INTERNATIONAL
STANDARD

ISO
10278

Steel — Determination of manganese content — Inductively coupled plasma atomic emission spectrometric method

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Acier — Dosage du manganèse — Méthode par spectrométrie d'émission atomique de plasma avec couplage inductif

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 10278 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

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

Steel — Determination of manganese content — Inductively coupled plasma atomic emission spectrometric method

1 Scope

This International Standard specifies an inductively coupled plasma atomic emission spectrometric method for the determination of the manganese content in unalloyed steels.

The method is applicable to manganese contents between 0,002 % (m/m) and 1,5 % (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 a mixture of hydrochloric and nitric acids and dilution of the solution to a known volume. If necessary, addition of scandium or yttrium as an internal standard. Nebulization of the solution into an inductively coupled plasma atomic emission spectrometer and measurement of the intensity of the emitted light from manganese at 257,61 nm and, optionally, emitted light from scandium at 361,38 nm or yttrium at 371,03 nm, simultaneously.

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, containing less than 0,000 1 % (m/m) of manganese.

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

4.3 Nitric acid, ρ about 1,40 g/ml, diluted 1 + 1.

4.4 Manganese standard solution.

4.4.1 Manganese standard solution A, corresponding to 0,5 g of Mn per litre.

Weigh, to the nearest 0,1 mg, 0,500 g of manganese metal [purity > 99,9 % (m/m)] (see note 1) and transfer to a 200 ml beaker. Add 30 ml of hydrochloric acid

(4.2), cover with a watch glass and heat gently to dissolve the manganese. Cool to ambient temperature, 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 0,5 mg of Mn.

NOTE 1   High purity manganese metal may contain high levels of oxygen. The oxygen content of the manganese should therefore be checked before it is used.

4.4.2 Manganese standard solution B, corresponding to 0,05 g of Mn per litre.

Transfer 20,0 ml of the manganese standard solution A (4.4.1) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,05 mg of Mn.

4.5   Scandium internal standard solution, corresponding to 1 g of Sc per litre.

Weigh, to the nearest 1 mg, 1,534 g of scandium oxide [Sc_2O_3, purity > 99,98 % (*m/m*)]. Transfer to a 500 ml beaker and dissolve in 40 ml of nitric acid (4.3). Transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this internal standard solution contains 1 mg of Sc.

4.6   Yttrium internal standard solution, corresponding to 1 g of Y per litre.

Weigh, to the nearest 1 mg, 1,270 g of yttrium oxide [Y_2O_3, purity > 99,98 % (*m/m*)]. Transfer to a 500 ml beaker and dissolve in 50 ml of hydrochloric acid (4.2). Transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this internal standard solution contains 1 mg of Y.

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 emission spectrometer, equipped with an inductively coupled plasma (ICP-AES).

The ICP-AES used will be satisfactory if, after opti-

mization according to 7.4.1, it meets the performance criteria given in 5.1.1 to 5.1.5.

The spectrometer can be either a simultaneous or sequential type. If a sequential spectrometer is equipped with an extra arrangement for simultaneous measurement of the internal standard line (scandium or yttrium), it can be used with the internal standard technique. If the sequential spectrometer is not equipped with this arrangement, an internal standard cannot be used and the alternative technique without an internal standard can be applied.

5.1.1   Practical resolution of the spectrometer (see A.1)

Calculate the bandwidth for Mn 257,61 nm, for Sc 361,38 nm and for Y 371,03 nm. The bandwidth shall be less than 0,040 nm for each line.

5.1.2   Short-term stability

Calculate the standard deviation of ten measurements of the absolute intensity or intensity ratio of the emitted light of the most concentrated calibration solution for manganese. The relative standard deviation shall not exceed 0,9 %.

5.1.3   Long-term stability

Calculate the standard deviation of seven mean values of three measurements of the absolute intensity or intensity ratio of the emitted light of the most concentrated calibration solution for manganese. Each mean value shall be determined every 0,5 h during a total time of 3 h. The relative standard deviation shall not exceed 1,8 % for the absolute intensity technique or 1,2 % for the internal standard technique.

5.1.4   Background equivalent concentration and detection limit (see A.2)

Calculate the background equivalent concentration (BEC) and detection limit (DL) for the analytical line in a solution containing only the analyte element. The value shall be below the values indicated in table 1.

Table 1 — BEC and DL values

Analytical line	Background equivalent concentration	Detection limit
nm	mg/l	mg/l
Mn 257,61	0,6	0,02
Sc 361,38	—	—
Y 371,03	—	—

5.1.5 Graph linearity

The linearity of the calibration graph is checked by calculating the correlation coefficient. This coefficient shall be more than 0,999.

6 Sampling

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

7 Procedure

7.1 Test portion

Weigh, to the nearest 1 mg, approximately 1,00 g of the test sample.

7.2 Blank test (corresponding to the zero member)

In parallel with the determination of the content 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 200 ml beaker. Add 10 ml of nitric acid (4.3), cover the beaker with a watch glass and heat gently until the effervescence ceases. Add 10 ml of hydrochloric acid (4.2) and continue heating until complete dissolution has taken place.

Cool to ambient temperature and transfer the solution quantitatively to a 200 ml one-mark volumetric flask. If the internal standard technique is used, using a pipette, add 2 ml of the scandium internal standard solution (4.5) or 10 ml of the yttrium internal standard solution (4.6). Dilute to the mark with water and mix.

7.3.2 Preparation of the calibration solutions

Introduce 1,00 g ± 0,01 g of the pure iron (4.1) into a series of six 200 ml beakers. Add 10 ml of nitric acid (4.3) to each beaker, cover with a watch glass and heat gently until the effervescence ceases. Add 10 ml of hydrochloric acid (4.2) and continue heating until complete dissolution has taken place.

Cool to ambient temperature and transfer the solutions into six 200 ml one-mark volumetric flasks, rinsing the beakers with a minimum quantity of water.

Using a pipette or burette, add to the volumetric flasks the volume of manganese standard solution A (4.4.1) indicated in table 2. If the calibration graph is found to be non-linear, additional calibration series may be used (for example, see tables 3 and 4). If the internal standard technique is used, using a pipette, add 2 ml of the scandium internal standard solution (4.5) or 10 ml of the yttrium internal standard solution (4.6). Dilute to the mark with water and mix.

Table 2 — Manganese contents between 0,002 % (*m/m*) and 1,50 % (*m/m*)

Volume of manganese standard solution A (4.4.1) ml	Concentration of manganese µg/ml	Corresponding manganese content in test portion % (*m/m*)
0 [1]	0	0
5,0	12,5	0,25
10,0	25,0	0,50
15,0	37,5	0,75
20,0	50,0	1,00
30,0	75,0	1,50
[1] Zero member		

Table 3 — Example for manganese contents up to 0,025 % (*m/m*)

Volume of manganese standard solution B (4.4.2) ml	Concentration of manganese µg/ml	Corresponding manganese content in test portion % (*m/m*)
0 [1]	0	0
0,5	0,125	0,002 5
1,0	0,250	0,005 0
2,0	0,500	0,010 0
3,0	0,750	0,015 0
5,0	1,25	0,025 0
[1] Zero member		

Table 4 — Example for manganese contents between 0,025 % (m/m) and 0,25 % (m/m)

Volume of manganese standard solution B (4.4.2) ml	Concentration of manganese µg/ml	Corresponding manganese content in test portion % (m/m)
0 [1]	0	0
5,0	1,25	0,025
10,0	2,50	0,050
20,0	5,00	0,100
30,0	7,50	0,150
50,0	12,5	0,250
1) Zero member		

7.4 Spectrometric measurements

7.4.1 Optimization of the instrument

Start the ICP-AES and let it run for at least 1 h before making any measurements.

Adjust all instrumental parameters, each gas (outer, intermediate or central) flow rate, torch position, entrance slits, exit slits, photomultiplier tube voltage, wavelength of the analytical line for manganese (257,61 nm), Sc (361,38 nm) or Y (371,03 nm), prespraying time and integrating time according to the instrument manufacturer's recommended operating practices and guidelines to give optimum intensity for manganese when measuring the highest concentration of calibration solution.

Prepare the software to measure the intensity, mean value and relative standard deviation of the manganese line.

If an internal standard is used, prepare the software to use the Sc line (361,38 nm) or the Y line (371,03 nm) as an internal standard and to calculate the ratio between the manganese intensity and scandium or yttrium intensity. The intensity of the internal standard shall be measured simultaneously with the analyte intensity.

Check the instrument performance requirements given in 5.1.1 to 5.1.5.

7.4.2 Measurements of the emitted intensities

Ensure that all solutions to be measured are within 1 °C of the same temperature if the absolute intensities are measured. Filter all solutions through a medium-texture filter paper. Discard the first 2 ml to 3 ml.

Measure the absolute intensity or intensity ratio of the analytical line beginning with the lowest calibration solution (zero member corresponding to the blank test).

Continue with two or three unknown test solutions, then the next lowest calibration solution, two or more unknown solutions, etc. In this way, all unknown test solutions are measured within the same time period as the calibration solutions, excluding any possible drift between calibration and unknown test solutions. For each solution, make five integrations and check that the short-term stability is the same as that specified in 5.1.2, then calculate the mean intensity or the mean intensity ratio for each solution.

Subtract the mean absolute intensity or the mean intensity ratio (I_0) of the zero member from the mean absolute intensity or the mean intensity ratio (I_i) of each solution giving the net absolute intensity or the net intensity ratio (I_N), as follows:

$$I_N = I_i - I_0$$

7.4.3 Preparation of the calibration graph

Use an electronic calculator to make a linear regression through the points with the net intensities or net intensity ratios on the y-axis and the concentration, expressed in micrograms per millilitre, of manganese in the calibration solution on the x-axis.

Calculate the correlation coefficient. This shall meet the specification given in 5.1.5.

8 Expression of results

8.1 Method of calculation

Using the electronic calculator, convert the net absolute intensity or net intensity ratio into the corresponding concentration, expressed in micrograms per millilitre, of manganese in the test solution, by using the calibration graph (see 7.4.3).

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

$$w_{Mn} = \frac{\rho_{Mn} \times 200}{10^6} \times \frac{100}{m} + w_{Mn,0} = \frac{\rho_{Mn}}{50m} + w_{Mn,0}$$

where

ρ_{Mn} is the concentration, expressed in micrograms per millilitre, of manganese in the test solution;

$w_{Mn,0}$ is the manganese content, expressed as a percentage by mass, in the pure iron (4.1) (this may be neglected when it does not affect the accuracy);

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

8.2 Precision

A planned trial of this method was carried out by 28 laboratories in 12 countries, using six levels of manganese contents, each laboratory making three determinations of manganese content at each level (see notes 2 and 3).

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

The results obtained were treated statistically in accordance with ISO 5725, using the data obtained from the samples containing six levels of manganese within the application range.

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 — Precision data

Manganese content	Repeatability	Reproducibility	
% (m/m)	r	R	R_w
0,002	0,000 23	0,000 64	0,000 38
0,005	0,000 44	0,001 2	0,000 71
0,010	0,000 73	0,001 9	0,001 1
0,020	0,001 2	0,003 0	0,001 8
0,050	0,002 3	0,005 5	0,003 4
0,100	0,003 8	0,008 8	0,005 4
0,200	0,006 3	0,013 9	0,008 6
0,500	0,012 1	0,025 7	0,016 0
1,00	0,019 9	0,040 8	0,025 6
1,50	0,026 6	0,053 5	0,033 7

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 result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

9 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;

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

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

(normative)

Procedure for the determination of instrumental criteria

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

A.1 Practical resolution of the spectrometer

Resolution is subject to theoretical definition but its practical assessment normally involves a wavelength scan across the spectral line of interest, plotting the profile, measurement of the peak width at half the peak height and calculation of the resolution in nanometers. An example is shown in figure A.1.

A.2 Background equivalent concentration and detection limit

Prepare three solutions each containing the analyte elements of interest at a concentration level of zero, 10 times the detection limit and 1 000 times the detection limit respectively. These solutions should also contain concentrations of acids, fusion agents and matrix elements similar to those in the samples to be analysed.

Spray the solution at 1 000 times the detection limit and wait about 10 s after the solution arrives in the plasma to ensure stable nebulization. Set operating and instrumental conditions for the element in question.

Carefully position on the maximum peak at the selected wavelength and select an appropriate photomultiplier gain (if the selection is not automatic) to ensure that the intensity is measured to four significant digits. Set an integration time of 3 s.

A.2.1 Determination of detection limit

Spray the blank test solution for approximately 10 s. Take 10 readings at the pre-set integration time.

Spray the solution containing 10 times the detection limit for about 10 s. Take 10 readings at the pre-set integration time.

From the intensity readings obtained for the blank and the solution at 10 times the detection limit, calculate the mean intensities $\overline{X}_1$ and $\overline{X}_b$ and the standard deviation of the blank s_b.

Calculate the net mean intensity ($\overline{X}_{n1}$) for the solution at 10 times the detection limit using the following equation:

$$\overline{X}_{n1} = \overline{X}_1 - \overline{X}_b$$

Calculate the detection limit (DL), for the element considered using the following equation:

$$DL = 3s_b \times \frac{\rho_1}{\overline{X}_{n1}}$$

where ρ_1 is the concentration, expressed in micrograms per millilitre, of the solution at 10 times the detection limit.

It should be pointed out that the detection limits calculated in this way have a wide margin of error owing to the limited number of replicate measurements.

A.2.2 Determination of background equivalent concentration

Calculate the background equivalent concentration (BEC) using the following equation:

$$BEC = \frac{\overline{X}_b}{\overline{X}_{n1}} \times \rho_1$$
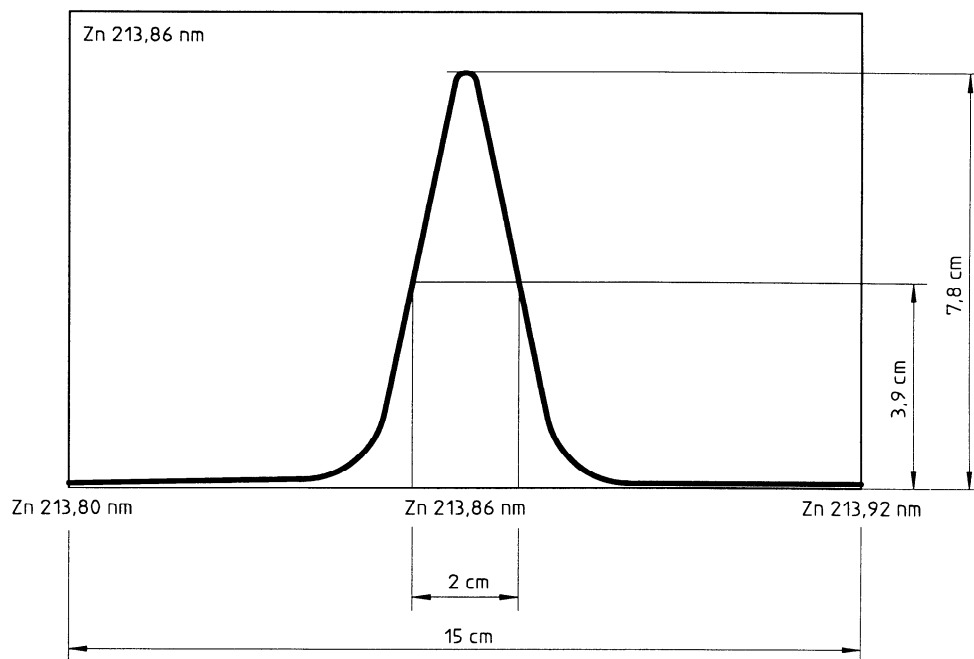
$$\text{Resolution} = (213{,}92 - 213{,}80) \times \frac{2{,}0}{15} = 0{,}016 \text{ nm}$$

Figure A.1 — Example of calculation of practical resolution