RP445

A METHOD FOR THE DETERMINATION OF COBALT IN MAGNET AND HIGH-SPEED TOOL STEELS

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ABSTRACT

A method for the accurate determination of cobalt in steel is described. Most of the iron is removed by extraction with ether; chromium, vanadium, etc., are eliminated by precipitation with sodium hydroxide and peroxide; the iron still remaining and the copper are precipitated by cupferron in a dilute hydrochloric-acid solution, and the cobalt is precipitated in the filtrate by α-nitroso-β-naphthol. Cupferron does not interfere in the precipitation of cobalt by α-nitroso-β-naphthol, and a method of testing the latter reagent is given. Quantitative data are presented which show the amount of cobalt that remains with the iron in an ether extraction and in a precipitation of iron by cupferron. Copper, chromium, vanadium, and tungsten are incompletely precipitated by α-nitroso-β-naphthol. With the exception of a small part of the copper all of these are removed in the preliminary separations, and a method for the elimination of the slight interference of copper is given.

CONTENTS

I. INTRODUCTION

In 1921 the author in collaboration with Dr. G. E. F. Lundell published a method for umpire determinations of cobalt and nickel in cobalt steels.[1] Briefly stated, the following steps are involved: (1) Dissolving the sample in hydrochloric acid and oxidizing tungsten and iron by means of nitric acid; (2) removing tungstic acid and recovering any cobalt in it; (3) separating most of the iron by means of ether; (4) separating chromium and vanadium by oxidizing with potassium persulphate, twice precipitating iron, cobalt, nickel, etc., with sodium hydroxide, and filtering; (5) dissolving the precipitate, and eliminating copper by precipitation with hydrogen sulphide; (6) after expelling hydrogen sulphide from the filtrate, removing the iron which still remains, by twice precipitating it with ammonium hydroxide and filtering; (7) determining nickel and cobalt in the

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[1] J. Ind. Eng. Chem., vol. 13, p. 540, 1921.

filtrate by electrolysis; (8) recovering the samll amount of cobalt which always remains in the electrolyte; and (9) separating nickel from cobalt by the use of dimethylglyoxime or α-nitroso-β-naphthol.

This method gives accurate results if properly applied, but it obviously requires too much time for use in the average laboratory excepting for standardization. Other methods, for example, those involving the basic acetate separation for the removal of iron and subsequent precipitation of nickel and cobalt by ammonuim sulphide, are equally time consuming and usually less accurate. The cyanide method is applicable in special cases but is usually employed only in routine work.

During an investigation of the zinc-oxide method for separating cobalt from iron and certain other constituents of steel,[2] it was found necessary to separate a few tenths of a milligram of cobalt from 1 to 2 g of iron. This was accomplished by extracting most of the iron with ether and then precipitating the remainder of the iron in the acid extract by the use of cupferron, which does not precipitate cobalt. Without destroying the excess of cupferron, the cobalt was precipitated in the filtrate by α-nitroso-β-naphthol and determined by igniting to the oxide, reducing in hydrogen, and weighing as the metal. This forms the basis of the following method, in which it is necessary to remove iron, copper, molybdenum, chromium, zirconium, titanium, vanadium, tin, and tungsten because these are precipitated either wholly or in part by α-nitroso-β-naphthol. (See Sec. III, 3 (c).)

II. METHOD FOR THE DETERMINATION OF COBALT

Transfer 1.000 g of sample to a 400 ml beaker, cover, add 20 ml of diluted hydrochloric acid (2+1),[3] and heat until solution is complete. Remove the solution from the source of heat and introduce 2 to 3 ml of diluted nitric acid (1+1) without uncovering the beaker. Boil gently for two to three minutes, wash and remove the cover glass and evaporate the solution to a volume of about 5 ml. Tungsten need not be removed even if some separates as tungstic acid. Transfer to a 150 to 300 ml separatory funnel, using small portions of diluted hydrochloric acid (1+1) to wash the beaker. The volume of the solution in the separatory funnel should not exceed 30 to 35 ml. Cool to about 5° C., add 50 ml of ether, stopper the funnel, and shake gently for one minute. Let stand in cold water for two to three minutes, and draw off the acid layer into another separatory funnel. Add 10 ml of diluted hydrochloric acid (1+1) to the ether extract remaining in the separatory funnel, stopper, and shake thoroughly. Allow to stand for two to three minutes, and drain the acid extract into the other separatory funnel. Add 50 ml of ether to the combined acid extracts in the second funnel, and repeat the extraction with ether and acid as before.

Allow the acid extracts to run into the original beaker, warm (gently and not over a free flame) to expel the ether, and then evaporate nearly to dryness. Add 15 ml of diluted nitric acid (2+1) and evaporate just to dryness. Add 50 ml of diluted hydrochloric acid (5+95) and heat until the salts are dissolved. If the material contains over

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[2] B. S. Jour. Research, vol. 7, p. 883, 1931.

[3] This denotes 2 volumes of hydrochloric acid, specific gravity 1.18, mixed with 1 volume of water. This system of designating diluted acids is used throughout this paper. If no dilution is specified, the concentrated reagent is intended.

10 per cent of cobalt, transfer the solution to a volumetric flask, and take an aliquot portion representing approximately 0.1 g of cobalt.[4] Pour the solution into 150 ml of a 5 per cent solution of sodium hydroxide to which has been added about 2 g of sodium peroxide. Dissolve any tungstic acid that may stick to the beaker in a few drops of the solution of sodium hydroxide and add it to the main solution. Set the beaker on the steam bath and digest for one-half to one hour to destroy the excess of peroxide. Allow to cool, filter through an 11 cm S. & S. blue band or a Whatman No. 42 paper, and wash thoroughly with hot water.

Transfer the paper and precipitate from the funnel to the original beaker, and add 15 ml of diluted hydrochloric acid (2+1). Heat on the steam bath until the precipitate is in solution, stir the paper to a pulp, and add 150 ml of water. Neutralize the hydrochloric acid with ammonium hydroxide, using litmus as indicator, and then add 5 ml of hydrochloric acid. Stir thoroughly and cool to about 10° C. Add a cold 6 per cent water solution of cupferron slowly and with stirring until no further precipitation takes place. An excess of reagent is indicated by the formation of a temporary flash of a fine white precipitate of cupferron which redissolves, as contrasted with the flocculent and insoluble precipitate of the compound of cupferron with the metals. In all of the experiments described in this paper 10 ml of the 6 per cent solution of cupferron was added and found to be sufficient. Allow the precipitate to settle for 10 minutes, then filter through an 11 cm S. & S. blue band or a Whatman No. 42 paper, and wash thoroughly with cold cupferron wash solution.[5] Between 150 and 200 ml of wash solution should ordinarily be used. If more than 0.03 g of cobalt is present, wash the beaker and precipitate five times with cupferron wash solution and reserve the filtrate. Tranfer the paper and precipitate to a 200 ml Erlenmeyer flask, and add 50 ml of cupferron wash solution. Shake the paper to a pulp, filter, catch the filtrate in a separate beaker, and wash thoroughly with cupferron wash solution. This filtrate is caught in a separate beaker because occasionally the first portion is cloudy and must again be poured on the paper.

To the filtrate and washings in a volume of about 400 ml add 15 ml of hydrochloric acid and then one and one-half times as much α-nitroso-β-naphthol[6] as is required to precipitate the cobalt. Never add less than 10 ml. Heat to 60° to 70° C. by digesting on the steam bath for 20 minutes (no longer). Remove from the source of heat, allow to stand about 15 minutes, filter through a No. 589 white band or a No. 40 Whatman paper, and wash with hot diluted hydrochloric acid (1+3) and then with hot water. Transfer the wet paper and precipitate to a porcelain crucible (15 ml capacity for less than 0.05 g of cobalt and 30 ml capacity for larger amounts), heat gently at first, preferably in a muffle furnace, then ignite to constant weight at 750° to 850° C.[7] Weigh as Co_3O_4 which contains

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[4] The flask should be well shaken just before withdrawing the aliquot portion so that approximately the proper proportion of tungstic acid is sucked into the pipette. About 0.1 g of cobalt is all that can be conveniently handled. This constitutes a weakness in the method when applied to materials containing high percentages of cobalt. For example, in the analysis of a steel containing 40 per cent of cobalt, a one-fourth aliquot portion, representing 0.25 g of sample, would be taken. Thus, an error of 0.1 mg in the weight of cobalt found would result in an error of 0.04 per cent. (See results Nos. 11 and 21 in Table 1.)

[5] Prepared by adding 20 ml of a 6 per cent water solution of cupferron to 1 liter of cold diluted hydrochloric acid (1+99).

[6] Prepared by dissolving 1 g of the dry reagent in 15 ml of glacial acetic acid and filtering. For the testing of the reagent, see Sec. III, 3 (*b*).

[7] See Sec. III, 3 (*d*).

73.4 per cent of cobalt. In all accurate work in which more than 0.01 g of cobalt is involved, the oxide must be reduced in hydrogen, cooled in an atmosphere of hydrogen, and the cobalt weighed as metal.

If more than 0.1 per cent of copper was present in the original material, the cobalt metal may contain a few tenths of a milligram of copper. To correct for this contamination, dissolve the cobalt metal in hydrochloric acid, dilute the solution so that it contains about 2 ml of hydrochloric acid per 100 ml, and treat with hydrogen sulphide. Filter, wash, and ignite the sulphide in a porcelain crucible. Dissolve the copper oxide in nitric acid, add an excess of ammonium hydroxide, and estimate the amount of copper colorimetrically. The standard and test solutions should be compared as nearly as possible under the same conditions, especially with respect to the concentration of ammonium hydroxide.

Results obtained by this method for the determination of cobalt are illustrated in Table 1.

TABLE 1.—*Results for cobalt obtained by the cupferron-α-nitroso-β-naphthol method*

Analysis No.	Material analyzed		Cobalt found		Error based on result obtained by ignition in H_2	Error based on result obtained by ignition in H_2 and assuming that exactly 1 g of sample was taken
	Bureau of Standards standard steels+copper	Cobalt added	Weighed as Co_3O_4	Weighed as metal		
		g	*g*	*g*	*g*	*Per cent*
1	1 g No. 50a	0.0005	0.0007			
2	do	.0483	.0481	0.0483	0.0000	0.00
3	do	.0528	.0521	.0525	−.0003	−.03
4	do	.1056	.1048	.1059	+.0003	+.03
5	do	.2640	.2640	.2648	+.0008	+.08
6	do	.2640	.2632	.2640	.0000	.00
7	do	.4226	.4216	.4228	+.0002	+.02
8	1 g No. 10d	.1056		.1054	−.0002	−.02
9	0.65 g No. 10d	.3698	.3680	.3700	+.0002	+.02
10	do	.3698	.3684	.3700	+.0002	+.02
11	do	.3698		.3688	−.0010	−.10
12	1 g No. 50a+0.005 g Cu	.0019	.0020			
13	do	.0097	.0098			
14	do	.0097	.0099			
15	do	.0483	.0479	.0483	.0000	.00
16	do	.0528	.0526	.0530	+.0002	+.02
17	do	.1322	.1322	.1326	+.0004	+.04
18	0.3 g No. 50a+0.3 g No. 73	.4226		.4224	−.0002	−.02
19	1 g No. 73+0.005 g Cu	.0097	.0098			
20	do	.0483	.0484	.0485	+.0002	+.02
21	0.3 g No. 50a+0.3 g No. 73+0.005 g Cu	.3960		.3948	−.0012	−.12
22	do	.3960		.3956	−.0004	−.04
23	do	.3960	.3936	.3960	.0000	.00
24	0.3 g No. 50a+0.3 g No. 73+0.01 g Cu	.4226		.4228	+.0002	+.02
25	do	.3698		.3692	−.0006	−.06

In analyses 5, 6, 7, 9, 10, 18, 21, 22, 23, 24, and 25 a one-fourth aliquot portion was taken for the determination. The numbers of the materials given in the second column of the table refer to Bureau of Standards standard samples which have the following percentage compositions:

No. 50a.—C, 0.66; Mn, 0.29; P, 0.02; S, 0.007; Si, 0.48; W, 18.25; Cr, 3.52; V, 0.97; Cu, 0.047; Ni, 0.045; Co, none found.

No. 10d.—C, 0.42; Mn, 0.92; P, 0.088; S, 0.03; Si, 0.063; Cu, 0.01; Ni, 0.002; Cr, 0.006; V, 0.006; Co, none found.

No. 73.—C, 0.31; Mn, 0.28; P, 0.023; S, 0.03; Si, 0.36; Cu, 0.033; Ni, 0.07; Cr, 13.9; V, 0.034; Co, none found.

The cobalt was added in the form of a solution of cobalt sulphate which was transferred to a beaker and evaporated to dryness before the steel chips were added and dissolved. The solution of cobalt sulphate is prepared and standardized as follows:

Dissolve 100 g of cobalt sulphate, $CoSO_4 \cdot 7H_2O$, in 1,500 ml of diluted hydrochloric acid (1+14), and add 250 g of potassium nitrite, KNO_2, dissolved in 500 ml of water. Allow to stand for 10 to 15 minutes, and then add 100 g more of potassium nitrite. After the precipitate has settled, decant the supernatant liquid, and transfer the potassium cobaltinitrite, $2K_3Co(NO_2)_6 \cdot 3H_2O$, to a large filter, and wash a few times with water. Transfer the potassium cobaltinitrite from the filter to the beaker in which the precipitation is made, and add 1,500 ml of diluted hydrochloric acid (1+9). Stir vigorously as the solution is heated to boiling. When the salt is dissolved, cool the solution, add 250 g of potassium nitrite dissolved in 400 ml of water and then add 200 g of potassium acetate, $KC_2H_3O_2$, dissolved in 250 ml of water. Allow the precipitate to settle, filter and wash as before. Transfer the precipitate of potassium cobaltinitrite to the beaker in which the precipitation is made, add 100 ml of diluted sulphuric acid (1+1), heat until the salt is dissolved, dilute to 2,000 ml, and treat with hydrogen sulphide. Allow to stand for four hours and filter. Add 50 ml of sulphuric acid to the filtrate, and evaporate it to a volume of about 200 ml. Add 25 ml of nitric acid, and heat until fumes of sulphuric acid are given off. Cool, dilute to 1 liter, and determine the approximate amount of cobalt in a 5 ml portion of the solution to ascertain the volume of water to be added to obtain a solution of the desired concentration. For this purpose the cobalt may be determined by precipitating it with α-nitroso-β-naphthol and igniting to the oxide, "Co_3O_4."

By following the above directions a liter of solution was obtained which was shown to contain 15.7 g of cobalt. This was diluted to 3 liters, giving a solution with a cobalt content of approximately 5 mg per milliliter. By a special test using formaldehyde and dimethylglyoxime[8] the solution was found to be free from nickel. Iron, chromium, and vanadium were also shown to be absent.

The solution was standardized (1) by electrolysis and (2) by precipitating the cobalt by α-nitroso-β-naphthol, igniting to oxide, reducing and cooling in hydrogen, and weighing as metal. By electrolysis 0.005283 g of cobalt per milliliter was obtained and by ignition in hydrogen 0.005288 g. In computing the results in Table 1 the value obtained by electrolysis was used. In the electrolysis the directions given by Lundell, Hoffman, and Bright, page 335, were followed. The cobalt remaining in the electrolyte was recovered, and correction was made for sulphur which contaminated the deposit.

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[8] See F. Feigl and H. J. Kapulitzas, Z. anal. Chem., vol. 82, p. 417, 1930, or G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 279. J. Wiley & Sons, New York, 1931.

III. DISCUSSION OF THE METHOD

1. EXTRACTION OF THE IRON WITH ETHER

The conditions given for the preparation of the solution for the extraction of most of the iron with ether are not so rigorous as those usually prescribed, but the separation is sufficiently complete for the purpose. The iron which remained in the acid extract when 1 g samples were used was determined in six cases and was found to average 1.1 mg per determination, with extreme values of 0.7 and 1.8 mg. By making only a single extraction with ether and acid in two similar determinations 6.6 and 7.0 mg of iron, respectively, were found in the acid extracts. In the case of steels containing tungsten it is not necessary to remove the tungstic acid, as this settles into the acid layer or remains in the beaker in which the steel was dissolved. In the subsequent precipitation by sodium hydroxide and sodium peroxide the tungstic acid is dissolved, and any cobalt retained by it is recovered without necessitating a separate operation.[9] Because of the retention of iron by tungstic acid, the iron content of the acid extract is usually slightly higher when tungsten is present than when it is absent.

In the analysis of magnet steels it may be necessary to extract the iron from solutions containing as much as 0.4 g of cobalt. It seemed advisable, therefore, to ascertain whether any cobalt is retained in the ether extract when a double extraction is made as described in the method. The ether extracts obtained in analysis No. 9 in Table 1 were combined, and the ether removed by evaporation. (In this analysis 0.65 g of iron had been separated from 0.37 g of cobalt.) Any reduced iron was oxidized by digestion with a little nitric acid. The iron was then precipitated by cupferron in a volume of 400 ml containing 20 ml of hydrochloric acid. The precipitate was removed by filtration on a large paper and the cobalt determined in the filtrate by precipitating it with α-nitroso-β-naphthol and igniting to oxide. An amount of cobalt estimated to be less than 0.3 mg was found. In a similar way the ether extract obtained in analysis No. 8 was found to contain approximately 0.1 mg of cobalt. To determine the efficacy of this method of separating such a small quantity of cobalt from such a large quantity of iron, 0.3 mg of cobalt was added to 0.6 g of iron and the latter precipitated by cupferron. A determination of cobalt in the filtrate showed between 0.2 and 0.3 mg. If much cobalt is present, more of it will be retained by the iron in the cupferron precipitate. (See Sec. III, 2.)

2. PRECIPITATION WITH CUPFERRON

Cupferron does not interfere in the precipitation of cobalt by α-nitroso-β-naphthol and is therefore a convenient reagent for removing iron and copper previous to the precipitation of cobalt. Iron is completely precipitated in solutions containing as much as 10 ml of hydrochloric acid in 100 ml, but a low concentration of acid is re-

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[9] The retention of cobalt by tungstic acid is of little consequence. A magnet steel containing 36 per cent of cobalt and 3.3 per cent of tungsten and a high-speed steel containing 7 per cent of cobalt and 18 per cent of tungsten were dissolved in hydrochloric acid, oxidized with nitric acid and the solution evaporated to dryness. The residues were digested on the steam bath for one-half hour with 50 ml of diluted hydrochloric acid (5+95) and the tungstic acid removed by filtration. After thorough washing with hot diluted hydrochloric acid (5+95), the residues of tungstic acid were examined for cobalt. Less than 0.1 mg was found in either case.

quired for complete precipitation of copper. In preliminary tests it was found that copper was completely precipitated in solutions containing 0.5 ml of hydrochloric acid in 100 ml of solution, but then a little cobalt was carried down by the iron. In two experiments, in each of which the iron was precipitated by adding 10 ml of a 6 per cent water solution of cupferron to 200 ml of solution containing 2 mg of iron, 0.1 g of cobalt, 5 mg of copper and 5 ml of hydrochloric acid, less than 0.1 mg of cobalt was found in each precipitate, and 0.5 and 0.6 mg of copper in the respective filtrates. The cupferron precipitates obtained in analyses Nos. 4, 5, 6, 8, 9, and 18 of Table 1, were combined, ignited in porcelain, and dissolved in hydrochloric acid. Most of the iron was extracted with ether, and the cobalt and small quantity of iron (less than 1 mg) in the acid extract were precipitated by ammonium sulphide after the ether was removed. The sulphides were caught on a small paper, ignited, and the iron and cobalt weighed as Fe_2O_3 and Co_3O_4. The oxides were dissolved in hydrochloric acid, and the iron was precipitated with ammonium hydroxide. After filtering and washing, the iron hydroxide was dissolved in hydrochloric acid and the precipitation and filtration repeated. The precipitate was ignited, and the weight of Fe_2O_3 was subtracted from the combined $Fe_2O_3 + Co_3O_4$ previously obtained. The results showed that about 0.1 mg of cobalt was retained in each cupferron precipitate. In two similar tests in which 0.15 g of iron was precipitated by cupferron in the presence of 0.1 g of cobalt, the precipitates of iron were found to contain 0.4 and 1 mg of cobalt, respectively.

3. PRECIPITATION WITH α-NITROSO-β-NAPHTHOL, AND IGNITION OF THE PRECIPITATE

(a) GENERAL DISCUSSION

If precipitations by α-nitroso-β-naphthol are made in solutions containing cupferron, the solution should not be heated for more than 15 to 20 minutes nor at temperatures above 70° C. In almost all cases the filtrate becomes cloudy even though all of the cobalt has been precipitated. This is unfortunate because it makes it impossible to tell whether precipitation is complete unless the solution is filtered a second time and the precipitate ignited. If the specified amount of reagent has been added and the filtrate is clear when it passes through the funnel stem, no cobalt will be found in the filtrate. On standing, some of the reagent in the filtrate usually separates and adheres to the beaker. This deposit can be loosened by the continued action of hot water or by digestion with alkaline solutions.

(b) TESTING THE REAGENT

Various directions for the preparation of the solution of the reagent are given, but the solution most commonly used in this type of work is one prepared by dissolving 1 g of α-nitroso-β-naphthol in 15 ml of glacial acetic acid. For every 0.01 g of cobalt present 6 ml of the reagent is usually specified. If these directions are followed in the case of determinations involving 0.1 g of cobalt, such a large excess of reagent is added that it separates with the cobalt precipitate and makes it almost impossible to complete the ignition without loss by frothing. On the other hand, the reagent may have deteriorated to such an extent that an insufficient amount is added. The quality of the reagent should be determined by the analyst, and a freshly prepared solution should always be used.

In this work three lots of the reagent were tested for their precipitating power as follows: Dissolve 1 g of reagent in 15 ml of glacial acetic acid, and add to it slowly and with vigorous stirring 300 ml of diluted hydrochloric acid (5+95) containing 0.25 g of cobalt. Digest, filter, wash, ignite, and weigh as described in the method for steels. One very old lot of reagent precipitated 0.048 g of cobalt, and two relatively new ones precipitated 0.068 g and 0.077 g, respectively. Theoretically 1 g should precipitate approximately 0.1 g of cobalt. Experimentally it was found that only a small excess of reagent is necessary for complete precipitation of the cobalt, and in the analysis of the steels listed in Table 1 the following procedure was adopted: First determine the precipitating power of the reagent in the manner just described, and then add one and one-half times as much as is required by the cobalt that is likely to be present. Never add less than 10 ml. In most of the work in this paper a reagent was used which precipitated 0.068 g of cobalt per gram. Approximately 35 ml of the prepared solution (1 g of reagent per 15 ml of glacial acetic acid) was thus used for 0.1 g of cobalt.

(c) INTERFERING SUBSTANCES

It is known that iron, copper, molybdenum, chromium, zirconium, titanium, vanadium, tin, and tungsten are also precipitated by α-nitroso-β-naphthol. Of these elements, all but small quantities of copper and possibly chromium are removed by the extraction with ether, by the precipitation with sodium hydroxide and sodium peroxide, or by the precipitation with cupferron. Copper, tungsten, chromium, vanadium, and molybdenum are only partially precipitated by α-nitroso-β-naphthol. Tests in which an excess of this reagent was added to a solution containing 5 ml of hydrochloric acid and 5 mg each of vanadium, tungsten, and molybdenum in 100 ml indicated that at least one-half of the vanadium, tungsten, and molybdenum passed into the filtrate. By precipitating 0.1 g of cobalt by the method outlined for steels and examining the precipitate of cobalt, 0.3 mg of copper was found in it when 1 mg of copper was present in the solution during the precipitation and 1.7 mg when 5 mg of copper was present. The final residues in analyses Nos. 15 to 25 in Table 1 were also examined for copper, and in no case was more than 0.2 mg found. This shows that interference by copper is not serious, but in very accurate work, copper in the weighed cobalt metal should be determined as described in the method. Similar tests with trivalent chromium showed that 0.4, 1.5 and 3.6 mg of chromium, respectively, were contained in the cobalt precipitates when 1.7, 9.0 and 43.0 mg of chromium were present in the solution during the precipitation of 0.1 g of cobalt with α-nitroso-β-naphthol. Nickel is not precipitated at all when alone. If cobalt is precipitated in a solution containing nickel, a little of the latter may come down with the cobalt, but this is not serious in the usual case. For example, only 0.2 mg was found in the cobalt metal in two analyses in which 0.05 g of cobalt was precipitated in the presence of 0.03 g of nickel.

(d) IGNITION OF THE PRECIPITATE

In most of this work the wet precipitate, with the filter paper folded around it, was placed in a porcelain crucible which was then put in a cold muffle furnace. The furnace was heated to a temperature of about 750° C. in the course of two to three hours. No mechanical loss resulted, and covering the precipitate with oxalic acid to prevent volatilization of cobalt was not necessary. If the residue is to be weighed as Co_3O_4, the temperature of ignition should be held between 750° and 850° C. At temperatures above 900° C. (and even at 900° C. in the case of large amounts) the compound loses oxygen and approaches the composition CoO. By heating this oxide for one-half to one hour at 750° C. it again approaches the composition Co_3O_4. For example, a residue, which by subsequent ignition in hydrogen was shown to contain 0.1056 g of cobalt, indicated a cobalt content of 0.1053 g after igniting at 750° C. for one hour and then calculating to metal on the basis of Co_3O_4 as the composition of the oxide. The same residue, ignited at 1,000° C. for one hour, indicated 0.1020 g of cobalt by using the factor for conversion of Co_3O_4 to metal, and 0.1093 g when the factor for CoO was used. Ignition for one hour at 750° C. brought the weight back to indicate a cobalt content of 0.1053 g on the basis of Co_3O_4 as the composition of the oxide. Further ignition of this oxide for one hour at 850° C. did not cause any change in weight. In all accurate work in which more than 0.01 g of cobalt is determined the oxide should be reduced and cooled in hydrogen and the cobalt weighed as metal.

The results in Table 1 were obtained by igniting to the oxide in a muffle furnace at a temperature of 750° to 850° C., cooling, and weighing. The crucible and contents were then heated over the full heat of a Tirrill burner, and covered with a perforated quartz cover (Rose crucible cover). A slow but steady stream of hydrogen from a cylinder was introduced and the heating continued for 10 minutes. The burner was removed, the hydrogen momentarily stopped and the metal then cooled to room temperature under a stream of hydrogen. There was no evidence of any reoxidation of the metal nor any appreciable retention of hydrogen. Substituting nitrogen for hydrogen at the end of the cooling process did not affect the results. In standardizing the solution of cobalt sulphate (p. 663) the results obtained by ignition in hydrogen checked those obtained by electrolysis within 1 part in 1,000.

4. POSSIBLE SOURCES OF ERROR

1. In the analysis of materials containing 5 per cent or more of cobalt, ample time must be allowed for separation of the solution into two layers during the ether extraction, and the subsequent evaporation of the acid extract must be conducted slowly and cautiously in order to avoid loss of cobalt by spraying.
2. Very thorough washing of the precipitate obtained by cupferron is necessary to minimize retention of cobalt by the precipitate.
3. Weighing as "Co_3O_4" after ignition even under closely controlled conditions almost invariably yields slightly low results.
4. The separation of copper from cobalt by the use of cupferron is not quite perfect, and if the content of copper is high, correction should be made for copper in the final residue.
5. Blanks on the reagents should be determined. In this work steels Nos. 50a and 10d (see Table 1) were used at various times and were taken through the whole process just as if cobalt were being determined in them. A blank averaging 0.8 mg was obtained, most

of which was shown to be iron coming from the α-nitroso-β-naphthol reagent. A determination of iron in three cobalt residues and in an accompanying blank showed 0.9, 0.8, and 0.8 mg, respectively, in the cobalt residues and 0.8 mg in the blank.

IV. APPLICATION OF THE METHOD

The method serves well for the accurate determination of from a few hundredths of 1 per cent to 40 per cent of cobalt in most kinds of ferrous materials. It is especially applicable to the determination of cobalt in high-speed tool steels and in magnet steels containing as much as 40 per cent of cobalt. If the sample in which cobalt is to be determined contains more than about 0.2 g of nickel and manganese, the zinc oxide method [10] is preferable because large quantities of nickel and manganese produce bulky precipitates with sodium hydroxide and peroxide, whereas in the zinc oxide method these remain in solution and do not interfere. In ferrocobalt and cobalt metal the determination can be made more conveniently and accurately by electrolysis.

V. ACKNOWLEDGMENT

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[10] B. S. Jour. Research, vol. 7, p. 883, 1931.

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