U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP853

Part of Journal of Research of the National Bureau of Standards, Volume 15, December 1935

DETERMINATION OF GALLIUM IN ALUMINUM

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ABSTRACT

Two procedures are described for the gravimetric determination of gallium in aluminum. One of these is based upon the separation of gallium from aluminum in sulphuric-acid solution by precipitation with cupferron. In this method, gallium is determined by difference in an oxide residue containing gallium, vanadium, titanium, and zirconium. The other procedure is based upon the separation of gallium from aluminum in hydrochloric-acid solution by extraction with ether. In this method, gallium is determined directly as the oxide Ga_2O_3.

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I. INTRODUCTION

In the preparation of a pure metal on a commercial scale, it is impossible to eliminate completely all impurities. The metal will be found to be slightly contaminated by those elements which are present in the ore and have somewhat similar properties, and by those which are unavoidably introduced from the reagents and the apparatus used.

Gallium is an element of the first type, for it is widely distributed in bauxites and accompanies aluminum to some extent in its reduction to metal. Methods for its determination are therefore of importance, not only to ascertain how much of it is present, but also to be able to correct for its effect in determinations of other constituents by methods that are subject to the interference of gallium.

Gallium is quantitatively precipitated by cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N.NO.ONH_4$) in sulphuric-acid solution. By this means it can be separated from aluminum. Gallium can also be separated from aluminum in hydrochloric-acid solution, by extraction with ether. If gallium only is being determined, the method of extraction with ether is preferable, because the final precipitate obtained is gallic oxide, Ga_2O_3. If, however, such elements as iron, vanadium, titanium, and zirconium are also being determined, the method in which the gallium is separated from aluminum by precipitation with cupferron is preferable. It should be observed that in the latter method gallium is determined by difference, and therefore the accuracy is less than can be attained by the method of extraction with ether.

II. METHODS RECOMMENDED FOR THE DETERMINATION OF GALLIUM IN ALUMINUM

1. PROCEDURE BASED UPON THE JOINT SEPARATION OF GALLIUM, VANADIUM, TITANIUM, ZIRCONIUM, IRON, TIN, AND COPPER BY PRECIPITATION WITH CUPFERRON

Place 10 g of the sample in a 600-ml beaker, add 200 ml of water, cover the beaker, and then add cautiously 200 ml of hydrochloric acid.[1] When the sample has dissolved, carefully add 60 ml of sulphuric acid (an excess of 30 ml over that which is necessary to combine with the aluminum), and evaporate the resulting solution until hydrochloric acid is expelled and vapors of sulphuric acid are evolved. Dilute the solution to 300 ml and filter it in order to remove any silica. Ignite the siliceous residue, treat it with about 10 ml of hydrofluoric acid (48 percent) and 1 ml of sulphuric acid, heat the resulting solution until vapors of sulphuric acid are evolved, dilute it, and finally add it to the filtrate obtained above. Dilute the solution to 375 ml, chill it in ice water, and add to it about 20 ml of a chilled, filtered, freshly prepared, 6-percent solution of cupferron. Allow the solution with the precipitate to stand in ice water for 1 hour, and stir it occasionally. In order to facilitate filtration, add a small amount of paper pulp.

Filter the solution and wash the precipitate with chilled diluted sulphuric acid (7+93) containing about 1.5 g of cupferron per liter. Place the filter and precipitate in a platinum crucible and ignite them at as low a temperature as possible, preferably by placing the crucible in a cold muffle furnace and gradually increasing the temperature to about 550° C. Dissolve the ignited residue in diluted hydrochloric acid (9+1), transfer the resulting solution to a 250-ml beaker, and add to it 5 ml of sulphuric acid. Evaporate the solution until vapors of sulphuric acid are evolved.

Since the precipitate obtained with cupferron consists not only of gallium but of a number of other elements as well, it is necessary to eliminate or to determine these other elements in order to evaluate the gallium.

(a) REMOVAL OF TIN AND COPPER

Dilute the sulphuric-acid solution to 100 ml, add 5 g of tartaric acid, and stir until the crystals are dissolved. Digest the solution on the steam bath until the iron is completely dissolved, and then dilute it to 250 ml. Pass a stream of hydrogen sulphide through the solution at room temperature for 15 to 20 minutes, and then let it stand for one-half hour before filtering it. Wash the filter and precipitate two or three times with diluted hydrochloric acid (1+200) which has been saturated with hydrogen sulphide. The

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[1] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; sulphuric acid, the concentrated acid of specific gravity 1.84; and nitric acid, the concentrated acid of specific gravity 1.42. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

precipitation and filtration are made in order to remove copper and tin, as well as any other metal which precipitates with hydrogen sulphide in acid solution.

(b) REMOVAL OF IRON

Nearly neutralize with ammonium hydroxide the filtrate obtained above, and pass in hydrogen sulphide for about 5 minutes to insure the reduction of iron to the bivalent state. Add an excess of 10 ml of ammonium hydroxide, and saturate the solution with hydrogen sulphide. Filter the solution, and wash the precipitate four times with a 2-percent solution of ammonium sulphide which also contains 1 percent of ammonium tartrate.

(c) RECOVERY OF GALLIUM, VANADIUM, TITANIUM, AND ZIRCONIUM BY CUPFERRON

After the removal of those metals which are precipitated by hydrogen sulphide in acid solution, and of iron, it is necessary to recover the gallium from solution. This is most conveniently done by again precipitating it with cupferron. It should be observed that the precipitate will be contaminated by those elements which also form insoluble compounds with cupferron under the same conditions.

Acidify with sulphuric acid the filtrate obtained in the removal of iron and boil it until the hydrogen sulphide is expelled. Filter the solution, dilute it to 375 ml, neutralize it with ammonium hydroxide, and finally add to it 30 ml of sulphuric acid. Chill the resulting solution in ice water, add to it 15 to 20 ml of the chilled 6-percent solution of cupferron, stir it well, and allow it to stand for about 1 hour. Filter the solution, and wash the precipitate with chilled diluted sulphuric acid (7+93) containing about 1.5 g of cupferron per liter. Place the filter and precipitate in a platinum crucible, dry them carefully, char them, and finally ignite them for a few minutes at 1,000° C. Weigh the residue as a mixture of Ga_2O_3, V_2O_5, TiO_2, and ZrO_2.

(d) DETERMINATION OF VANADIUM

Fuse the mixture of oxides obtained above with 0.5 g of potassium pyrosulphate. Dissolve the fused mass in 10 ml of diluted sulphuric acid (1+9), and add to the resulting solution 5 ml of a solution of ferric sulphate (equivalent to 25 mg of iron) and 12 ml of a 25-percent solution of sodium hydroxide. The solution at this stage should have a volume of about 30 ml and should contain an excess of about 1.5 g of sodium hydroxide. Boil the solution for 1 to 3 minutes, filter it, and wash the precipitate twice with a 1-percent solution of sodium hydroxide. Because the amount of vanadium involved is so small, it is rarely necessary to repeat the precipitation. Neutralize the filtrate with diluted sulphuric acid (1+4), then add 5 ml of sulphuric acid, and concentrate by evaporation to a volume of about 25 ml. Cool the solution to room temperature, transfer it to a comparison cylinder, and add 3 ml of a 3-percent solution (by volume) of hydrogen peroxide. The volume should not be over 30 ml at this stage. Determine the vanadium colorimetrically by comparing the solution with one of known vanadium content which has been similarly treated.

(e) DETERMINATION OF TITANIUM

Dissolve the precipitate obtained with sodium hydroxide by pouring 20 ml of hot diluted sulphuric acid (1+9) repeatedly through the filter, and then wash the filter with sulphuric acid of the same strength.

If necessary, concentrate the solution by evaporation until its volume is not greater than 20 ml. Cool the solution to room temperature, transfer it to a comparison cylinder, and add 3 ml of a 3-percent solution of hydrogen peroxide. Determine the titanium colorimetrically by comparing the solution with one of known titanium content which has been similarly treated.

(f) DETERMINATION OF ZIRCONIUM

After the colorimetric determination of titanium, transfer the solution to a small beaker, add to it an excess of diammonium phosphate (10 to 50 mg usually suffices), and allow it to stand at 50° C for several hours, or until the zirconium phosphate is coagulated. It should be noted that a sufficient amount of hydrogen peroxide should be in the solution during this treatment to keep the titanium in the peroxidized condition. Filter the solution and wash the phosphate precipitate with a 5-percent solution of ammonium nitrate. Transfer the filter and the precipitate to a platinum crucible, ignite carefully until the paper is destroyed, and then heat for a few minutes at 1,000° C. Weigh the residue as $ZrO(PO_3)_2$.

(g) DETERMINATION OF GALLIUM BY DIFFERENCE

In order to arrive at a determination of gallium, it is necessary to subtract from the weight of the mixed oxides of gallium, vanadium, titanium, and zirconium, obtained from the second precipitation by cupferron, the weights of V_2O_5, TiO_2, and ZrO_2 determined as has just been described. It is to be noted that gallium is thus determined by difference.

2. PROCEDURE BASED UPON THE EXTRACTION OF GALLIUM BY ETHER

Gallium can be determined directly by proceeding in the following manner:

Place 10 g of the sample in a 600-ml beaker, add 200 ml of water, cover the beaker, and then add cautiously 250 ml of hydrochloric acid. When the sample has dissolved, evaporate the solution to about 300 ml, cool it, and dilute it to 400 ml with diluted hydrochloric acid (1+1). Transfer the solution to a separatory funnel, and cool in ice water. Add to the cooled solution 150 ml of ether which has also been cooled. If both the ether and the acid solution are cold when mixed, the formation of a yellow color, which usually appears, can be to a great extent prevented. Shake the contents of the separatory funnel thoroughly, and then chill again by immersion in ice water. When the layers have separated, draw off the acid solution and transfer the ether extract to a beaker. In this treatment the gallium as chloride passes into the ether while the aluminum remains in the acid solution. Make two more ether extractions, using 50 ml of ether in each extraction. In the third extraction, allow the separatory funnel to stand at room temperature for about 1 hour before removing the acid solution.

Combine the three ether extracts and let stand at room temperature or in a warm place until the ether layer becomes entirely separated from the small amount of acid solution which had been unavoidably entrained. Carefully remove this small amount of acid solution and treat it with two small portions of ether. Transfer the entire ether fraction, which now contains all the gallium, to a clean beaker and evaporate it carefully to dryness. Dissolve the residue obtained in nitric acid, add 5 ml of sulphuric acid, and heat until vapors of sulphuric acid are evolved. Insure the destruction of organic matter by adding small portions of nitric acid from time to time, and continue to heat until vapors of sulphuric acid appear.

Remove the metals which are precipitable by hydrogen sulphide in acid solution, and also iron, as previously directed. Recover the gallium by precipitation with cupferron as previously directed. Weigh the ignited residue as Ga_2O_3.

The results obtained in the recovery of known quantities of gallium, which had been added to solutions containing 10-g portions of aluminum (Standard Sample 44c), by the method of extraction with ether are given in table 1.

TABLE 1.—*Recovery of gallium from solutions of aluminum to which known quantities of gallium were added*

Gallium present [1]	Gallium recovered	Error
g	g	g
0.0006	0.0006	0.0000
.0007	.0009	+.0002
.0011	.0013	+.0002
.0100	.0099	−.0001
.0102	.0101	−.0001

[1] This includes the gallium added as well as that contained in the aluminum.

The results obtained in the determination of gallium in four different samples of aluminum by the two procedures described are given in table 2.

TABLE 2.—*Comparison of the results obtained in the determination of gallium in aluminum by the two procedures*

Cupferron method	Ether method	NBS sample number of aluminum used
Percent	*Percent*	
0.017	0.016	44
.017	.017	
	.018	
.020	.020	44a
.020	.021	
.020	.024	
.022		
.011	.010	44b
.012	.010	
.013	.011	
.013		
.0003	.0004	44c
.0004	.0007	

In the case of Standard Sample 44c, gallium was determined in the combined cupferron precipitates, as well as in the combined ether extracts, of five 10-g portions of aluminum. The final residues of Ga_2O_3 were examined spectrochemically by Bourdon F. Scribner, of this Bureau, who identified gallium, and found in them only minute amounts of impurities originally in the aluminum.

III. DISCUSSION OF THE METHODS

Although it has been generally believed that gallium is not completely precipitated by cupferron in solutions containing as much as 5 percent of sulphuric acid by volume, when tartaric acid is present, and that complete precipitation is not attained in solutions having an acidity greater than 6 ml of sulphuric acid in 400 ml,[2] it was found that no difficulty was encountered in producing complete precipitation in solutions containing as much as 7 to 8 percent of sulphuric acid by volume, provided that an excess of cupferron (15 to 20 ml of a 6-percent solution) was added. It was found necessary with this method to work with volumes of 400 ml, in order to prevent precipitation of aluminum salts by crystallization when the solutions were chilled.

In the determination of gallium in aluminum, if the gallium content is as much as 0.01 percent, a 10-g portion is sufficient. If the content is smaller, the cupferron precipitates resulting from a number of 10-g portions should be combined to yield at least 0.001 g of ignited mixed oxides. In the mixed oxide residue, 0.1 mg of either titanium or vanadium can be easily determined colorimetrically if the volumes of the solutions are kept small. The determination of small amounts of zirconium is somewhat difficult, but 0.1 mg (0.3 mg of $ZrO(PO_3)_2$) of this element can be handled if again the volume of the solution is kept small.

It had been found by Swift [3] that 97 percent of the gallium contained in a hydrochloric-acid solution of acidity 4.9 to 5.9 *N* could be extracted by ether in one operation. In order to ascertain the number of extractions necessary to remove all the gallium, the following experiments were made. Two hydrochloric-acid solutions, each containing 10 g of aluminum and 0.0076 g of gallium, were extracted four times. There was recovered from the first extraction 0.0069 and 0.0065 g of gallium, respectively; from the second, 0.0004 and 0.0006 g; and from the third, 0.0003 and 0.0003 g. The fourth extract was found to contain less than 0.0001 g of gallium. The total amounts of metal recovered were 0.0076 and 0.0074 g, respectively. In another experiment, in which 0.0102 g of gallium was added, the recoveries from three extractions were 0.0078, 0.0016, and 0.0008 g, a total recovery of 0.0102 g. It thus appeared that three extractions were necessary and sufficient. It should be observed that in the extraction with ether a quantity of aluminum greater than 10 g cannot be handled conveniently. In this method the volume of the acid solution is kept large enough to prevent the precipitation of $AlCl_3.6H_2O$, the solubility of which decreases with increasing concentration of hydrochloric acid and which is also affected by the presence of ether. A concentration of hydrochloric acid greater than 6 *N* should not be used, because of the solubility of the ether in solutions of higher acid concentration than this.

It should be noted that no titanium, vanadium, nor zirconium was ever found in the final residue of Ga_2O_3 obtained by the method of extraction with ether. The residue always contained a minute amount of iron, probably introduced through the reagents used. Determinations of iron in three of these residues ranged from 0.02 to 0.05 mg.

WASHINGTON, September 20, 1935.

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[2] E. S. von Bergkampf, Z. anal. Chem. **83**, 345 (1931); **90**, 333 (1932).

[3] E. H. Swift, J. Am. Chem. Soc. **46**, 2375 (1924).