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Analysis of Microquantities of Antimony, Tin and Arsenic in Ferrotungsten*

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Synopsis

It is very difficult to determine microamounts of impurities in ferrotugsten. Antimony, tin and arsenic have been determined by volumetric or gravimetric method in JIS and A. S. T. M., so the determination of microquantities of these elements is difficult. The photometric method would be suitable for this purpose. The spectrophotometric determinations of antimony, tin and arsenic in ferrotungsten by a routine method developed in our laboratory are described here, that is, after these elements were separated as sulfide from main elements such as iron, tungsten and others, the precipitates obtained were dissolved and a certain definite amount of this solution was used in the following procedure. Arsenic with one protion of it was determined with molybdenum blue method directly, and antimony and tin with other portion of it were separated from copper and others by the coprecipitation with manganese dioxide and then determined respectively by methyl violet-amyl acetate extraction method and cacotherine method.

I. Introduction

It is difficult to determine the microquantity of impurities in ferrotungsten. The analyses of antimony, tin and arsenic are made by volumetric or gravimetric method in JIS and A. S. T. M., and these are unapplicable to the determination of microamount of these metals. It seemed that photometry would be the most suitable method for their microdetermination and the present authors carried out the determination of microquantities of antimony, tin and arsenic in ferrotungsten by the photometric method reported earlier.

II. Analytical method

Photometric determination of microquantities of antimony, tin and arsenic in ferrotungsten was carried out in the following manner. Antimony was determined by the sensitive method with methyl violet-amyl acetate extraction(1)(2) discovered by the authors, tin by using cacotheline also reported previously,(3) and arsenic by using molybdenum blue.(4)

In carrying out these methods, the impurities must be separated from the chief constituents, iron and tungsten, and from other impurities.

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* The 907th report of the Research Institute for Iron, Steel and Other Metals. Reported in Journal of the Japan Institute of Metals, **21** (1957), 385.

(1) H. Gotô and Y. Kakita, J. Chem. Soc. Japan, **73** (1952), 399.

(2) H. Gotô and Y. Kakita, J. Japan Inst. Metals, **16** (1952), 560.

(3) H. Gotô and Y. Kakita, Ibid. , **17** (1953), 220, 223.

(4) Y. Kakita, Ibid., **8** (1944), 415.

Copper, vanadium, chromium, molybdenum, tungsten and iron interfere in the determination of antimony and tin, and phosphorus and silicon interfere in the determination of arsenic.

From the foregoing facts, it seemed appropriate to isolate antimony, tin and arsenic as sulfides by precipitation with hydrogen sulfide in weak acidity, in the presence of tartaric acid, as in the method adopted by JIS,(5) which would separate them from iron, tungsten, phosphorus, chromium and vanadium. Copper and molybdenum would be precipitated as sulfides with antimony, tin, and arsenic but can be separated by coprecipitation of antimony and tin with manganese dioxide.

III. Apparatus and reagents

Apparatus

Hitachi spectrophotoelectric photometer, model EPU-2, with 1 cm cell.

Reagents

Standard antimony solution: metallic antimony (analytical reagent grade) is accurately weighed, dissolved in hydrochloric acid (10N) containing a small amount of hydrogen peroxide, with warming, the mixture is further heated to decompose hydrogen peroxide, and cooled. This is diluted with hydrochloric acid (10N) to a definite volume so as to containing 0.1 mg of antimony in 1 ml of the solution. A definite portion of this solution is taken and diluted accurately to the desired volume on use.

Standard tin solution: 0.2500 g metallic tin (analytical reagent grade) was dissolved with aliquot amount of hydrochloric acid (1:1) by heating and after the solution was cooled, it was diluted to 500 ml in total volume by adding hydrochloric acid (1:1). The stock solution thus prepared was, when used, diluted five times by hydrochloric acid (1:1).

Standard arsenic solution: 0.1321 g of pure arsenic trioxide (standard substance) is weighed accurately, dissolved in 20 ml of sodium hydroxide solution (ca. 5 per cent) with warming, and diluted to 100 ml with water. This is acidified with sulfuric acid (1:5), potassium permanganate solution (0.5 per cent) is added while boiling the solution until a faint pink color remains, and the mixture is boiled further for a few minutes. This solution is cooled, and neutralized with sodium hydroxide solution. This solution contains 0.1 mg of arsenic in 1 ml and this is dilute dexactly to 5 volumes on use.

Tartaric acid washing solution: about 1 g of tartaric acid is dissolved in 100 ml of sulfuric acid (1:99) satuarted with hydrogen sulfide.

Other reagent: all reagent used were that of analytical reagent grade.

IV. Analytical procedure

1. Method of separation

Two g of the sample is weighed into a nickel crucible, 10 g of sodium

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(5) JIS G 1316 (1953) Analysis of Ferrotungsten.

carbonate-sodium peroxide mixture (1:1) is added, and mixed thoroughly. This is fused for about 30 minutes, cooled, and digested with water in a beaker. The nickel crucible is taken out and washed thoroughly. 10 g of tartaric acid is added to the beaker, neutralized with ammonia, and further 10 ml of ammonia is added. This mixture is heated to near boiling for a few minutes, neutralized with sulfuric acid, and 2 ml of sulfuric acid is added for each 100 ml of the solution to bring the sample solution to approximately 300 ml. Hydrogen sulfide is bubbled vigorously through this solution for at least 30 minutes and the resultant mixture is allowed to stand for some time to complete the precipitation. The precipitate is collected by filtration, washed thoroughly with the tartaric acid washing solution, and the sulfide precipitate is transferred to a beaker with the filter paper. The precipitate and the filter are heated with 10 ml of sulfuric acid and a suitable amount of nitric acid to effect decomposition and heated until white fumes of sulfur dioxide evolve. The residual solution is transferred to a 250 ml measuring flask, diluted exactly to 250 ml, and 50 ml of this solution is used as the sample solution for the photometric determination of antimony, tin, or arsenic.

2. Determination of antimony

50 ml of the sample solution prepared as described in the foregoing section is taken and to it 10 ml of nitric acid (1:1) and 40 ml of water, 5 ml of manganese sulfate solution (5 per cent) are added, and while boiling the solution, 3 ml of potassium permanganate solution (3 per cent) is added dropwise with agitation. The mixture is boiled further with agitation until manganese dioxide precipitates completely, the mixture is allowed to stand for 5~10 minutes without heating, and filtered. The precipitate on the filter is washed with warm water, transferred to the original beaker, and 20 ml of hydrochloric acid (1:1) containing a small amount of hydrogen peroxide is poured through the filter into the same beaker to dissolve the precipitate. The filter is futher washed with a small amount of hydrochloric acid (1:1) and water, and the washings are added to the precipitate in the beaker. The solution in the beaker is evaporated to a volume of a few ml, 20 ml of hydrochloric acid is added, and again heated for a few minutes. When cooled, the solution is transferred to a 50 ml measuring flask and diluted exactly to 50 ml. To 5~10 ml of this solution, 0.3 ml of ceric sulfate solution (2 per cent in 1N sulfuric acid) is added to effect oxidation, 5 ml of hydrazine sulfate solution (1 per cent) is added to decompose the excess of ceric sulfate, and 1 ml of methyl violet solutian (0.2 per cent) is added. The color of this solution is adjusted to bluish green to green by the addition of sodium citrate solution (30 per cent).

To this solution, 5 ml of amyl acetate is added and the mixture is shaken vigorously for about 30 seconds. After allowing this mixture to stand to separate into two layers, the amyl acetate layer is collected and the absorbance of this solution is measured at 600 mμ. Calibration curve is prepared by using standard antimony solution in various amounts, diluted with 5 ml of hydrochloric acid (1:1), and processed in the same manner as the sample solution. When the amount of antimony is small, the precipitate separated by coprecipitation on manganese dioxide is used wholly, this precipitate is treated as described above and evaporated to a few ml, and warmed with 10 ml of hydrochloric acid. This cooled solution is submitted wholly to extraction.

3. Determination of tin

50 ml of the sample solution is taken and diluted with 10 ml of nitric acid and 40 ml of water, and 5 ml of manganese sulfate solution (5 per cent) is added, and the mixture is boiled. While boiling, 3 ml of potassium permanganate solution (3 per cent) is added in small portions and the mixture is further boiled to precipitate manganese dioxide. After allowing the mixture to stand for 5~10 minutes, the mixture is filtered through a paper filter, the precipitate on the filter is washed with warm water, and returned to the original beaker. The filter is washed with 12~14 ml of hydrochloric acid (1 : 1) containing a small amount of hydrogen peroxide, the washing is allowed to enter the beaker containing the precipitate, and the filter is again washed thoroughly with warm water, combining this washing also in the beaker. The mixture in the beaker is boiled to decompose hydrogen peroxide, and the solution is allowed to evaporate gently until the volume is reduced to 10 ml. (If the mixture in the beaker is turbid due to filter paper bits, it is filtered, the filter is washed thoroughly with warm water, and the filtrate is again evaporated to about 10 ml.) The solution is transferred to a 50 ml Erlenmeyer flask, the beaker is washed with water, and the washing is added to the content in the Erlenmeyer flask, bringing the total volume to about 20 ml. To this solution, 0.16 g of aluminium foil is added, the flask is connected to the Kipp apparatus, and the atomosphere inside the flask is changed with carbon dioxide. The flask is then heated to dissolve the aluminium and the heating is continued further until the solution becomes clear and fine bubbles have changed into large bubbles. This is cooled rapidly with water while still passing the carbon dioxide and 0.5 ml of cacotheline solution (0.2 per cent) is added. The atmosphere inside it is again exchanged with carbon dioxide, the flask is stoppered closely with a rubber stopper, and this is allowed to stand for about 10 minutes. The solution is then diluted to a total volume of 20 ml and its absorbance is measured at 530 mμ.

For the plotting of the calibration curve, the standard tin solution of various amounts is taken in a 50 ml Erlenmeyer flask, hydrochloric acid, water, and aluminium foil are added, and reduced in the same way as above. For the reduction, a 50 ml Erlenmeyer flask is stoppered with a rubber stopper, into which two glass tubes are inserted for the introduction and exit of gas, one being connected to the Kipp apparatus.

4. Determination of arsenic

To 50 ml of the sample solution, a few drops of potassium permanganate solution (0.5 per cent) is added, boiled to effect oxidation, and cooled. This is neutralized with sodium hydroxide solution (ca. 5 per cent), 10 ml of sulfuric acid (1:10), 7 ml of ammonium molybdate solution (1 per cent), and 10 ml of hydrazine sulfate solution (1 per cent) are added, and the whole is diluted to 100 ml with water. This mixture is heated in a boiling water bath to effect coloration, the solution is cooled immediately in running water, and the optical density is measured at 850 mμ. The heating for coloration requires 2～3 minutes at 80°C, and about 10 minutes would be necessary when heating a cold solution.

For the calibration curve, the standard arsenic solution and 10 ml of sulfuric acid (1:10) are treated in the same way as for the sample solution.

V. Analytical results

Analyses were carried out by the foregoing methods on Japanese Standard Iron and Steel Sample No. 16 (a), ferrotungsten, and two other samples, and results obtained are shown in Table 1.

Table 1. Results of analyses.

Sample	Sb (%)	Sb mean (%)	Sn (%)	Sn mean (%)	As (%)	As mean (%)
Japanese S. S. No. 16 (a) Ferrotungsten	0.00159 0.00157 0.00159	0.00158	0.338 0.350 0.350	0.346	0.044 0.047 0.048	0.046
Japanese S.S. No. 16 Ferrotungsten	0.00090 0.00087 0.00085	0.00087	0.318 0.331 0.294	0.314	0.041 0.042 0.039	0.041
Ferrotungsten	0.00031 0.00027 0.00028	0.00029	0.094 0.106 0.118	0.106	0.010 0.011 0.012	0.011

Summary

(1) Determination of microquantities of antimony, tin and arsenic in ferrotungsten was carried out by the photometric method.

(2) Antimony, tin, arsenic and other elements were separated as sulfides from the chief constituents by precipitation with hydrogen sulfide in weakly acid solution in the presence of tartaric acid.

(3) Arsenic was determined by the molybdenum blue method from a part of the solution of its sulfide.

(4) Antimony was determined by the methyl violet-amyl acetate extraction method after the separation by coprecipitation from a part of the same solution with manganese dioxide.

(5) Tin was also coprecipitated with manganese dioxide and determined by the cacotheline method.

(6) This analytical procedure was applied to some samples of ferrotungsten.