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Methods for Chemical Analysis of Graphite

石墨化学分析方法

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Methods for Chemical Analysis of Graphite

WARNING: personnel using this document needs to have practical experience in laboratory work. This document does not point out all safety, health and environmental protection issues related to its use. It is the users' responsibility to take appropriate safety, health and environmental protection measures, and ensure compliance with relevant national laws and regulations.

1 Scope

This document describes methods for the analysis of moisture, volatile matter, ash content, fixed carbon content, sulfur content, acid-soluble iron content and iron content of graphite products.

This document is applicable to the chemical analysis of natural graphite products.

2 Normative References

The contents of the following documents constitute indispensable clauses of this document through the normative references in the text. In terms of references with a specified date, only versions with a specified date are applicable to this document. In terms of references without a specified date, the latest version (including all the modifications) is applicable to this document.

GB/T 6679 General Rules for Sampling Solid Chemical Products

GB/T 6682 Water for Analytical Laboratory Use - Specification and Test Methods

GB/T 8170 Rules of Rounding off for Numerical Values & Expression and Judgement of Limiting Values

3 Terms and Definitions

This document does not have terms or definitions that need to be defined.

4 General Stipulations

4.1 Samples for chemical analysis obtained in accordance with the sampling method specified in GB/T 6679 shall be packed in plastic bags or ground-mouth bottles, and the sampling size shall be no less than 50 g.

4.2 Except for moisture determination, all other analysis items shall be analyzed after the specimens are baked to a constant weight at 105 °C ~ 110 °C.

4.3 The weighing of high, medium and low carbon specimens shall be accurate to 0.1 mg, and when constant weight is required, the difference between the two weighing values shall not be greater than 0.3 mg. The weighing of high-purity graphite specimens shall be accurate to 0.02 mg, and when constant weight is required, the difference between the two weighing values shall not be greater than 0.05 mg.

4.4 Each analysis item shall be determined at least twice in parallel. Take the arithmetic mean of two parallel determination results as the analysis result.

4.5 The calculation results of high-purity graphite are rounded to four decimal places in accordance with GB/T 8170, and the calculation results of other items are rounded to two decimal places in accordance with GB/T 8170.

4.6 Unless otherwise stated, the water used in this Method shall not be lower than Grade-3 water specified in GB/T 6682.

4.7 The concentration of a solution is expressed as molar concentration or mass concentration. Others, such as: (1 + 1), (1 + 2) and (m + n), etc. refer to the ratio of solute volume to water volume. Unless otherwise specified, the solutions used are all aqueous solutions.

4.8 Unless otherwise stated, the reagents used in this Method are only those confirmed to be of analytical purity or guaranteed purity; the reagents used for calibration are only those confirmed to be primary reagents or of spectral purity or high purity; the acid and ammonia water used are only confirmed concentrated acid or concentrated ammonia water.

5 Determination of Moisture

5.1 Instruments, Equipment and Materials

5.1.1 Electric drying oven: room temperature to 200 °C, with a temperature control accuracy of ± 2 °C.

5.1.2 Analytical balance: with an accuracy not lower than 0.1 mg.

5.1.3 Ground-mouth weighing bottle: 20 mL.

5.2 Analytical Procedures

Accurately weigh-take 2 g ~ 5 g of undried specimen, accurate to 0.1 mg, and record it as m_0. Put it into a ground-mouth weighing bottle that has been dried to a constant weight, slightly open the lid, and place it in an oven at 105 °C ~ 110 °C. After drying for 2 hours, take out the ground-mouth weighing bottle and properly put on the lid of the weighing bottle. Place it in a desiccator to cool for 30 minutes, weigh it and record it as m. Repeat this, until reaching a constant weight.

5.3 Result Calculation

8.2.2.4 Graphite standard sample: graphite mineral composition analysis standard substance, GBW 03118, GBW 03119, GBW 03120.

8.2.2.5 Oxygen: with a purity not less than 99.5%.

8.2.3 Instruments, equipment and materials

8.2.3.1 High-frequency infrared carbon and sulfur analyzer: carbon determination accuracy is not less than 0.0001%.

8.2.3.2 Analytical balance: with an accuracy not lower than 0.1 mg.

8.2.3.3 Box-type resistance furnace: the maximum temperature is not lower than 1,200 °C, with a temperature control accuracy of ± 10 °C.

8.2.3.4 Temperature controllable electric heating plate: room temperature to 300 °C, with a temperature control accuracy of ± 2 °C.

8.2.3.5 Electric drying oven: room temperature to 300 °C, with a temperature control accuracy of ± 2 °C.

8.2.3.6 Desiccator: equipped with color-changing silica gel.

8.2.3.7 Porcelain crucible.

8.2.4 Porcelain crucible treatment

Burn the porcelain crucible at 1,000 °C for 2 hours, then, place it in a desiccator to cool and reserve it for later use.

8.2.5 Sample treatment

Weigh-take 10.00 g (accurate to 0.1 mg) of dried specimen and place it in a porcelain crucible that has been subjected to the burning treatment; slowly dropwise add excess hydrochloric acid solution (1 + 1) to thoroughly acidify the sample. Then, on a temperature controllable electric heating plate with a temperature below 150 °C, slowly dry and cool it. Dropwise add water in several times, wash the specimen, until it becomes neutral, then, move it into the box-type resistance furnace. Raise the temperature from room temperature to 350 °C, leave a gap in the furnace door, and thoroughly burn for 2 hours. Then, take it out and cool it for later use.

8.2.6 Analytical procedures

8.2.6.1 Calibration test

Actuate the instrument and pre-heat for 30 minutes. Adjust the instrument to determine the fixed carbon state. Turn on the oxygen; in accordance with the sample to be determined, select the standard substance and perform system calibration, until the repeatability of the determination results reaches the uncertainty range required by the graphite standard sample. Thus, the system

5---high-temperature porcelain tube (1,300 °C);

6---tubular electric furnace (1,300 °C);

7---porcelain boat;

8---burette;

9, 10---sulfur determination cups.

Figure 2 -- Sulfur Determination Device

9.1.4 Analytical procedures

9.1.4.1 Device tightness inspection: rapidly raise the furnace temperature to 1,200 °C ~ 1,250 °C, introduce oxygen or air, adjust the flow rate to 0.7 L/min ~ 0.8 L/min, and check whether there is any air leakage in the device before conducting the test.

9.1.4.2 Specimen determination: add 2/3 volume of hydrochloric acid solution (3 + 197) into the sulfur determination cup, add 10 mL of starch-potassium iodide solution, and dropwise add potassium iodate standard solution to make the solution in the sulfur determination cup turn light blue. Use the same method to prepare a reference solution for judging the end point. Ventilate for 4 minutes ~ 5 minutes. If the blue color of the solution in the sulfur determination cup disappears, then, dropwise add potassium iodate standard solution, until the blue color does not disappear. Accurately weigh-take 0.2 g ~ 1.0 g of dried specimen (depending on the sulfur content), accurate to 0.1 mg, and record it as m_{12}. Put it into the burned porcelain boat, use a sulfur-free metal hook to quickly push the porcelain boat into the combustion tube, and immediately block the mouth of the tube. At 1,200 °C ~ 1,250 °C, perform ventilation combustion. The ventilation rate should be 80 ~ 100 bubbles per minute. When the gas enters the lower part of the sulfur determination cup, which makes the blue color disappear, immediately dropwise add the potassium iodate standard solution. The dropwise adding speed shall be such that the solution in the absorber maintains the light blue color of the original blank, until the light blue color of the solution remains constant for 1 minute ~ 2 minutes, which is the end point.

9.1.4.3 Determination of correction coefficient: in accordance with the sample content, select a coke standard sample with an appropriate sulfur content; accurately weigh-take 0.1 g ~ 1.0 g of standard sample, accurate to 0.1 mg, and record it as m_{11}. In the burned porcelain boat, follow the subsequent steps in 9.1.4.2.

9.1.5 Result calculation

9.1.5.1 The correction coefficient (F) is calculated in accordance with Formula (7):

$$F = \frac{m_{11} \times A}{V_0} \qquad \cdots\cdots (7)$$

Where,

9.2.2.1 Graphite standard sample: graphite mineral composition analysis standard substance, GBW 03118, GBW 03119, GBW 03120.

9.2.2.2 Tungsten trioxide: analytically pure.

9.2.2.3 Sodium hydroxide: analytically pure.

9.2.2.4 Potassium iodide: analytically pure.

9.2.2.5 Potassium bromide: analytically pure.

9.2.2.6 Glacial acetic acid: analytically pure.

9.2.2.7 Electrolyte: weigh-take 5.0 g each of potassium iodide and potassium bromide, dissolve it in 250 mL ~ 300 mL of distilled water, and add 10 mL of glacial acetic acid to the solution.

9.2.3 Instruments, equipment and materials

9.2.3.1 Analytical balance: with an accuracy not lower than 0.1 mg.

9.2.3.2 Coal sample: with a particle size less than 0.3 mm, not less than 100 mg.

9.2.3.3 Color-changing silica gel.

9.2.3.4 Porcelain boat: bisque or corundum product; the length of the sample-holding part is about 60 mm, and the temperature resistance is greater than 1,200 °C.

9.2.3.5 Coulomb sulfur meter: it mainly consists of the following parts.

a) Tubular high-temperature furnace: it can be heated to above 1,200 °C and has a high-temperature constant-temperature zone at 1,150 °C of at least 70 mm long. It is equipped with a platinum-rhodium-platinum thermocouple temperature measurement and control device, and the furnace is equipped with a reducing diameter combustion tube with heat resistance greater than 1,300 °C.

b) Electrolytic cell and electromagnetic stirrer: the electrolytic cell is 120 mm ~ 180 mm high, with a capacity of not less than 400 mL. It contains a platinum electrolytic electrode pair with an area of 150 mm^2 and a platinum indicator electrode pair with an area of approximately 15 mm^2. The response time of the indicator electrode shall be less than 1 s, and the electromagnetic stirrer speed is about 500 r/min and continuously adjustable.

c) Coulomb integrator: the integral linear error within the range of electrolytic current 0 mA ~ 350 mA shall be less than 0.1% and equipped with a 4 ~ 6 digits digital display or printer.

d) Sample delivery program controller: it can move forward and backward in accordance with the prescribed procedures.

e) Air supply and purification device: it consists of electromagnetic pump and purification pipe. The air supply volume is about 1,500 mL/min, and the gas extraction volume is about 1,000 mL/min. The purification tube is filled with sodium hydroxide and color-changing silica gel.

9.2.4 Analytical procedures

9.2.4.1 Turn on the power of the Coulomb sulfur meter and adjust the temperature control device to control the furnace temperature at around 1,150 °C.

9.2.4.2 Add 300 mL of electrolyte to the electrolytic cell and turn on the magnetic stirrer.

9.2.4.3 Turn on the electromagnetic pump, adjust the air flow to 1,000 mL/min, and check the air tightness.

9.2.4.4 Coal sample test: take about 50 mg of coal sample and put it into a porcelain boat that has been pre-burned at 800 °C. Use a thin layer of tungsten trioxide to cover the surface and put it into he high-temperature part of the tubular electric furnace. After 5 minutes, the porcelain boat automatically returns. If the mass of sulfur on the automatic sulfur meter shows zero, a re-determination shall be performed, until it is not zero.

9.2.4.5 Graphite standard sample test: weigh-take 50 mg of the graphite standard sample, accurate to 0.1 mg, put it into a porcelain boat, and use a thin layer of tungsten trioxide to cover the surface of the graphite standard sample. Then, put it into the porcelain boat at the entrance of the tubular electric furnace, and press the “START” button. The graphite standard sample is automatically sent to the high-temperature part of the tubular electric furnace by a nickel-chromium wire hook. After 5 minutes, the porcelain boat automatically returns. Record the displayed sulfur mass (mg). If it is inconsistent with the graphite standard sample, the coefficient can be corrected.

9.2.4.6 Weigh-take 50 mg of specimen, accurate to 0.1 mg and record it as m_{14}. Put it into a porcelain boat that has been pre-burned at 800 °C and use a thin layer of tungsten trioxide to cover the surface. Then, put the porcelain boat into the entrance of the tubular electric furnace, press the “START” button, and record the displayed sulfur mass as m_{13}.

9.2.4.7 At the end of the test, successively close the straight-through valve, magnetic stirrer and electromagnetic pump, release the electrolyte (reusable), clean the electrolytic cell and turn off the power supply.

9.2.5 Result calculation

The sulfur content (w_8) in the specimen is calculated in accordance with Formula (9):

$$w_8 = \frac{m_{13}}{m_{14}} \times 100\% \qquad \cdots\cdots (9)$$

Where,

10.1.2.4 Sulfosalicylic acid solution (200 g/L).

10.1.2.5 Ammonium thiocyanate solution (100 g/L).

10.1.2.6 Iron standard stock solution [ρ(Fe) = 1.00 mg/mL]: accurately weigh-take 1.4297 g of high-purity (or spectrally pure) iron trioxide that has been dried at 105 °C ~ 110 °C for 2 hours and cooled to room temperature, add 50 mL of hydrochloric acid solution (1 + 1), dissolve it, then, transfer to a 1,000 mL volumetric flask. Use water to dilute to the scale and shake it well.

10.1.2.7 Iron standard solution [ρ(Fe) = 0.04 mg/mL]: accurately draw-take 10.0 mL of the iron standard stock solution (10.1.2.6) and place it in a 250 mL volumetric flask. Use water to dilute to the scale and shake it well.

10.1.3 Instruments and equipment

10.1.3.1 Analytical balance: with an accuracy not lower than 0.1 mg.

10.1.3.2 Electric drying oven: room temperature to 200 °C, with a temperature control accuracy of ± 2 °C.

10.1.3.3 Spectrophotometer: with a 1 cm cuvette, and a wavelength range of 300 nm ~ 800 nm.

10.1.4 Analytical procedures

10.1.4.1 Drawing of standard curve

Take 0.00 mL, 1.00 mL, 3.00 mL, 5.00 mL, 7.00 mL, 10.00 mL, 15.00 mL and 20.00 mL of the iron standard solution (10.1.2.7), respectively place them in a set of 100 mL volumetric flasks. Use water to dilute to about 50 mL, add 2 mL of sulfosalicylic acid solution (200 g/L), and shake it well. Dropwise add ammonia solution (1 + 1) to make the color of the solution change from purple to yellow with an excess of 4 mL, use water to dilute to the scale and shake it well. Leave it for 10 minutes. Use a 1 cm cuvette, use water as a reference, at a wavelength of 420 nm, determine the absorbance of the solution. Take iron content as the x-coordinate and the absorbance as the y-coordinate to draw a working curve.

10.1.4.2 Determination

10.1.4.2.1 Accurately weigh-take 0.5 g [when the iron content (mass fraction) is lower than 0.5%, take 1 g ~ 3 g] of dried specimen, accurate to 0.1 mg, and record it as the mass of the specimen. Place it in a 150 mL beaker and use a small amount of water to wet the specimen. Add 25 mL of concentrated hydrochloric acid, stir it, until the specimen is completely immersed in the acid. Use a watch glass to cover it, place it on the electric heating plate, keep it slightly boiling for 20 minutes. Then, remove it, and use water to wash the watch glass and cup wall. Let it slightly cool, then, use a medium-speed qualitative filter paper to filter it into a 250 mL volumetric flask. Use hot water to wash it, until there is no iron ion (check with ammonium thiocyanate solution, and there shall be no red color). After cooling, dilute it to the scale and shake it well. This is the specimen solution.

and the temperature control accuracy is ± 10 °C.

11.1.3.4 Platinum crucible: with a volume of not less than 30 mL.

11.1.4 Analytical procedures

11.1.4.1 Drawing of standard curve

Take 0.00 mL, 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, 2.50 mL, 3.00 mL, 4.00 mL and 5.00 mL of iron standard solution (11.1.2.6), and respectively place them in a set of 100 mL volumetric flasks. Add water to dilute to about 50 mL, add 10 mL of sulfosalicylic acid solution (100 g/L), use ammonia solution (1 + 1) to neutralize it, until the test solution just turns yellow, and with an excess of 2 mL. Use water to dilute it to the scale and shake it well. At a wavelength of 420 nm, determine the absorbance. Select a 1 cm cuvette, use water as a reference, at a wavelength of 420 nm, determine the absorbance of the solution. Take iron content as the x-coordinate and absorbance as the y-coordinate to draw a working curve.

11.1.4.2 Determination

11.1.4.2.1 Weigh-take 1 g ~ 3 g (accurate to 0.1 mg) of specimen, place it in a platinum crucible, and record it as the mass of the specimen. Burn it at 950 °C ~ 1,000 °C to remove all carbon, add 3 g ~ 4 g of anhydrous sodium carbonate and mix it well. Then, use 1 g of anhydrous sodium carbonate to cover it and put it into a high-temperature furnace. At 950 °C ~ 1,000 °C, melt it for 20 minutes, then, take it out to cool. Use a filter paper to wipe the outer wall of the crucible, put it into a 250 mL beaker containing 100 mL of boiling water. Use a watch glass to cover it, cool for 5 minutes, and carefully dropwise add hydrochloric acid solution (1 + 1) to dissolve the melt. After complete dissolution, place it on an electric furnace and boil for 5 minutes, then, cool and reserve it for later use. Transfer the above-mentioned to a 250 mL volumetric flask, dilute to the scale and mix it well. This is the specimen solution.

11.1.4.2.2 Dispense 5 mL ~ 25 mL of specimen solution into a 100 mL volumetric flask, add water to dilute to about 50 mL, add 10 mL of sulfosalicylic acid solution (100 g/L) and shake it well. Follow 11.1.4.1 for the subsequent steps. Meanwhile, carry out a blank test.

11.1.5 Result calculation

The iron content (w_{11}) is calculated in accordance with Formula (13):

$$w_{11} = \frac{(\rho_3 - \rho_2) \times V_4 \times 10^{-6}}{m_{19} \times V_5} \times 100\% \quad \cdots\cdots (13)$$

Where,

w_{11}---the iron content (mass fraction);

ρ_3---the mass concentration of iron in the solution to be tested obtained from the standard series curve (or direct reading of the concentration), expressed in (μg);

11.3 Inductively Coupled Plasma Optical Emission Spectrometry

11.3.1 Method summary

When a completely dissolved specimen is introduced into the inductively coupled plasma torch, the iron element in the solution is excited by high temperature and emits characteristic spectral lines. The intensity of the characteristic spectral lines has a corresponding functional relationship with the content of the element. By determining the intensity of the characteristic spectral lines, determine the element content.

11.3.2 Reagent

Hydrochloric acid solution (1 + 1).

11.3.3 Instruments, equipment and materials

11.3.3.1 Analytical balance: with an accuracy not lower than 0.1 mg.

11.3.3.2 Inductively coupled plasma optical emission spectrometer.

11.3.4 Analytical procedures

11.3.4.1 Preparation of working curve series of solutions

Accurately transfer-take 0.00 mL, 0.50 mL, 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL and 6.00 mL of iron standard solution (11.1.2.6), respectively place them into seven 100 mL volumetric flasks, add 4 mL of hydrochloric acid solution (1 + 1), use water to dilute to the scale and shake them well.

11.3.4.2 Preparation of test solution

Dispense 5 mL ~ 10 mL of the specimen solution in 11.1.4.2.1 and place it in a 100 mL volumetric flask. Add 4 mL of hydrochloric acid solution (1 + 1), use water to dilute to the scale and shake it well. Meanwhile, carry out a blank test.

11.3.5 Determination

On the inductively coupled plasma emission spectrometer, in accordance with the instrument model, set the required working parameters (use a high-salt atomizer). Successively and respectively determine the emission spectral intensity of the blank solution, working curve series of solutions and test solution preparation, and draw a working curve. From the working curve, obtain the mass concentration of iron element or use direct reading of the mass concentration of iron element.

11.3.6 Result calculation

The iron content (w_{13}) is calculated in accordance with Formula (15):

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