ICS 77.100
CCS H 11

NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 24194-2024

Replacing GB/T 24194-2009

Ferrosilicon - Determination of multi-element contents - Inductively coupled plasma atomic emission spectrometric method

硅铁 多元素含量的测定 电感耦合等离子体原子发射光谱法

Issued on: May 28, 2024 **Implemented on: December 1, 2024**

Issued by: State Administration for Market Regulation;
Standardization Administration of the PRC

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1 Scope

The document gives a method for determining the contents of iron, aluminium, calcium, manganese, chromium, titanium, phosphorus, copper, nickel, magnesium, vanadium, niobium, lead, antimony, zirconium and boron in ferrosilicon by inductively coupled plasma atomic emission spectrometry.

It applies to the determination of aluminium, calcium, manganese, chromium, titanium, phosphorus, copper, nickel, magnesium, vanadium, niobium, lead, antimony, zirconium and boron in ferrosilicon, and of iron in high-silicon ferrosilicon.

Table 1 gives the determination range, as a mass fraction, for each element: iron 0.50 % to 3.00 %; aluminium 0.005 % to 3.00 %; calcium 0.005 % to 3.00 %; manganese 0.005 % to 0.50 %; chromium 0.005 % to 0.50 %; titanium 0.005 % to 0.50 %; phosphorus 0.005 % to 0.06 %; copper 0.002 % to 0.10 %; nickel 0.002 % to 0.10 %; magnesium 0.002 % to 0.20 %; vanadium 0.001 % to 0.20 %; niobium 0.0005 % to 0.02 %; lead 0.0005 % to 0.01 %; antimony 0.0005 % to 0.01 %; zirconium 0.005 % to 0.05 %; boron 0.0010 % to 0.03 %.

A warning placed at the head of the document states that persons using it should have practical experience of regular laboratory work, that the document does not point out all possible safety problems, and that the user is responsible for taking suitable safety and

health measures and for meeting the conditions of the relevant national regulations.

4 Principle

The test portion is decomposed with nitric acid, hydrofluoric acid and hydrochloric acid; silicon and fluorine are driven off by fuming with perchloric acid; the salts are dissolved in hydrochloric acid and the test solution is diluted to the prescribed volume. The emission intensity of each analyte in the solution, or its intensity relative to yttrium, is measured with an inductively coupled plasma atomic emission spectrometer, and the mass fraction of the analyte is calculated from a calibration curve made with standard solutions.

5 Reagents

Unless otherwise stated, only recognised analytically pure reagents and grade two or better distilled water complying with GB/T 6682, or water of equivalent purity, are used.

The acids and reagents listed are nitric acid of density about 1.42 g/mL, hydrofluoric acid about 1.15 g/mL, perchloric acid about 1.67 g/mL, hydrochloric acid about 1.19 g/mL, hydrogen peroxide about 1.10 g/mL, hydrochloric acid 1+3, and mannitol at 2.5 g/L.

Standard stock and working solutions are prescribed for iron, aluminium, calcium, manganese, chromium, titanium, phosphorus, copper, nickel, magnesium, vanadium, niobium, lead, antimony, zirconium, boron and yttrium. For each one the clause states the substance and mass to be weighed, the dissolution medium, the final volume and the resulting concentration, and requires the solution to be kept in a dedicated polypropylene or polyethylene reagent bottle.

Certified series standard solutions of the elements, and series obtained by diluting certified series, may be used. Pure iron with a mass fraction greater than 99.98 %, or of known analyte content, is also listed among the reagents.

6 Apparatus and equipment

Single-mark pipettes, graduated pipettes and single-mark volumetric flasks shall comply with GB/T 12806, GB/T 12807 and GB/T 12808.

Any model of inductively coupled plasma atomic emission spectrometer may be used provided the instrument meets GB/T 36244 and JJG 768; its performance is tested by the method of Annex A. The document does not prescribe particular analytical lines but recommends those of Table 2, and requires the background correction positions of the lines and the spectral interferences to be checked carefully according to the characteristics of the instrument.

Table 2 lists, for each analyte and for yttrium, one or more recommended wavelengths in nanometres together with the elements that may interfere at those wavelengths. Yttrium at

371.03 nm is the line used as internal standard in 8.4.3.

7 Sampling and sample preparation

Sampling and sample preparation are carried out according to GB/T 4010, and the whole of the test sample shall pass a 0.125 mm sieve aperture.

8 Analytical procedure

8.1 At least two independent determinations are made on the same test sample.

8.2 The test portion is weighed according to Table 3 to the nearest 0.0001 g. Table 3 gives 0.2000 g for group I, applicable to the routine elements of high-silicon ferrosilicon, ordinary ferrosilicon and low-aluminium ferrosilicon, and 0.5000 g for groups II and III, applicable to high-purity ferrosilicon and to the determination of boron.

8.3 A blank test is run alongside the test portions on a mass of pure iron corresponding to the iron content of the test portion, weighed to the nearest 0.001 g. Table 4 gives 0.045 g of pure iron for a 0.2000 g test portion and 0.110 g for a 0.5000 g test portion. Two notes state that no pure iron is added when impurities in high-silicon ferrosilicon are determined, and that for the grades PGFeSi65 and PGFeSi40 the mass of pure iron is calculated from the corresponding iron content of the sample to be tested.

8.4.1 Three groups of test solution are prepared in polytetrafluoroethylene beakers. Group I uses nitric acid, hydrofluoric acid added dropwise from a plastic tube until the violent reaction stops, hydrochloric acid 1+3 and low-temperature heating to complete dissolution, then perchloric acid fuming down to about 2 mL to 3 mL of solution, dissolution of the salts in hydrochloric acid 1+3 and dilution to 100 mL. Group II follows the same sequence with larger volumes and with concentrated hydrochloric acid, and is diluted in a polytetrafluoroethylene or quartz flask. Group III uses hydrofluoric acid added with a polyethylene pipette or graduated dropper, mannitol, and nitric acid added slowly with the beaker turned gently between additions until the solution is clear, the solution then standing 30 min at room temperature before dilution in a polytetrafluoroethylene flask. Where the internal standard method is used, 5.00 mL of the 10.0 μg/mL yttrium standard solution is added before dilution to the mark.

8.4.2 Calibration solutions are prepared on seven portions of pure iron corresponding to the iron content of the test portion, dissolved as in 8.4.1, with the analyte calibration solutions added according to Tables 5, 6 and 7. The concentration range of the calibration solutions is to cover the concentration range of the elements analysed, no single calibration solution is to hold all the analytes at their highest or their lowest level, and each calibration curve needs at least five calibration solutions in a suitable gradation. Where linearity is insufficient the series may be extended; where the concentration is so high that the curve becomes non-linear, a less sensitive line is used or the test and calibration solutions are diluted. The

amount of each coexisting element in the calibration series is to match the amount of that element in the sample solution.

8.4.2 Tables 5, 6 and 7 hold the calibration series for groups I, II and III respectively. Each row names the analyte, the standard solution used and its concentration, and then gives, for the six points numbered 0 to 5, the volume in millilitres added to a 100 mL volumetric flask and the resulting concentration in micrograms per millilitre. Group I runs iron, aluminium and calcium from 0 μg/mL to 60.00 μg/mL, manganese, chromium and titanium from 0 μg/mL to 10.00 μg/mL and phosphorus from 0 μg/mL to 1.20 μg/mL; group II runs fourteen elements with top points between 2.00 μg/mL for niobium and 12.50 μg/mL for aluminium and calcium; group III runs boron alone from 0 μg/mL to 2.00 μg/mL. Notes state that the ranges of Table 5 correspond to a 0.2000 g test portion and those of Tables 6 and 7 to a 0.5000 g test portion, and that iron applies only to the determination of iron in high-silicon ferrosilicon.

8.4.3 The spectrometer is switched on and its state checked; after ignition the running parameters are confirmed to be within the set range, the nebulising system and the plasma flame are confirmed to be working normally, and the instrument is stabilised for more than 30 min. The most concentrated calibration solution is measured and the working conditions are optimised according to the instrument manual, adjusting parameters such as the outer, intermediate and central gas flow rates, the torch position, the entrance and exit slits, the photomultiplier voltage, the analytical line wavelength, the pre-flush time and the integration time. Where an internal standard is used, software is prepared that takes yttrium at 371.03 nm as internal standard and computes the intensity ratio of each element to yttrium, the internal standard intensity being measured at the same time as the analyte intensity. A nebuliser resistant to hydrofluoric acid is needed for group III solutions.

8.4.4 Measurement starts with the calibration solution of lowest concentration, the zero solution corresponding to the blank test, and the calibration solutions are then aspirated in order, with deionised water or dilute nitric acid aspirated between solutions. At least two repeat measurements are made and the mean of the two readings is taken. The curve is plotted with the concentration of the element as abscissa and the spectral intensity as ordinate, a linear regression is made by least squares, and the correlation coefficient shall be greater than 0.999. The blank test solution and the sample solutions are measured under the same conditions, with deionised water aspirated between measurements and at least two repeat measurements taken; the net intensity of the analyte in the sample solution is collected and the content of each element is calculated from the calibration curve.

9 Calculation and expression of results

9.1 The analyte content is obtained from an equation whose symbols are the analyte content in percent, the concentration of the analyte in the sample solution in micrograms per millilitre, the concentration of the analyte in the blank test solution in micrograms per