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Replacing GB/T 223.11-1991

Iron, steel and alloy - Determination of chromium content - Visual titration or potentiometric titration method

(ISO 4937:1986, MOD)

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Foreword

This Part of GB/T 223 replaces GB/T 223.11 - 1991 “Methods for Chemical Analysis of Iron, Steel and Alloy - The Ammonium Persulfate Oxidation Volumetric Method for the Determination of Chromium Content”.

In this revision, the name of this Part is changed to "Iron, Steel and Alloy-Determination of Chromium Content-Visual Titration or Potentiometric Titration Method", including two analysis methods: method I visual titration method and method II potentiometric titration method.

Compared with GB/T 223.11 - 1991, method I of this Part has the following main revisions:

- modified the content range of determination;
- added the content related to correct vanadium interference by theoretical calculation method;
- modified the description content for reagents and water in the analysis is added, and the expression method for solution concentration;
- modified the specimen quantity and its expression;
- added quantity units in result calculation formulae are revised, and calculation formula for correcting vanadium interference by theoretical calculation method;
- re-organized precision test.

Method II in this Part is modified in relation to ISO 4937: 1986 "Steel and iron -- Determination of chromium content -- Potentiometric or visual titration method". Compared with ISO 4937: 1986, it has the following main revisions:

- only potentiometric titration method therein is adopted, and the technical contents are consistent with it;
- a note is added respectively to "instrument" and "titration of specimen containing vanadium".

Annex A, Annex B and Annex C in this Part are informative.

This Part was proposed by China Iron and Steel Association.

This Part shall be under the jurisdiction of National Technical Committee on Iron and Steel of Standardization Administration of China.

Iron, steel and alloy - Determination of chromium content - Visual titration or potentiometric titration method

WARNING: the personal using this Part of GB/T 223 shall have the practical experience of regular laboratory working. This Part does not point out all possible safety problems. The users are under the obligation to adopt proper safety and health measures and shall ensure meet the requirements specified in national relevant regulations.

1 Scope

This Part of GB/T 223 specifies the determination of chromium content with visual titration or potentiometric titration method.

Method I of this Part is applicable to the determination of chromium content with mass fraction 0.10%~35.00% in pig iron, carbon steel, alloy steel, high-temperature alloy and precision alloy; method II of this Part is applicable to the determination of chromium content with mass fraction 0.25%~35.00% in iron and steel.

2 Normative references

The following standards contain provisions which, through reference in this Part of GB/T 223, constitute provisions of this Part. For dated reference, subsequent amendments to (excluding correction to), or revisions of, any of these publications do not apply. However, the parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards. For undated references, the latest edition of the normative document referred to applies.

GB/T 223.13, *Methods for chemical analysis of iron, steel and alloy - The ammonium ferrous sulfate titration method for the determination of vanadium content*

GB/T 223.14, *Methods for chemical analysis of iron, steel and alloy - The N-benzoy-N-phenylhydroxylamine extraction photometric method for the determination of vanadium content*

GB/T 223.76, *Methods for chemical analysis of iron, steel and alloy - The flame atomic absorption spectrometric method for the determination of vanadium content*

GB/T 6379.1, *Accuracy (trueness and precision) of measurement methods and*

3.2.4 Nitric acid, ρ is about 1.42 g/mL.

3.2.5 Phosphoric acid, ρ is about 1.69 g/mL.

3.2.6 Sulfuric acid, ρ is about 1.84 g/mL, diluted to 1+1.

3.2.7 Sulfuric acid, ρ is about 1.84 g/mL, diluted to 5+95.

3.2.8 Hydrofluoric acid, ρ is about 1.15 g/mL.

3.2.9 Sulfuric acid - phosphoric acid mixture: add 320mL of sulfuric acid (3.2.6) and 80mL of phosphoric acid (3.2.5) in 600mL of water, and blend.

3.2.10 Silver nitrate solution, 10g/L: weigh out 1.0g of silver nitrate, dissolve in 100mL of water, dropwise add several drops of nitric acid (3.2.4), and store in a brown bottle.

3.2.11 Ammonium persulfate solution, 300 g/L, prepare before use.

3.2.12 Sodium chloride solution, 50 g/L.

3.2.13 Manganese sulfate solution, 40 g/L.

3.2.14 Phenyl anthranilic acid solution, 2 g/L: weigh out 0.2 g of reagent, place in a 300mL beaker, add 0.2 g of anhydrous sodium carbonate, add 20 mL of water, heat and dissolve, dilute with water to 100 mL, and blend.

3.2.15 Ferrous-phenanthroline solution: weigh out 1.49 g of phenanthroline and 0.98 g of ferrous ammonium sulfate, place in a 300 mL beaker, add 50 mL of water, heat, dissolve, cool, dilute with water to 100 mL, and blend.

3.2.16 Chromium standard solution

3.2.16.1 Chromium stock solution, 2.000 g/L.

weigh out 5.6578 g of potassium bichromate (reference) baked at 150°C for 1h and cooled in a dryer to the room temperature, place it in a beaker, add water for dissolving it, shift it in a 1000 mL volumetric flask, dilute with water to the scale, and blend.

1 mL of this solution contains 2.000 mg of chromium.

3.2.16.2 Chromium standard solution A, 1.000 g/L.

Take and shift 50.00 mL of chromium stock solution (3.2.16.1) and place in 100-mL volumetric flask, dilute it with water to the scale, and blend.

1 mL of this solution contains 1.000 mg of chromium.

3.2.16.3 Chromium standard solution B, 0.500 g/L.

Take and shift 25.00 mL of chromium stock solution (3.2.16.1), place in a 100-mL volumetric flask, dilute it with water to the scale, and blend.

1 mL of this solution contains 0.500 mg of chromium.

3.2.17 Ferrous ammonium sulfate standard titration solution

3.2.17.1 Preparation

Weigh out 6 g, 12 g and 24 g of ferrous ammonium sulfate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$], respectively dissolve in the sulfuric acid (3.2.7), dilute it with sulfuric acid (3.2.7) to 1000 mL, and blend. Ferrous ammonium sulfate solutions with 0.015 mol/L, 0.03 mol/L and 0.06 mol/L concentration respectively are obtained.

3.2.17.2 Calibration and indicator correction

Take 3500 mL conical flasks, respectively add 50 mL of sulfuric acid - phosphoric acid mixture (3.2.9) into them, heat for evaporating until sulfuric acid smoke appears, slightly cool, add 50 mL of water, cool to the room temperature; respectively add chromium standard solution (its chromium content shall be close to the chromium mass in the specimen), dilute with water to 200 mL, titrate with ferrous ammonium sulfate standard titration solution (3.2.17.1) until the solution is light yellow, add 3 drops of phenyl anthranilic acid solution (3.2.14), continue titrating until the solution turns from rose red to brilliant green; and then read the volume (mL) of ferrous ammonium sulfate standard titration solution consumed. Add the same quantity of chromium standard solution again, and then titrate with ferrous ammonium sulfate standard titration solution (3.2.17.1) until the solution turns from rose red to brilliant green. The difference of two volumes of ferrous ammonium sulfate standard titration solution consumed is the corrected value of 3 drops of phenyl anthranilic acid solution. The calculation shall be carried out after adding this value into the volume (mL) of ferrous ammonium sulfate standard titration solution consumed for titration. The mean value of extreme difference value of ferrous ammonium sulfate standard titration solution volume (mL) consumed by 3 portions of chromium standard solution, not greater than 0.05 mL, shall be taken.

The mass of chromium equivalent to unit volume ferrous ammonium sulfate standard titration solution shall be calculated according to Formula (1):

$$T = \frac{V \times c}{V_1} \qquad \cdots\cdots\cdots\cdots (1)$$

where,

T - Mass of chromium equivalent to unit volume ferrous ammonium sulfate standard

3.4.3.3 Titration

3.4.3.3.1 Vanadium free specimen

Titrate the test solutions obtained from 3.4.3.2 with ferrous ammonium sulfate standard titration solution (3.2.17.1) until the solutions take on light yellow, add 3 drops of phenyl anthranilic acid solution (3.2.14), continue titration until the solutions turn from rose red to brilliant green.

3.4.3.3.2 Specimen containing vanadium

3.4.3.3.2.1 Back titration method of potassium permanganate

Titrate the test solutions obtained in 3.4.3.2 with proper concentration of ferrous ammonium sulfate standard titration solution (3.2.17.1), add 5 drops ferrous-phenanthroline solution (3.2.15) before sexavalent chromium turns from yellow to brilliant green, continue titration until the solutions take on steady red, excessively titrate 5mL, add 5 drops of ferrous-phenanthroline solution (3.2.15), back titrate with potassium permanganate solution (3.2.18) of close concentration until red preliminarily disappears, add anhydrous sodium acetate (3.2.1) according to Table 2, after sodium acetate dissolves, continue slowly titrate with potassium permanganate solution (3.2.18) until light blue (blue-green when the chromium content is high).

Potassium permanganate solution (3.2.18) consumed by ferrous-phenanthroline solution must be corrected according to the following method:

In the two portions of solutions completing calibration of volume ratio of potassium permanganate equivalent to ferrous ammonium sulfate standard titration solution, 10 drops of ferrous-phenanthroline solution (3.2.15) shall be added into one portion and 20 drops shall be added into the other portion. Both of them shall be titrated with potassium permanganate solution (3.2.18) of the same concentration as test solutions. Difference of consumed potassium permanganate solution (3.2.18) volumes is the corrected value of 10 drops of ferrous-phenanthroline solution (3.2.15). This value shall be subtracted from the volume (mL) of potassium permanganate solution consumed by excess ferrous ammonium sulfate standard titration solution.

3.4.3.3.2.2 Theoretical value calculation

Titration shall be carried out according to 3.4.3.3.1, and resultant of chromium and vanadium will be obtained, which shall be corrected according to the theoretical value. 1% vanadium is equivalent to 0.34% chromium.

Vanadium content may be determined according to the operations specified in GB/T 223.13, GB/T 223.14, GB/T 223.76 or GB/T 20125, or may be determined according to proper international vanadium standards.

greater than the repetitiveness limit (r), it shall not exceed 5%;

Under the reproducibility condition, the absolute difference of two obtained independent test results shall not be greater than the reproducibility limit (R); if greater than the reproducibility limit (R), it shall not exceed 5%.

4 Method II -- Potentiometric Titration Method

4.1 Principle

After the specimen is dissolved by acid, when silver sulfate exists, in the acid medium, chromium is oxidized to chromium (VI) by ammonium persulfate, manganese (VII) is reduced by hydrochloric acid, and chromium (VI) is reduced by ferrous ammonium sulfate standard solution.

During the potentiometric titration, equivalence points are determined through changes of measuring potential, as the continuous adding of ferrous ammonium sulfate standard solution.

4.2 Reagents

Unless otherwise specified, during the analysis, only confirmed analytical reagent and distilled water or equivalent purity water is used; there is no oxidation or reduction phenomenon.

4.2.1 Urea.

4.2.2 Perchloric acid, ρ is about 1.67 g/mL.

4.2.3 Hydrofluoric acid, ρ is about 1.15 g/mL.

4.2.4 Phosphoric acid, ρ is about 1.69 g/mL.

4.2.5 Nitric acid, ρ is about 1.42 g/mL.

4.2.6 Hydrochloric acid, ρ is about 1.19 g/mL, diluted to 1+1.

4.2.7 Hydrochloric acid, ρ is about 1.19 g/mL, diluted to 1+10.

4.2.8 Sulfuric acid, ρ is about 1.84 g/mL, diluted to 1+1.

4.2.9 Sulfuric acid, ρ is about 1.84 g/mL, diluted to 1+5.

4.2.10 Sulfuric acid, ρ is about 1.84 g/mL, diluted to 1+19.

4.2.11 Silver sulfate solution, 5 g/L.

4.2.12 Ammonium persulfate [$(NH_4)_2S_2O_8$] solution, 500 g/L, prepare before use.

4.2.13 Manganese sulfate [$MnSO_4 \cdot H_2O$] solution, 4 g/L.

4.2.14 Manganese sulfate [$MnSO_4 \cdot H_2O$] solution, 100 g/L.

4.2.15 Potassium permanganate solution, 5 g/L.

4.2.16 Sodium nitrite solution, 3 g/L, prepare before use.

4.2.17 Sulfamic acid solution [NH_2SO_3H], 100 g/L.

This solution can only be stable for 1 week.

4.2.18 Ferrous ammonium sulfate standard solution, in the medium of sulfuric acid, 1mL of this solution is equivalent to 2mg of chromium.

4.2.18.1 Preparation of solution

Weigh out 46g of hexahydrated ferrous ammonium sulfate [Fe(NH4)2(SO4)2·6H2O], dissolve in 500mL of water, add 110 mL of sulfuric acid (4.2.8), cool, dilute to 1000mL, and blend.

4.2.18.2 Potential calibration of solution (carry out before use)

Weigh out 30.0mL of potassium bichromate standard solution (4.2.19), shift into a 600 mL beaker, add 45 mL of sulfuric acid (4.2.9), add water to about 400 mL, titrate according to the conditions specified in 4.5.3.3.1.

Concentration c_1 of corresponding ferrous ammonium sulfate shall be calculated according to Formula (6), expressed by mass (mg) of chromium per milliliter.

$$c_1 = \frac{30.0 \times 1.733}{V_7} \qquad \cdots\cdots (6)$$

where,

V_7 - Volume of ferrous ammonium sulfate consumed for calibration, in milliliters (mL);

30.0 - Volume of taken and shifted potassium bichromate standard solution (4.2.19), in milliliters (mL);

1.733 - Mass of chromium (VI) in 1mL of potassium bichromate standard solution (4.2.19), in milligrams (mg).

4.2.19 Potassium bichromate standard solution

Weigh 4.9031 g (to the accuracy of 0.0001g) of potassium bichromate which has been dried to constant quantity at 150℃ and cool in the dryer in advance, dissolve

Place the specimen (4.5.1) in a 600-mL beaker, add 60 mL of sulfuric acid (4.2.9) and 10 mL of phosphoric acid (4.2.4), heat for dissolving, oxidize with 15 mL of nitric acid (4.2.5), heat until white dense smoke appears, cool and add 100mL of water.

In order to accelerate dissolution of high silicon specimen, a few drops of hydrofluoric acid (4.2.3) may be added (see note 1 of 4.5.3.2).

4.5.3.1.2 Chromium-nickel alloy steel and iron

Place specimen (4.5.1) into a 600mL beaker, add 25mL of hydrochloric acid (4.2.6), heat for dissolving, and oxidize with 15mL of nitric acid (4.2.5). If the specimen is especially not dissolvable, add 1~2mL of hydrofluoric acid (4.2.3), add 20mL of sulfuric acid (4.2.8) and 10mL of phosphoric acid (4.2.4), and heat until white dense smoke appears.

After cooling down, add 15mL of nitric acid (4.2.5) to the smoky solution, if necessary, add nitric acid again until carbide is completely decomposed, continue smoking to exhaust oxynitride, cool, add 100mL of water (see note 1 in 4.5.3.2).

4.5.3.1.3 Steel containing tungsten

Place the specimen (4.5.1) in a 600-mL beaker, add 25 mL of hydrochloric acid (4.2.6), add 20 mL of sulfuric acid (4.2.8) and 10 mL of phosphoric acid (4.2.4), heat until bubbling stops. If the specimen is especially not dissolvable, add 1~2 mL of hydrofluoric acid (4.2.3), oxidize with 15 mL of nitric acid (4.2.5), heat until white dense smoke appears.

After cooling down, add 15 mL of nitric acid (4.2.5) to the smoky solution, if necessary, add nitric acid again until carbide is completely decomposed, continue smoking to exhaust oxynitride, cool, add 100mL of water (see note 1 in 4.5.3.2).

4.5.3.1.4 High alloy steel and iron or high silicon steel and iron

Place the specimen (4.5.1) in a 750-mL conical flask, add 20mL of hydrochloric acid (4.2.6), 10mL of nitric acid (4.2.5) and 1 mL of hydrofluoric acid (4.2.3).

When bubbling stops, add 30 mL of perchloric acid (4.2.2), heat until white smoke appears, cover the surface vessel, continue heating until the alloy is completely dissolved (white smoke is reserved in the conical flask), cool.

Add 30 mL of water, boil for 5 minutes, cool (see note 1 of 4.5.3.2), quantitatively shift into a 600-mL beaker, add 20 mL of sulfuric acid (4.2.8), 10 mL of phosphoric acid (4.2.4) and 70 mL of water.

4.5.3.2 Chromium oxidation and titration preparation

If necessary, filter graphite carbon with filter lined with pulp, wash with sulfuric acid (4.2.10), dilute to about 350 mL with warm water, add 20 mL of silver sulfate potassium permanganate, add 3g of urea (4.2.1) after about 1 minute, after the potential is stable around 800 mV, and mix and titrate according to 4.5.3.3.1.

- Excess potassium permanganate may also be reduced by dropwise adding sodium nitrite solution (4.2.16) until the potential is stable around 770 mV. Add 5 mL of sulfamic acid solution (4.2.17) (potential is 780 mV), add 30 mL of phosphoric acid (4.2.4), and mix and titrate according to 4.5.3.3.1.

Titration volume V_{11} (mL) shall be recorded.

Note: titration may be carried out according to 4.5.3.3.1, and content of chromium and vanadium will be determined which shall be corrected according to the theoretical value.1% vanadium is equivalent to 0.34% chromium.

4.6 Result representation

4.6.1 Calculation method

4.6.1.1 Vanadium free specimen

Chromium content w_{Cr}, represented by mass fraction, shall be calculated according to Formula (7):

$$w_{Cr} = \frac{(V_9 - V_8) \times c_1}{m \times 1\ 000} \times 100 \quad \cdots\cdots\cdots\cdots (7)$$

where,

V_8 - Volume of ferrous ammonium sulfate standard solution (4.2.18) consumed for blank test solution (4.5.2) titration, in milliliters (mL);

V_9 - Volume of ferrous ammonium sulfate standard solution (4.2.18) consumed for chromium (4.5.3.3.1) titration, in milliliters (mL);

c_1 - Concentration of corresponding ferrous ammonium sulfate standard solution (4.2.18), expressed by mass (mg) of chromium per milliliter;

m - Specimen quantity; unit: gram (g).

4.6.1.2 Specimen containing vanadium

Chromium content w_{Cr}, represented by mass fraction, shall be calculated according to Formula (8):

$$w_{Cr} = \frac{(V_{10} - V_{11}) \times c_1}{m \times 1\ 000} \times 100 \quad \cdots\cdots\cdots\cdots (8)$$

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