BS EN 10071:2012

BSI Standards Publication

Chemical analysis of ferrous materials — Determination of manganese in steels and irons — Electrometric titration method

National foreword

This British Standard is the UK implementation of EN 10071:2012. It supersedes BS EN 10071:1991 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee ISE/102, Methods of Chemical Analysis for Iron and Steel.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Chemical analysis of ferrous materials - Determination of manganese in steels and irons - Electrometric titration method

Analyse chimique des matériaux ferreux - Détermination du manganèse dans les aciers et les fontes - Méthode par titrage électrométrique

Chemische Analyse von Eisenwerkstoffen - Bestimmung von Mangan in Stahl und Eisen - Elektrometrisches Titrierverfahren

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Foreword

This document (EN 10071:2012) has been prepared by Technical Committee ECISS/TC 102 “Methods of analysis for iron and steel”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2013, and conflicting national standards shall be withdrawn at the latest by April 2013.

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This document supersedes EN 10071:1989.

In comparison with EN 10071:1989, the following significant technical change was made:

— Clause 3, Principle, rewording of the third sentence in order to correct the erroneous mention of “pyrophosphoric irons”.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies an electrometric titration method for the determination of manganese in steels and irons.

The method is applicable to unalloyed, low alloy or alloyed steels and to irons with manganese contents greater than or equal to 0,5 % (m/m).

2 Normative references

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

EN ISO 648, *Laboratory glassware — Single-volume pipettes (ISO 648)*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042)*

EN ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition (ISO 14284)*

3 Principle

Dissolution of the test portion with appropriate acids, followed by a partial neutralisation of the acids with sodium hydrogen carbonate.

Precipitation of the interfering cations with zinc oxide.

Titration of Mn (II) with a potassium permanganate solution, in a pyrophosphoric medium at a pH of about 6,5.

The oxidation-reduction reaction [oxidation of Mn (II) to Mn (III)] is controlled by an electrometric measurement.

4 Reagents

During the analysis, use only reagents of recognised analytical grade.

4.1 **Water,** free from reducing compounds.

For each 1 000 ml of water add 6 ml of sulphuric acid (ρ_{20} = 1,84 g/ml) and boil. Add a few crystals of sodium periodate and maintain the boiling for about 10 min. Cool and transfer into an appropriate vessel.

4.2 **Zinc oxide,** free from compounds which can reduce the permanganate ions.

4.3 **Nitric acid solution,** 1 + 1.

Add 500 ml of nitric acid (ρ_{20} = 1,40 g/ml) to 500 ml of water (4.1).

4.4 **Hydrochloric acid solution,** 1 + 1.

Add 500 ml of hydrochloric acid (ρ_{20} = 1,19 g/ml) to 500 ml of water (4.1).

4.5 Aqua regia.

Mix three volumes of hydrochloric acid (ρ_{20} = 1,19 g/ml) with one volume of nitric acid (ρ_{20} = 1,40 g/ml).

4.6 Sodium hydrogen carbonate, saturated solution at room temperature.

NOTE The concentration of the saturated solution corresponds to about 100 g/l $NaHCO_3$, in water (4.1).

4.7 Sodium pyrophosphate solution, 120 g/l.

Dissolve 120 g of hydrated sodium pyrophosphate ($Na_4P_2O_7 \,.\, 10\, H_2O$) in a one-litre beaker with hot water (4.1). After cooling, transfer this solution into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water (4.1) and mix.

NOTE The temperature shall not exceed 70 °C.

4.8 Manganese standard solution, 0,500 g/l Mn.

Weigh ($1{,}438_5 \pm 0{,}001$) g of potassium permanganate ($KMnO_4$) and transfer it into a 500 ml conical flask. Dissolve with 40 ml of hydrochloric acid (4.4) and then heat the solution until dryness. Add 5 ml of hydrochloric acid (4.4), 100 ml of water (4.1) and mix.

Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, cool, dilute to the mark with water (4.1) and mix.

1 ml of this solution contains 0,500 mg of Mn.

4.9 Potassium permanganate standard solution, about 0,002 2 mol/l.

4.9.1 Preparation of the solution.

Dissolve approximately 0,36 g of potassium permanganate with 1 000 ml of water (4.1) and allow the solution to stand out of the light, for at least two weeks. Filter through a glass wool or a sintered glass filter, transfer the filtrate into a brown glass bottle and mix.

4.9.2 Standardization of the solution.

Transfer 350 ml of the sodium pyrophosphate solution (4.7) into a 600 ml beaker. With calibrated pipettes or a burette, add 30 ml of the manganese standard solution (4.8).

Mix carefully and then add small amounts of nitric acid (4.3) in order to set up the pH to about 6,5.

NOTE The pH setting up can be controlled either by means of a pH-meter (5.2) or by means of a pH indicator paper (4.10).

Titrate with the potassium permanganate standard solution (4.9) and determine the end point by means of an electrometric measurement.

4.9.3 Calculation of the titre of the solution.

The manganese concentration, C_1, of the potassium permanganate standard solution (4.9), expressed in mg/ml is given by the Formula (1):

$$C_1 = \frac{0{,}5000 \times 30}{V_1} \tag{1}$$

where

V_1 is the volume, expressed in millilitres, of the potassium permanganate standard solution (4.9) used for the titration.

4.10 pH indicator paper, range 5 to 7.

5 Apparatus

All volumetric glassware shall be Class A and calibrated, in accordance with EN ISO 648 or EN ISO 1042 as appropriate.

5.1 Magnetic stirrer.

5.2 pH-meter, fitted with glass electrode and a calomel electrode.

5.3 Potentiometer, fitted with platinum electrode and a calomel electrode.

6 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 or an appropriate national standard for steel and iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, 1,25 g of the test sample.

7.2 Determination

7.2.1 Dissolution of the test portion

7.2.1.1 Unalloyed and low alloyed steels and irons

Transfer the test portion (7.1) into a 500 ml conical flask and dissolve it with 30 ml of nitric acid solution (4.3).

7.2.1.2 Alloyed steels

Transfer the test portion (7.1) into a 500 ml conical flask and start the dissolution by adding 20 ml of hydrochloric acid solution (4.4).

NOTE Larger volumes of hydrochloric acid solution (4.4) can be necessary.

Oxidise with 10 ml of nitric acid solution (4.3) or with 15 ml of aqua regia (4.5).

7.2.2 Preparation of the test solution

Heat the test solution (7.2.1) until boiling, in order to expel nitrogen oxides. Cool and add water until about 80 ml. Whilst stirring slowly add, 80 ml of the sodium hydrogen carbonate solution (4.6).

NOTE 1 The addition of the sodium hydrogen carbonate solution (4.6) will partially neutralise the acids added for the sample dissolution. This will minimise the zinc amount that can be dissolved during the hydroxides precipitation with zinc oxide.

NOTE 2 Before the zinc oxide addition, the solution needs to be perfectly limpid. The precipitate that can appear during the addition of the sodium hydrogen carbonate solution (4.6) will lead to a manganese loss. Consequently, if the test solution is not perfectly limpid, the precipitate needs to be dissolved by adding a minimum amount of nitric acid solution (4.3) and then boiling until the nitrogen oxides have been expelled.

In all cases, boil the solution once again and add about 5 g of zinc oxide (4.2), whilst stirring vigorously.

Transfer the solution and the precipitate into a 250 ml volumetric flask, cool, dilute to the mark with water (4.1) and mix.

Filter the solution through a dry, fluted filter paper and collect the filtrate in an appropriate dry vessel, after having rejected the first fractions of the filtrate (a few millilitres).

7.2.3 Titration

Transfer 350 ml of the sodium pyrophosphate solution (4.7) into a 600 ml beaker.

According to the expected manganese content of the sample, add the aliquot portion of the filtrate (7.2.2) specified in Table 1, whilst continuously and vigorously stirring by means of a magnetic stirrer (5.1), in order to avoid the precipitation of zinc phosphate.

Table 1 — Aliquot portion of the filtrate

Expected manganese content of sample %	**Aliquot portion of the filtrate (7.2.2)** ml	**Dilution ratio (D)**
0,5 ≤ Mn ≤ 4	100,0	2,5
4 ≤ Mn ≤ 8	50,0	5,0
8 < Mn	20,0	12,5

Adjust the pH to approximately 6,5 by adding nitric acid solution (4.3). This setting up is controlled either by means of a pH-meter (5.2) or by means of a pH indicator paper (4.10).

Titrate with the potassium permanganate standard solution (4.9). Follow the progress of the titration by an electrometric measurement as for example, by means of a potentiometer (5.3).

Let V_2 be the volume, expressed in millilitres, of the potassium permanganate standard solution (4.9) used for the titration.

NOTE In presence of an excess of pyrophosphate, the pH of the test solution after the addition of the aliquot portion of the filtrate (7.2.2) is greater than 6,5. The adjustment of the pH value is therefore carried out by addition of an acid solution: this will avoid the formation of precipitates difficult to redissolve, which can happen when the pH value has to be increased by addition of an alkaline solution.

8 Expression of results

The manganese mass fraction (w_{Mn}), in percent (%), is given by the Formula (2):

$$w_{\mathrm{Mn}} = \frac{V_2 \text{ x } \mathrm{C}_1 \text{ x } \mathrm{D}}{10 \text{ x } \mathrm{m}} \qquad (2)$$

where

V_2 is the volume in millilitres, of the potassium permanganate standard solution (4.9) used for the titration;

C_1 is the manganese concentration of the potassium permanganate standard solution (4.9), expressed in mg/ml;

D is the dilution ratio (see Table 1);

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

9 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) method used;

c) results;

d) any unusual characteristics noted during the determination;

e) any operation not included in this European Standard or in the document to which reference is made or regarded as optional;

f) date of the test and/or date of preparation or signature of the test report;

g) signature of the responsible person.

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