[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

DINITROSO-RESORCINOL AS A REAGENT FOR THE QUANTITATIVE DETERMINATION OF COBALT IN THE PRESENCE OF NICKEL AND OTHER METALS OF THE IRON GROUP[1]

BY W. R. ORNDORFF AND M. L. NICHOLS

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There is at present no simple and accurate method available for the determination of cobalt in the presence of other metals of the iron group unless it is the use of phenyl-thiohydantoic acid.[2] Many methods have been recommended for the determination of cobalt including gravimetric, electrolytic, volumetric and colorimetric methods. Of these the gravimetric and electrolytic methods are the most often used. For the gravimetric determination of cobalt the best two methods are the use of α-nitroso-β-naphthol as proposed by Illinski and Knorre[3] and the ignition of cobalt sulfate proposed by Gauhe.[4] The electrolytic method also gives excellent results according to the modification of Lundell and Hoffman.[5]

Experimental Part

The dinitroso-resorcinol used in this investigation was that described in another article.[6] All nitrogen determinations were made by the Kjeldahl method by first reducing the compound with zinc dust and dil. sulfuric acid. The determinations of cobalt by the electrolytic, α-nitroso-β-naphthol and the cobalt sulfate methods were made according to the directions given in the previous references. The buret used had been calibrated by the Bureau of Standards. The values used for the atomic weights are those given in the 1922 International Table of Atomic Weights.[7]

Method of Precipitation.—A solution of cobalt chloride or sulfate containing approximately 0.03 g. of the crystallized salt was diluted to 50 cc. and 1 cc. of hydrochloric acid, d. 1.17, was added.[8] This was warmed and 300 cc. of a hot aqueous solution of dinitroso-resorcinol, 1 g. per liter, was added. This caused the formation of a deep red color but no precipitate. Then while the mixture was stirred, 10 cc. of a solution of sodium

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[1] From a dissertation presented by M. L. Nichols in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Willard and Hall, THIS JOURNAL, **44**, 2219 (1922).

[3] Illinski and Knorre, *Ber.*, **18**, 699 (1885); *Z. anal. Chem.*, **24**, 595 (1885).

[4] Gauhe, *Z. anal. Chem.*, **4**, 55 (1865).

[5] Lundell and Hoffman, *J. Ind. Eng. Chem.*, **13**, 540 (1921).

[6] Orndorff and Nichols, THIS JOURNAL, **45**, 1536 (1923).

[7] *Ibid.*, **44**, 427 (1922).

[8] The addition of 1 cc. of HCl with the subsequent addition of sodium acetate gave a flocculent precipitate. If more than this amount of HCl is added the precipitation is prevented and only a deep red solution results. In the latter case precipitation is brought about by the addition of a large quantity of sodium acetate but the precipitate is not satisfactory.

acetate (10 g. of $NaC_2H_3O_2.3H_2O$ in 100 cc. of water) was added slowly. This caused the formation of a colloidal precipitate. The solution was then digested over a low flame for 15 minutes and stirred once after 5 minutes. This gave a voluminous brownish-red precipitate which settled readily on standing for a short time, leaving a clear reddish-yellow supernatant liquid.

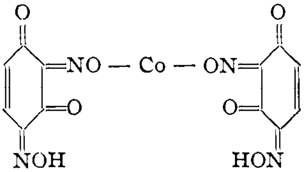
Composition of the Precipitate.—As the moisture content of the air-dried cobalt precipitate varied considerably, some of the material was dried to constant weight at 105° in an atmosphere of carbon dioxide, using an electrically-heated drying tube.[6] This dried precipitate was analyzed for nitrogen and cobalt and the following results were obtained.

Nitrogen: Subs., 0.6614, 0.0918: 66.95, 9.28 cc. of 0.1 N H_2SO_4. Calc. for $(C_6H_3N_2O_4)_2Co$: N, 14.26. Found: 14.18, 14.16.

Cobalt as $CoSO_4$: Subs., 0.2178, 0.1532: $CoSO_4$, 0.0860, 0.0605. Calc. for $(C_6H_3N_2O_4)_2Co$: Co, 15.00. Found: 15.02, 15.02.

Cobalt electrolytically: Subs., 0.1535, 0.1889: cobalt, 0.0230, 0.0284. Calc. for $(C_6H_3N_2O_4)_2Co$: Co, 15.00. Found: 14.98, 15.03.

These results show that the formula of the dried cobalt salt is $(C_6H_3N_2O_4)_2Co$ or structurally



The decomposition point of the cobalt salt was found to be 160° to 161°.

Preparation of Standard Solutions.—In order to determine whether this method of precipitation of cobalt would give accurate quantitative results, standard solutions of cobalt chloride and cobalt sulfate were prepared. Imported crystallized salts, free from nickel, were standardized by determining the cobalt in each by the electrolytic, cobalt sulfate and α-nitroso-β-naphthol methods. The cobalt chloride solution was found to contain 0.000434 g. of cobalt per cc. and the cobalt sulfate solution 0.000400 g. of cobalt per cc.

Analysis of the Cobalt Solutions with Dinitroso-resorcinol.—The cobalt solutions[9] were analyzed for cobalt by precipitation with dinitroso-resorcinol. The precipitation was carried out exactly as described on the preceding page. After the precipitate had settled, the solutions were filtered through a Gooch crucible which had been previously dried at 125° to 130° and weighed. In filtering the precipitate, care must be taken to use gentle suction at first or some of the precipitate will be drawn through the Gooch crucible. The precipitate was washed with 0.5 to 1% hy-

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[9] A quantity of cobalt that will give a precipitate of not over 0.15 g. should be used. The precipitate is so bulky that more than this amount is very difficult to handle.

drochloric acid until the filtrate was colorless and then dried at 125° to 130° to constant weight and weighed. It was found that 2 hours' drying was generally sufficient.

TABLE I

ANALYSIS OF STANDARD SOLUTIONS

	Cobalt chloride				Cobalt chloride		
Co taken G.	Precipitate G.	Co found G.	Error Mg.	Co taken G.	Precipitate G.	Co found G.	Error Mg.
0.0022	0.0134	0.0020	−0.2	0.0217	0.1463	0.0219	+0.2
.0022	.0140	.0021	− .1	.0217	.1446	.0217	0.2
.0022	.0138	.0021	− .1	.0217	.1431	.0215	− .2
.0065	.0435	.0065	.0	.0217	.0146	.0219	+ .2
.0065	.0431	.0065	.0		Cobalt sulfate		
.0108	.0721	.0108	.0	.0020	.0141	.0021	+ .1
.0108	.0713	.0107	− .1	.0040	.0254	.0038	− .2
.0108	.0721	.0108	.0	.0040	.0257	.0039	− .1
.0108	.0725	.0109	+ .1	.0200	.1350	.0203	+ .3
.0108	.0725	.0109	+ .1	.0200	.1345	.0202	+ .2

Determination of Cobalt in the Presence of Nickel.—When a solution of nickel sulfate or chloride, free from cobalt, containing 0.06 g. of nickel was treated with an aqueous solution of dinitroso-resorcinol, as in the precipitation of cobalt a green solution resulted but no precipitate was formed. The determination of the cobalt in 50 cc. of the standard solutions in the presence of 0.06 g. of nickel was then tried by the previous method. Under these conditions some of the nickel was carried down with the voluminous cobalt precipitate, giving a high result.

However, the cobalt can be determined quantitatively in the presence of small amounts of nickel in the following manner. The cobalt was precipitated in exactly the same manner as previously described. After the precipitate had settled out the clear supernatant liquid was decanted through a Gooch crucible which had been previously dried at 125° to 130° and weighed. A very small amount of the precipitate collected on the Gooch crucible. This was washed with 50 cc. of 0.085 *N* hydrochloric acid. This same acid was then transferred from the suction flask to the beaker containing the precipitate and it was digested over a low flame

TABLE II

DETERMINATION OF COBALT IN THE PRESENCE OF 0.06 GRAMS OF NICKEL

Using cobalt chloride solution				Using cobalt sulfate solution			
Co taken G.	Precipitate G.	Co found G.	Error Mg.	Co taken G.	Precipitate G.	Co found G.	Error Mg.
0.0043	0.0294	0.0044	+0.1	0.0020	0.0141	0.0021	+0.1
.0217	.1432	.0215	− .2	.0040	.0268	.0040	.0
.0217	.1440	.0216	− .1	.0200	.1316	.0197	− .3
.0217	.1444	.0217	.0	.0200	.1338	.0201	+ .1
.0217[a]	.1427	.0214	− .3	.0200	.1332	.0200	.0
....	....	....	...	.0200[a]	.1316	.0197	− .3
....	....	....	...	.0200[a]	.1333	.0200	.0
....	....	....	...	.0200[a]	.1331	.0200	.0

[a] In order to ascertain whether the digestion with HCl dissolved the cobalt precipitate, no nickel was added in these determinations.

for 30 minutes. The precipitate settled out on standing for a short time, leaving a clear, yellow, supernatant liquid. It was then filtered on the same Gooch crucible, washed thoroughly with 0.5 to 1.0% hydrochloric acid, dried to constant weight at 125° to 130° and weighed.

Determination of Cobalt in the Presence of Manganese.—The addition of an aqueous solution of dinitroso-resorcinol to one of a manganese salt did not cause the formation of either a precipitate or a colored solution under the conditions of the precipitation of cobalt. However, some of the manganese might be carried down with the cobalt precipitate as in the case of nickel, so the cobalt was determined in the presence of manganese according to the previous method used for cobalt alone and also by the method used for cobalt in the presence of nickel.

TABLE III

DETERMINATION IN THE PRESENCE OF 0.15 GRAM OF MANGANESE

Method for cobalt alone				Method for cobalt in the presence of nickel			
Co taken G.	Precipitate G.	Co found G.	Error Mg	Co taken G.	Precipitate G.	Co found G.	Error Mg.
0.0200	0.1351	0.0203	+0.3	0.0200	0.1347	0.0202	+0.2
.0217	.1445	.0217	.0	.0217	.1442	.0216	− .1

These results show that no modification in the method for the determination of cobalt by precipitation with dinitroso-resorcinol is necessary when manganese is present, as it remains completely in solution.

Determination of Cobalt in the Presence of Zinc.—Since the zinc salt also gave no precipitate or colored solution with an aqueous solution of dinitroso-resorcinol, the cobalt was determined in the presence of zinc by the method given for the determination of cobalt alone.

TABLE IV

DETERMINATION OF COBALT IN THE PRESENCE OF 0.15 GRAM OF ZINC

Co taken G.	Precipitate G.	Co found G.	Error Mg.
0.0200	0.1350	0.0203	+0.3
.0200	.1344	.0202	+ .2

These results show that also in the case when zinc is present, no modification of the method is necessary.

Determination of Cobalt when Copper is Present.—When a solution of a copper salt is treated with an aqueous solution of dinitroso-resorcinol a deep brownish-red solution results and the copper is precipitated to some extent. Moreover, this copper precipitate is not separated from the cobalt by digestion with hydrochloric acid, as in the case of nickel. Therefore, the copper must be removed from the solution before the cobalt is precipitated.

This determination was made in the following manner. The solution containing 0.0200 g. of cobalt and 0.06 g. of copper as cupric sulfate was acidified and the copper removed by electrolysis. The solution was neutralized with 1 : 1 ammonium hydroxide and 1 cc. of hydrochloric acid, d. 1.17, was added. The cobalt was then precipitated and determined in the manner previously described. Two analyses gave 0.1324 and 0.1348 g. of precipitate, corresponding to 0.0199 and 0.0202 g. of cobalt, with errors of —0.1 and +0.2 mg., respectively.

Determination of Cobalt when Iron is Present.—When a solution of either a ferrous or a ferric salt is treated with an aqueous solution of dinitroso-resorcinol a deep green solution results with the formation of an appreciable quantity of precipitate. This precipitate cannot be separated from the cobalt precipitate by digestion with hydrochloric acid, which makes it necessary to remove the iron before precipitation of the cobalt.

The determination was made in the following manner. Five cc. of hydrochloric acid, d. 1.17, was added to a solution of both metals as chlorides and the solution evaporated to about 25 cc. The major portion of the iron was extracted by ether[10] and the ether remaining was removed by boiling. The small amount of iron remaining in the solution was removed by precipitation with dil. ammonium hydroxide, the precipitate dissolved in hot, dil. hydrochloric acid and reprecipitated with ammonium hydroxide. The combined filtrates were evaporated to 50 cc., neutralized with dil. hydrochloric acid, and 1 cc. of hydrochloric acid, d. 1.17, was added. The cobalt was then precipitated with an aqueous solution of dinitroso-resorcinol and determined by the method described previously.

TABLE V

DETERMINATION OF COBALT AFTER REMOVAL OF ADDED IRON

0.0108 G. of cobalt and 1.0 G. of iron

Precipitate G.	Co found G.	Error Mg.	Precipitate G.	Co found G.	Error Mg.
0.0727	0.0109	+0.1	0.0719	0.0108	0.0
.0718	.0108	.0	.0715	.0107	− .1

Determination of Cobalt in Steel.—The method described in this paper was then applied to the analysis of Kinite. The steel was first analyzed for cobalt and nickel by the method given by Lundell and Hoffman[5] and the following results were obtained.

Subs., 1.0095, 1.0103: Co and Ni, 0.0354, 0.0370; Ni dimethylglyoxime salt, 0.0239, 0.0249. Found: Co, 3.03, 3.16; Ni, 0.48, 0.50.

Some of the same steel was also analyzed for cobalt by precipitation with dinitroso-resorcinol. The procedure described by Lundell and Hoffman was followed until all of the iron was removed. The solution was evaporated to 100 cc. and acidified with 2 cc. of hydrochloric acid, d. 1.17. The cobalt was then precipitated and determined by the previous method for the determination of cobalt in the presence of nickel. It was found

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[10] Rothe, *Mitt. kgl. Tech. Versuchsanstalt Berlin,* **1892**, part III. Hall and Williams, "Examination of Iron, Steel and Brass," **1921**, p. 71.

that in the presence of such a large quantity of ammonium salts the cobalt precipitate formed immediately unless 2 cc. of acid was added. The following results were obtained.

TABLE VI

DETERMINATION OF COBALT IN KINITE

Sample G.	Precipitate G.	Cobalt %
0.5392	.1077	3.00
.5932	.1245	3.15
.5091	.1069	3.15

This steel[11] has been analyzed by many companies and the results vary for cobalt from 3.12 to 3.49 and for nickel from 0.41 to 0.61 with an average for cobalt of 3.23% and for nickel of 0.52%.

Determination of Cobalt in Nickel.—The method for the determination of cobalt in the presence of nickel when applied to the analysis of shot nickel or a United States 5-cent coin did not give satisfactory results. In the presence of such large quantities of nickel, the nickel is partially precipitated by the dinitroso-resorcinol and it is impossible to separate the nickel from the cobalt precipitate. Several methods for the removal of the nickel were tried but none of them gave satisfactory results.

Summary

1. When an aqueous solution of dinitroso-resorcinol is added to a solution of cobalt sulfate or chloride a precipitate is formed, which in the dry condition has the composition $(C_6H_3N_2O_4)_2Co$.

2. The conditions for the quantitative precipitation of cobalt with dinitroso-resorcinol have been carefully determined.

3. The cobalt precipitate decomposes at 160° to 161°.

4. The precipitate can be filtered on a Gooch crucible, dried to constant weight at 125° to 130°, weighed and the amount of cobalt calculated from the above formula.

5. The conditions for the quantitative determination of cobalt in the presence of small amounts of nickel have been determined.

6. Manganese and zinc do not interfere in this determination.

7. Copper and iron interfere in this determination and must be removed from the solution before the cobalt is precipitated.

8. This method is not applicable in the presence of large quantities of nickel.

ITHACA, NEW YORK

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[11] Personal communication from L. L. Tatum, manager of the Kinite Company.