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Steel and iron — Determination of manganese content — Flame atomic absorption spectrometric method

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*Aciers et fontes — Dosage du manganèse — Méthode par spectrométrie
d'absorption atomique dans la flamme*

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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.

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.

International Standard ISO 10700 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

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Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

Steel and iron — Determination of manganese content — Flame atomic absorption spectrometric method

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the manganese content in steel and iron.

The method is applicable to manganese contents between 0,002 % (*m/m*) and 2,0 % (*m/m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition*.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*.

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids followed by evaporation with perchloric acid until white fumes appear.

Spraying of the solution into an air-acetylene flame.

Spectrometric measurement of the atomic absorption of the 279,5 nm spectral line emitted by a manganese hollow cathode lamp.

4 Reagents

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

4.1 Pure iron, free from manganese or with a known low manganese content.

4.2 Hydrochloric acid, ρ about 1,19 g/ml.

4.3 Hydrofluoric acid, ρ about 1,15 g/ml.

4.4 Nitric acid, ρ about 1,40 g/ml.

4.5 Perchloric acid, ρ about 1,54 g/ml (see note 1).

NOTE 1 Perchloric acid (ρ about 1,67 g/ml) may also be used. 100 ml of perchloric acid (ρ about 1,54 g/ml) is equivalent to 79 ml of perchloric acid (ρ about 1,67 g/ml).

4.6 Background solution.

WARNING — See clause 7.

Weigh, to the nearest 0,01 g, 10,00 g of the pure iron (4.1). Place in a 1 litre beaker. Add 200 ml of hydrochloric acid (4.2), cover the beaker with a watch glass and heat gently until the iron is dissolved. Then oxidize by adding 50 ml of nitric acid (4.4) in small portions. Add 150 ml of perchloric acid (4.5). Heat strongly and evaporate until dense white fumes of perchloric acid appear. Continue fuming for 15 min at a temperature that maintains a steady reflux of white perchloric acid fumes on the walls of the beaker. Allow to cool, add 300 ml of water and heat gently to dissolve the salts.

Transfer quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this background solution contains 0,010 g of Fe.

4.7 Manganese, standard solution

4.7.1 Manganese stock solution, corresponding to 1,00 g of Mn per litre.

Weigh, to the nearest 0,1 mg, 1,00 g of pure manganese metal [purity $\geq 99,9\%$ (*m/m*)]. Place in a 250 ml beaker and add 40 ml of hydrochloric acid (4.2). Cover with a watch glass and heat gently until the manganese has dissolved. Cool, 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.

4.7.2 Manganese standard solution, corresponding to 0,02 g of Mn per litre.

Transfer 20,0 ml of the stock solution (4.7.1) to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 0,02 mg of Mn.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory apparatus, and

5.1 Atomic absorption spectrometer, equipped with a manganese hollow cathode lamp and supplied with air and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from manganese.

The atomic absorption spectrometer used will be satisfactory if, after optimization according to 7.3.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the precision criteria given in 5.1.1 to 5.1.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 5.1.4.

5.1.1 Minimum precision (see A.1)

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,5 % of the mean absorbance of this solution.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

5.1.2 Limit of detection (see A.2)

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element at a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of manganese in a matrix similar to the final test portion solution shall be less than 0,02 μg of Mn per millilitre.

5.1.3 Graph linearity (see A.3)

The value of the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.1.4 Characteristic concentration (see A.4)

The characteristic concentration of manganese in a matrix similar to the final test portion solution shall be better than 0,1 µg of Mn per millilitre.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.1.1 to 5.1.3 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring the absorbances of a suitable solution with and without scale expansion and using the ratio of the signals obtained.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general. All evaporations must be carried out in fume cupboards suitable for use with perchloric acid.

Ensure that the spray system and drainage system are washed free from perchloric acid after use.

7.1 Test portion

Weigh, to the nearest 1 mg, approximately 1,0 g of the test sample.

7.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents, including the pure iron (4.1).

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add 20 ml of hydrochloric acid (4.2), cover the beaker with

a watch glass and heat gently until solvent action ceases. Add 5 ml of nitric acid (4.4), and boil for 1 min to remove oxides of nitrogen. Add 15 ml of perchloric acid (4.5), and heat strongly without a cover until fuming commences. Cover with a watch glass and continue heating at a temperature at which a steady reflux of white perchloric acid fumes is maintained on the walls of the beaker. Continue heating until there are no perchloric acid fumes visible inside the beaker.

For samples not readily soluble in hydrochloric acid and nitric acid, add 2 ml of hydrofluoric acid (4.3) before the addition of 15 ml of perchloric acid and continue as described above.

7.3.2 Treatment of the solution

7.3.2.1 Manganese contents up to 0,10 % (m/m)

Allow to cool, add 25 ml of water and heat gently to dissolve the salts. Cool again and transfer quantitatively to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Filter by decantation through a dry, medium-texture filter paper to remove any residue or precipitate, and collect the filtrate in a dry beaker after discarding the first portions.

The filtrate is the test solution for determining manganese contents up to 0,10 % (m/m).

7.3.2.2 Manganese contents between 0,10 % (m/m) and 0,40 % (m/m)

Transfer 50,0 ml of the filtrate (7.3.2.1) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

7.3.2.3 Manganese contents between 0,40 % (m/m) and 2,0 % (m/m)

Transfer 10,0 ml of the filtrate (7.3.2.1) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

7.3.3 Preparation of the calibration solutions

7.3.3.1 Manganese contents up to 0,10 % (m/m)

Introduce 40,0 ml of the background solution (4.6) into a series of eight 100 ml one-mark volumetric flasks. Using a burette or pipette, add the volumes of manganese standard solution (4.7.2) indicated in table 1. Dilute to the mark with water and mix.

Table 1

Volume of manganese standard solution (4.7.2) ml	Mass of manganese mg	Corresponding content of manganese in test sample % (m/m)
0 ¹⁾	0	0
0,4	0,008	0,002
2,0	0,04	0,010
4,0	0,08	0,020
8,0	0,16	0,040
12,0	0,24	0,060
16,0	0,32	0,080
20,0	0,40	0,100
1) Zero member.		

7.3.3.2 Manganese contents between 0,10 % (m/m) and 0,40 % (m/m)

Introduce 10,0 ml of the background solution (4.6) into a series of six 100 ml one-mark volumetric flasks. Using a burette or pipette, add the volumes of manganese standard solution (4.7.2) indicated in table 2. Dilute to the mark with water and mix.

Table 2

Volume of manganese standard solution (4.7.2) ml	Mass of manganese mg	Corresponding content of manganese in test sample % (m/m)
0 ¹⁾	0	0
4,0	0,08	0,08
8,0	0,16	0,16
12,0	0,24	0,24
16,0	0,32	0,32
20,0	0,40	0,40
1) Zero member.		

7.3.3.3 Manganese contents between 0,40 % (m/m) and 2,0 % (m/m)

Introduce 2,0 ml of the background solution (4.6) into a series of six 100 ml one-mark volumetric flasks. Using a burette or pipette, add the volumes of manganese standard solution (4.7.2) indicated in table 3. Dilute to the mark with water and mix.

Table 3

Volume of manganese standard solution (4.7.2) ml	Mass of manganese mg	Corresponding content of manganese in test sample % (m/m)
0 ¹⁾	0	0
4,0	0,08	0,40
8,0	0,16	0,80
12,0	0,24	1,20
16,0	0,32	1,60
20,0	0,40	2,00
1) Zero member.		

7.3.4 Adjustment of atomic absorption spectrometer

See table 4.

Table 4

Element	Characteristic
Type of lamp	Manganese hollow cathode
Wavelength	279,5 nm
Flame	Air-acetylene fuel-lean flame adjusted for maximum manganese response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations
WARNING — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:	
a) the explosive nature of acetylene, and regulations concerning its use;	
b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;	
c) the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;	
d) the need to ensure that the liquid trap is filled with water;	
e) the need always to spray water between the test solutions, blank solution and/or calibration solutions.	

7.3.5 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized.

Set the absorbance value at zero using water.

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria given in 5.1.1 to 5.1.3.

Adjust the flame to be fuel-lean and the burner height to about 10 mm below the light path. Spraying, alternately, the calibration solution of the highest concentration and the zero member (see tables 1 to 3), adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum.

Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 5.1.1 to 5.1.3 and the additional performance requirement of 5.1.4, to ensure that the instrument is suitable for the determination of manganese.

7.3.6 Spectrometric measurements

Set the scale expansion so that the calibration solution of the highest concentration gives nearly full scale deflection. Spray the calibration solutions in ascending order repeatedly until each gives the specified precision, thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Spray these first in ascending order, then in descending order, with the test solution as the middle solution, in each case measuring the absorption in relation to water. Spray the complete range of calibration solutions, including the zero member, again in ascending and descending order. The means of the last ascending and descending series of calibration solutions are used for the calibration graph.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two "sandwiching" solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the mean absorbance of each calibration solution.

Obtain the mean absorbance of the test solution and the mean absorbance of the blank test solution.

7.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations, and for the range of manganese contents expected.

Usually the zero member has a negligibly small absorbance, but if the zero member has a significant absorbance, a more complicated procedure is required. In this case, the concentration of manganese $\rho_{Mn,z}$ in the zero member can be calculated using the formula

$$\rho_{Mn,z} = \rho_{Mn,c1} \times \frac{A_z}{A_{Mn,c1} - A_z}$$

where

$\rho_{Mn,c1}$ is the concentration of manganese, expressed in micrograms per millilitre, added to the first calibration solution;

A_z is the absorbance of the zero member;

$A_{Mn,c1}$ is the absorbance of the first calibration solution.

The derived value $\rho_{Mn,z}$ is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin.

Refer the absorbances of the two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria, then the test solution readings are also acceptable.

8 Expression of results

8.1 Method of calculation

Convert the absorbances of the test solution and the blank solution to micrograms of manganese per millilitre by means of the calibration graph (7.4).

The manganese content w_{Mn} , expressed as a percentage by mass, is given by the equation

$$w_{\text{Mn}} = \frac{(\rho_{\text{Mn},1} - \rho_{\text{Mn},0}) \times 250}{10^6} \times \frac{100}{m} \times D$$

$$= \frac{(\rho_{\text{Mn},1} - \rho_{\text{Mn},0}) \times 25D}{10^3 m}$$

where

$\rho_{\text{Mn},0}$ is the concentration, expressed in micrograms per millilitre, of manganese in the blank test (7.2);

$\rho_{\text{Mn},1}$ is the concentration, expressed in micrograms per millilitre, of manganese in the test solution derived from the calibration graph (7.4);

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

D is the dilution factor:

$D = 1$ for manganese contents up to 0,10 % (m/m),

$D = 4$ for manganese contents between 0,10 % (m/m) and 0,40 % (m/m),

$D = 20$ for manganese contents between 0,40 % (m/m) and 2,0 % (m/m).

8.2 Precision

A planned trial of this method was carried out by 20 laboratories using 10 levels of manganese contents, each laboratory making three determinations (see notes 2 and 3) of manganese at each level.

The test samples used are listed in table B.1.

The results obtained were treated statistically in accordance with ISO 5725.

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 4), as summarized in table 5. The graphical representation of the data is shown in figure C.1.

Table 5

Manganese content % (m/m)	Repeatability r	Reproducibility	
		R	R_w
0,002	0,000 29	0,000 62	0,000 30
0,005	0,000 52	0,001 2	0,000 59
0,010	0,000 81	0,001 8	0,000 99
0,020	0,001 3	0,002 9	0,001 7
0,050	0,002 3	0,005 3	0,003 3
0,100	0,003 6	0,008 4	0,005 5
0,20	0,005 6	0,013	0,009 2
0,50	0,010	0,024	0,018
1,00	0,016	0,038	0,030
2,00	0,024	0,061	0,051

NOTES

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

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

4 From the results obtained on day 1, the repeatability (r) and reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

9 Test report

The test report shall include the following information:

- all information necessary for the identification of the sample, the laboratory and the date of analysis;
- the method used by reference to this International Standard;
- the results, and the form in which they are expressed;
- any unusual features noted during the determination;
- any operation not specified in this International Standard or any optional operation which may have influenced the results.

Annex A (normative)

Procedures for the determination of instrumental criteria

For the preparation of standard methods of analysis using flame atomic absorption spectrometry, the values for the instrumental criteria should be decided from interlaboratory test results, by the working group in charge.

A.1 Determination of minimum precision

Spray the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings A_{Ai} and calculate the mean value $\bar{A}_A$.

Spray the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings A_{Bi} and calculate the mean value $\bar{A}_B$.

The standard deviations s_A and s_B of the most and least concentrated calibration solutions respectively are obtained from the equations

$$s_A = \sqrt{\frac{\sum (A_{Ai} - \bar{A}_A)^2}{9}}$$

$$s_B = \sqrt{\frac{\sum (A_{Bi} - \bar{A}_B)^2}{9}}$$

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_A \times 100/\bar{A}_A$ and $s_B \times 100/\bar{A}_B$, respectively.

A.2 Determination of limit of detection,

$\rho_{Mn,min}$

Prepare two solutions each containing the same matrix concentration as the sample solution, but with the

element of interest at the following known concentrations;

- ρ'_{Mn} µg/ml to give an absorbance A' of approximately 0,01;
- matrix blank to give an absorbance A_0 .

Spray the ρ'_{Mn} solution and blank solution 10 times each, recording each reading for about 10 s, and using sufficient scale expansion to make the fluctuations in signal clearly visible.

Obtain the mean absorbance readings $\bar{A}'$ and $\bar{A}_0$.

The standard deviation $s_{A'}$ is given by the equation

$$s_{A'} = \sqrt{\frac{\sum (A'_i - \bar{A}')^2}{9}}$$

where

A'_i is the individual measured absorbance reading;

$\bar{A}'$ is the mean value of A'_i .

The limit of detection $\rho_{Mn,min}$ is given by the equation

$$\rho_{Mn,min} = \frac{\rho'_{Mn} \times s_{A'} \times k}{\bar{A}' - \bar{A}_0}$$

(k is normally taken as 2)

A.3 Criterion for graph linearity

Having established the calibration graph (see figure A.1), before the application of any curve-straightening device, obtain the net absorbance value A_A corresponding to the top 20 % of the concentration range and the net absorbance A_B corresponding to the bottom 20 % of the concentration range. Calculate A_A/A_B . This must not be less than 0,7.