DETERMINATION OF ALUMINUM IN NITRIDING STEELS BY THE USE OF 8-HYDROXYQUINOLINE

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ABSTRACT

A rapid method for the determination of aluminum in nitriding steels is described. The procedure consists in (*a*) separating aluminum from most of the iron by precipitating with sodium bicarbonate, (*b*) dissolving this precipitate in acid and precipitating the rest of the iron with sodium hydroxide, (*c*) treating the filtrate with 8-hydroxyquinoline to precipitate aluminum, and (*d*) either titrating with a standard solution of potassium bromate and potassium bromide after dissolving the aluminum quinolate in acid, or weighing the quinolate after drying at 135° C. The bicarbonate and sodium hydroxide precipitations and the determination of aluminum by 8-hydroxyquinoline are discussed briefly.

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I. INTRODUCTION

Practically all types of nitriding steels contain aluminum as a major alloying constituent, the amounts varying from 0.25 to 2 per cent. The "Nitralloy" type, containing 0.60 to 1.2 per cent of aluminum, 0.8 to 1.3 per cent of chromium, and 0.15 to 0.25 per cent of molybdenum, is perhaps the one most widely used. Special grades of nitriding steels may also contain 0.5 to 1.0 per cent of vanadium, 0.10 to 2.5 per cent of nickel and 7 per cent or more of chromium. The Bureau of Standards' standard sample No. 106 contains 1.06 per cent of aluminum (total), 0.017 per cent of aluminum present as Al_2O_3, 1.29 per cent of chromium and 0.16 per cent of molybdenum. At the bureau the aluminum content of the standard was found by using a slight modification of a method of analysis described by Cunningham (3).[1] In this method most of the iron is removed by the Rothé ether method, the remaining iron separated with cupferron, the filtrate boiled with nitric and perchloric acids to oxidize chromium and destroy organic matter, the aluminum precipitated twice with ammonium hydroxide and the ignited and weighed oxide corrected for impurities. This method, while very accurate, requires considerable time and hence is not suitable for rapid commercial determinations. Precipitation with 8-hydroxyquinoline (1, 4), after suitable separations, seemed to

[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

offer promise of more rapid and sufficiently accurate determinations. A method of analysis based on this principle is described in one of the following sections. The procedure consists in (*a*) separating aluminum from manganese and most of the iron and nickel by precipitating with sodium bicarbonate; (*b*) dissolving the precipitate in acid and precipitating chromium and the rest of the iron and nickel with sodium hydroxide; (*c*) precipitating aluminum in the filtrate with 8-hydroxyquinoline in a slightly ammoniacal solution containing tartrate and hydrogen peroxide, whereby aluminum is separated from molybdenum, vanadium, tin, phosphorus, and small amounts of chromium (which escaped the sodium hydroxide separation), and (*d*) either titrating with a standard solution of potassium bromate and potassium bromide after dissolving the aluminum quinolate in acid, or weighing the quinolate after drying at 135° C. By this method duplicate determinations of aluminum that are accurate to ± 0.02 per cent of the sample can be made in about three hours. Certain experimental data relating to the several separations upon which the method is based are presented before giving the detailed description of the recommended procedure.

II. DISCUSSION OF THE METHOD

1. PRECIPITATION OF ALUMINUM BY SODIUM BICARBONATE

Precipitation with bicarbonate has been used successfully in procedures for the determinations of chromium, vanadium, manganese, and small amounts of aluminum in steels (6). Its suitability for steels of relatively high aluminum content, such as aluminum bearing steels, has been somewhat in doubt because of uncertainty as to the conditions that must be established to insure complete precipitation. In the bicarbonate precipitation, it is desirable to use the minimum amount of bicarbonate, as an unnecessary excess increases the amount of iron precipitated.

The data given in Table 1 were obtained by dissolving 4 g portions of steel in dilute sulphuric acid, adding various amounts of solutions of aluminum and chromium sulphate, and then adding different quantities of an 8 per cent solution of sodium bicarbonate. The aluminum in the precipitate was determined by the Cunningham method already outlined in the introductory section. Experiments 1 and 2 demonstrate that 0.05 ml of the bicarbonate solution per 1 mg of aluminum in excess of the amount required to form a permanent precipitate is not enough for complete precipitation. The term "excess bicarbonate" is used throughout this article to denote the amount of bicarbonate added after the first permanent precipitate is obtained. Experiments 3 to 9 indicate that an excess of 0.13 to 0.18 ml of bicarbonate per 1 mg of aluminum sufficies for complete precipitation in plain steels and in chromium steels containing no more than 3 per cent of chromium. If this excess is used about 0.2 g of iron is precipitated. It should be mentioned in passing that it is desirable to filter and wash the bicarbonate precipitate as soon as it has settled. Exposure to air causes oxidation of ferrous iron and consequent precipitation of ferric hydroxide by hydrolysis. This reaction tends to lower the pH of the solution, though it is not known whether the slight increase in acidity would cause some resolution of aluminum hydroxide.

TABLE 1.—*Data on the precipitation of aluminum by sodium bicarbonate in the presence of ferrous iron*

[4 g of steel used in each experiment]

Experiment No.	Steel [1]	Other elements added	Al present or added	Aluminum found	Error	Excess $NaHCO_3$ added	
						Per mg of Al	Total
		g	*g*	*g*	*mg*	*ml*	*ml*
1	16b	----------	0.0756	0.0564	−19.2	0.05	4.0
2	16b	----------	.0756	.0526	−23.0	.05	4.0
3	16b	----------	.0756	.0746	−1.0	.11	8.5
4	16b	----------	.0756	.0756	.0	.13	10.0
5	55	----------	.0376	.0377	+.1	.16	6.0
6	16b	----------	.0378	.0382	+.4	.16	6.0
7	16b	----------	.0378	.0375	−.3	.16	6.0
8	55	----------	.0400	.0398	−.2	.18	7.0
9	55	0.120 Cr	.0400	.0404	+.4	.18	7.0
10	55	.367 Cr	.0400	.0387	−1.3	.18	7.0
11	55	.420 Cr	.0400	.0388	−1.2	.23	9.0
12	55	.550 Cr, .250 Ni	.0400	.0400	.0	.35	14.0
13	55	.550 Cr, .250 Ni	.0400	.0398	−.2	.35	14.0

[1] Percentage compositions of the steels used are as follows: 16b, basic open hearth, C=1.01, Mn=0.38, P=0.025, Si=0.08, Ni=0.003, Cr=0.007, V=0.004, Al=0.008, Sn=0.001; 55, ingot iron, C=0.013, P=0.003, Si=−0.001, Ni=0.020, Cr=0.002, Al=0.002, Sn=0.008.

With high-chromium steels a larger excess of bicarbonate is needed, for it is apparently necessary to precipitate a considerable part of the chromium before all of the aluminum is precipitated. This is in accord with the hydrolysis curves for aluminum and chromium published by H. T. S. Britton (2). Experiments 12 and 13 show that an excess of 0.35 ml of bicarbonate per 1 mg of aluminum suffices for high-chrome steels.

Nickel divides in the bicarbonate separation. With high-nickel steels about 10 per cent of nickel remains in the precipitate. In steels of low-nickel content, the percentage retained is higher. For example, with 250 mg of nickel present, the bicarbonate precipitate contained approximately 30 mg of nickel whereas with 8.5 mg about 5 mg of nickel was retained.

Experiments 4, 6, and 7 show that organic matter which may be formed when a high-carbon steel is dissolved in a nonoxidizing acid does not prevent complete precipitation of aluminum in the bicarbonate procedure.

2. SEPARATION OF ALUMINUM FROM NICKEL AND IRON BY PRECIPITATION WITH SODIUM HYDROXIDE

It has been stated that separations of aluminum are incomplete if precipitations are made with sodium hydroxide in solutions containing bivalent or trivalent nickel (5, 9). H. A. Buchheit, of the Bureau of Standards, in tests (unpublished) on the separation of 0.05 g of aluminum from 0.10 g of nickel by means of a double precipitation with sodium hydroxide, found that approximately 14 mg of aluminum was retained in the second sodium hydroxide precipitate in the case of bivalent, and 5 mg in the case of trivalent nickel. Additional tests were made by the authors to ascertain the amount

of aluminum retained in the sodium hydroxide precipitate by the small amounts of nickel present in most nitriding steels. The data obtained are given in Table 2. For these experiments faintly acid solutions (volume 150 ml) containing varying amounts of nickel, aluminum, and iron were poured slowly into 150 ml of a hot 10 per cent solution of sodium hydroxide (while stirring vigorously), boiled one minute and cooled. In experiments 1 to 6 the precipitate was filtered off and washed with a cold 1 per cent solution of sodium hydroxide. In experiments 1 to 3, aluminum was determined in the sodium hydroxide precipitate, after solution in acid, by double precipitation with ammonium hydroxide in the presence of considerable ammonium chloride. In experiments 4 to 6, aluminum was determined in the sodium hydroxide filtrates by double precipitation with ammonium hydroxide. In experiments 7 to 11, the solution, after precipitation with sodium hydroxide, was made up to 500 ml and aluminum determined in a filtered 250 ml aliquot portion by double precipitation with ammonium hydroxide. The aluminum thus found was multiplied by 2 to obtain, by difference, the total aluminum lost. Experiments 1 to 3 and 7 to 8 show that appreciable amounts of aluminum are carried down by the precipitate if moderate amounts of aluminum and nickel are treated with sodium hydroxide. However, experiments 4, 5, 9, and 10 show that the loss is negligible when nickel is precipitated in the presence of the amount of iron (approximately 0.2 g) usually retained in the bicarbonate precipitate. Experiment 6 shows that 0.350 g of chromium causes no significant retention of aluminum.

TABLE 2.—*Retention of aluminum by the sodium hydroxide precipitate*

Experiment No.	Al present	Other elements present	Al lost in NaOH precipitation	
			Single	Double
	g	*g*	*g*	*g*
1	0.0376	0.014 Ni	0.0025	0.0000
2	.0400	.044 Ni	.0062	.0025
3	.0100	.100 Ni	.0089	.0070
4	.0400	.014 Ni, .200 Fe	.0004	----------
5	.0400	.014 Ni, .200 Fe	.0004	----------
6	.0400	.350 Cr	.0003	----------
7	.0400	.014 Ni	.0022	----------
8	.0400	.040 Ni	.0058	----------
9	.0400	.040 Ni, .220 Fe	.0005	----------
10	.0400	.004 Ni, .050 Cr, .240 Fe	.0004	----------

In some procedures for the rapid determination of aluminum in steel, a faintly acid solution of all of the iron in a 2 to 5 g sample is slowly poured into an excess of sodium hydroxide, the solution diluted to a definite volume, and aluminum determined in a filtered aliquot portion. Such a procedure gives low results because some of the aluminum is retained by the very large precipitate of ferric hydroxide. For example, tests on a 3 g sample of a steel containing

1 per cent of aluminum showed an average loss corresponding to 0.06 per cent of aluminum. These tests were made by pouring the faintly acid solution (volume 250 ml) into 150 ml of a hot 12 per cent solution of sodium hydroxide, diluting to exactly 500 ml, determining aluminum in a filtered 300 ml portion by precipitating twice with ammonium hydroxide and correcting the ignited and weighed alumina for phosphorus, silica, and chromium. As would be expected, less aluminum is lost with steels of lower aluminum content. For example, tests on 2.5 g samples of steels containing 0.8 and 0.4 per cent of aluminum gave average losses corresponding to 0.05 and 0.03 per cent of aluminum, respectively. These errors are fairly constant, so that for rapid routine determinations on material of approximately constant composition a correction factor can be determined and applied. In such determinations, the bicarbonate separation is, of course, omitted, whereby the time required for an analysis (with final titration of the quinolate precipitate) is shortened to 1.5 to 2 hours.

3. PRECIPITATION OF ALUMINUM BY 8-HYDROXYQUINOLINE

In addition to aluminum, the sodium hydroxide filtrate will contain more or less of any molybdenum, vanadium, tin, arsenic, and phosphorus that may be present in the steels under test. Very small amounts of chromium, usually less than 0.5 mg, may also be present. Lundell and Knowles (8) have shown that aluminum can be precipitated with 8-hydroxyquinoline in the presence of molybdenum and vanadium by adding hydrogen peroxide to the solution prior to the addition of the quinoline reagent. By a combination of this method with Berg's (1) tartaric acid procedure aluminum can be separated from all of the elements that have been mentioned. This method of precipitation is described in Section III. The results obtained by titrating the aluminum quinolate thus precipitated in mixtures of known amounts of aluminum with various elements are shown by experiments 1 to 7 of Table 3.

TABLE 3.—*Results obtained in the determination of aluminum by titration of aluminum quinolate*

Experiment No.	Al present	Elements added	Al found	Difference
	g	*g*	*g*	*mg*
1	0.0099	----------	0.0100	+0.1
2	.0200	----------	.0201	+.1
3	.0200	----------	[1].0202	+.2
4	.0260	----------	.0259	−.1
5	.0200	0.010 Mo .003 Cr	.0203	+.3
6	.0200	.010 Sn	.0201	+.1
7	.0199	.020 V	.0200	+.1
8	[2].0250	----------	.0251	+.1
9	[3].0250	.01 Mo .05 Cr .004 Ni	.0251	+.1

[1] Dried at 135° C and weighed as aluminum quinolate.
[2] 0.05 g of Al plus 0.22 g of iron treated with NaOH as directed in Section III, the mixture diluted to 500 ml and aluminum determined in a filtered 250 ml portion by precipitation as quinolate and subsequent titration.
[3] Same as experiment 8, but 0.01 g Mo, 0.05 g Cr, and 0.004 g Ni were added before the sodium hydroxide precipitation.

III. RECOMMENDED PROCEDURE

Transfer 4 g of sample to a 500 ml Erlenmeyer flask, add exactly 50 ml of diluted sulphuric acid (1+9, accurately measured), cover with a watch glass, and heat gently. When action ceases, dilute to 150 ml with hot water, heat to boiling, and while agitating the solution add from a burette a solution containing 8.0 g of sodium bicarbonate per 100 ml of water until a permanent precipitate appears (approximately 38 ml in the usual case). At this point add 0.20 ml more for each miligram of aluminum anticipated. A 4 g sample of a steel containing 1:2 per cent of aluminum would require an excess of 9.6 ml of the bicarbonate solution. In no case, however, should less than 5 ml excess be added; that is, for steels containing less than 0.6 per cent of aluminum add a 5 ml excess of the bicarbonate solution. For high-chromium steels more bicarbonate will be needed. (See Section II.)

After adding the proper amount of bicarbonate solution, cover the flask, boil for one minute and let the precipitate settle. Filter immediately through a rapid 12.5 cm paper (No. 40 Whatman or equal) and wash the flask and precipitate twice with hot water. The filtrate will become cloudy in the funnel stem and receiving vessel owing to oxidation and hydrolysis of the iron, but this is of no consequence. Dissolve the bicarbonate precipitate by pouring 25 ml of hot diluted hydrochloric acid (1+2) drop by drop on it, and catch the solution in the original flask. Wash the paper and residue 8 to 10 times with hot diluted hydrochloric acid (1+19).[2] Add 1 ml of nitric acid (specific gravity 1.42) to the acid solution and washings, boil for two minutes and cool somewhat.

Nearly neutralize with a 30 per cent solution of sodium hydroxide, adjust the volume of the solution to 150 to 175 ml, warm to 70° C. and pour slowly into 150 ml of a hot 10 per cent solution of sodium hydroxide as the latter is vigorously stirred. Boil for one minute and cool the solution to room temperature. Transfer to a 500 ml volumetric flask and dilute to the mark. Pour into a dry 600 ml beaker. Stir well and let settle for about 30 minutes. Filter through a tight 12.5 cm paper (No. 42 Whatman or equal). Discard the first 25 to 35 ml portion and collect the next 250 ml in a 250 ml volumetric flask. Transfer the contents of the flask to a 600 ml beaker, washing the flask several times with water.

Neutralize the alkaline solution with hydrochloric acid (specific gravity 1.18), add an excess of 3 to 5 ml and 1 g of tartaric acid (5 ml of a 20 per cent solution). Add ammonium hydroxide (specific gravity 0.90) until the solution is just alkaline to litmus and then add 3 to 4 drops more. Add 10 to 15 ml of a fresh 3 per cent solution of hydrogen peroxide (or 1 to 1.5 ml of fresh perhydrol). Heat to 50° to 55° C. and add, dropwise and with constant stirring, a clear 2.5 per cent solution of 8-hydroxyquinoline [3] until 0.7 ml has been added for each milligram of aluminum anticipated, and then 5 ml more.

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[2] Any aluminum which was present in the steel as Al_2O_3 will remain on the paper at this point. This can be included in the analysis, if the percentage of total aluminum is desired, by igniting the paper and residue, fusing with potassium pyrosulphate, dissolving the melt and adding to the main acid solution. This correction rarely exceeds 0.018 per cent of aluminum (equivalent to 0.035 Al_2O_3).

Since aluminum nitride is soluble in diluted hydrochloric acid (1+3), it is also probably soluble in diluted sulphuric acid (1+9), though this point was not checked.

[3] Prepared by triturating 2.5 g of 8-hydroxyquinoline with 5 ml of glacial acetic acid, pouring the resulting solution into 100 ml of water at 60° C., cooling and filtering.

For a steel containing 1.2 per cent of aluminum the volume needed would be $24 \times 0.7 = 16.8 + 5$, or 22 ml. Then add dropwise while stirring 2 ml of ammonium hydroxide (specific gravity 0.90) and stir with a mechanical stirrer for 12 to 15 minutes. Let settle for about 15 minutes, while cooling to room temperature, and filter by suction through a 50 cm fritted glass crucible of fine porosity such as a No. 4 Jena glass filtering crucible.[4] Wash the beaker and precipitate with about 60 ml diluted ammonium hydroxide (1 + 99) heated to about 50° C.

The precipitate can be either weighed or titrated.[5] In gravimetric determinations, dry the precipitate for 1.5 hours at 135° C. and weigh as $Al(C_9H_6ON)_3$ which contains 5.87 per cent of aluminum.

The titration procedure is equally accurate and is particularly suited for rapid work. If this procedure is to be used, place a clean flask under the funnel and pour 40 ml of hot (75° C.) diluted hydrochloric acid (1 + 6) on the washed precipitate. Let the reaction proceed for a few minutes and stir occasionally with a small glass rod before applying suction. As soon as the precipitate has dissolved apply suction, and wash the crucible first with about 75 ml of the hot diluted hydrochloric acid (75° C.) and then with 50 ml of water.

Dilute the acid solution to 250 ml, add 15 ml of hydrochloric acid, and cool to room temperature (21° C. ± 4°). The hydrochloric acid content of the solution during the subsequent bromination should not be less than 8 per cent.

Add a standard 0.35 *N* solution of potassium bromate-potassium bromide until in moderate excess (about 3 ml excess), as determined by test,[6] or by calculation if the approximate amount of aluminum is known. If the bromate solution is 0.35 *N* approximately 1.3 ml are required for each milligram of aluminum, and hence for a steel containing 1.2 per cent of aluminum there would be needed $24 \times 1.3 = 31.2 + 3$ ml excess, or 34 ml. Stir and let stand for 30 to 60 seconds to make sure that bromination is complete. Add 15 ml of a 25 per cent solution of potassium iodide, stir well to make sure that the reaction between bromine and iodide is complete, and then titrate with a standard solution of sodium thiosulphate until the color of the iodine becomes faintly yellow. At this point add 2 ml of starch solution and titrate to the disappearance of the blue color.

The following solutions are required for the titration method:

Potassium bromate-bromide solution (0.35 N).—Dissolve 9.743 g of potassium bromate and approximately 34 g of potassium bromide in 400 ml of water and dilute to exactly 1 liter. If pure bromate is used the theoretical titer for aluminum can be used. Usually it is more convenient to obtain the titer of the bromate by determining the ratio of the bromate solution to a thiosulphate solution which has been

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[4] If fritted glass crucibles are not available the precipitate can be filtered through a tight paper, such as a Whatman No. 42. In this case the paper and precipitate should be washed about 10 times with 10 ml portions of cold diluted ammonium hydroxide (1+99).

[5] If a good grade of sodium hydroxide is used the blank will represent about +0.2 mg of aluminum. If it does not exceed this amount it can be neglected because it compensates for the small loss of aluminum that occurs in the sodium hydroxide precipitation. The blank on the alkali used was determined by precipitating 0.24 g of aluminum-free iron with sodium hydroxide, diluting to 500 ml filtering off a 250 ml portion, adding a definite amount of aluminum and then precipitating and titrating the aluminum quinolate. The difference between the aluminum value so obtained and that obtained by directly precipitating and titrating the same amount of aluminum represented the blank on the alkali.

[6] Made by adding a drop of the solution to a mixture of 1 drop of potassium iodide solution and 1 drop of starch solution on a spot plate. If the mixture turns blue, stir the test solution for one minute and again test. If the blue color does not again appear, more bromate solution must be added and the test repeated. Berg (1) uses a few drops of a 1 per cent aqueous solution of indigo-carmine. Hahn and Vieweg (3) use diazobenzene-sulphonic acid paper instead of iodide and starch.

standardized against a standard solution of 0.1 *N* permanganate. This ratio is obtained as follows: To 250 ml of water add 25 ml of the bromate solution, stir, add 25 ml of hydrochloric acid (specific gravity 1.19) and immediately add 15 ml of a 25 per cent solution of potassium iodide. Stir and titrate with the thiosulphate solution until the solution is nearly colorless. At this point add 2 ml of starch solution and titrate to the disappearance of the blue color. In titrating quinolates with potassium bromate 4 atoms of bromine are required for each quinolate radical. Consequently 12 atoms of bromine represent 1 atom of aluminum, and 1 ml of an exactly *N* solution of the bromate bromide would equal

$$\frac{26.97}{12}\times\frac{1}{1{,}000}=0.002248 \text{ g of aluminum}$$

The titer of the bromate solution is then obtained as follows:

$$\text{Normality factor of the thiosulphate solution}\times\frac{\text{ml of thiosulphate solution}}{\text{ml of bromate solution}}=\text{the normality factor of the bromate solution}$$

The latter $\times$ 0.002248 = g of Al per ml of the bromate solution.

Sodium thiosulphate solution (0.35 N).—Dissolve 88 g of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in 300 ml of recently distilled water, add 0.1 g of sodium carbonate and dilute to one liter. Standardize by means of 0.1 *N* permanganate. (See (6) p. 118.)

Starch solution.—To 500 ml of boiling water add a cold suspension of 5 g of soluble starch in 25 ml of water. Cool, add a cool solution of 5 g of sodium hydroxide in 50 ml of water, then add 15 g of potassium iodide and mix thoroughly.

Potassium iodide solution (25 per cent).—Dissolve 25 g of potassium iodide in 100 ml of water.

The results that were obtained when this method was applied in the analysis of standard steel No. 106 are shown in Table 4. In addition to the data shown in the table, determinations of aluminum in synthetic mixtures designed to simulate a steel containing 0.5 per cent of aluminum, 1.25 per cent of chromium, and 0.2 per cent of molybdenum gave values of 0.49, 0.51, and 0.49.

TABLE 4.—*Results obtained by applying the recommended method in analysis of steel No. 106*

[Total Al = 1.06 per cent, Al as Al_2O_3 = 0.017 per cent]

PERCENTAGE OF ALUMINUM OBTAINED

By titration	By weighing precipitate after drying at 135° C
1.05	1.06
1.05	1.06
1.03	1.06
1.05	
1.06	[1] 1.08
1.05	
1.04	[1] 1.07
Average 1.05	----------

[1] Includes recovery of aluminum in the residue from the acid treatment of the bicarbonate precipitate. The other values in this table do not include this recovery.

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