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Alloyed steel — Determination of manganese — Potentiometric and visual titration method

Aciers alliés — Détermination de la teneur en manganèse — Méthodes de titration visuelle et potentiométrique

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 18632 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Alloyed steel — Determination of manganese — Potentiometric and visual titration method

1   Scope

This International Standard specifies a potentiometric or visual titration method for the determination of the mass fraction of manganese in alloyed steels. The method is applicable to mass fractions of manganese between 2 % and 25 %. Vanadium and cerium interfere with the measurement. 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. If the mass fraction of cerium in the sample is greater than 0,01 %, or the mass fraction of vanadium in the sample is greater than 0,005 %, a theoretical correction is necessary.

2   Normative references

The following referenced documents are indispensable for the application 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 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 4942, *Steel and iron — Determination of vanadium content — N-BPHA spectrophotometric method*

ISO 4947:1986, *Steel and cast iron — Determination of vanadium content — Potentiometric titration method*

ISO 9647:1989, *Steel and iron — Determination of vanadium content — Flame atomic absorption spectrometric method*

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3   Principle

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

4   Reagents

During the analysis, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

4.1   Ammonium nitrate, NH_4NO_3.

4.2   **Urea**.

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

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

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

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

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

4.8   **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.

4.9   **Potassium dichromate solution**, 0,002 50 mol/l.

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

4.10   **Manganese standard solution**, corresponding to 1,00 g of Mn per litre.

Weigh, to the nearest 0,1 mg, 1,000 g of pure manganese metal [purity ⩾ 99,9 % (mass fraction)]. Place it in a 250 ml beaker and add 40 ml of hydrochloric acid (4.5). Cover with a watch glass and heat gently until 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 Mn.

4.11   Ferroammoniumdisulfate solution, standard volumetric solution, 0,015 mol/l.

4.11.1   Preparation of the solution.

Dissolve 5,9 g of ferroammoniumdisulfate [(NH_4) Fe$(SO_4)_2$·6H$_2$O] in 1 000 ml of sulfuric acid (4.7) and mix.

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

4.11.2.1   Visual titration method.

4.11.2.1.1   Titration.

Transfer three portions of 20,00 ml of the potassium dichromate solution (4.9) to three 250 ml conical flasks.

Add 20 ml of sulfuric acid (4.6), 5 ml of phosphoric acid (4.3). Add water up to a volume of approximately 150 ml. Proceed as specified in 7.2.2.1.

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

4.11.2.1.2   Correction for N-phenylanthranilic acid.

Transfer three portions of 5,00 ml of the potassium dichromate solution (4.9) to three 250 ml conical flasks. Add 20 ml of sulfuric acid (4.6) and 5 ml of phosphoric acid (4.3). Titrate the solution with the ferroammoniumdisulfate solution (4.11.1) until the end point is approached[1]. Add 2 drops of N-phenylanthranilic acid solution (4.8), continue the titration until disappearance of the purplish red color and

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1)   The purplish red colour of the solution becomes light.

record the volume added. Add 5 ml more of potassium dichromate solution (4.9), titrate with the ferroammoniumdisulfate solution (4.11.1) 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 of V_0.

4.11.2.1.3   Calculation.

The corresponding concentration, c, in moles per litre (mol/l), of the ferroammoniumdisulfate solution (4.11.1) is given by the equation:

$$c = \frac{0,015\,00 \times 20,00}{V_1 - V_0}$$

where

V_1 is the mean volume, in millilitres, of the ferroammoniumdisulfate solution (4.11.1) added;

V_0 is the mean volume, in millilitres, of the ferroammoniumdisulfate solution (4.11.1) added for correction of N-phenylanthranilic acid.

4.11.2.2   Potentiometric titration method.

4.11.2.2.1   Titration.

Transfer three portions of 20,00 ml of the manganese standard solution (4.10) to three 300 ml conical flasks. Add 15 ml of phosphoric acid (4.3). Heat until the surface of the solution calms down[2] and white fumes are just given off (controlling the temperature from 200 °C to 240 °C). Remove the flask from the heater, add 2 g of ammonium nitrate (4.1) immediately and shake the conical flask to remove nitrogen oxide. Nitrogen oxide must be eliminated thoroughly by blowing with a pipette or by adding 0,5 g to 1,0 g of urea (4.2). 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 (4.7) and mix. Make up the volume to approximately 150 ml and cool to room temperature.

Proceed as specified in 7.2.2.2.

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

4.11.2.2.2   Calculation.

The corresponding concentration, c_1, in moles per litre, of the ferroammoniumdisulfate solution (4.11.1) is given by the equation:

$$c_1 = \frac{1,00 \times 20,00}{54,94 \times V_2}$$

where

V_2 is the mean volume, in millilitres, of the ferroammoniumdisulfate solution (4.11.1) required to titrate the manganese solution;

54,94   is the molar mass, in grams per mole, of manganese.

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2) A stage where no bubble is observed on the surface of the solution.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 or ISO 1042, as appropriate. Ordinary laboratory apparatus shall be used, and also a potentometric titration device, consisting of

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

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

NOTE   A redox electrode can also be used.

6 Sampling and samples

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

7 Procedure

7.1 Test portion

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

Table 1 — Test portion

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

7.2 Determination

7.2.1 Preparation of the test solution

Transfer the test portion (7.1) to a 300 ml conical flask. Add 15 ml of phosphoric acid (4.3) [first add 15 ml of *aqua regia*, hydrochloric acid (4.5) + nitric acid (4.4) = 3 + 1, for some high-alloy steels] and heat gently until effervescence ceases. Decompose the carbides by the addition of nitric acid (4.4) drop by drop.

Continue heating until the surface of the solution calms down[2)] and white fumes are just given off (controlling the temperature from 200 °C to 240 °C). Remove the flask from the heater, add 2 g of ammonium nitrate (4.1) immediately and shake the conical flask to remove nitrogen oxide. Nitrogen oxide must be eliminated thoroughly by blowing with a pipette or by adding 0,5 g to 1,0 g of urea (4.2). Wait for 1 min to 2 min. Cool the solution to 80 °C to 100 °C.

7.2.2 Titration

7.2.2.1 Visual titration

Add 60 ml of sulfuric acid (4.7) to the test solution (7.2.1) and mix. Make up the volume to approximately 150 ml and cool to room temperature.

Titrate the solution with the ferroammoniumdisulfate solution (4.11) until the end point is approached. Add 2 drops of N-phenylanthranilic acid (4.8). Continue the titration until the purplish red colour of the solution just disappears. Record the volume, V_3, of the ferroammoniumdisulfate solution (4.11) added.

7.2.2.2 Potentiometric titration

Transfer the test solution (7.2.1) to a 400 ml beaker. Add 60 ml of sulfuric acid (4.7) and mix. Make up the volume to approximately 150 ml and cool to ambient temperature.

Place the beaker containing the solution on the magnetic stirrer and start it.

Immerse the indicator and reference electrodes [5 a) and 5 b)] or a redox electrode in the solution. Titrate slowly with the ferroammoniumdisulfate solution (4.11) until the end point is approached. Continue the titration in 0,05 ml or one drop increments, and record the volume added 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 first derivative of the potential difference divided by the first derivative of the volume of titrant (dE/dV). Record the end-point volume, V_4, of the ferroammoniumdisulfate solution (4.11).

7.2.3 Theoretical correction of vanadium and cerium

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

Manganese, percent = vanadium, percent × 1,08; manganese, percent = cerium, percent × 0,4.

The mass fraction of vanadium may also be determined by the procedures specified in ISO 4942, ISO 4947 or ISO 9647 and the corresponding mass fraction shall be subtracted from the raw mass fraction of manganese.

8 Expression of results

8.1 Method of calculation

8.1.1 Visual titration

The mass fraction of manganese in the sample, w_{Mn}, expressed as a percentage, is given by the equation:

$$w_{Mn} = \frac{c \times (V_3 - V_0) \times 54,94}{m_0 \times 1\,000} \times 100 - 1,08 \times w_V - 0,4 \times w_{Ce}$$

where

c is the concentration, in moles per litre, of the ferroammoniumdisulfate solution (4.11);

V_0 is the volume, in millilitres, of the ferroammoniumdisulfate solution (4.11) for correction of N-phenylanthranilic acid;

V_3 is the volume, in millilitres, of the ferroammoniumdisulfate solution (4.11) required to titrate manganese, vanadium and cerium;

m_0 is the mass, in grams, of the test portion;

54,94   is the molar mass, in grams per mole, of manganese;

w_V is the mass fraction of vanadium in the sample, expressed as a percentage;

w_{Ce} is the mass fraction of cerium in the sample, expressed as a percentage.

8.1.2   Potentiometric titration

The mass fraction of manganese in the sample, w_{Mn}, expressed as a percentage, is given by the equation:

$$w_{Mn} = \frac{c_1 \times V_4 \times 54,94}{m_0 \times 1\,000} \times 100 - 1,08 \times w_V - 0,4 \times w_{Ce}$$

where

c_1 is the concentration, in moles per litre, of the ferroammoniumdisulfate solution (4.11);

V_4 is the volume, in millilitres, of the ferroammoniumdisulfate solution (4.11) required to titrate manganese, vanadium and cerium;

m_0 is the mass, in grams, of the test portion;

54,94   is the molar mass, in grams per mole, of manganese;

w_V is the mass fraction of vanadium in the sample, expressed as a percentage;

w_{Ce} is the mass fraction of cerium in the sample, expressed as a percentage.

8.2   Precision

A planned trial of this method was carried out by 10 laboratories, at 7 levels of manganese; each laboratory making three determinations of mass fraction of manganese at each level.

NOTE 1   Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

NOTE 2   The third determination was carried out at a different time (on a different day) by the same operator as in Note 1, using the same apparatus with a new calibration.

The test samples used are listed in Table A.1. The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between the mass fraction of manganese and repeatability (r) and reproducibility (R and R_w) of the test results (see Note 3) as summarized in Table 2. The graphical representation of the data is shown in Annex B.

NOTE 3   From the two values obtained on day 1 and the value obtained on day 2, the repeatability limit (r) and reproducibility limit (R and R_w) were calculated using the procedure specified in ISO 5725-3.

Table 2 — Results for repeatability limit and reproducibility limits

Mass fraction of manganese %	Repeatability limit r	Reproducibility limits	
		R_w	R
2,00	0,023 2	0,035 6	0,067 8
5,00	0,041 3	0,061 3	0,131 2
10,00	0,063 7	0,092 6	0,216 4
12,00	0,071 4	0,103 3	0,246 8
15,00	0,082 2	0,117 9	0,289 9
20,00	0,098 4	0,139 9	0,356 7
22,00	0,104 5	0,148 1	0,382 1
25,00	0,113 2	0,159 8	0,419 0

9 Test report

The test report shall include the following information:

a) the method used by reference to this International Standard;

b) all information necessary of the identification of the sample, the laboratory and the data of analysis;

c) the results and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A
(informative)

Additional information on the international cooperative test

The test samples used are listed in Table A.1. Detailed results for the mass fraction of manganese obtained in international cooperative tests are shown in Table A.2.

Table A.2 was derived from the results of international analytical trials carried out in 2006 on steel samples in 5 countries involving 10 laboratories.

The results of the trials were reported. The precision data are presented in graphical form in Annex B.

Table A.1 — Test samples used

Sample No.	No. of certified reference material (CRM)	Chemical composition % (mass fraction)									
		C	Si	Mn	P	S	Cr	Ni	Mo	V	Cu
1	GBW 01301	0,9	0,06	2,09	0,05	0,03	0,1	0,08			0,2
2	GBW 01657	0,07	0,5	4,76	0,03	0,01	11,5	4,5	3,1	0,02	0,1
3	YSBC 11301-93	0,06	0,9	10,03	0,02	0,003	18	5,7			
4	YSBC 11315-94	1,2	0,6	12,61	0,08	0,007	0,2	0,1			
5	BH1004-1	0,06	0,6	17,22	0,09	0,008	9,3				
6	BH 0227	0,2	0,2	22,44	0,02	0,001	0,02	0,003			Al 2,2