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

THE SEPARATION AND DETERMINATION OF COBALT. II. GRAVIMETRIC DETERMINATION OF COBALT[1]

BY H. H. WILLARD AND DOROTHY HALL

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.

More satisfactory results were obtained by ignition in a porcelain crucible at the full heat of the Meker burner, possibly due to a slightly more reducing atmosphere. From the results given below it is evident that

TABLE I

EFFECT OF INCREASING IGNITION TEMPERATURE

Co taken G.	Co_3O_4 found at 850° G.	Co found G.	Co_3O_4 found at 900° G.	Co found G.
0.0568	0.0779	0.0572	0.0782	0.0574
0.0429	0.0588	0.0432	0.0583	0.0428

upon ignition pure cobalt nitrate forms the oxide Co_3O_4, which may then be reduced in a stream of hydrogen to metal, so as to check with the theoretical value.

TABLE II

OXIDE IGNITED OVER MEKER BURNER THEN REDUCED IN HYDROGEN

Co taken G.	Co found as Co_3O_4 G.	Co after ignition in hydrogen G.
0.0842	0.0844	0.0844
0.0640	0.0639	0.0638
0.0646	0.0648	0.0648

Ignition to Oxide after Precipitation with Phenyl-thiohydantoic Acid

In order to determine whether cobalt could be ignited to oxide after precipitation by phenyl-thiohydantoic acid, samples of the pure metal were dissolved and precipitated by this reagent, as described in Paper I

TABLE III

IGNITION TO OXIDE

Co taken G.	Oxide found G.	Error assuming Co_2O_3 Mg. Co	Error assuming Co_3O_4 Mg. Co	Error, Co reduced in H Mg.
0.0214	0.0354	+0.5	+1.7	...
0.0296	0.0432	+1.1	+2.3	...
0.0325	0.0463	+0.4	+1.5	...
0.0225	0.0326	+0.7	+1.4	...
0.0264	0.0386	+1.0	+2.2	...
0.0178	0.0252	+0.1	+0.7	...
0.0342	0.0472	−0.7	+0.4	...
0.0272	0.0388	+0.4	+1.3	...
0.0316	0.0446	+0.1	+1.2	...
0.0306	0.0431	0	+1.0	...
0.0327	0.0462	+0.1	+1.2	...
0.0171	0.0243	+0.2	+0.7	+0.9
0.0333	0.0456	−0.9	+0.1	−0.3
0.0278	0.0401	+0.6	+1.6	+1.7
0.0354	0.0504	+0.4	+1.6	+1.6
		Av. +0.3	Av. +1.3	Av. +1.0

(p. 2221) and, after drying, ignited in porcelain crucibles to constant weight at the full heat of the Meker burner. In the preceding table it is evident that

more accurate results are obtained by assuming that the oxide is Co_2O_3 rather than Co_3O_4. In the last 8 experiments oxalic acid was added before ignition, and in the last 4 the oxide was reduced in hydrogen and the metal weighed.

In the following experiments every precaution was taken to make sure that none of the reagents gave non-volatile residues. Precipitation was made in a platinum dish to exclude silica from glass. Freshly distilled nitric acid and water were also used. Ammonium carbonate free from non-volatile matter was employed to make the solution ammoniacal. Phenyl-thiohydantoic acid recrystallized from water was used for the precipitation. These samples were ignited to oxide and then converted to sulfate after solution in perchloric acid. The results given here are excellent, assuming the oxide to be Co_2O_3.

TABLE IV

IGNITION TO OXIDE. FOLLOWED BY CONVERSION TO SULFATE

Co taken G.	Oxide found G.	Co calc. from Co_2O_3 G.	Error Mg.	$CoSO_4$ found G.	Co calc. from sulfate G.	Error Mg.
0.0272	0.0384	0.0273	+0.1	0.0709	0.0270	−0.2
0.0296	0.0518	0.0297	+0.1	0.0798	0.0303	+0.7
0.0404	0.0570	0.0405	+0.1	0.1054	0.0401	−0.3

Since it has been shown that the oxide formed on ignition corresponds to the formula Co_3O_4, the excess in weight must be due to some impurity or to the presence of cobalt in some form other than oxide. That this is not due to carbon, at least in any appreciable amount, was shown by the fact that the oxide was completely soluble in hydrochloric acid in the presence of a reducing agent. This solution of the oxide, however, gave a distinct test for sulfate.

It is evident, therefore, that during ignition some of the sulfur in the precipitate was converted into sulfate, thus causing the excess weight.

TABLE V

OXIDE CORRECTED FOR SULFATE

Co taken G.	SO_3 in ppt. Mg.	Corr.-wt. of oxide G.	Co found G.	Error Mg.
0.0566	1.6	0.0801	0.0576	+1.0
0.0404	1.3	0.0561	0.0402	−0.2
0.0308	1.2	0.0445	0.0318	+1.0
0.0329	0.7	0.0455	0.0329	0.0
0.0301	0.4	0.0412	0.0302	+0.1
0.0337	0.6	0.0467	0.0342	+0.5
0.0283	0.5	0.0386	0.0283	0.0
0.0334	0.5	0.0462	0.0339	+0.5
			Av.	+0.4

To detect the presence of sulfate, the cobalt oxide was dissolved in hydrochloric acid, evaporated to dryness, dissolved with water, diluted to 100

cc., the solution acidified with a few drops of hydrochloric acid and the sulfate precipitated as barium sulfate. The solutions were allowed to stand for 12 hours before filtration.

In all cases sulfate was found to be present, but this did not always account for the total excess weight. Possibly some of it was due to carbon, notwithstanding its seeming absence as stated above. The results are shown in Table V.

Electrolytic Determination of Cobalt

The electrolytic determination of cobalt is not always satisfactory. The deposit is often dark colored and contains impurity causing high results. Moreover, it is often impossible to obtain complete deposition. Lundell and Hoffman[2] have made a careful investigation of this matter and shown that excellent results may be obtained when the electrolyte contains a high concentration of ammonia and ammonium sulfate and a few grams of sodium sulfite. A few determinations were made under the conditions recommended and excellent results were indeed obtained. This method can, therefore, be considered satisfactory.

Determination as Cobalt Sulfate

In previous work in this laboratory it was shown that cobalt sulfate could be ignited at temperatures up to 550° without decomposition; above this there is a loss of sulfur trioxide. This temperature was, therefore, taken as most suitable for the ignition of the sulfate. Results are given in the preceding paper.[3]

Determination as Sulfate after Precipitation with Phenyl-thiohydantoic Acid

While it was possible to convert pure cobalt to the theoretical weight of sulfate, it was found that after precipitation with phenyl-thiohydantoic

TABLE VI
DETERMINATION AS SULFATE

Co taken G.	CoSO₄ found G.	Co found G.	Error Mg.
0.0294	0.0780	0.0297	+0.3
0.0591	0.1541	0.0586	−0.5
0.0349	0.0929	0.0354	+0.5
0.0304	0.0803	0.0305	+0.1
0.0167	0.0489	0.0185	+1.8
0.0330	0.0877	0.0333	+0.3
0.0250	0.0666	0.0253	+0.3
0.0310	0.0814	0.0310	0.0
0.0343	0.0925	0.0352	+0.9
0.0522	0.1380	0.0525	+0.3
		Av.	+0.4

[2] Lundell and Hoffman, *J. Ind. Eng. Chem.*, **13**, 540 (1921).
[3] Table I, p. 2221.

acid and conversion to sulfate, results were high. The cobalt sulfate never dissolved in water to give a solution entirely clear. A yellow precipitate separated which dissolved upon the addition of a drop of acid. The exact nature of this substance could not be determined because of the extremely small amount available. In the attempt to avoid this error, cobalt was precipitated according to the directions given in Part I and the precipitate treated in various ways.

1. After the carbon had been burned these samples were dissolved in hydrochloric acid, evaporated to dryness with sulfuric acid, ignited at 550°, and weighed as sulfate. The results are shown in Table VI.

2. If any of the excess weight were due to insoluble matter, filtering the solution and again evaporating to dryness should reduce the error. This process was used in 8 experiments. The insoluble portion was weighed and was found to contain about 0.1 mg. of iron and 0.1 mg. of cobalt. This does not account for the error in some of the results, and it would appear that part of the increased weight must be due to impurities which are soluble. The results obtained were even worse than the preceding, the average error being +1.0 mg., perhaps due to impurities derived from the glass vessels used in the second operation.

3. The dried precipitate was dissolved in perchloric acid, evaporated with sulfuric acid and weighed as cobalt sulfate. Care must be taken in dissolving the precipitate in perchloric acid, since the acid attacks organic matter quite vigorously. The cobalt sulfate did not dissolve in water to give a clear solution, but the results were more satisfactory.

TABLE VII

DETERMINATION OF SULFATE AFTER SOLUTION IN PERCHLORIC ACID

Co taken	CoSO₄ found	Co found	Error
G.	G.	G.	Mg.
0.0235	0.0624	0.0237	+0.2
0.0257	0.0681	0.0259	+0.2
0.0137	0.0375	0.0143	+0.6
0.0325	0.0861	0.0327	+0.2

4. To make sure that no impurities were introduced by the reagents used, precipitation was made with the utmost care to exclude foreign substances, using specially purified materials, as described on p. 2228. After conversion to sulfate, the results (Table IV, p. 2228) show a slight error. The cobalt sulfate did not dissolve in water to give an entirely clear solution.

5. Ignition in a current of oxygen to oxide and then in a current of hydrogen to metal was tried, but it was impossible to obtain cobalt with a metallic luster. In 4 experiments the errors varied from +0.7 to +3.1 mg.

Determination of Cobalt as Pyrophosphate

The precipitation of cobalt as double ammonium phosphate has been

used by several investigators,[4] some of whom recognized that it gave rather erratic results. Precipitation is never complete and the cobalt in the filtrate must be recovered by precipitation as sulfide.

Fourteen experiments were made to test the accuracy of this method. The results were invariably too high, the error varying from 0.5 mg. to 4.2 mg. The filtrate and washings contained from 0.3 mg. to 2.9 mg. of cobalt. The method was as follows.

The cobalt solution was made neutral to litmus paper and 10 g. of di-ammonium hydrogen orthophosphate dissolved in 100 cc. of water was at first added drop by drop to the boiling solution, which contained 1 g. of ammonium chloride. The volume of the solution during precipitation was about 300 cc. Some solutions after cooling were filtered at once, some after standing for 2 hours and some after standing overnight. The character or solubility of the precipitate was not influenced by any of these modifications. The precipitate was filtered on a Gooch crucible, washed 20 times with a 1% solution of the ammonium phosphate, 10 times with cold water, and ignited at the full heat of the Meker burner to cobalt pyrophosphate, $Co_2P_2O_7$. The cobalt in the filtrate was precipitated as sulfide from an ammoniacal solution and ignited to oxide.

It is possible that the addition of less ammonium phosphate or some other change in the conditions of precipitation would have given better results; but the method must always be subject to the error due to solubility.

Summary

1. Although pure cobalt nitrate can be accurately ignited to the oxide, Co_3O_4, and the latter reduced by hydrogen to metal, the oxide obtained by ignition of the phenyl-thiohydantoic acid precipitate contains a little sulfate. If the oxide is empirically assumed to be Co_2O_3, the results are fairly good.

2. Ignition of cobalt sulfate at 550° is the most accurate method for cobalt. When applied to the phenyl-thiohydantoic acid precipitate the results are usually slightly high and the sulfate is not completely soluble in water.

3. The electrolytic determination of cobalt is very satisfactory when the proper conditions and precautions are observed.

4. Precipitation as cobalt ammonium phosphate followed by ignition to pyrophosphate is less accurate than the preceding methods.

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[4] Dirvell, Chem. News, **40**, 268 (1880). Clarke, ibid., **48**, 262 (1884). Hope, J. Soc. Chem. Ind., **9**, 375 (1890). Dakin, Z. anal. Chem., **39**, 784 (1900). Dufty, J. Iron Steel Inst., **90**, 52 (1914).