INTERNATIONAL STANDARD

ISO 18632

Second edition
2018-08

Alloyed steels — Determination of manganese — Potentiometric or visual titration method

Aciers alliés — Détermination du manganèse — Méthodes par titration visuelle ou potentiométrique

Reference number
ISO 18632:2018(E)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 18632:2010), which has been technically revised. The following changes have been made:

- a procedure has been added for the removal of the oxidized layer when the manganese standard solution is prepared;
- superfluous figures have been deleted in Table A.2;
- Annex C has been added to explain the main redox reaction and the correction of vanadium and cerium content in the document.

Alloyed steels — Determination of manganese — Potentiometric or visual titration method

1 Scope

This document specifies a potentiometric or visual titration method for the determination of manganese content in alloyed steels.

The method is applicable to manganese mass fractions between 2 % and 25 %. Vanadium and cerium interfere with the determination. If the mass fraction of cerium in the sample is less than 0,01 %, or the mass fraction of vanadium in the sample is less than 0,005 %, the interference is negligible, otherwise theoretical corrections are necessary.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Dissolution of a test portion in appropriate acids. Addition of phosphoric acid. Oxidation of manganese to manganese(III) in phosphoric acid medium by ammonium nitrate. Visual titration of manganese(III) with a ferroammoniumdisulfate standard solution with N-phenylanthranilic acid as indicator, or potentiometric titration with a ferroammoniumdisulfate standard solution. If the sample contains vanadium and/or cerium, the manganese content shall be corrected.

5 Reagents

During the analysis use only reagents of recognized analytical grade and only grade 2 water in accordance with ISO 3696.

5.1 **Ammonium nitrate,** NH_4NO_3.

5.2 **Urea**.

5.3 **Phosphoric acid,** ρ approximately 1,69 g/ml.

5.4 **Nitric acid,** ρ approximately 1,42 g/ml.

5.5 **Hydrochloric acid,** ρ approximately 1,19 g/ml.

5.6 **Sulfuric acid,** diluted 1 + 3.

5.7 **Sulfuric acid,** diluted 5 + 95.

5.8 **N-phenylanthranilic acid solution,** $C_6H_5NHC_6H_4COOH$, approximately 2 g/l.

Dissolve 0,20 g of N-phenylanthranilic acid and 0,20 g of sodium carbonate in 100 ml of water and filter.

5.9 **Potassium dichromate solution,** $K_2Cr_2O_7$, 0,002 5 mol/l.

Weigh 0,735 5 g of high purity potassium dichromate, previously dried at 150 °C for at least 2 h and cooled in a desiccator. Introduce it into a 250 ml beaker and dissolve in some water. Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.10 **Manganese standard solution,** corresponding to 1,00 g/l of manganese.

Weigh, to the nearest 0,1 mg, 1,000 g of pure manganese [purity ≥ 99,9 % (mass fraction)].

When the surface of manganese seems oxidized, the oxide layer should be removed before weighing as follows:

a) introduce several grams of manganese into a beaker containing sulfuric acid (5.7) and stir;

b) decant, discard the sulphuric acid solution and immediately rinse the metal several times, firstly with water and then with ethanol or acetone;

c) dry the metal for about 2 min at 100 °C and cool in a desiccator.

Introduce it in a 250 ml beaker and add 40 ml of hydrochloric acid (5.5). Cover with a watch glass and heat gently to complete dissolution. Cool and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1,00 mg of manganese.

5.11 **Ferroammoniumdisulfate standard solution,** $[(NH_4)_2Fe(SO_4)_2\cdot 6H_20]$ 0,015 mol/l.

5.11.1 Preparation of the solution

Dissolve 5,9 g of ferroammoniumdisulfate in 1 000 ml sulfuric acid (5.7) and mix.

5.11.2 Standardization of the solution (to be carried out just before use)

5.11.2.1 Visual titration method

5.11.2.1.1 Titration

Transfer three aliquots of 20,0 ml of the potassium dichromate solution (5.9) to three 250 ml conical flasks.

Add 20 ml of sulfuric acid (5.6), 5 ml of phosphoric acid (5.3) and water up to a volume of approximately 150 ml. Proceed as specified in 8.2.2.1.

Calculate the mean (V_1) of the three volumes values of the ferroammoniumdisulfate solution. The difference between the values should not exceed 0,05 ml.

5.11.2.1.2 Correction for N-phenylanthranilic acid

Transfer three aliquots of 5,0 ml of the potassium dichromate solution (5.9) to three 250 ml conical flasks. Add 20 ml of sulfuric acid (5.6), 5 ml of phosphoric acid (5.3). Titrate the solution with the ferroammoniumdisulfate solution (5.11) until the end point is approached (i.e. when the purplish red colour of the solution becomes lighter). Add two drops of N-phenylanthranilic acid solution (5.8), continue the titration until the purplish red colour disappears and record the volume added. Add another 5,0 ml of potassium dichromate solution (5.9), titrate with the ferroammoniumdisulfate solution (5.11) until the end point and record the volume added again. The mean of the differences between the volumes of the two titrations is the corrected value, V_0.

5.11.2.1.3 Calculation

The corresponding concentration, *c*, expressed in moles per litre, of the ferroammoniumdisulfate solution (5.11) is given by Formula (1):

$$C = \frac{0{,}015 \times 20{,}0}{V_1 - V_0} \qquad (1)$$

where

V_1 is the mean volume, expressed in millilitres, of the ferroammoniumdisulfate solution (5.11) used for the titration;

V_0 is the mean volume, expressed in millilitres, of the ferroammoniumdisulfate solution (5.11) used for the correction of N-phenylanthranilic acid titration;

0,015 is the molar concentration, expressed in moles per litre, of the potassium dichromate solution (5.9) times six;

20,0 is the volume, expressed in millilitres, of the potassium dichromate solution (5.9) used for the standardization.

5.11.2.2 Potentiometric titration method

5.11.2.2.1 Titration

Transfer three aliquots of 20,0 ml of the manganese standard solution (5.10) to three 300 ml conical flasks. Add 15 ml of phosphoric acid (5.3). Heat until the surface of the solution calms down (i.e. a state where no bubble is observed on the surface of the solution) and white fumes are just given off (at this stage the temperature should be about 200 °C to 240 °C). Remove the flask from the heater, add 2 g of ammonium nitrate (5.1) immediately and shake the conical flask for removing nitrogen oxide. Nitrogen oxide shall be eliminated thoroughly by blowing with a pipette or by adding 0,5 g to 1,0 g of urea (5.2). Wait for 1 min to 2 min. Cool the solution to 80 °C to 100 °C.

Transfer the solution to a 400 ml beaker. Add 60 ml of sulfuric acid (5.7) and mix. Make up the volume to approximately 150 ml with water and cool to room temperature.

Proceed as specified in 8.2.2.2.

Calculate the mean, V_2, of the three values of the ferroammoniumdisulfate solution volumes. The difference between the values should not exceed 0,05 ml.

5.11.2.2.2 Calculation

The corresponding concentration, c_1, expressed in moles per litre, of the ferroammoniumdisulfate solution (5.11) is given by Formula (2):

$$c_1 = \frac{1{,}00 \times 20{,}0}{54{,}94 \times V_2} \qquad (2)$$

where

V_2	is the mean volume, expressed in millilitres, of the ferroammoniumdisulfate solution (5.11) used for the titration of the manganese solution;
54,94	is the molar mass, expressed in grams per mole, of manganese;
1,00	is the concentration, expressed in grams per litre, of the manganese standard solution (5.10);
20,0	is the volume, expressed in millilitres, of the manganese standard solution (5.10) used for the standardization.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385, ISO 648 or ISO 1042, as appropriate. Use ordinary laboratory apparatus and a potentometric titration device, consisting of:

a) indicator electrode, of bright platinum, which shall be kept in a clean, highly polished condition;

b) reference electrode, of silver/silver chloride, calomel or mercury(I) sulfate.

NOTE A redox electrode can also be used.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,000 1 g, a test portion of the sample according to Table 1.

Table 1 — Test portion

Expected mass fraction of manganese %	Mass of test portion g
2 to 5	0,50
5 to 15	0,20
15 to 25	0,10

8.2 Determination

8.2.1 Preparation of test solution

Introduce the test portion (8.1) into a 300 ml conical flask. Add 15 ml of phosphoric acid (5.3) [for some high-alloy steels, first add 15 ml of aqua regia: three volumes hydrochloric acid (5.5) plus one volume nitric acid (5.4)] and heat gently until effervescence ceases. Decompose the carbides by addition of nitric acid (5.4) drop by drop.

Continue heating until the surface of the solution calms down and white fumes are just given off (at this stage the temperature should be about 200 °C to 240 °C). Remove the flask from the heater, add 2 g of ammonium nitrate (5.1) immediately and shake the conical flask for removing nitrogen oxide. Nitrogen oxide shall be eliminated thoroughly by blowing with a pipette or by adding 0,5 g to 1,0 g of urea (5.2). Wait for 1 min to 2 min. Cool the solution to 80 °C to 100 °C.

8.2.2 Titration

8.2.2.1 Visual titration

Add 60 ml of sulfuric acid (5.7) to the solution (8.2.1) and mix. Make up the volume to approximately 150 ml with water and cool to room temperature.

Titrate the solution with the ferroammoniumdisulfate solution (5.11) until the end point is approached. Add two drops of N-phenylanthranilic acid (5.8). Continue the titration until the purplish red colour of the solution disappears. Record the volume, V_3, of the ferroammoniumdisulfate solution (5.11) used for the titration.

8.2.2.2 Potentiometric titration

Transfer the solution (8.2.1) to a 400 ml beaker. Add 60 ml of sulfuric acid (5.7) and mix. Make up the volume to approximately 150 ml with water and cool to room temperature.

Place the beaker on the magnetic stirrer and switch it on.

Immerse the indicator and reference electrodes [see Clause 6 a) and b)] or a redox electrode in the solution. Titrate slowly with the ferroammoniumdisulfate solution (5.11) until the end point is approached. Continue the titration in 0,05 ml or one drop increments and record the burette and potential readings when equilibrium is reached after each incremental addition. Continue the titration through the end point. Determine the end point by the titration curve or the derivative ratio dE/dV. Record the volume, V_4, of the ferroammoniumdisulfate solution (5.11) used for the titration.

8.2.3 Theoretical correction of vanadium and cerium

For the samples containing vanadium and/or cerium, mass fraction of manganese shall be corrected on the following theoretical basis.

Manganese, per cent = vanadium, per cent × 1,08; manganese, per cent = cerium, per cent × 0,39

For detailed information, see Annex C.