible to add much concentrated ammonia without interfering with the precipitation of cobalt. Most metals of the hydrogen sulfide group are precipitated. The various separations will be described in detail.

¹ From a dissertation presented by Dorothy Hall in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

² Pozzi-Escot, *Ann. chim. anal. chim. appl.*, 10, 147 (1905).

Preparation of Materials

Phenyl-thiohydantoic acid, $C_6H_5NC(NH_2)SCH_2COOH$, was prepared by the method of Nencki and Jaeger.³ The procedure is as follows.

To a mixture of 189 g. of monochloro-acetic acid and 152 g. of ammonium thiocyanate in a round-bottom flask are added 186 g. of aniline and 930 cc. of ethyl or methyl alcohol. The mixture is heated under a reflux condenser on the water-bath for several hours, after which the undissolved part is allowed to settle and the clear, brown-yellow liquid is poured into a large evaporating dish. It is allowed to cool, whereupon crystallization takes place. Sometimes the liquid crystallizes slowly, probably because of impurities. Stirring then often hastens crystallization. The yellow crystals are filtered on a Büchner funnel, washed with water and dried. The product is recrystallized from alcohol and then from water. By further refluxing the mother liquor with the undissolved part from which the liquid was decanted, a second crop of crystals may be obtained. A 60–70% yield is possible.⁴

Phenyl-thiohydantoic acid crystallizes in flat plate-like crystals, which are perfectly white when pure. As usually prepared, it possesses a characteristic odor which is much decreased by recrystallization from water.

The solubility in 100 cc. of water at 100° was found to be about 10 g. and at 20° less than 1 g.; that in alcohol is similar, but the acid is much more soluble in acetone. A saturated aqueous or alcoholic solution may be used as a reagent. If this is too dilute, acetone may be used or the solid dissolved in hot water when needed.

The cobalt used was in the form of metallic cobalt, which was prepared by electrolysis from chloropentammine cobaltic chloride, the form in which cobalt is most readily purified.

To a cold solution of 50 g. of cobalt chloride, "nickel free," (containing 25.8% of cobalt) and 100 g. of ammonium chloride in 300 cc. of conc. ammonia (sp. gr. 0.90), 25 cc. of 30% hydrogen peroxide solution was added at once, then 2 or 3 cc. at a time, until 50 cc. had been added. Other oxidizing agents were less satisfactory since larger amounts of the other amines were formed. After the oxidation was complete the solution was neutralized with conc. hydrochloric acid and 50 cc. excess added, after which the solution was heated to boiling and allowed to cool. The purple precipitate was filtered off and dissolved in a 2% ammonia solution, filtered hot, acidified with hydrochloric acid and boiled. Practically the theoretical yield of amine was obtained. The purity of the original cobalt chloride was shown by the fact that the mother liquors from the precipitation of the chloropentammine salt contained only a trace of nickel.

The chloropentammine chloride was dissolved in ammonia and electrolyzed by a current of 2 amperes for 24 hrs. The cathode was a piece of platinum foil covered with a thin film of vaseline. The cobalt deposit was then peeled off as a sheet and ignited in hydrogen at a bright red heat to reduce any oxide or chloride that might have been occluded. To make sure of the purity of the cobalt, weighed amounts were dissolved in nitric acid, evaporated with sulfuric acid to dryness and ignited in a muffle furnace at 550° until constant weight was obtained, which required

³ Nencki and Jaeger, *J. prakt. chem.*, [2] **16**, 17 (1877).

⁴ This reagent is now obtainable from the Eastman Kodak Company.

about 2 ignitions of 1 hour each. Previous work⁵ showed that above this temperature the sulfate slowly decomposes.

The cobalt sulfate thus formed dissolved clear in water and was neutral. The following results were obtained.

TABLE I
ANALYSES OF METALLIC COBALT

Co taken G.	CoSO ₄ found G.	Co found G.	Error Mg.
0.1329	0.3500	0.1332	+0.3
0.0211	0.1869	0.0211	0.0
0.1009	0.2649	0.1008	-0.1
0.1212	0.3181	0.1211	-0.1

Method of Precipitation

Amounts of metallic cobalt equivalent to about 25 mg. were used for each determination. For every 25 mg. of cobalt 0.7 to 1 g. of phenylthiohydantoic acid dissolved in 30 cc. of water or alcohol was added to the hot ammoniacal cobalt solution in a volume of 200–300 cc. After boiling for a few seconds with constant stirring, the precipitate separated at the top so that it was possible to detect any pink color in the clear solution, indicating incomplete precipitation. Unless the solution is distinctly alkaline, precipitation will be incomplete. The least amount of ammonia which will induce complete precipitation is 1 cc. (sp. gr. 0.90) in a volume of 300 cc., but as much as 10 cc. may be present without interference. With 20 cc., however, precipitation is again not quite complete. Continuous stirring or shaking tends to hasten the process. The bulky precipitate was washed with hot water and then dried, whereupon it shrank to a convenient size and was easily ignited to the oxide.

Composition of the Precipitate

Various experiments were tried to ascertain the composition of the cobalt precipitate. From the amount of reagent required to give complete precipitation, no definite information could be obtained. The smallest amount of reagent that would completely precipitate 25 mg. of cobalt was 400 mg., or 16 times the weight of the metal.

Cobalt sulfate and chloropentammine cobalt chloride were precipitated with phenylthiohydantoic acid and the precipitates dried in a vacuum desiccator over sulfuric acid for 3 days. Samples of these were weighed, ignited, fused with potassium pyrosulfate, dissolved and the cobalt determined volumetrically, as described later. Using the same material the percentage of cobalt found varied from 9.1% to 11.6% and the 2 preparations were essentially alike, although they were precipitated from salts of bivalent and trivalent cobalt, respectively. The average value was 9.9%, while the theoretical percentage for bivalent cobalt is 12.3

⁵ By Mr. R. D. Smith.

and for trivalent, 8.6. One determination of sulfur gave 17.86% as compared with a theoretical value of 13.2%, assuming the formula $(C_9H_9O_2-N_2S)_2Co$. It is obvious that the precipitate is contaminated with sulfide or some other sulfur compound, as might be expected from the varying color of the different precipitates. Therefore, the precipitate cannot be weighed directly.

Separation of Iron

Iron and cobalt are usually separated by precipitating the iron as the basic acetate⁶ or as hydroxide by adding zinc oxide or some similar neutralizing agent.⁷ Iron may be separated by shaking out with ether,⁸ but usually traces of cobalt remain in the ether extract. Cobalt may be extracted from a solution containing thiocyanate by means of a mixture of ether and amyl alcohol; sodium pyrophosphate is added to retain the iron in the water solution.⁹ There is, however, no reagent which precipitates cobalt and separates it completely from iron.

Phenyl-thiohydantoic acid may be used to separate cobalt from iron. The latter does not precipitate in the presence of citrate, although very small amounts are carried down each time when cobalt is present, the exact amount depending on the conditions of precipitation. Vigorous agitation of the solution is necessary as soon as the reagent has been added and before the cobalt begins to precipitate. If the cobalt precipitate is red, then the proper procedure for precipitation has been followed and very little iron will be found with the cobalt; but if a black precipitate forms (probably due to the presence of ferrous sulfide) it may contain as much as 50 mg. of iron and must be discarded. Small amounts of iron will cause no trouble unless gravimetric methods are used in the final determination of the cobalt.

To determine whether precipitation was complete the precipitate was filtered off, and to the filtrate more of the reagent was added. The second precipitate, consisting mainly of the reagent with a little iron, was ignited, fused with potassium hydrogen sulfate, dissolved in water and tested for cobalt with nitroso- β -naphthol in ammoniacal citrate solution by the method of Atack¹⁰ modified by Jones.¹¹ Since 0.01 mg. of cobalt gives a deep red color, it was possible by using a standardized solution to estimate quite closely the amount of cobalt present.

The most satisfactory removal of cobalt from iron was obtained by the following method, using a 500cc. Erlenmeyer flask. The total volume of the solution was kept at about 300 cc. The solution, containing 25 mg. of cobalt, 1 g. of iron in the form of ferric alum, and 8 g. of citric acid,

⁶ McIntosh, *Chem. News*, **56**, 64 (1887). Hare, *THIS JOURNAL*, **17**, 537 (1895). Campbell, *Z. anal. Chem.*, **30**, 616 (1893).

⁷ Vortman, *Jahresber.*, **1894**, 2534. Slavik, *Chem.-Ztg.*, **38**, 514 (1914).

⁸ Brunck, *Chem.-Ztg.*, **37**, 1374 (1913).

⁹ Rosenheim and Huldshinsky, *Ber.*, **34**, 2050 (1901).

¹⁰ Atack, *J. Soc. Chem. Ind.*, **34**, 64 (1915).

¹¹ Jones, *Analyst*, **43**, 317 (1918).

was neutralized with ammonia (sp. gr. 0.90) and 5 cc. excess was added. To the warm solution (35°) was added 0.7 to 1.0 g. of phenyl-thiohydantoic acid dissolved in 30 cc. of water or alcohol. The flask was quickly stoppered and shaken for several minutes. The cobalt precipitated at once, and when heated to boiling for several minutes it filtered easily. The filtrate was tested for complete precipitation of the cobalt, as described above. After washing with 0.5% ammonium citrate solution until the wash water gave no test for iron, the precipitate was dried, ignited, and then fused with potassium pyrosulfate. The fused mass was then dissolved in water, diluted to 200 cc., and 10 g. of ammonium chloride added. The iron was precipitated twice by adding dil. ammonia to the hot solution, ignited to oxide, and weighed as such. Proceeding as indicated above, and adding 1 g. of reagent, the amount of iron precipitated varied irregularly in 20 experiments from a trace to 9. mg., the average being 3.7 mg. Cobalt was completely precipitated in all cases.

When only 0.7 g. of reagent was added, the minimum amount required for complete precipitation in the presence of 1 g. of iron, somewhat less of the latter was precipitated the amounts varying from 2.1 to 4.5 mg. with an average of 2.9 mg. With 10 mg. of iron present in 2 experiments, 1.0 and 2.3 mg. were precipitated. The presence of nickel still further decreases the amount of iron precipitated, probably because in this case the precipitate is more finely divided and easier to wash, but the iron rarely falls below 1.5 mg. The reason for this effect of adding a large excess of the reagent is doubtless because the excess crystallizes out on cooling slightly even though the solution is filtered hot, and these crystals carry iron.

If instead of a flask a 600cc. beaker is used for the precipitation, the separation is not as good, since the agitation of the solution is more difficult. When precipitated under such conditions the reagent was added to the boiling solution and boiling was continued for a few minutes. The amount of iron in the precipitate varied from 3 to 10 mg., the average being 8 mg., and even when precipitated twice it varied from 2 to 6 mg.

The only objection to using an Erlenmeyer flask is the difficulty of removing the precipitate, for usually the last trace cannot be transferred; but the precipitate is so bulky that the slight amount adhering to the flask is negligible.

In the following experiments cobalt was precipitated in the presence of 1 g. of iron as described above, and then determined volumetrically

TABLE II
PRECIPITATION OF COBALT IN THE PRESENCE OF IRON

Co taken G.	Co found G.	Error Mg.
0.0321	0.0319	-0.2
0.0245	0.0250	+0.5
0.0238	0.0241	+0.3
0.0270	0.0265	-0.5
0.0306	0.0303	-0.3
0.0337	0.0339	+0.2

by oxidation to cobaltic hydroxide and reduction with titanous sulfate as outlined later.

Precipitation in the Presence of Nickel

The literature on the subject of the separation of nickel and cobalt is extensive, but since the method used here is not a separation of these 2 elements, no other methods will be discussed. Nickel is precipitated by phenyl-thiohydantoic acid under the same conditions as is cobalt, but not quantitatively. Nickel forms a brown precipitate which is soluble in hot dil. ammonia to a certain extent and is completely soluble in hot conc. ammonia. It would be impossible, however, to remove the nickel with hot conc. ammonia without affecting the cobalt precipitate, nor can the precipitated nickel be dissolved with hot alcohol.

In the presence of more than 20 cc. of ammonia (sp. gr. 0.90), complete and immediate precipitation of cobalt is not possible. The following results show the effect of adding more ammonia during precipitation.

TABLE III
EFFECT OF ADDITION OF AMMONIA

Ammonia added (Sp. gr. 0.90)	Ni added	Ni in ppt.
Cc.	Mg.	Mg.
50	19	6.0
16	19	9.0
10	19	7.2
10	10	9.4
10	5	1.4

In the presence of 1 g. of iron and 19 mg. of nickel the amount of iron in the precipitate varied from 0 to 5.5 mg., the average being 2.8 mg. The addition of more nickel had no effect. When only 5 mg. of iron was present 0.8 mg. was carried down; 0.7 g. of reagent was used in these experiments.

TABLE IV
NICKEL AND IRON IN PRECIPITATE

Ni added	Ni in ppt.	Fe added	Fe in ppt.
Mg.	Mg.	G.	Mg.
9.5	4.2	1	4.2
19.0	3.9	1	2.6
19.0	9.0	0.01	0.9
19.0	6.7	0.008	0.8
19.0	12.0	0.004	0.8
38.0	11.4	1	3.8
50.0	11.9	1	2.5
50.0	9.0
60.0	14.0

The amounts of both nickel and iron carried by the precipitate were determined in the following experiments, 0.7 g. of phenyl-thiohydantoic acid being used in each case. These precipitates were washed with hot

0.5% ammonium citrate solution until the wash water gave no test for iron or nickel. It was noticed that the filtrate immediately after the filtration of the cobalt gave no test for nickel with dimethylglyoxime, but as soon as washing of the precipitate was started nickel began to precipitate. This shows that nickel is precipitated with the cobalt and by washing is partially removed. When the volume during precipitation was increased to 700 cc. no improvement was apparent.

Separation from Zinc

Cobalt is usually separated from zinc by precipitation with nitroso- β -naphthol; zinc may be separated from cobalt by precipitation as sulfide from a solution slightly acid with formic or monochloro-acetic acid,¹² or containing the cobalt as cobaltcyanide.¹³

Experimental.—Cobalt was completely separated from zinc in one precipitation by phenyl-thiohydantoic acid. The solution, 400 cc. in volume, contained citrate and 10 cc. of ammonia (sp. gr. 0.90) in excess. The reagent was added to the boiling cobalt solution and the boiling continued for several minutes. Zinc has a very noticeable effect in retarding the precipitation of cobalt, but by keeping the solution warm and stirring frequently all of the cobalt was precipitated in $\frac{1}{2}$ hour, and a clear, colorless filtrate left. The cobalt precipitate was washed with hot 0.5% ammonium citrate 15 times and then dried. After burning off the carbon, the cobalt oxide was fused with potassium pyrosulfate, the fused mass dissolved in water, the solution diluted to 200 cc. and tested for zinc by passing hydrogen sulfide into the hot, slightly acid solution. No test for zinc could be obtained.

Separation from Manganese

Funk's method¹⁴ of separating cobalt from manganese is based on the fact that manganous sulfide is soluble in formic acid and acetic acid. He was also able to separate cobalt from very small amounts of manganese by precipitation as potassium cobaltinitrite.¹⁵ One of the best methods is precipitation of the cobalt with nitroso- β -naphthol.

Experimental.—The same conditions of precipitation were used as for the separation from iron. Precipitation was complete at once. After washing, the precipitate was dried, ignited and fused with potassium pyrosulfate. Manganese was tested for by oxidation to permanganate with potassium periodate,¹⁵ using a blank to make sure of the color change. No trace of manganese could be detected.

Separation from Other Metals

By precipitating cobalt in a volume of 400 cc. with 7 g. of citric acid and 10 cc. excess of ammonia (sp. gr. 0.90) complete separation from arsenic, titanium, uranium, vanadium, tungsten, molybdenum, aluminum, chromium, calcium and magnesium was accomplished in one precipitation. The cobalt was not determined, but the precipitate was entirely

¹² (a) Berg, *Z. anal. Chem.*, **25**, 512 (1886). (b) Rosenheim and Huldshinsky, *Z. anorg. Chem.*, **32**, 84 (1902).

¹³ Funk, *Z. anal. Chem.*, **46**, 1 (1907). Ref. 12 b.

¹⁴ Funk, *ibid.*, **45**, 562 (1906).

¹⁵ Willard and Greathouse, *THIS JOURNAL*, **39**, 2366 (1917).

free from the other metals present. The precipitate was sometimes a little slow in forming, but when the solution was boiled, frequently stirred and allowed to stand, complete precipitation and separation were always obtained.

Summary

1. Cobalt may be quantitatively separated in one operation from arsenic, uranium, vanadium, titanium, tungsten, molybdenum, zinc, manganese, chromium, aluminum, magnesium, and calcium by precipitation with phenyl-thiohydantoic acid in slightly ammoniacal solution.

2. In the presence of iron the precipitate is rarely entirely free from this impurity, and usually contains from 1 to 5 mg., regardless of the amount originally present. This does not, however, interfere with the volumetric determination of cobalt.

3. Nickel is always partially precipitated.

4. The cobalt precipitate does not have a definite composition. It is probably contaminated with cobalt sulfide, thus making it necessary to convert the cobalt into some more definite form.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SEPARATION AND DETERMINATION OF COBALT. II. GRAVIMETRIC DETERMINATION OF COBALT¹

BY H. H. WILLARD AND DOROTHY HALL

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When determined gravimetrically cobalt is weighed as the oxide, Co_3O_4 , as metal (obtained electrolytically or by reduction of the oxide in hydrogen), as sulfate, as double ammonium phosphate, or as pyrophosphate. Although other methods have been proposed they have proved unsatisfactory. The above methods were investigated in order to determine in what form cobalt could best be weighed after precipitation with phenyl-thiohydantoic acid.

Ignition to Oxide

Ignition to oxide is the method most commonly used when cobalt is precipitated by nitroso- β -naphthol or when it is obtained in any other suitable form.

To ascertain whether it is possible to ignite cobalt to a definite oxide, Co_3O_4 , samples of the pure metal were dissolved in nitric acid and, after evaporation to dryness, ignited to constant weight in an electric furnace. Increase in the ignition temperature did not appreciably affect the results, as the following table indicates.

¹ From a dissertation presented by Dorothy Hall in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.