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Ferromanganese and ferrosilicomanganese — Determination of manganese content — Potentiometric method

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

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FOREWORD

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INTERNATIONAL STANDARD **ISO 4159-1978 (E)**

Ferromanganese and ferrosilicomanganese – Determination of manganese content – Potentiometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a potentiometric method for the determination of the manganese content of ferromanganese and ferrosilicomanganese.

The method is applicable to alloys containing from 55 to 95 % (*m*/*m*) of manganese.

2 REFERENCE

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

3 PRINCIPLE

Dissolution of a test portion with hydrochloric, hydrofluoric and perchloric acids.

Potentiometric determination (see note) of manganese with potassium permanganate in a pyrophosphoric medium at a controlled pH, according to the reaction :

$$4\,Mn^{2+} + MnO_4^{-} + 8\,H^{+} + 15\,(P_2O_7H_2)^{2-} \rightarrow 5\,Mn(P_2O_7H_2)_3^{3-} + 4\,H_2O$$

NOTE – The method may be completed by any other electrometric method : amperometric titration, dead-stop, etc.

4 REAGENTS

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

4.1 Perchloric acid[2], ρ 1,61 g/ml.

4.2 Hydrofluoric acid, ρ 1,14 g/ml.

4.3 Hydrochloric acid, ρ 1,19 g/ml.

4.4 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 2.

4.5 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 4.

4.6 Sodium pyrophosphate, saturated solution.

Dissolve 145 g of sodium pyrophosphate ($P_2O_7Na_4.10H_2O$) in a 2 litre conical flask, with about 1 litre of hot water; heat without exceeding, even locally, the temperature of 60 °C, until the salt is completely dissolved. Cool.

Prepare this solution at the time of use.

4.7 Potassium permanganate, recrystallized.

Place 50 g of pure analytical grade potassium permanganate in the conical flask (5.1), and dissolve it in 200 ml of warm distilled water (70 to 80 °C).

Fit the reflux condenser (5.2) to the flask and boil the solution for 20 min. Filter the warm solution quickly under vacuum through a sintered glass funnel (5.3).

Cool the filtrate in iced water, stirring vigorously, and allow the fine, crystalline precipitate to settle for 10 min.

Decant the solution; then, using a glass spatula, transfer the crystalline mass into a funnel with a filter plate, porosity 4, and place under suction for a few minutes to remove most of the mother liquor.

Dissolve the crystalline mass in 160 ml of distilled water (deionized water is not permitted for this phase), and repeat the recrystallization.

After filtering and placing under suction for approximately 5 min, transfer the crystalline mass onto a 150 mm diameter watch glass using a glass spatula, and dry it in air, protected from light and dust. When the crystalline mass no longer agglomerates when crushed with the spatula, dry it at 110 °C for 2 h, then transfer it to a weighing bottle fitted with a ground glass stopper.

Store in the dark.

This salt contains 34,76 % (*m*/*m*) of Mn.

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[1] At present at the stage of draft.

[2] Attention is drawn to the hazards associated with perchloric acid when heated to fuming.

4.8 Potassium permanganate, about 0,1 N standard volumetric solution.

4.8.1 *Preparation*

Dissolve 3,20 g of potassium permanganate in 1 000 ml of water. Allow to stand for 6 days. Filter through glass wool or a sintered glass filter, then transfer to a brown glass bottle. Mix.

4.8.2 *Standardization*

Place about 2,5 g of the recrystallized potassium permanganate (4.7), weighed to the nearest 0,000 2 g, in a 250 ml conical flask, and follow exactly the procedure specified in 7.3. It is recommended that this standardization be carried out in parallel with the determination.

The manganese equivalent *T* of the potassium permanganate solution (4.8), expressed in grams of manganese corresponding to 1 ml of solution, is given by the formula

$$T = \frac{m_1 \times 34{,}76}{100\,(V_1 - V_0)} \times \frac{50}{250}$$

$$= \frac{0{,}069\,52\,m_1}{V_1 - V_0}$$

where

m_1 is the mass, in grams, of the crystallized potassium permanganate (4.7) used;

V_0 is the volume, in millilitres, of the potassium permanganate solution (4.8) used for the blank test;

V_1 is the volume, in millilitres, of the potassium permanganate solution (4.8) used for the standardization.

5 APPARATUS

Usual laboratory equipment, and in particular :

5.1 Erlenmeyer conical flask with ground neck.

5.2 Reflux condenser with ground glass joint, to fit the flask (5.1).

5.3 Filter crucibles (porosity 4) or **filter funnels,** capacity 40 ml.

5.4 Volumetric flask, capacity 250 ml.

5.5 Beaker, capacity 600 ml.

5.6 Conical flask, capacity 250 ml.

5.7 Dish, capacity 250 ml, or beaker, capacity 400 ml, of polytetrafluoroethylene.

5.8 Magnetic stirrer.

5.9 pH meter, fitted with glass and calomel electrodes.

5.10 Potentiometer, fitted with platinum and calomel electrodes.

6 SAMPLE

Use powder which will pass through a sieve with a mesh size of 160 µm, prepared in accordance with ISO 3713.

7 PROCEDURE

7.1 Test portion

Take a test portion of 1 ± 0,000 2 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same reagents.

7.3 Determination

7.3.1 Attack the test portion as specified in 7.3.1.1 or 7.3.1.2, as appropriate.

7.3.1.1 *Ferromanganese*

Transfer the test portion (7.1) to the conical flask (5.6) and attack it with 20 ml of the hydrochloric acid (4.3) and 0,2 ml of the hydrofluoric acid (4.2), then add 10 ml of the perchloric acid (4.1).1)

Proceed as specified in 7.3.2.

7.3.1.2 *Ferrosilicomanganese*

Transfer the test portion (7.1) to a dish or beaker (5.7). Attack it with 10 ml of the hydrochloric acid (4.3), add 10 ml of the perchloric acid (4.1) then, slowly, about 20 ml of the hydrofluoric acid (4.2).1)

Proceed as specified in 7.3.2.

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1) Oxidize the solution with nitric acid prior to adding the perchloric acid.

7.3.2 Heat gently at first, then progressively increase the heat until the formation of heavy perchloric fumes. Continue heating until a syrupy consistency is obtained and manganese dioxide begins to precipitate. Allow to cool.

7.3.3 Take up with 20 ml of the hydrochloric acid solution (4.5). Heat gently until the solution clears. Rinse the sides of the vessel carefully with a jet from a wash-bottle and continue heating for a few minutes. Add 100 ml of hot water, and cool to room temperature. Transfer, without filtering, to the volumetric flask (5.4). Rinse the vessel used for the attack carefully, cool and make up to the mark. Shake to mix the solution.

7.3.4 By means of a pipette, transfer 50 ml of the solution to the beaker (5.5). Dilute to 100 ml with water. Add 250 ml of the sodium pyrophosphate solution (4.6). Place the beaker on the magnetic stirrer (5.8) and add a magnetized bar.

7.3.5 Adjust the pH of the solution to a value between 6,5 and 7, using the pH meter (5.9), by adding the hydrochloric acid solution (4.4).

NOTE — In the case of ferromanganese containing chromium, it is necessary to wait for 30 min after the adjustment of the pH of the solution before carrying out the titration.

Titrate with the potassium permanganate solution (4.8), adding it slowly to the beaker. Follow the indications of the potentiometer : the end of the titration is obtained when a sudden increase in potential of at least 100 mV is observed.

It is recommended that a second titration be carried out under the same conditions on another aliquot portion of the test solution.

8 EXPRESSION OF RESULTS

The manganese content, expressed as a percentage by mass of the sample, is given by the formula

$$T\,(V_2 - V_0) \times \frac{250}{50} \times \frac{100}{m_0}$$

$$= \frac{500\,T\,(V_2 - V_0)}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (7.1);

V_0 is the volume, in millilitres, of the potassium permanganate solution (4.8) used for the blank test;

V_2 is the volume, in millilitres, of the potassium permanganate solution (4.8) used for the determination (7.3.5);

T is the manganese equivalent of the potassium permanganate solution (4.8), expressed in grams of manganese corresponding to 1 ml of the solution.

9 REPRODUCIBILITY

Experience has shown that the 95 % confidence limits for an experienced operator are ± 0,20 %.

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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