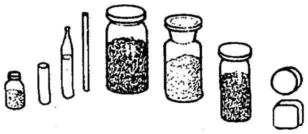

NBS MISC. PUBL. **260-6**

Standard Reference Materials:

Methods for the Chemical Analysis of White Cast Iron Standards

U.S. Department of Commerce

National Bureau of Standards

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Standard Reference Materials:

Methods for the Chemical Analysis of White Cast Iron Standards

J. I. Shultz
Institute for Materials Research
National Bureau of Standards
Washington, D.C.

National Bureau of Standards Miscellaneous Publication 260–6

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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

W. Wayne Meinke, Chief
Office of Standard Reference Materials.

OTHER NBS PUBLICATIONS IN THIS SERIES

NBS Misc. Publ. 260, Standard Reference Materials:
Catalog and Price List of Standard Reference Materials Issued by the National Bureau of Standards, January 1965. In press.*
(Supersedes NBS Misc. Publ. 241, March 1962).

NBS Misc. Publ. 260-1, Standard Reference Materials:
Preparation of NBS White Cast Iron Spectrochemical Standards, June 1964. 30 cents.*

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

STANDARD REFERENCE MATERIALS: METHODS FOR THE CHEMICAL ANALYSIS OF WHITE CAST IRON STANDARDS

J. I. Shultz

Institute for Materials Research
National Bureau of Standards

The procedures described in this publication are those used at the National Bureau of Standards in the analysis of white cast iron standard reference materials for the ten (10) major elements; namely, carbon, manganese, phosphorus, sulfur, silicon, copper, nickel, chromium, vanadium, and molybdenum.

Carbon and sulfur are determined by combustion; manganese, chromium and vanadium by titrimetry; phosphorus, copper, and molybdenum by photometry; and silicon and nickel by gravimetry.

These procedures, which are slight modifications of well-established and previously published methods, were selected for their accuracy and dependability.

1. INTRODUCTION

These methods cover the procedures for the chemical analysis of ten major elements for eight white cast iron Standard Reference Materials 1176-1183 that were issued by the National Bureau of Standards in April 1961. Details of the planning and preparation of these alloys are given in NBS Miscellaneous Publication 260-1 entitled, "Preparation of NBS White Cast Iron Spectrochemical Standards" [1]. Although the standards contain a graded composition for twenty-one (21) elements, they were initially analyzed and certified for carbon, manganese, phosphorus, sulfur, silicon, copper, nickel, chromium, vanadium, and molybdenum. The residual elements having concentration ranges for which values have more recently been determined include titanium, arsenic, antimony, tin, cobalt, tellurium, boron, bismuth, zirconium, lead and aluminum.

The methods of analysis used at the National Bureau of Standards were selected or designed to give the best obtainable results. In some instances, more than one procedure was employed for an element as a cross-check on both the precision and accuracy of the composition.

The analysis is of little value unless the sampling procedure is carefully controlled. Not only must care be taken to assure that the sample is representative of the whole, but it is equally important that the sample be prepared in such a manner that contamination is avoided. Similarly, the materials to be used as composition standards must be homogeneous and in a form suitable for use. The homogeneity of the samples was established by metallographic, spectroscopic and chemical examination before sampling for the final analysis.

Although limited in engineering applications, these white iron standards have been prepared for the cast iron industry to meet the needs for analytical control by rapid instrumental methods. White iron represents the only metallurgical structure that would provide the requisite homogeneity for optical emission spectroscopic analyses. In addition, the fact that carbon is present in the combined form permits, by vacuum techniques, the determination of carbon, phosphorus and sulfur which would otherwise not be possible.

The samples for chemical analysis were prepared from 1 1/4 inch square and 3/4 inch thick solid sections by breaking brittle segments, cut from the certified portion of the samples, in a hardened iron mortar with an iron pestle. The material was then sized to pass through a No. 14 sieve.

Samples for cooperative analysis were sent to five (5) selected laboratories whose experience in the analysis of these types of alloys is well established. Those laboratories assisting with the analysis were: The American Cast Iron Pipe Co., Birmingham, Alabama, R. Elder and R. Deas; General Motors Corp., Warren, Michigan, M. D. Cooper and R. B. Loranger; Naval Research Laboratory, Washington, D. C., D. Walter and O. Mylting; Applied Research Laboratory, United States Steel Corp., Pittsburgh, Pa., L. M. Melnick; and Canton Roll and Machine Works, United States Steel Corp., Canton, Ohio, D. J. Henderson.

These methods cover the chemical analysis of white cast irons having chemical compositions within the limits shown in table 1.

Table 1. Composition limits of the ten major elements for white cast iron.

Element determined	Limit (%)
Carbon	1.5 - 4.0
Manganese	0.3 - 1.5
Phosphorus	.01 - 0.8
Sulfur	.03 - .2
Silicon	.3 - 4.0
Copper	.1 - 1.5
Nickel	.01 - 3.0
Chromium	.01 - 3.0
Vanadium	.005 - 0.3
Molybdenum	.01 - 1.5

Table 2 gives the revised certified values which are based on the results obtained at NBS and five cooperating laboratories.

Table 2. Certified values of the ten major elements for white cast iron.

NBS No:	1176	1177	1178	1179	1180	1181	1182	1183
Type:	Piston ring	Wear plate	Die	Brake drum	Mold	Special 1	Special 2	Special 3
Element	Percent							
C	3.47	2.74	3.11	3.35	3.28	3.63	1.97	3.05
Mn	0.63	0.37	0.86	0.64	1.12	1.32	0.45	0.91
P	.42	.61	$.11_5$	.23	0.05_5	0.29	.85	.011
S	.061	.037	.026	$.16_5$	.086	.052	.046	.025
Si	3.19	.88	1.91	1.34	3.04	2.54	.31	1.76
Cu	0.76	$.08_7$	0.16	0.41	0.20	1.47	.49	1.01
Ni	$.05_5$	2.97	2.25	1.31	.044	0.11	.22	0.53
Cr	.51	1.39	0.89	0.23	.14	2.04	.029	$.07_7$
V	.17	0.00_5	$.01_7$	$.03_6$	.26	0.11	$.06_0$	.080
Mo	.59	1.49	.94	.31	$.15_5$	$.04_2$	$.01_8$	$.02_9$

2. CARBON IN WHITE CAST IRON

Carbon is undoubtedly the most important element in ferrous materials and the one which has greater influence on the properties of a metal than any other, with the possible exception of large amounts of some of the alloying elements. As a result of this importance, many methods of analysis have been developed [2,3,4,5] but carbon is determined most rapidly and accurately by direct combustion in oxygen. During the many years this method has been in general use, variations in apparatus and procedure have been introduced to meet specific requirements.

In white cast iron, as in steels, virtually all of the carbon exists in the combined form as Fe_3C with essentially no free graphite present; hence, the combined carbon is represented as total carbon.

Scope

This method is recommended for the determination of carbon in the range of 1.5 to 4.0 percent. For this concentration range, the relative standard deviation is 0.02 percent.

Principle of Method

The sample is burned in a stream of oxygen, and the carbon dioxide in the evolved gases is collected in a suitable absorbent and weighed.

Interferences

Oxides of sulfur are removed by means of a manganese dioxide trap, or by a tube of platinized silica gel heated to 440°C, followed by a tube containing ironized asbestos and anhydrous $Mg\ (ClO_4)_2$.

Apparatus

Apparatus for determination of carbon by the direct-combustion gravimetric method is available commercially or may be constructed. A schematic of the apparatus for the combustion carbon method is given in figure 1.

(a) Resistance furnace, using silicon carbide resistance elements and capable of maintaining a temperature of at least 1100°C.

(b) Miscellaneous apparatus. Additional equipment required includes absorption bulbs, catalyst heater, combustion tubes, sample inserters, oxygen flow indicators, oxygen pressure gages, oxygen drying and purifying trains.

(c) Absorption bulbs. No special types of bulbs are specified, but the Fleming, Nesbitt and the Midvale bulbs are preferred. The bulbs should be filled in such a manner that the gas passes through the absorbent for CO_2 and the absorbent for water, in that order. A layer of glass wool immediately adjacent to the entrance and exit is required to prevent plugging by particles of the solid absorbent and to aid in diffusing the gases.

The absorbents should be added in increments with gentle tapping, to compact the charge adequately.

(d) Purifying train, consisting of a carbon dioxide absorbent and magnesium perchlorate trap, H_2SO_4 trap and a flowmeter.

Reagents and Materials

(a) Alundum, granular (60 mesh or finer), specially prepared for carbon determination.

(b) Boats, ceramic, clay, or nickel. Ignite in a muffle furnace, or preferably in a tube furnace in the presence of oxygen, at 1100°C or higher for at least 1 hour before use until a constant blank is obtained.

(c) Carbon dioxide absorbent, inert base, 8 to 20 mesh impregnated with NaOH (Ascarite and Caroxite have been found satisfactory for this purpose).

(d) Magnesium perchlorate, anhydrous ($Mg(ClO_4)_2$).

(e) Manganese dioxide (MnO_2) specially prepared for removal of oxides of sulfur.

(f) Oxygen, minimum 99.6 percent pure.

(g) Platinized silica gel.

Preparation of Apparatus

(a) Assemble the apparatus and provide for purification of the oxygen by passing it through a catalyst heater and purifying train. Turn on the current and adjust the furnace temperature to at least 1100°C.

(b) Open the stopcocks of one of the absorption bulbs and connect it to the combustion train. If the absorption bulb has not been in use for 8 hours or longer, condition it as follows:

(c) Transfer several grams of a sample containing approximately 0.5 percent carbon to the combustion boat containing alundum bedding material. Cover the boat with a suitable cover and introduce it into the combustion tube. Close the tube and preheat the sample for 2 minutes. Turn on the oxygen, adjust the flow rate to about 800 to 1000 ml per min. and maintain this rate for 8 min.

(d) Shut off the oxygen. Detach the absorption bulb, close the stopcocks, and place the bulb in the balance case to cool. (Note: the time allowed for the absorption bulb to cool before weighing it must be held to a definite time limit. The requirement is easily fulfilled by employing two bulbs and by weighing the bulb just prior to its use.) Remove the sample from the combustion tube.

(e) Repeat the steps outlined in Paragraphs (b) through (d) inclusive with the second absorption bulb.

Procedure

(a) Weigh the tared absorption bulb which has been conditioned as described above, (b) through (d), and attach it to the combustion train.

(b) Transfer a 1 g sample, weighed to the nearest 1 mg, to the boat containing the alundum bedding.

(c) Cover the boat and proceed as described above, (c) and (d), collecting the evolved carbon dioxide in one of the weighed absorption bulbs.

(d) Weigh the bulb. The increase in weight represents CO_2.

Blank

Determine a blank on each absorption bulb, following the same procedure and using the same amounts of all materials.

Calculation

Calculate the percentage of carbon as follows:

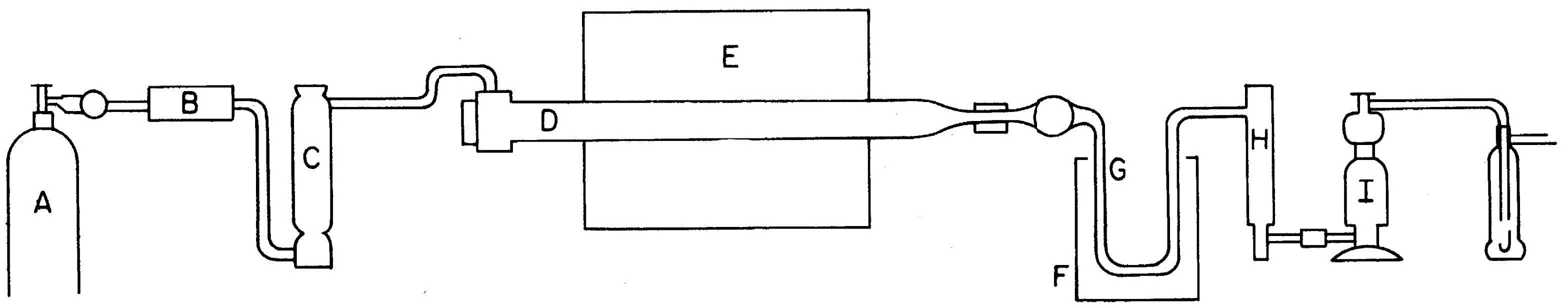
$$\text{Carbon, percent} = \frac{(A - B) \times 0.2729}{C} \times 100$$

where:

A = grams of CO_2

B = correction for blank, in grams, and

C = grams of sample used.



A - Oxygen supply
B - Preheating furnace
C - Purifying tower containing ascarite
D - Combustion tube
E - Electric furnace

F - Furnace for heating catalyst at 440° C
G - Tube containing platinized silica gel
H - Tower containing ironized asbestos and anhydrone
I - Fleming bulb containing ascarite and anhydrone
J - Bubble tube containing H_2SO_4

Figure 1. Schematic of combustion carbon method apparatus.

3. MANGANESE IN WHITE CAST IRON

When correct conditions are closely observed, oxidation with ammonium persulfate, followed by a measured reduction with sodium arsenite, is a reliable and rapid method for the determination of manganese, and thus is preferred to the bismuthate method.

Manganese may also be determined gravimetrically as the pyrophosphate or as the sulfate, and photometrically as the colored permanganate ion. However, it is commonly determined volumetrically by one of two methods - the persulfate or the bismuthate methods, which terms refer to the reagents used in oxidizing the manganese in solution [2,3,4,6].

While the bismuthate method is reliable, it is time-consuming and requires great care to obtain accurate results.

Scope

This method is recommended for the determination of manganese in the range of 0.3 to 1.5 percent. The relative standard deviations at the low and high ranges are 0.005 and 0.02 percent, respectively.

Principle of Method

Manganese ions in a sulfuric-phosphoric-nitric acid medium are oxidized to permanganate by ammonium persulfate in the presence of silver ions. The permanganic acid is titrated with standard sodium arsenite solution.

Interferences

Elements ordinarily present in white iron do not interfere when the titration is performed potentiometrically. If the samples contain between 5 and 20 mg of chromium, the background is compensated for by the addition of potassium dichromate solution to the solution used for standardization.

Apparatus

Apparatus for potentiometric titration is available commercially.

Reagents

(a) Ammonium persulfate solution (250 g per liter). Dissolve 25 g of ammonium persulfate ($(NH_4)_2S_2O_8$) in water and dilute to 100 ml. Do not use solutions that are more than one day old.

(b) Iron, high purity (low manganese). Determine the manganese content of a suitably milled and well-mixed portion of the metal by the periodate photometric method.

(c) Manganese, standard solution (1 ml = 0.0008 g Mn). Transfer an amount of high-purity manganese of known assay, equivalent to 0.8 g of manganese, weighed to the nearest 0.1 mg, to a 250-ml beaker. Add 15 ml of HNO_3 (1+1) and heat gently to dissolve the metal and expel brown fumes. Cool, transfer to a 1-liter volumetric flask, dilute to volume, and mix.

(d) Mixed acids. Add 100 ml of H_2SO_4 to 525 ml of water slowly, while stirring. Cool, add 125 ml of H_3PO_4 and 250 ml HNO_3, and mix.

(e) Potassium dichromate solution (1 ml = 0.001 g Cr). Dissolve 2.830 g of potassium dichromate ($K_2Cr_2O_7$) in water, transfer to a 1-liter volumetric flask, dilute to volume, and mix.

(f) Silver nitrate solution (8 g per liter). Dissolve 8 g of silver nitrate ($AgNO_3$) in water and dilute to 1 liter.

(g) Sodium arsenite solution (54 g per liter). Dissolve 54 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 liter.

(h) Sodium arsenite, standard solution (1 ml = 0.0008 g Mn). Dilute 100 ml of the sodium arsenite solution described in Paragraph (g) to 1 liter and filter, if not clear. Saturate the solution with carbon dioxide.

Procedure

(a) Transfer a 1 g sample, weighed to the nearest 0.5 mg, to a 250-ml beaker.

(b) Add 30 ml of water, 30 ml of mixed acids and 2-3 drops of HF. Heat until dissolution of the sample is complete, and boil the solution until brown fumes have been expelled. Dilute to 75 ml with water, filter through a coarse paper, collecting the filtrate in a 500-ml

Erlenmeyer flask. Wash the residue with hot water, adjust the volume to 125 ml and proceed as directed in paragraphs (d) and (e).

(c) Dissolve approximately the same weight of iron as the weight of the sample in 30 ml of the mixed acids. Transfer by pipet a portion of the manganese solution (1 ml = 0.0008 g Mn) to the iron solution. The amount of manganese added should be approximately the same amount as expected in the sample. Dilute to 130 ml with water and proceed as directed in paragraphs (d) and (e). Use this solution for the standardization of the sodium arsenite solution.

(d) Add 10 ml of $AgNO_3$ solution and 15 ml of $(NH_4)_2S_2O_8$ solution. Heat the solution to boiling, and boil briskly for 90 sec. Cool to 5 to 10°C in an ice bath.

(e) Transfer the solution to a 400-ml beaker and rinse the flask with 50 ml of cold water (5 to 10°C). Position the electrodes of the titrimeter in the solution, stir vigorously, and titrate with sodium arsenite solution until a maximum change in potential is indicated.

(f) Calculate the manganese equivalent of the arsenite solution as g of manganese per ml.

Calculation

Calculate the percentage of manganese as follows:

$$\text{Manganese, percent} = \frac{AB}{C} \times 100$$

where:

A = milliliters of sodium arsenite solution required to titrate the sample,

B = manganese equivalent of the sodium arsenite solution, in grams per milliliter, and

C = grams of sample used.

4. PHOSPHORUS IN WHITE CAST IRON

In this method, phosphorus is converted to the blue complex by adding a solution containing hydrazine sulfate and ammonium molybdate and heating at 98°C for several minutes. The transmittance or absorbance is read at 650 mμ.

Other widely used methods for the determination of phosphorus in ferrous materials involve its precipitation as the yellow ammonium phosphomolybdate and subsequent conversion to magnesium pyrophosphate or by titration of the phosphomolybdate with standard alkali solution. These methods are dependable, but time-consuming [3].

More rapid and sensitive photometric methods which utilize the molybdenum-blue reaction are generally preferred because of their relative freedom from interferences by alloying elements [7].

Scope

This method is recommended for the determination of phosphorus in the range of 0.01 to 0.8 percent. The relative standard deviations at the low and high ranges are 0.002 and 0.01 percent, respectively.

Principle of Method

Phosphorus as the ortho acid forms a blue complex with ammonium molybdate-hydrazine sulfate. Photometric measurement is made at approximately 650 mμ.

Concentration Range

The recommended concentration range is from 0.001 to 0.04 mg of phosphorus in 50 ml of solution, using a cell path of 2 cm.

Stability of Color

The color develops within 5 minutes at 98°C and is stable for at least 24 hours.

Interferences

Arsenic above 0.05 percent interferes and must be removed by volatilization with HBr.

Reagents

(a) Ammonium molybdate solution (2 percent in 11 N H_2SO_4). Add 300 ml of H_2SO_4 (sp gr 1.84) to 500 ml of water and cool. Dissolve 20 g of ammonium molybdate in the acid and dilute to 1 liter with water.

(b) Hydrazine sulfate solution (0.15 percent). Dissolve 1.5 g of hydrazine sulfate in 1 liter of water.

(c) Ammonium molybdate-hydrazine sulfate solution. Dilute 25 ml of ammonium molybdate solution to 80 ml with water, add 10 ml of the hydrazine sulfate solution and dilute to 100 ml with water. Prepare this solution as needed.

(d) Sodium sulfite solution (10 percent). Dissolve 100 g of anhydrous sodium sulfite in 500 ml of water and dilute to 1 liter.

(e) Standard phosphorus solution (A) (1 ml = 0.4 mg of P). Dissolve 1.8312 g of Na_2HPO_4 in 200 ml of water, add 35 ml of HNO_3 (1+1), dilute to 1 liter in a volumetric flask with water, and mix.

(f) Standard phosphorus solution (B) (1 ml = 0.01 mg of P). Transfer 5.0 ml of standard phosphorus solution (A) with a pipet to a 200-ml volumetric flask, dilute to the mark with water, and mix. Prepare this solution as needed.

Preparation of Calibration Curve

(a) Transfer 0, 0.5, 1.0, 2.0, 3.0 and 4.0 ml aliquot portions of standard phosphorus solution (B) to each of six 125-ml Erlenmeyer flasks.

(b) Add 5 ml of HNO_3 (1+1) and 3.0 ml of $HClO_4$ (60 percent). Evaporate the solution to fumes and fume gently for 3 to 4 minutes to remove HNO_3.

(c) Cool and add 5 ml of HBr (1+4). Evaporate to fuming and fume gently to remove HBr. Cool, wash the wall of the flask with 5 ml of water, and evaporate to fumes. Cool somewhat and add 10 ml of water and 15 ml of Na_2SO_3 solution. Heat the solution to boiling and boil gently for 30 seconds. Add 20 ml of the ammonium molybdate-hydrazine sulfate reagent, heat to about 95-98°C and digest at this temperature for 4 to 5 minutes. Then heat rapidly just to the boiling temperature, but do not boil. Cool rapidly to room temperature and transfer the solution to a 50-ml volumetric flask. Wash the Erlenmeyer flask with 2-ml portions of a dilute solution of the ammonium molybdate-hydrazine sulfate reagent (1+4) and transfer the washings to the 50-ml flask. Dilute to the mark with the diluted solution of the reagent and mix.

(d) Transfer a portion of the solution to a 2-cm absorption cell and measure the transmittance or absorbance at about 650 mμ, using water as a reference solution for 100 percent transmittance or zero absorbance.

(e) Plot the transmittance values obtained against milligrams of phosphorus in 50 ml on semi-log paper. Calculate the phosphorus value in milligrams per absorbance unit from the A-scale readings.

Procedure

(a) Transfer an aliquot portion, containing from 0.001 mg to 0.04 mg of phosphorus, of a solution to a 125-ml Erlenmeyer flask. Proceed as directed in (b), (c), and (d) of section above.

(b) Using the value obtained, read from the calibration curve the number of milligrams of phosphorus present in 50 ml of the final solution.

Blank

Determine the blank correction by following the same procedure and using the same amounts of all reagents.

Calculation

Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, percent} = \frac{A - B}{C \times 10}$$

where:

A = milligrams of phosphorus in 50 ml of final solution

B = milligrams of phosphorus in 50 ml of the blank, and

C = grams of sample in 50 ml of the final solution.

5. SULFUR IN WHITE CAST IRON

The combustion-titration procedure given, though not stoichiometric, has gained widespread acceptance because of its speed and general application. The procedure permits various modifications in apparatus and reagents, but because it is empirical, close adherence to the details of the method is necessary to yield reproducible and accurate results [3,5].

A number of other methods are available for the determination of sulfur in ferrous materials. The gravimetric procedure in which the sulfur is weighed as barium sulfate; the evolution method in which it is evolved as hydrogen sulfide and then oxidized by a solution of iodine or iodate; and the combustion - titration procedure all have been widely used. Difficulties attending to accurate determinations by the gravimetric method are generally well known. The evolution method is rapid, but it is empirical and the details must be carefully worked out and followed if satisfactory results are to be obtained [2,3,4].

Scope

This method is recommended for the determination of sulfur in the range of 0.01 to 0.2 percent. The relative standard deviations at the low and high ranges are 0.002 and 0.003 percent, respectively.

Principle of Method

A major part of the sulfur in the sample is converted to sulfur dioxide (SO_2) by combustion in a stream of oxygen. The SO_2 is absorbed in an acidified starch-iodide solution and determined, during the combustion, by titration with a potassium iodate solution. The latter is standardized against materials similar in composition to those being analyzed, since the percentage of sulfur evolved as SO_2 varies with different materials.

Interferences

Elements ordinarily present in white iron do not interfere.

Apparatus

Apparatus for determination of sulfur by combustion-titration method is available commercially or may be constructed. A schematic of the apparatus for the combustion sulfur method is given in figure 2.

(a) Resistance furnace, using silicon carbide resistance elements and capable of maintaining a temperature of at least 1425°C.

(b) Miscellaneous apparatus. Additional equipment required: absorption and titration apparatus, boats, buret, combustion tube, oxygen flow indicator, oxygen pressure gages, porous filter.

Reagents and Materials

(a) Boats and covers, ceramic. Ignite in a tube furnace in the presence of oxygen at 1000°C or higher for at least 1 hour before use.

(b) Copper, foil strips for use as an accelerator.

(c) Oxygen, minimum 99.6 percent pure.

(d) Potassium iodate, standard solution (1 ml = 0.0001 g S). Dissolve 0.207 g of KIO_3 in 900 ml of water, and dilute to 1 liter in a volumetric flask. (Note: Experimental work indicates that the recovery of sulfur as sulfur dioxide is 93 to 95 percent complete with the apparatus and procedure used. The standard iodate solution is prepared by weighing 93 percent of the stoichiometric amount of potassium iodate.)

(e) Starch solution (9 g per liter). Transfer 9 g of soluble starch to a small beaker, add 5 to 10 ml of water, and stir until a smooth paste is obtained. Pour the mixture slowly into 500 ml of boiling water. Cool, add 15 g of KI, and stir until the KI is dissolved. Dilute to 1 liter.

Procedure

(a) Adjust the temperature of the furnace to 1425 to 1440°C.

(b) Add approximately 65 to 70 ml of HCl (3+197) and 2 ml of starch solution to the titration vessel. Pass oxygen through the system and add a small amount of KIO_3 (1 ml = 0.0001 g S) until the intensity of the blue color is that which is to be taken as the endpoint of the final titration. Read the buret and record as the initial reading. Turn off the oxygen.

(c) Transfer a 1 g sample, weighed to the nearest 1 mg, to the preignited combustion boat, spreading the sample evenly over the length of the boat. Select as a control, a sample whose sulfur content and alloy characteristics are similar to those of the sample being analyzed. Cover the sample with approximately 0.2 g of copper foil. Place a preignited cover on the boat and introduce the boat and contents into the center of the combustion zone of the combustion tube. Close the tube and allow the sample to heat for 1.5 min. Start the flow of oxygen at a rate of approximately 1.5 liters per min.

(d) As the stream of gas begins to bubble through the absorption solution, the blue color will fade. Titrate continuously with standard KIO_3 solution (1 ml = 0.0001 g S) at such a rate as to maintain as nearly as possible, the initial intensity of the blue color. A 5 to 6 minute combustion period will usually suffice. Near the end of the combustion period, carefully adjust the blue color of the endpoint to that taken initially, paragraph (b). Read the buret and record the reading. Subtract the initial reading. The difference is the volume of KIO_3 solution required for titration of the sample.

Blank

Make a blank determination, following the same procedure and using the same amounts of all reagents.

Some refractory boats may contain sulfur compounds liberated only in the presence of a burning sample, and each lot should be checked on a low sulfur standard to insure proper performance.

Calculation

Calculate the percentage of sulfur as follows:

$$\text{Sulfur, percent} = \frac{(A - B)C \times 100}{D}$$

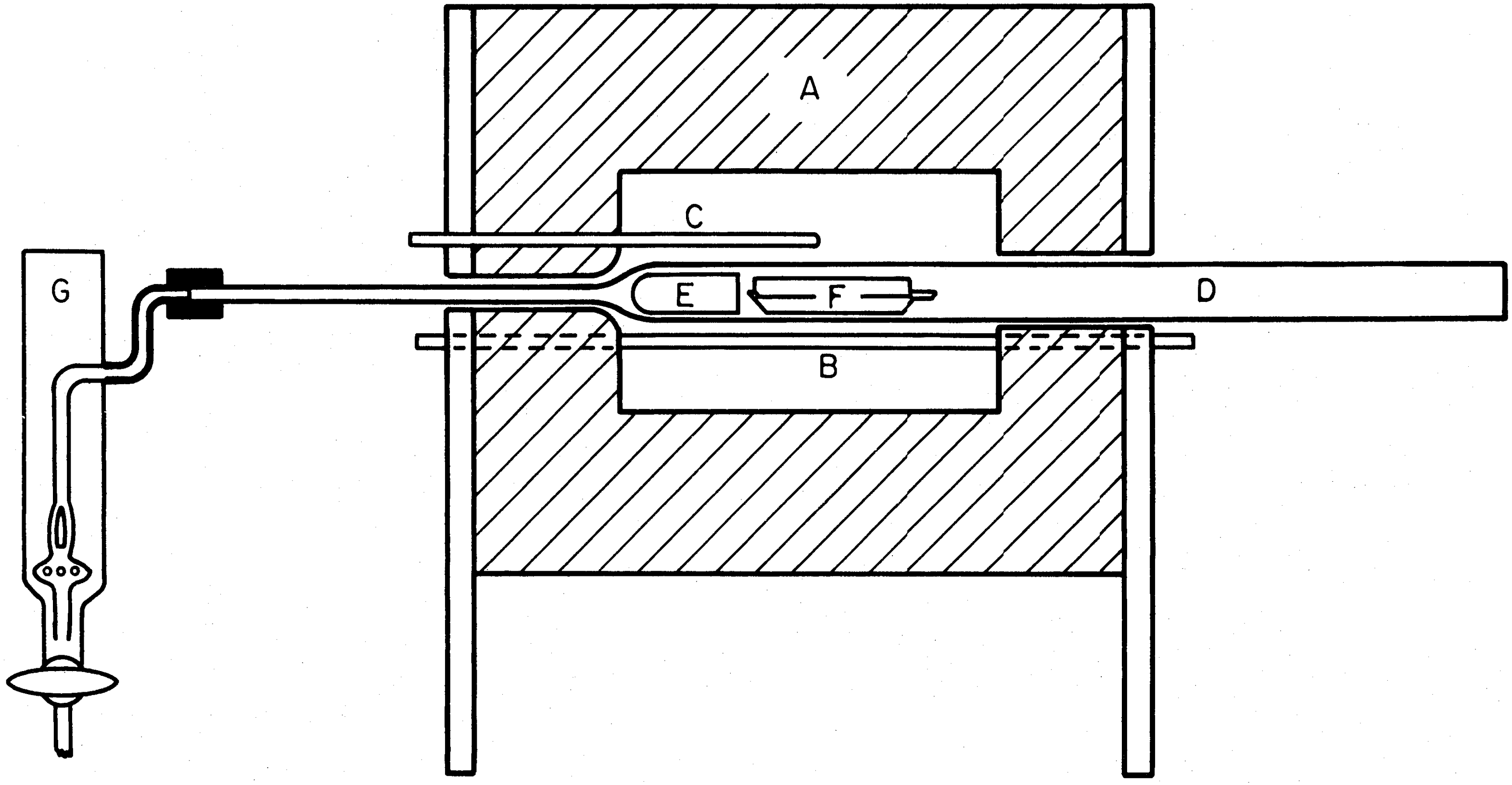
where:

A = milliliters of standard KIO_3 solution required for titration of the sample

B = milliliters of standard KIO_3 solution required for titration of the blank

C = sulfur equivalent of the KIO_3 solution, in grams per milliliter, and

D = grams of sample used.



A – High temperature furnace
B – Silicon carbide heating elements
C – High temperature thermocouple
D – Combustion tube
E – Porous filter
F – Combustion boat and cover
G – Titration vessel

Figure 2. Schematic of combustion-titration method for sulfur.

6. SILICON IN WHITE CAST IRON

The most reliable methods for the determination of silicon in white cast iron involve solution of the sample in a mineral acid or a mixture of these acids, dehydration with sulfuric or perchloric acid, and final purification of the residue by volatilizing the silica with hydrofluoric acid [2,3,5,8].

In this method, the use of perchloric acid as the dehydrating acid has the advantage that most anhydrous perchlorates are readily soluble; thus, little difficulty is encountered in dissolving the salts after the silicic acid has been dehydrated. Since single evaporations never yield all of the silica, double dehydrations are recommended.

Scope

This method is recommended for the determination of silicon in the range of 0.3 to 4.0 percent. The relative standard deviations at the low and high ranges are 0.0004 and 0.002 percent, respectively.

Principle of Method

After dissolution of the sample, silicic acid is dehydrated by fuming with perchloric acid. The solution is filtered, and the silica is ignited, weighed, and then volatilized with hydrofluoric acid. The residue is ignited and weighed. The loss in weight represents silica (SiO_2).

Interferences

Elements ordinarily present in white iron do not interfere.

Procedure

(a) Transfer a sample to a 400-ml beaker, selecting the sample weight in accordance with the following table and weighing it to the nearest 3 or 5 mg as specified.

Silicon percent	Sample Weight g	Tolerance of Sample Weight g
0.30 to 2.0	4.675	0.005
2.0 to 4.0	2.337	.003

(b) Add 40 ml of HNO_3 (3+5), cover and heat cautiously until dissolution of the sample is complete. Raise the cover and add 40 ml of $HClO_4$ for a 2.337 g sample, or 60 ml for a 4.675 g sample. Evaporate the solution to fumes and heat at such a rate that the $HClO_4$ refluxes on the sides of the beaker for 15 to 20 min. Discontinue heating and when the solution has cooled sufficiently add 100 ml of warm water (40 to 50°C). Stir to dissolve the salts and heat gently, if necessary.

(c) Add pulp and filter immediately, using an 11-cm medium paper. Collect the filtrate in a 600-ml beaker. Transfer the precipitate to the paper, scrubbing the beaker thoroughly with a rubber-tipped rod. Wash the paper and residue alternately but not more than 8 to

10 times with 3 to 5 ml portions of hot HCl (5+95) and hot water to remove the iron salts. Transfer the paper to a platinum crucible and reserve.

(d) Add 15 ml of HNO_3 to the filtrate and evaporate the solution as directed in paragraph (b). Filter immediately, using a 9-cm fine paper and wash as directed in paragraph (c).

(e) Transfer the paper to the reserved platinum crucible and heat carefully at 600°C until the carbon is removed. Finally ignite for at least 30 min., or to constant weight, at 1100 to 1150°C. Cool in a desiccator, and weigh.

(f) Add enough H_2SO_4 (1+1) to moisten the SiO_2, and then 3 to 5 ml of HF. Evaporate to dryness and then at a gradually increasing rate until H_2SO_4 is removed. Ignite for 15 min. at 1100 to 1150°C, cool in a desiccator, and weigh.

Calculation

Calculate the percentage of silicon as follows:

$$\text{Silicon, percent} = \frac{(A-B) \times 0.4675}{C} \times 100$$

where:

A = initial weight, crucible and impure SiO_2,

B = final weight, crucible and residue, and

C = grams of sample used.

7. COPPER IN WHITE CAST IRON

Accurate methods for the determination of copper include gravimetric, electrolytic, titrimetric and photometric approaches. All give satisfactory results when properly applied and carried out. All, except the photometric procedure, generally require preliminary and time-consuming separations of the copper, either as the sulfide or the thiocyanate [2,3].

A rapid, one-step photometric procedure [9], specifically designed for the determination of copper in all types o of ferrous alloys, has been readily adapted to white cast iron. In this method, citrate and ethylenediaminetetraacetate (versene) are added as complexing agents, the copper carbamate complex is then formed and extracted with butyl acetate. The absorbance of the copper carbamate complex is measured at 560 mμ.

Scope

This method is recommended for the determination of copper in the range of 0.1 to 1.5 percent. The relative standard deviations at the low and high range are 0.002 and 0.02 percent, respectively.

Principle of Method

After dissolution of the sample, citric acid and ammonium hydroxide are added. The sodium salt of ethylenediaminetetraacetic acid is added as a complexing agent and sodium diethyldithiocarbamate is added to form the copper complex. The copper complex is extracted with butyl acetate and the photometric measurement is made at approximately 560 mμ.

Concentration Range

The recommended concentration range is from 0.002 mg to 0.04 mg of copper in 25 ml of butyl acetate using a cell path of 2 cm.

Stability of Color

The color is stable for several hours.

Interfering Elements

Provision has been made to complex all commonly encountered interfering elements.

Reagents

(a) Citric acid solution (250g per liter). Dissolve 125 g of citric acid in about 250 ml of water, add 10 ml of H_2SO_4 (1+1), and dilute to 500 ml with water.

(b) Disodium ethylenediaminetetraacetate solution (40 g per liter). Dissolve 20 g of disodium ethylenediaminetetraacetate dihydrate in 400 ml of water and dilute to 500 ml.

(c) Sodium diethyldithiocarbamate solution (1.0 g per liter). Dissolve 0.1 g of sodium diethyldithiocarbamate trihydrate in 100 ml of water.

(d) Standard copper solution (1 ml = 200 μg Cu). Dissolve 100.0 mg of copper in 20 ml of H_2SO_4 (1+1) and 5 to 6 drops of HNO_3 by heating. Evaporate the solution to fumes of H_2SO_4, cool, add 100 ml of water, and cool to room temperature. Transfer the solution to a 500-ml volumetric flask, dilute to the mark with water, and mix well.

(e) Standard copper solution (1 ml = 4.00 μg Cu). Transfer exactly 10 ml of standard copper solution (1 ml = 200 μg Cu) to a 500-ml volumetric flask, dilute to the mark with water, and mix well. Prepare this solution as needed.

Preparation of Calibration Curve

Calibration Solutions. Transfer 0, 1.0, 3.0, 5.0, 7.0, and 10.0 ml of standard copper solution (1 ml = 4.00 μg Cu) to each of six 125 ml Erlenmeyer flasks. Add 10 ml of H_2SO_4 (1+1), dilute to 25 ml with water, and add 10 ml of citric acid solution.

(a) Neutralize the above solution to a pH 7, using litmus paper, with ammonium hydroxide, cooling, if necessary, and add 3 to 5 ml in excess. Add 15 ml ethylenediaminetetraacetate solution to the warm solution and cool to room temperature. Transfer the solution to a 125-ml separatory funnel, washing the Erlenmeyer flask with 10 ml of water. Add 10 ml of diethyldithiocarbamate solution and shake for 10 to 15 seconds. Pipet exactly 25 ml of butyl acetate into the funnel, shake for 30 seconds and cool in running water for 2 to 3 minutes. Repeat the shaking for

15 seconds, cool, and allow the layers to separate. Drain off completely the lower aqueous layer and discard. Transfer the butyl acetate layer to a dry test tube and stopper.

(b) Photometry. Fill the reference cell with butyl acetate and adjust the photometer to the initial setting, using a light band centered at approximately 560 mμ. While maintaining this photometric adjustment, take the photometric readings of the calibration solutions.

(c) Calibration curve. Plot the photometric readings of the calibration solutions against the micrograms of copper per 25 ml of butyl acetate extract.

Procedure

(a) Transfer a 0.100 g sample, containing not more than 40 μg of copper, to a 125-ml Erlenmeyer flask, add 15 ml of H_2SO_4 (1+4), 1 to 2 drops of HF and heat until the sample dissolves. Evaporate the solution to fumes of H_2SO_4. Cool, (Note), add 20 ml of water and 10 ml of citric acid solution and continue as directed in paragraphs (a) and (b) above.

(Note) For samples containing more than 40 μg Cu, transfer to a 100 ml volumetric flask, add 5 ml H_2SO_4 (1+1) and dilute to the mark with water. Transfer an aliquot, containing not more than 40 μg of copper to a 125-ml Erlenmeyer flask, adjust the amount of H_2SO_4 and water to provide a volume of 25 ml containing 5 ml of H_2SO_4. Add 10 ml of citric acid solution and continue as directed in paragraphs (a) and (b) above.

(b) By means of a calibration curve, convert the photometric readings of the sample solutions to micrograms of copper.

Blank

Make a blank determination following the same procedure and using the same amounts of all reagents.

Calculation

Calculate the percentage of copper as follows:

$$\text{Copper, percent} = \frac{A - B}{C \times 10^4}$$

where:

A = micrograms of copper found in the 25 ml of butyl acetate extract of the sample

B = micrograms of copper found in the 25 ml of butyl acetate extract of the blank

C = grams of sample represented in the 25 ml of butyl acetate extract of the sample.

8. NICKEL IN WHITE CAST IRON

(Nickel greater than 1 percent)

The dimethylglyoxime-gravimetric procedure, as applied to ferrous materials, is virtually specific for nickel when the necessary precautions are observed. This procedure has the desirable feature of requiring few, if any preliminary separations.

Nickel can also be determined volumetrically by titration with silver nitrate after treatment of an oxidized solution with potassium iodide and potassium cyanide, gravimetrically or volumetrically after precipitation with dimethylglyoxime, or electrolytically [2,3,4].

Scope

This method is recommended for the determination of nickel in the range of 1.0 to 3.0 percent. For this concentration range, the relative standard deviation is 0.02 percent.

Principle of Method

After dissolution of the sample, nickel is precipitated with dimethylglyoxime, filtered and weighed.

Interferences

Interferences due to copper and cobalt are eliminated by double precipitation of the nickel dimethylglyoxime.

Apparatus

Crucible, filtering. Fritted-glass filtering crucibles or porous-bottom porcelain filtering crucibles are recommended for general use.

Reagents

(a) Citric acid solution (250 g per liter). Dissolve 250 g of citric acid in 750 ml of water, add 20 ml of diluted H_2SO_4 (1+1), dilute to 1 liter and filter, if necessary.

(b) Dimethylglyoxime (10 g per liter of ethyl alcohol). Dissolve 10 g of dimethylglyoxime in 1 liter of ethyl alcohol and filter, if necessary.

Procedure

(a) Transfer a 2 g sample to a 600-ml beaker, add 100 ml of HNO_3 (1+3), and digest until solution is complete. Evaporate the solution to dryness. Dissolve the residue in 20 ml of HCl and heat gently. Add 75 ml of hot water, and filter, using an 11 cm coarse paper containing pulp, into a 600-ml beaker. Transfer any insoluble material to the filter, wash alternately with hot HCl (5+95) and hot water until most of the iron salts are removed and then 3 times with hot water. Dilute the filtrate to 200 ml with water.

(b) Transfer the paper and precipitate to a platinum crucible, ignite at 850 to 900°C, cool, and add enough H_2SO_4 (1+1) to moisten the residue, and then 3 to 5 ml of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue in a minimum of $Na_2S_2O_7$ and add the fusion to the reserved filtrate.

(c) Add 75 ml of citric acid solution and neutralize with NH_4OH. Add 40 ml, or a sufficient amount, of dimethylglyoxime solution, and add a slight excess of NH_4OH. Digest for 1 hour at $60^{\circ}C$. Cool to room temperature and filter through an 11 cm fine paper. Wash the beaker and precipitate 3 times with water. Add 5 ml of dimethylglyoxime to the filtrate to determine whether precipitation is complete.

(d) Transfer the paper and precipitate to the beaker, add 5 ml of H_2SO_4 and mix thoroughly to char the paper. Add 20 ml of HNO_3, digest until the solution is clear, and evaporate to dense fumes of H_2SO_4. Continue the fuming for 5 to 10 minutes to destroy all organic matter, cool, and wash the sides of the beaker. Add 25 ml of water and 5 ml of citric acid solution. Mix well, and filter, using a 9 cm fine paper containing pulp, into a 400-ml beaker. Wash the beaker 3 to 4 times and finally wash the paper 12 to 15 times with hot water. Adjust the volume to 200 ml. Discard any residue.

(e) Nearly neutralize the filtrate with NH_4OH, add 40 ml, or a sufficient amount, of dimethylglyoxime solution, and add a slight excess of NH_4OH. Digest for 1 hour at $60^{\circ}C$. Cool to room temperature. Filter the precipitate through a weighed fritted crucible, wash well with water.

(f) Dry the precipitate at 130°C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

Calculation

Calculate the percentage of nickel as follows:

$$\text{Nickel, percent} = \frac{A \times 0.2032}{B} \times 100$$

where:

A = grams of nickel dimethylglyoxime, and

B = grams of sample used.

8. NICKEL IN WHITE CAST IRON

(Nickel less than 1 percent)

Scope

This method is recommended for the determination of nickel in the range of 0.01 to 1.0 percent. The relative standard deviations at the low and high ranges are 0.003 and 0.02 percent, respectively.

Principle of Method

After dissolution of the sample, the bulk of the iron is separated from nickel by extraction with ether. The nickel is then precipitated with dimethylglyoxime, filtered and weighed.

Interferences

Interferences due to copper and cobalt are eliminated by double precipitation of the nickel dimethylglyoxime.

Apparatus

Crucible, filtering. Fritted-glass filtering crucibles or porous-bottom porcelain filtering crucibles are recommended for general use.

Reagents

(a) Citric acid solution (250 g per liter). Dissolve 250 g of citric acid in 750 ml of water, add 20 ml of diluted H_2SO_4 (1+1), dilute to 1 liter and filter, if necessary.

(b) Dimethylglyoxime (10 g per liter of ethyl alcohol). Dissolve 10 g of dimethylglyoxime in 1 liter of ethyl alcohol and filter, if necessary.

(c) Ethyl ether.

Procedure

(a) Transfer a 10 g sample to a 600-ml beaker, add 100 ml of HCl (1+1), and digest until solution is complete. Cool somewhat, cautiously add 8 to 12 ml of HNO_3 to oxidize the solution, and evaporate to dryness. Dissolve the residue in 20 ml of HCl and heat gently. Add 75 ml of hot water, and filter using an 11 cm coarse paper containing pulp into a 600-ml beaker. Transfer any insoluble material to the filter, wash alternately with hot HCl (5+95) and hot water until most of the iron salts are removed, and then 3 times with hot water. Evaporate the filtrate to dryness on the steam bath, cool, and dissolve in 50 ml of HCl (1+1).

(b) Transfer the paper and precipitate to a platinum crucible, ignite at 850 to 900°C, cool, and add enough H_2SO_4 (1+1) to moisten the residue, and then 3 to 5 ml of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue in a minimum of $Na_2S_2O_7$ and add the fusion to the reserved filtrate.

(c) Transfer the solution in paragraph (a) above to a 600-ml cylindrical separatory funnel, rinse the beaker several times with small portions of HCl (1+1), and dilute to a volume of 130 ml with HCl (1+1). Cool in an ice bath to 5 to 10°C, add 300 ml of cooled ethyl ether and shake thoroughly. Allow the funnel to cool 5 to 10 minutes in the ice bath, and repeat the shaking. Allow the layers to separate, and draw off the lower acid layer into the 600-ml beaker. Wash the funnel with approximately 25 ml of cold HCl (1+1) and repeat the above operations, finally draining the lower acid layer into the beaker. Discard the ether layer.

(d) Cautiously heat the ether-extracted acid layer on a steam bath to remove the ether, add 3 ml of HNO_3 and finally evaporate to dryness. Dissolve in 5 ml of HCl (1+1) and dilute to 75 ml with water. Heat gently until the salts are in solution and adjust the volume to 200 ml.

(e) Add 25 ml of citric acid solution, nearly neutralize with NH_4OH, add 20 ml, or a sufficient amount, of dimethylglyoxime solution. Add NH_4OH until slightly alkaline, and digest for 1 hour at about $60^\circ C$. Cool to room temperature. Filter using an 11-cm fine paper containing a little pulp into a 600 ml beaker. Wash the beaker and precipitate 3 times with water. Add 5 ml of dimethylglyoxime to the filtrate to determine whether precipitation is complete.

(f) Transfer the paper and precipitate to the beaker, add 5 ml of H_2SO_4, and mix thoroughly to char the paper. Add 20 ml of HNO_3, digest until the solution is clear, and evaporate to dense fumes of H_2SO_4. Continue the fuming for 5 to 10 minutes to destroy all organic matter, cool, and wash the sides of the beaker. Add 25 ml of water and 5 ml of citric acid solution. Mix well, and filter using a 9 cm fine paper containing pulp into a 400-ml beaker. Wash the beaker 3 to 4 times, and finally wash the paper 12 to 15 times with hot water. Adjust the volume to 200 ml. Discard any residue.

(g) Nearly neutralize the filtrate with NH_4OH, add 20 ml, or a sufficient amount, of dimethylglyoxime solution. Add NH_4OH until slightly alkaline and digest for 1 hour at about $60^\circ C$. Cool to room temperature.

Filter the precipitate through a weighed fritted crucible, wash well with water.

(h) Dry the precipitate at 130°C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

Calculation

Calculate the percentage of nickel as follows:

$$\text{Nickel, percent} = \frac{A \times 0.2032}{B} \times 100$$

where:

A = grams of nickel dimethylglyoxime, and

B = grams of sample used.

9. CHROMIUM IN WHITE CAST IRON

The most satisfactory methods for determining chromium in ferrous materials are volumetric and differ only in the reagents that are used to oxidize the chromium and in the details of titrating the oxidized chromium.

The basis for one of the most commonly used volumetric procedures is the oxidation to hexavalent chromium with ammonium persulfate and reduction to the trivalent form by potentiometric titration with ferrous ammonium sulfate. Any vanadium present is oxidized to vanadate with persulfate and is reduced to the vanadyl state by the ferrous sulfate. This is the basis for the determination of both chromium and vanadium on the same sample [2,4,5].

Scope

This method is recommended for the determination of chromium in the range of 0.2 to 3.0 percent. The relative standard deviations at the low and high. ranges are 0.002 and 0.02 percent, respectively.

Principle of Method

After dissolution of the sample, chromium is oxidized with $(NH_4)_2S_2O_8$ and titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$.

Vanadium is titrated with the chromium and it must be determined and the proper corrections applied to the chromium.

Apparatus

Apparatus for potentiometric titration.

Reagents

(a) Ammonium persulfate solution (15 percent). Dissolve 15 g of $(NH_4)_2S_2O_8$ in 85 ml of water. This solution should be prepared as needed.

(b) Ferrous ammonium sulfate (23 g per liter). Dissolve 23 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1 liter of cool H_2SO_4 (1+19).

(c) Potassium dichromate, standard solution (1 ml = 0.0010 g Cr). Dissolve 2.829 g of $K_2Cr_2O_7$ in 500 ml of water contained in a 1 liter volumetric flask, and dilute to volume with water.

(d) Silver nitrate solution (0.25 percent). Dissolve 2.5 g of $AgNO_3$ in 1 liter of water.

Procedure

(a) Transfer a 2 g sample to a 600-ml beaker, add 75 ml of water and 20 ml of H_2SO_4. Heat gently until the sample is dissolved. Evaporate until salts separate, cool, and dilute with about 50 ml of warm water, and digest until the salts are dissolved.

(b) Filter, using an 11 cm coarse paper containing pulp and collect the filtrate in a 600-ml beaker. Wash the beaker and paper 10 to 12 times with warm H_2SO_4 (2+98). Reserve the filtrate.

(c) Transfer the paper and residue to a platinum crucible, ignite at 850 to 900°C, cool, and add enough H_2SO_4 (1+1) to moisten the residue, and then 3 to 5 ml of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue in a minimum of $Na_2S_2O_7$ and add the fusion to the reserved filtrate.

(d) Dilute the solution to a volume of 300 ml with water, add 10 ml of $AgNO_3$ solution and 20 ml of ammonium persulfate solution. Heat to boiling and boil 20 minutes to oxidize the chromium. At this point a pink color due to permanganic acid should develop, indicating the complete oxidation of the chromium (and vanadium). If this does not occur, add more $AgNO_3$ and $(NH_4)_2S_2O_8$ and continue the boiling for several minutes until a pink color appears. Boil for 10 to 15 minutes after the last addition of the $(NH_4)_2S_2O_8$. Add 5 ml of HCl (1+3) and boil for 10 minutes after the pink color has disappeared. Cool to room temperature.

(e) Position the electrodes of the titrimeter in the solution, stir vigorously and titrate the chromium with ferrous ammonium sulfate (23 g per liter) until a maximum change in potential is indicated. Standardize the ferrous ammonium sulfate solution by titrating potentiometrically an equivalent amount of chromium as potassium dichromate in 300 ml of boiled and cooled H_2SO_4 (1+19). Vanadium is also titrated and a correction must be applied to the chromium.

Calculation

Calculate the percentage of chromium as follows:

A = grams of sexivalent chromium used as standard

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution used to titrate A.

$$\frac{A}{B} = C$$

C = chromium titer, in grams, of $Fe(NH_4)_2(SO_4)_2$ solution

D = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution used to titrate the sample

E = grams of sample used

$$\text{Chromium + (vanadium), percent} = \frac{C \times D}{E} \times 100$$

In this method, vanadium is also titrated, and the chromium value obtained must be corrected for vanadium as follows:

$$\text{Chromium, percent (corrected)} = \left(\frac{C \times D}{E} \times 100\right) - \left(\frac{F}{2.94}\right)$$

F = Percent of vanadium in sample.

10. CHROMIUM AND VANADIUM IN WHITE CAST IRON

(Sodium Bicarbonate Separation)

Scope

This method is recommended for the determination of chromium in the range of 0.01 to 0.2 percent and vanadium in the range of 0.005 to 0.3 percent. For chromium in this concentration range, the relative standard deviation is 0.002 percent. For vanadium in this concentration range, the relative standard deviations are 0.001 and 0.003 percent, respectively.

Principle of Method

After dissolution of the sample, chromium and vanadium are separated from the bulk of the iron by hydrolytic precipitation with $NaHCO_3$, oxidized with $(NH_4)_2S_2O_8$ and titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$.

Vanadium is titrated with the chromium and must also be determined and the proper corrections applied to the chromium.

Apparatus

Apparatus for potentiometric titration.

Reagents

(a) Ammonium persulfate solution (15 percent). Dissolve 15 g of $(NH_4)_2S_2O_8$ in 85 ml of water. This solution should be prepared as needed.

(b) Ferrous ammonium sulfate solution (8 g per liter). Dissolve 8 g of $Fe(NH_4)_2(SO_4)_2$, $\cdot 6H_2O$ in 1 liter of cool H_2SO_4 (1+19).

(c) Ferrous ammonium sulfate solution (23 g per liter). Dissolve 23 g of $Fe(NH_4)_2(SO_4)_2$, $\cdot 6H_2O$ in 1 liter of cool H_2SO_4 (1+19).

(d) Potassium dichromate standard solution (1 ml = 0.0010 g Cr). Dissolve 2.829 g of $K_2Cr_2O_7$ in 500 ml of water contained in a 1 liter volumetric flask, and dilute to volume with water.

(e) Silver nitrate solution (0.25 percent). Dissolve 2.5 g of $AgNO_3$ in 1 liter of water.

(f) Sodium bicarbonate solution (80 g per liter). Dissolve 80 g of $NaHCO_3$ in 900 ml of water, dilute to 1 liter and filter, if necessary.

Procedure

(a) Transfer a 10 g sample to a 500-ml Erlenmeyer flask, add exactly 110 ml of H_2SO_4 (1+9), cover and heat gently until the sample is dissolved. Dilute the solution with 50 ml of hot water and heat to boiling. Add the $NaHCO_3$ solution from a buret while constantly swirling the flask to avoid a local excess, until a slight permanent precipitate forms and then add 6 to 8 ml in excess. Cover the flask, boil gently for several minutes, and allow the precipitate to settle. Immediately filter using a 12.5 cm coarse paper, decanting the supernatant liquid, and finally transfer the precipitate to the paper. Wash the flask and paper 2 to 3 times with hot water and discard the filtrate. The filtrate may become cloudy through oxidation and hydrolysis of the iron, but this is of no consequence.

(b) Return the paper and precipitate to the flask, add 20 ml of H_2SO_4 and swirl until the filter is in solution. Add 25 ml of HNO_3, digest and evaporate to fumes of H_2SO_4. Repeat the digestion with an additional 25 ml of HNO_3 and evaporate to fumes, if necessary, to destroy organic matter. Add 75 ml of water, digest until salts are dissolved, and filter using an 11 cm coarse paper containing pulp, and collect the filtrate in a 600-ml beaker. Wash the flask and paper 10 to 12 times with warm water. Reserve the filtrate.

(c) Transfer the paper and residue to a platinum crucible, ignite at 850 to 900°C, cool, and add enough H_2SO_4 (1+1) to moisten the residue, and then 3 to 5 ml of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue in a minimum of $Na_2S_2O_7$ and add the fusion to the reserved filtrate.

(d) Add 3 ml of water saturated with SO_2, heat to boiling, and boil 5 minutes to expel the excess SO_2. Cool somewhat and oxidize any reduced iron with 3 ml of HNO_3. Boil to expel nitrous oxides, dilute to 200 ml, and add 40 ml of HNO_3. Remove the cover glass and boil gently for at least 1 hour at such a rate that the final volume is 125 ml. Cool, dilute to 300 ml with water and cool to 5°C in an ice bath.

(e) Position the electrodes of the titrimeter in the solution, stir vigorously and titrate the vanadium with standard ferrous ammonium sulfate solution (8 g per liter) until a maximum change in potential is indicated. Standardize the ferrous ammonium sulfate solution by titrating potentiometrically an equivalent amount of potassium dichromate in 300 ml of boiled and cooled H_2SO_4 (1+19).

(f) Evaporate the solution to fumes of H_2SO_4 and continue the fuming until most of the HNO_3 is expelled. Cool, add 75 ml of water, and digest until the salts are in solution.

(g) Dilute the solution to a volume of 300 ml with water, add 10 ml of $AgNO_3$ solution and 20 ml of ammonium persulfate solution. Heat to boiling and boil 20 minutes to oxidize the chromium. At this point a pink color due to permanganic acid should develop indicating the complete oxidation of the chromium (and vanadium). If this does not occur, add 2 drops of $KMnO_4$ solution (25 g per liter) and additional ammonium persulfate solution until a pink color appears. Add 5 ml of HCl (1+3) and continue the boiling for 10 minutes after the pink color has disappeared. Cool to room temperature.

(h) Position the electrodes of the titrimeter in the solution, stir vigorously and titrate the chromium with ferrous ammonium sulfate solution (23 g per liter) until a maximum change in potential is indicated. Standardize the ferrous ammonium sulfate solution by titrating potentiometrically an equivalent amount of chromium as potassium dichromate in 300 ml of boiled and cooled H_2SO_4 (1+19). Vanadium is also titrated and a correction must be applied to the chromium.

Calculation

Calculate the percentage of vanadium as follows:

A = grams of sexivalent chromium used as standard

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate A

C = vanadium titer, in percent, of $Fe(NH_4)_2(SO_4)_2$ solution

$$C = \frac{A \times 29.4}{B}$$

D = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate the sample

$$\text{Vanadium, percent} = C \times D$$

Calculate the percentage of chromium as follows:

E = grams of sexivalent chromium used as standard

F = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate E

G = chromium titer, in percent, of $Fe(NH_4)_2(SO_4)_2$ solution

$$G = \frac{E \times 10}{F}$$

H = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate the sample

$$\text{Chromium, percent} = G \times H - \frac{(C \times D)}{(2.94)}$$

11. VANADIUM IN WHITE CAST IRON

The principal methods for the determination of vanadium are volumetric and depend either on a measured reduction from the pentavalent to the tetravalent state, or on a measured oxidation from the tetravalent to the pentavalent state. The procedure utilizing the reduction of the vanadium is preferred because it can be readily performed in solutions at room temperature, while its oxidation, on the other hand, does not proceed as easily and is best done at 60 to 80°C.

A number of reagents are used to oxidize vanadium to vanadate and include nitric acid, permanganate, bromate, and hydrogen peroxide. The reduction is generally performed with ferrous ammonium sulfate.

In this method, the use of nitric acid for the oxidation and subsequent reduction with ferrous sulfate has the desirable feature of a rapid, direct potentiometric titration requiring no preliminary separations [2,4,10].

Scope

This method is recommended for the determination of vanadium in the range of 0.1 to 0.3 percent. For this concentration range, the relative standard deviation is 0.003 percent.

Principle of Method

After dissolution of the sample, vanadium is oxidized with HNO_3 and titrated potentiometrically with $Fe(NH_4)_2(SO_4)_2$.

Interference

Elements ordinarily present in white iron do not interfere.

Apparatus

Apparatus for potentiometric titration.

Reagents

(a) Ferrous ammonium sulfate solution (8 g per liter). Dissolve 8 g of $Fe(NH_4)_2(SO_4)_2, \cdot 6H_2O$ in 1 liter of cool H_2SO_4 (1+19).

(b) Potassium dichromate standard solution (1 ml = 0.0010 g Cr). Dissolve 2.829 g of $K_2Cr_2O_7$ in 500 ml of water contained in a liter volumetric flask, and dilute to volume with water.

Procedure

(a) Transfer a 2 g sample to a 600-ml beaker, and add 100 ml of H_2SO_4 (1+4). Heat gently until the sample is dissolved. Evaporate until salts separate, cool, and dilute with about 50 ml of warm water, and digest until the salts are dissolved.

(b) Add 10-15 ml of HNO_3 to oxidize the iron and any carbides that may persist. Filter, using an 11 cm coarse paper containing pulp and collect the filtrate in a 600-ml beaker. Wash the beaker and paper 10 to 12 times with warm H_2SO_4 (2+98). Reserve the filtrate.

(c) Transfer the paper and residue to a platinum crucible, ignite at 850 to 900°C, cool, and add enough

H_2SO_4 (1+1) to moisten the residue, and then add 3 to 5 ml of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue in a minimum of $Na_2S_2O_7$ and add the fusion to the reserved filtrate.

(d) Add 3 ml of water saturated with SO_2, heat to boiling, and boil 5 minutes to expel the excess SO_2. Cool somewhat and oxidize any reduced iron with 3 ml of HNO_3. Boil to expel nitrous oxides, dilute to 200 ml, and add 40 ml of HNO_3. Remove the cover glass and boil gently for at least 1 hour at such a rate that the final volume is 125 ml. Cool, dilute to 300 ml with water and cool to 5°C in an ice bath.

(e) Position the electrodes of the titrimeter in the solution, stir vigorously and titrate the vanadium with standard ferrous ammonium sulfate solution (8 g per liter) until a maximum change in potential is indicated. Standardize the ferrous ammonium sulfate solution by titrating potentiometrically an equivalent amount of potassium dichromate in 300 ml of boiled and cooled H_2SO_4 (1+19).

Calculation

Calculate the percentage of vanadium as follows:

A = grams of sexivalent chromium used in standard

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate A

C = vanadium titer, in percent, of $Fe(NH_4)_2(SO_4)_2$ solution

$$C = \frac{A \times 2.94}{B}$$

D = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution to titrate the sample

E = grams of sample used

$$\text{Vanadium, percent} = \frac{C \times D}{E}$$

12. MOLYBDENUM IN WHITE CAST IRON

A direct, one-step photometric procedure, readily adapted to white cast iron, is based on the formation and extraction of the molybdenum thiocyanate complex and subsequent measurement at 470 mμ [3].

Methods for the determination of molybdenum vary and include numerous photometric, gravimetric and volumetric approaches.

There is little to choose between the gravimetric methods in which the molybdenum is precipitated with alpha-benzoinoxime and ignited to the oxide, or precipitated and weighed as lead molybdate, and the volumetric method in which it is reduced by zinc, collected under a solution of ferric sulfate, and titrated with a standard solution of potassium permanganate. Both methods, however, are time consuming and require great care to obtain accurate results [4,5].

Scope

The photometric method is recommended for the determination of molybdenum in the range of 0.01 to 1.5 percent. The relative standard deviations at the low and high ranges are 0.002 and 0.02 percent, respectively.

Principle of Method

After dissolution of the sample, the thiocyanate complex of the molybdenum is developed. The complex is extracted with butyl acetate and the photometric measurement is made at approximately 470 mμ.

Concentration Range

The recommended concentration range is from 0.002 mg to 0.03 mg of molybdenum in 20 ml of butyl acetate using a cell depth of 2 cm.

Stability of Color

The intensity of the color is stable for several hours.

Interferences

Elements ordinarily present do not interfere.

Reagents

(a) Citric acid solution (250 g per liter). Dissolve 125 g of citric acid in about 250 ml of water, add 10 ml of H_2SO_4 (1+1), and dilute to 500 ml with water.

(b) Ferric sulfate solution (50 g per liter). Dissolve 5 g of $Fe_2(SO_4)_3 \cdot H_2O$ in 90 ml of H_2SO_4 (1+9) and dilute to 100 ml with H_2SO_4 (1+9).

(c) Sodium thiocyanate solution (100 g per liter). Dissolve 50 g of NaCNS in 400 ml of water and dilute to 500 ml.

(d) Stannous chloride solution (350 g per liter). Dissolve 175 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of HCl (1+1) by heating, and dilute to 500 ml with water.

(e) Standard molybdenum solution (1 ml = 150 µg Mo). Dissolve 189.1 mg of $Na_2MoO_4 \cdot 2H_2O$ in 100 ml of H_2SO_4 (1+9), transfer to a 500-ml volumetric flask, dilute to the mark with water, and mix well.

(f) Standard molybdenum solution (1 ml = 3.00 µg Mo). Transfer exactly 10 ml of standard molybdenum solution (1 ml = 150 µg) to a 500-ml volumetric flask, dilute to the mark with H_2SO_4 (1+99) and mix well. Prepare this solution as needed.

Preparation of Calibration Curve

Calibration solutions. Transfer 0, 1.0, 3 0, 5.0, 7.0 and 10.0 ml of standard molybdenum solution (1 ml = 3 µg Mo) to each of six 125-ml Erlenmeyer flasks, add 15 ml of H_2SO_4 (1+1) and dilute to 60 ml with water.

(a) Add 1 ml of ferric sulfate solution and 10 ml of citric acid solution, heat to 80°C for 5 minutes and cool. Transfer the solutions to 250-ml separatory funnels and cool in running water. Add 10 ml of sodium thiocyanate solution and shake for 30 seconds. Add 10 ml of stannous chloride solution and shake for exactly 1 minute. Pipet exactly 20 ml of butyl acetate into the funnel, shake for 30 seconds and cool in running water for 2 to 3 minutes. Repeat the shaking for 30 seconds and allow the layers to separate. Drain off and discard the lower aqueous layer. Add 50 ml of H_2SO_4 (1+9), 10 ml sodium thiocyanate solution and 5 ml of stannous chloride solution. Shake for 30 seconds, let stand for 2 to 3 minutes, repeat the shaking for 30 seconds and allow the layers to separate. Drain off and discard the lower aqueous layer. Transfer the butyl acetate layer to a dry test tube, stopper the tube, and allow to stand until the solution is clear.

(b) Photometry. Fill the reference cell with butyl acetate and adjust the photometer to the initial setting, using a light band centered at approximately 470 mμ. While maintaining this photometric adjustment, take the photometric readings of the calibration solutions.

(c) Calibration curve. Plot the photometric readings of the calibration solution against the micrograms of molybdenum per 20 ml of butyl acetate extract.

Procedure

(a) Transfer a 0.100 g sample, containing not more than 30 μg of molybdenum, to a 125-ml Erlenmeyer flask, add 15 ml of H_2SO_4 (1+1), 1 to 2 drops of HF and heat until the sample dissolves. Cool, add 1 ml of H_2O_2 (30 percent) and evaporate to fumes of H_2SO_4. Cool, (Note), dilute to 60 ml with water, add 10 ml of citric acid solution, heat to 80°C for 5 minutes and cool. Transfer the solutions to 250-ml separatory funnels and cool in running water. Continue the color development and extraction as directed in paragraphs (a) and (b) above.

(Note) For samples containing more than 30 μg Mo, add 5 ml of H_2SO_4 (1+1), dilute to 50 ml with water, cool, transfer to a 100-ml volumetric flask, and dilute to the mark with water. Transfer an aliquot, containing not more than 30 μg, to a 125-ml Erlenmeyer flask, and adjust the amount of H_2SO_4 to give about 7.5 ml of H_2SO_4 in the flask, add 1 to 2 drops of HF and heat to fumes of H_2SO_4. Cool, dilute to 60 ml with water and proceed as directed in paragraphs (a) and (b) above.

(b) By means of a calibration curve, convert the photometric readings of the sample solutions to micrograms of molybdenum.

Blank

Make a blank determination following the same procedure and using the same amounts of all reagents.

Calculation

Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, percent} = \frac{A - B}{C \times 10^4}$$

where:

A = micrograms of molybdenum found in the 20 ml butyl acetate extract of the sample

B = micrograms of molybdenum found in the 20 ml butyl acetate extract of the blank

C = grams of sample in the 20 ml butyl acetate extract of the sample

REFERENCES

[1] Michaelis, R.E., Wyman, L.L., "Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards", NBS Misc. Publ. 260-1 (1964).

[2] Lundell, G.E.F., Hoffman, J.I., Bright, H.A., "Chemical Analysis of Iron and Steel", John Wiley and Sons, Inc., New York, 1931.

[3] Am. Soc. Testing and Materials, Philadelphia, "ASTM Methods Chemical Analysis of Metals", 1960.

[4] Hillebrand, W.F., Lundell, G.E.F., Bright, H.A., Hoffman, J.I., "Applied Inorganic Analysis", 2nd edition, John Wiley and Sons, Inc., New York, 1953.

[5] Pigott, E.C., "Ferrous Analysis", 2nd edition, John Wiley and Sons, Inc., New York, 1953.

[6] Bright, H.A., Larrabee, C.D., "Determination of Manganese in Steel and Iron by the Persulfate-Arsenite Method", J. Res. Natl. Bur. Std. 3, 573 (1929).

[7] Hague, J.L., Bright, H.A., "Colorimetric Determination of Phosphorous in Steel and Cast Iron". J. Res. Natl. Bur. Std., 26, 405 (1941).

[8] Fowler, R.M., "Determination of Silicon in Steels", Ind. and Eng. Chem., Anal. Ed. 4, No. 4, 382 (1932).

[9] Hague, J.L., Brown, E.D., Bright, H.A., "Photometric Determination of Copper in Iron and Steel with Diethyldithiocarbamate", J. Res. Natl. Bur. Std. 47, 5 (1951).

[10] Westwood, W., Mayer, A., "Chemical Analysis of Cast Iron and Foundry Materials", George Allen and Unwin Ltd., London, 1951.

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