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Ferrochromium and ferrosilicochromium — Determination of chromium content — Potentiometric method

Ferro-chrome et ferro-silico-chrome — Dosage du chrome — Méthode potentiométrique

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4140 was developed by Technical Committee ISO/TC 132, *Ferroalloys*, and was circulated to the member bodies in January 1978.

It has been approved by the member bodies of the following countries :

- Australia
- Austria
- Bulgaria
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- France
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- Poland
- Romania
- South Africa, Rep. of
- Spain
- Sweden
- Turkey
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- USA
- USSR
- Yugoslavia

No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD **ISO 4140-1979 (E)**

Ferrochromium and ferrosilicochromium — Determination of chromium content — Potentiometric method

1 Scope and field of application

This International Standard specifies a potentiometric method for the determination of the chromium content of ferrochromium and ferrosilicochromium.

The method is applicable to all grades of these ferroalloys.

2 Reference

ISO 3713, *Ferroalloys — Sampling and preparation of samples — General rules.*[1]

3 Principle

Fusion of a test portion with sodium peroxide, dissolution of the melt in water, and acidification of the aqueous solution with sulphuric acid; alternatively, for some ferroalloys, dissolution of a test portion by direct acid attack. Oxidation of chromium with ammonium persulphate in the presence of silver ions as catalyst. Determination of the sum of chromium and vanadium by potentiometric titration with ammonium iron(II) sulphate. Reoxidation of vanadium with potassium permanganate; destruction of the excess of permanganate by nitrite, and destruction of the excess of nitrite by urea. Determination of vanadium by potentiometric titration with ammonium iron(II) sulphate, and determination of the chromium content by difference.

The reactions are the following :

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7H_2O$$

$$VO_2^+ + Fe^{2+} + 2H^+ \rightarrow VO^{2+} + Fe^{3+} + H_2O$$

$$5\,VO^{2+} + MnO_4^- + H_2O \rightarrow 5\,VO_2^+ + Mn^{2+} + 2H^+$$

$$5\,NO_2^- + 2\,MnO_4^- + 6H^+ \rightarrow 5\,NO_3^- + 2\,Mn^{2+} + 3H_2O$$

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

4.1 Sodium peroxide.

4.2 Sodium carbonate.

4.3 Ammonium persulphate [$(NH_4)_2S_2O_8$].

4.4 Urea.

4.5 Phosphoric acid, ϱ 1,7 g/ml.

4.6 Nitric acid, ϱ 1,42 g/ml.

4.7 Hydrofluoric acid, ϱ 1,14 g/ml.

4.8 Sulphuric acid, 50 % (*V*/*V*) solution.

To 400 ml of water, add cautiously 500 ml of sulphuric acid (ϱ 1,84 g/ml), mix, cool, dilute to 1 000 ml and mix.

4.9 Hydrochloric acid, 40 % (*V*/*V*) solution.

To 600 ml of water, add 400 ml of hydrochloric acid (ϱ 1,19 g/ml), and mix.

4.10 Silver nitrate solution.

Dissolve 5 g of silver nitrate in water and dilute to 1 000 ml.

4.11 Potassium permanganate solution.

Dissolve 2,5 g of potassium permanganate in water and dilute to 100 ml.

4.12 Potassium nitrite solution.

Dissolve 1 g of potassium nitrite in water and dilute to 100 ml.

4.13 Potassium dichromate.

Dissolve pure potassium dichromate in water, recrystallize, dry the crystals at 150 °C and melt them at 415 °C. Grind the product to about 8 mesh and store in a glass bottle with a ground glass stopper.

NOTE — The potassium dichromate reagent may be purchased as high-grade material for volumetric analysis and dried at 105 °C before use.

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[1] At present at the stage of draft.

4.14 Ammonium iron(II) sulphate, approximately 0,17 N standard volumetric solution.

4.14.1 Preparation

Dissolve 65 g of ammonium iron(II) sulphate in 500 ml of water in a 1 000 ml volumetric flask. When dissolution is complete, add 100 ml of the sulphuric acid solution (4.8), cool, make up to the mark and mix.

4.14.2 Standardization

Transfer 1,000 ± 0,000 2 g of the potassium dichromate (4.13) to a 600 ml beaker. Dissolve in 100 ml of water, add 30 ml of the sulphuric acid solution (4.8) and dilute to 300 ml. Proceed as described in 7.2.3 and 7.2.4.

The chromium equivalent, T, of the ammonium iron (II) sulphate solution, expressed in grams of chromium corresponding to 1 ml of solution, is given by the formula

$$T = \frac{0{,}353\,5}{V_1}$$

where V_1 is the volume, in millilitres, of the ammonium iron(II) sulphate solution added.

5 Apparatus

Usual laboratory equipment and in particular :

5.1 Crucible, of capacity 40 ml, of iron, nickel, zirconium, alumina or pocelain.

5.2 Beaker, of capacity 600 ml.

5.3 Potentiometer.

Any high-impedance voltmeter of the type used for pH measurements is suitable.

5.4 Calomel/platinum electrodes.

5.5 Motor-driven stirrer, or a **magnetic stirrer.**

6 Sample

Use a sample prepared in accordance with ISO 3713.

7 Procedure

7.1 Test portion

Take a test portion of 0,5 ± 0,000 2 g.

7.2 Determination

7.2.1 Place the test portion (7.1) in the crucible (5.1), containing 10 g of the sodium peroxide (4.1), or 7 g of the sodium peroxide (4.1) and 3 g of the sodium carbonate (4.2), and mix carefully. Holding the crucible in tongs, swirl it over a flame, heating gently at first, then more strongly until fusion is complete and particles of metal disappear from the bottom of the crucible (approximately 6 min). Allow the crucible to cool.

Place the crucible in the beaker (5.2). Add carefully approximately 150 ml of water and cover with a watch glass. Heat carefully and, after effervescence has ceased, allow to cool. Add 40 ml of the sulphuric acid solution (4.8). When the solution is completely clear, rinse the watch glass with a jet from a wash-bottle and remove the crucible after having thoroughly washed it with water. Dilute the solution to approximately 300 ml.

7.2.1.1 Dissolution of low carbon ferrochromium (0,5 % C max.) soluble in acids

Transfer the test portion (7.1) to the beaker (5.2). Add 25 ml of the sulphuric acid solution (4.8) and heat very gently, avoiding reduction in volume, for 20 min or until solvent action has apparently ceased.[1] Add 5 ml of the phosphoric acid (4.5) and evaporate just to fuming. Cool, add 40 ml of cold water, heat to boiling, oxidize with the nitric acid (4.6) and boil for 2 min. Dilute to 400 ml with hot water.

7.2.1.2 Dissolution of ferrosilicochromium (1 % C max.) soluble in acids

Place the test portion (7.1) in a platinum dish, add 10 to 15 ml of the hydrofluoric acid (4.7) and, carefully, drop by drop, 15 ml of the nitric acid (4.6).

Heat the contents of the dish until the test portion is completely decomposed. Add 20 ml of the sulphuric acid solution (4.8) and 5 ml of the phosphoric acid solution (4.5) and evaporate until sulphuric acid fumes appear. Cool the dish, rinse the walls with water and again evaporate until sulphuric acid fumes appear. Cool the dish, dissolve the salts in 40 to 60 ml of water and transfer the solution into a 600 ml beaker. Rinse the dish with water and collect the washings in the beaker. Dilute to 300 ml and heat until dissolution of salts is complete.

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[1] It is important to ensure that the whole of the test portion is covered by the acid and that no particles adhere to the wall of the beaker during transfer of the test portion or following shaking of the beaker during dissolution.

7.2.2 Add 20 ml of the silver nitrate solution (4.10), 3 drops of the potassium permanganate solution (4.11), and 8 g of the ammonium persulphate (4.3) and boil for 10 min.[1] Add 0,5 ml of the hydrochloric acid solution (4.9) to reduce excess permanganate and continue to boil for 5 min after the permanganate colour has disappeared.[2] Allow the solution to cool to room temperature.

7.2.3 Add 10 ml of the phosphoric acid (4.5) in the case of dissolution as in 7.2.1, and 5 ml of phosphoric acid in the case of dissolution as in 7.2.1.1 and 7.2.1.2. Set up the stirrer (5.5). Place the electrodes (5.4) in the solution and connect them to the potentiometer (5.3).

7.2.4 Titrate with ammonium iron(II) sulphate solution (4.14), with continuous stirring, to a potential deflection of about 200 mV.[3] The amount of ammonium iron(II) sulphate solution used corresponds to chromium + vanadium.

7.2.5 Add the potassium permanganate solution (4.11) drop by drop until a distinct pink colour which lasts for more than 1 min is obtained[4]. Add the potassium nitrite solution (4.12) drop by drop until the permanganate colour disappears and a change in potential is observed, then 2 drops in excess. Add approximately 0,5 g of the urea (4.4) to destroy excess nitrite. Titrate with the ammonium iron(II) sulphate solution to a potential deflection. This titration corresponds to the vanadium content.

8 Expression of results

The chromium content, expressed as a percentage by mass, is given by the formula

$$\frac{100\,T\,(V_2 - V_3)}{m}$$

where

T is the chromium equivalent of the ammonium iron(II) sulphate solution (4.14), expressed in grams of chromium corresponding to 1 ml of solution;

V_2 is the volume, in millilitres, of the ammonium iron(II) sulphate solution (4.14) used in the first titration (chromium + vanadium);

V_3 is the volume, in millilitres, of the ammonium iron(II) sulphate solution (4.14) used in the second titration (vanadium);

m is the mass, in grams, of the test portion (7.1).

9 Reproducibility

Experience has shown that the 95 % confidence limits for an experienced operator are ± 0,20 % (*m*/*m*) for chromium contents in the neighbourhood of 70 % (*m*/*m*).

10 Test report

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or regarded as optional.

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[1] If the colour of permanganic acid does not develop after boiling for 5 min, make 0,5 g additions of ammonium persulphate to the hot solution until the colour is obtained.

[2] If the colour of permanganic acid is not discharged, make further 0,5 ml additions of the hydrochloric acid solution, boiling after each addition, until the colour disappears.

[3] If the chromium content of the sample exceeds 31 % (*m*/*m*), start by adding 50 ml of the ammonium iron(II) sulphate solution from a pipette; if it exceeds 68 % (*m*/*m*), start by adding 100 ml.

[4] The appearance of the pink colouration indicates the reoxidation of vanadium. This may also be recognized by the corresponding increase in potential.