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

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

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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):

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

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):

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

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 potentiometric 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.

Vanadium can be determined by the procedures specified in ISO 4942, ISO 4947 or ISO 9647, or by any other appropriate wet chemistry method. The corresponding content shall be subtracted from the raw mass fraction of manganese.

9 Expression of results

9.1 Method of calculation

9.1.1 Visual titration

The mass fraction of manganese in the sample, w_{Mn}, expressed in per cent, is given by Formula (3):

$$w_{Mn} = \frac{c \times (V_3 - V_0) \times 54{,}94}{m_0 \times 1\,000} \times 100 - 1{,}08 \times w_V - 0{,}39 \times w_{Ce} \quad (3)$$

where

c is the concentration, expressed in moles per litre, of the ferroammoniumdisulfate solution (5.11);

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

V_3 is the volume, expressed in millilitres, of the ferroammoniumdisulfate solution (5.11) used to titrate manganese, vanadium and cerium;

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

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

w_V is the mass fraction of vanadium in the sample, expressed in per cent;

w_{Ce} is the mass fraction of cerium in the sample, expressed in per cent.

9.1.2 Potentiometric titration

The mass fraction of manganese in the sample, w_{Mn}, expressed in per cent, is given by Formula (4):

$$w_{Mn} = \frac{c_1 \times V_4 \times 54{,}94}{m_0 \times 1\,000} \times 100 - 1{,}08 \times w_V - 0{,}39 \times w_{Ce} \quad (4)$$

where

c_1 is the concentration, expressed in moles per litre, of the ferroammoniumdisulfate solution (5.11);

V_4 is the volume, expressed in millilitres, of the ferroammoniumdisulfate solution (5.11) used to titrate manganese, vanadium and cerium;

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

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

w_V is the mass fraction of vanadium in the sample, expressed in per cent;

w_{Ce} is the mass fraction of cerium in the sample, expressed in per cent.

9.2 Precision

A planned trial of this method was carried out by ten laboratories, at seven levels of manganese, each laboratory making three determinations of manganese content 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.

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

The data obtained showed a logarithmic relationship between manganese content 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 one and the value obtained on day two, the repeatability limit (r) and reproducibility limits (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	Reproducibility limits	
%	r	R_w	R
2	0,023 2	0,035 6	0,067 8
5	0,041 2	0,061 5	0,131 2
10	0,063 6	0,092 8	0,216 3
12	0,071 3	0,103 4	0,246 7
15	0,082 0	0,118 1	0,289 8
20	0,098 3	0,140 2	0,356 6
22	0,104 3	0,148 3	0,382 0
25	0,113 0	0,160 0	0,418 9

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or the date of the test report;

b) the method used by reference to this document;

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

d) any unusual features noted during the determination;

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

Annex A
(informative)

Additional information on the international interlaboratory test

The test samples used are listed in Table A.1. Detailed results for manganese content obtained from the international interlaboratory test are shown in Table A.2.

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

The precision data are presented in graphical form in Annex B.

Table A.1 — Test samples used

Sample No.	ID No. of 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[a]	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

[a] Need to be corrected.

Table A.2 — Detailed results obtained in the international cooperative test

No.	Sample	Mass fraction of manganese %		Precision data %		
		Certified	Found	Repeatability limit	Reproducibility limits	
			$\overline{w}_{Mn}$	r	R_w	R
1	GBW 01301	2,09	2,089	0,020	0,035	0,072
2	GBW 01657	4,76	4,752	0,056	0,063	0,113
3	YSBC 11301-93	10,03	10,080	0,055	0,083	0,251
4	YSBC 11315-94	12,61	12,658	0,060	0,119	0,263

$\overline{w}_{Mn}$ General mean.

[a] When the international cooperative test started, the scope of the working draft concerned the determination for manganese mass fractions between 2 % and 30 %. Since there was no certified reference material (CRM) available for the level of 30 % manganese (mass fraction), CRM BH0227 was used as two samples: one for its normal level of manganese, 22,44 % (mass fraction) and the other for the 30 % level of manganese (mass fraction) by weighing 0,13 g, which is more than the normal, but being calculated as 0,1 g. On this base, the "reference value" was calculated by multiplying its manganese certified value by the factor 1,3.

According to an ISO TC 17/SC 1 Resolution on October 18–20, 2006, the scope was changed to the mass fraction range of 2 % to 25 %, and the results obtained for sample No. 7 were removed from the statistical calculation of precision data.

Table A.2 *(continued)*

No.	Sample	Mass fraction of manganese %		Precision data %		
		Certified	Found	Repeatability limit	Reproducibility limits	
			$\overline{w}_{Mn}$	r	R_w	R
5	BH1004-1	17,22	17,228	0,131	0,164	0,284
6	BH 0227	22,44	22,363	0,087	0,117	0,399
7	— [a]	29,17[a]	29,092	0,124	0,146	0,506

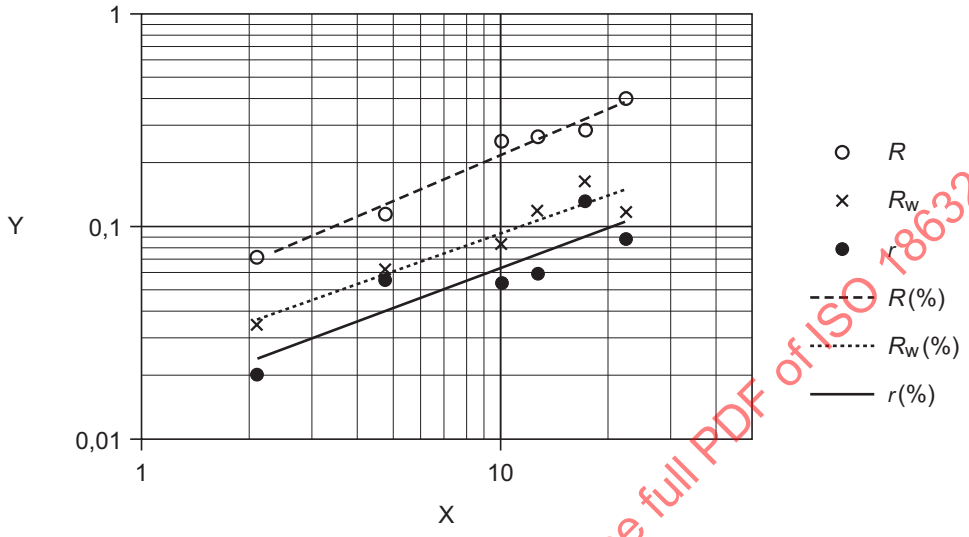
$\overline{w}_{Mn}$ General mean.

[a] When the international cooperative test started, the scope of the working draft concerned the determination for manganese mass fractions between 2 % and 30 %. Since there was no certified reference material (CRM) available for the level of 30 % manganese (mass fraction), CRM BH0227 was used as two samples: one for its normal level of manganese, 22,44 % (mass fraction) and the other for the 30 % level of manganese (mass fraction) by weighing 0,13 g, which is more than the normal, but being calculated as 0,1 g. On this base, the "reference value" was calculated by multiplying its manganese certified value by the factor 1,3.

According to an ISO TC 17/SC 1 Resolution on October 18–20, 2006, the scope was changed to the mass fraction range of 2 % to 25 %, and the results obtained for sample No. 7 were removed from the statistical calculation of precision data.

Annex B
(informative)

Graphical representation of precision data



Key

X mass fraction of manganese, %

Y precision, mass fraction, %

$$\lg r = 0{,}627\,4\ \lg \overline{W}_{Mn} - 1{,}823\,9$$

$$\lg R_w = 0{,}594\,7\ \lg \overline{W}_{Mn} - 1{,}627\,1$$

$$\lg R = 0{,}721\,3 \lg \overline{W}_{Mn} - 1{,}386\,2$$

where $\overline{W}_{Mn}$ is the average mass fraction of manganese obtained from three determinations in each laboratory.

Figure B.1 — Logarithmic relationship between mass fraction of manganese ($\overline{W}_{Mn}$), repeatability limit, r, and reproducibility limits, R_w and R