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Iron ores - Determination of fluorine content - Ion-selective electrode method

铁矿石 氟含量的测定 离子选择电极法

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Iron ores - Determination of fluorine content - Ion-selective electrode method

WARNING -- Personnel using this document shall have regular laboratory work experience. This document does not point out all possible safety issues. It is the user's responsibility to take appropriate safety and health measures and ensure compliance with the conditions specified in relevant national regulations.

1 Scope

This document specifies a method for the determination of fluorine content using ion-selective electrode method.

This document applies to the determination of fluorine content in natural iron ores, iron concentrates, and lump ores, including sintered products. The determination range (mass fraction): 0.005 % ~ 1.00 %.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 6379.1 Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions

GB/T 6379.2 Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method

GB/T 6682 Water for analytical laboratory use - Specification and test methods

GB/T 6730.1 Iron ores - Preparation of predried test samples for chemical analysis

GB/T 8170 Rules of rounding off for numerical values & expression and judgement of limiting values

GB/T 10322.1 Iron ores - Sampling and sample preparation procedures

GB/T 12806 Laboratory glassware - One-mark volumetric flasks

GB/T 12807 Laboratory glassware - Graduated pipettes

GB/T 12808 Laboratory glassware - One-mark pipettes

3 Terms and definitions

There are no terms or definitions to be defined in this document.

4 Principle

The sample is melted with sodium hydroxide and dissolved in water and hydrochloric acid. After dry filtration, in the presence of sodium citrate buffer solution, adjust the pH value of the test solution to 5.0 ± 0.1, and directly conduct potentiometric determination with a fluoride ion-selective electrode.

5 Reagents and materials

Unless otherwise stated, only approved analytical reagents and secondary water complying with GB/T 6682 or water equivalent to its purity shall be used in the analysis.

5.1 Sodium hydroxide, granular, dry.

5.2 Sodium hydroxide solution, 300 g/L.

DISSOLVE 75 g of sodium hydroxide in 250 mL of water.

5.3 Sodium hydroxide solution, 20 g/L.

DISSOLVE 5 g of sodium hydroxide in 250 mL of water.

5.4 Hydrochloric acid, $\rho \approx 1.19$ g/mL.

5.5 Hydrochloric acid, 1 + 2.

5.6 Hydrochloric acid, 1 + 9.

5.7 Sodium citrate buffer solution, $c_{(Na_3C_6H_5O_7 \cdot 2H_2O)} = 1$ mol/L.

In a 1 L beaker, WEIGH 294.1 g of sodium citrate and DISSOLVE it in 800 mL of water, USE hydrochloric acid (see 5.5) to adjust the pH to 5.0 ± 0.1. TRANSFER to a 1 L volumetric flask, DILUTE with water to the mark, and MIX well.

5.8 Fluorine standard solution A, stored in plastic bottles.

DRY an appropriate amount of sodium fluoride (purity greater than 99.7 %) at 105 °C. WEIGH 1.108 g of dried sodium fluoride, DISSOLVE it in water, TRANSFER it to a

1 L volumetric flask, DILUTE it with water to the mark, and MIX well. 1 mL of this solution contains 500 μg of fluorine.

5.9 Fluorine standard solution B, stored in plastic bottles.

USE a pipette to transfer 100.00 mL of fluorine standard solution A (see 5.8), PUT it into a 500 mL volumetric flask, DILUTE it with water to the mark, and MIX well. 1 mL of this solution contains 100 μg of fluorine.

5.10 Fluorine standard solution C, stored in plastic bottles.

USE a pipette to transfer 50.00 mL of fluorine standard solution B (see 5.9), PUT it into a 500 mL volumetric flask, DILUTE it with water to the mark, and MIX well. This solution shall be prepared fresh before use. 1 mL of this solution contains 10 μg of fluorine.

5.11 Fluorine standard solution D, stored in plastic bottles.

USE a pipette to transfer 50.00 mL of fluorine standard solution C (see 5.10), PUT it into a 500 mL volumetric flask, DILUTE it with water to the mark, and MIX well. This solution shall be prepared fresh before use. 1 mL of this solution contains 1 μg of fluorine.

6 Instruments and equipment

Unless otherwise stated during analysis, use ordinary experimental instruments. One-mark volumetric flasks, graduated pipettes, and one-mark pipettes shall comply with the requirements of GB/T 12806, GB/T 12807, and GB/T 12808, respectively.

6.1 Balance: the scale value is 0.1 mg.

6.2 Ion meter (or pH meter): the scale value is 0.1 mV.

6.3 Magnetic stirrer: with a 2.5 cm × 0.4cm stirring rod covered with polyethylene.

6.4 Fluoride ion-selective electrode.

6.5 Calomel reference electrode.

6.6 pH glass electrode.

6.7 Silver crucible or nickel crucible: the generally used capacity is 25 mL ~ 30 mL, but 100 mL can also be used.

6.8 Muffle furnace: temperature control of 650 ℃ ~ 700 ℃.

6.9 Plastic beaker: 100 mL and 200 mL.

8.3 Blank test and verification test

8.3.1 Blank test

A blank test is performed along with the sample analysis, and all reagents shall be taken from the same reagent bottle.

8.3.2 Verification test

During each analysis, an iron ore reference material of the same type and similar properties to the analyzed sample is used and analyzed under the same analysis conditions at the same time. Pre-drying of iron ore reference materials shall be carried out in accordance with 7.2.

When analyzing several similar types of ores at the same time, it can use only one reference material for analysis at the same time.

8.4 Determination

WARNING: It is recommended to wear safety glasses and gloves when melting sodium hydroxide, and be careful when dissolving the melt.

8.4.1 Decomposition of sample

PUT the sample (see 8.2) into a crucible, ADD 3 g of sodium hydroxide (see 5.1) to cover the sample, PUT the crucible into a muffle furnace at 600 ℃ ~ 650 ℃ to melt for 10 minutes, TAKE OUT the crucible and ROTATE it for a few seconds, then PUT it back into the furnace to melt for 5 minutes.

TAKE OUT the crucible, COOL it and PLACE it in a 200 mL plastic beaker, ADD 60 mL of hot water to extract the melt, WASH the crucible with 10 mL of hydrochloric acid (see 5.5) and WIPE the crucible wall. After the test solution is cooled to room temperature, TRANSFER it to a 100 mL plastic volumetric flask, DILUTE it with water to the mark, and MIX well. DRY FILTER with slow quantitative filter paper, DISCARD the initial filtrate, and COLLECT the filtrate in a plastic beaker. COLLECT about 40 mL of the filtrate for splitting.

Before using a silver crucible or nickel crucible, it shall be cleaned by melting a small amount of sodium hydroxide (see 5.1).

When using a 100 mL silver crucible or nickel crucible, extract the melt directly in the crucible.

8.4.2 Preparation of calibration solutions

In a set of 100 mL plastic volumetric flasks, ADD fluorine standard solution (see 5.8 ~ 5.11) according to the amount given in Table 2, ADD 5 mL of sodium hydroxide

fluorine electrode, and STIR the solution at a constant speed. Quickly DETERMINE the test solution and calibration solution in order of increasing concentration. During the initial determination, after introducing the electrodes, wait 2 minutes before reading the potential value. According to the determination results, in order of increasing concentration, intersperse the test solution and the reference material solution in the calibration solutions, and then carry out the second determination. Starting from the solution with the lowest concentration, in order from low to high concentration, introduce the electrodes for determination. For all test solutions, it shall read stable potential values according to the same fixed response time. The response time shall be greater than 5 minutes. All test solutions shall be stirred at the same speed. All abnormalities shall be eliminated to make the readings accurate.

Before determination, the fluoride ion-selective electrode shall be adjusted to a stable potential in the solution with the lowest fluorine concentration. The time required for potential stabilization varies with the reaction of the electrode, and can be 15 min ~ 1 h. After each reading, wash the electrode carefully with water and dry it with a cloth.

8.4.5 Calibration curve

On semi-logarithmic paper, take the potential value as the ordinate, the fluoride ion concentration as the abscissa, plot a calibration curve segmentally with 0.30 μg/mL as the node, and read the fluorine content in the test solution on the calibration curve. Or take the potential value as the ordinate, the negative logarithm of the fluoride ion concentration as the abscissa, plot a calibration curve segmentally with 0.30 μg/mL as the node.

Calibration curve regression equations can be established using a computer.

9 Result calculation and representation

9.1 Calculation of fluorine content

Calculate the fluorine content ω_F in the sample according to formula (1) or formula (2), expressed in mass fraction (%). Formula (1) is used when plotting a calibration curve on semi-logarithmic paper, and formula (2) is used when establishing a calibration curve with the negative logarithm of the fluoride ion concentration and using the potential value as the ordinate.

$$\omega_F = \frac{\rho_F \times 20}{m} \quad \cdots\cdots (1)$$

$$\omega_F = \frac{10^{-y} \times 20}{m} \quad \cdots\cdots (2)$$

where:

ω_F - the fluorine content in the sample, %;

The correctness check uses a certified reference material (CRM) or a reference material (RM) for verification. The final laboratory result is compared with the standard value A_c of CRM or RM. There will be two possibilities.

a) $|\mu_c - A_c| \leq C$, in this case, there is no significant difference between the determined value and the standard value.

b) $|\mu_c - A_c| > C$, in this case, there is a significant difference between the determined value and the standard value.

where:

μ_c - the determined value of CRM or RM;

A_c - the standard value of CRM or RM;

C - the value depends on the type of CRM or RM used.

The C value of the certified reference material (CRM) or reference material (RM) determined by multiple laboratories is calculated according to formula (4):

$$C = \frac{1}{\sqrt{2}} \sqrt{R^2 - \frac{n-1}{n} r^2 + 8u^2} \qquad \cdots\cdots (4)$$

where:

R - the inter-laboratory reproducibility limit;

r - the in-laboratory repeatability limit;

n - the number of repeated determinations of reference material;

u - the uncertainty of the standard value of CRM or RM.

9.2.5 Calculation of final result

The final result of the sample is the arithmetic mean of the acceptable analytical values, or the value determined in accordance with the provisions in Annex B, and is rounded off in accordance with the provisions of GB/T 8170. When the fluorine content is less than 0.01 %, the final result is rounded off to the fourth decimal place; when the fluorine content is greater than or equal to 0.01 %, the final result is rounded off to the third decimal place.

10 Test report

The test report shall include the following information:

a) laboratory name and address;

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