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Steel and iron — Determination of calcium and magnesium — Inductively coupled plasma atomic emission spectrometric method

Aciers et fontes - Détermination du calcium et du magnésium - Méthode par spectrométrie d'émission atomique avec plasma induit

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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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The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Steel and iron — Determination of calcium and magnesium — Inductively coupled plasma atomic emission spectrometric method

1 Scope

This International Standard specifies a method for determination of calcium and magnesium contents in iron, cast iron, steel, and alloyed steel by inductively coupled plasma (ICP) atomic emission spectrometry.

The method is applicable to the determination of calcium and magnesium contents (mass fraction) in the range of 0,000 5 % to 0,006 % and 0,000 5 % to 0,20 %, respectively.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 Principle

A test portion is dissolved in a hydrochloric, nitric and hydrofluoric acid mixture and fumed with perchloric acid. Hydrochloric acid, nitric acid, and an internal standard element (if used) are added and the solution is diluted to a known volume. The solution is filtered if necessary, nebulized into an ICP spectrometer and the intensity of the emitted light from each element measured simultaneously with the intensity of the light emitted by the internal standard element.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade with very low calcium and magnesium contents and only grade 2 water as specified in ISO 3696.

4.1 Pure iron, containing less than 0,5 µg/g of calcium and magnesium.

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

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

4.4 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 4.

4.5 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 100.

4.6 Nitric acid, ρ about 1,42 g/ml.

4.7 Hydrofluoric acid, ρ about 1,14 g/ml.

4.8 Perchloric acid, ρ about 1,67 g/ml.

4.9 Acid mixture.

Mix two volumes of hydrochloric acid (4.2), one volume of nitric acid (4.6), and three volumes of water.

4.10 Calcium standard solutions.

4.10.1 Calcium stock solution, corresponding to 1 000 mg of calcium per litre.

Dry several grams of calcium carbonate [purity ≥99,9 % (mass fraction)] in an oven at 100 °C ± 5 °C for at least 1 h and cool to room temperature in a desiccator. Weigh, to the nearest 0,000 1 g, 2,497 g of the dried product into a 400 ml beaker, add 20 ml of hydrochloric acid (4.3), cover with a watch-glass and heat gently until the product is completely dissolved. Cool to room temperature and transfer the solution into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this stock solution contains 1,000 mg of calcium.

4.10.2 Calcium standard solution A, corresponding to 100 mg of calcium per litre.

Transfer 10,00 ml of calcium stock solution (4.10.1) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,100 mg of calcium.

4.10.3 Calcium standard solution B, corresponding to 10 mg of calcium per litre.

Transfer 10,00 ml of calcium standard solution A (4.10.2) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,010 mg of calcium.

4.10.4 Calcium standard solution C, corresponding to 1,0 mg of calcium per litre.

Transfer 10,00 ml of calcium standard solution B (4.10.3) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,001 mg of calcium.

4.11 Magnesium standard solutions

4.11.1 Magnesium stock solution, corresponding to 1 000 mg of magnesium per litre.

Weigh, to the nearest 0,000 1 g, 1,000 g of pure magnesium [purity ≥99,9 % (mass fraction)] and transfer into a 250 ml beaker. Add 20 ml of water, then add hydrochloric acid (4.3) drop by drop while swirling until the acid action ceases and continue adding hydrochloric acid (4.3) to a total volume of 20 ml. Cover with a watch-glass and heat to boil for 10 min. After cooling, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this stock solution contains 1,000 mg of magnesium.

4.11.2 Magnesium standard solution A, corresponding to 100 mg of magnesium per litre.

Transfer 10,00 ml of magnesium stock solution (4.11.1) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,100 mg of magnesium.

4.11.3 Magnesium standard solution B, corresponding to 10 mg of magnesium per litre.

Transfer 10,00 ml of magnesium standard solution A (4.11.2) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,010 mg of magnesium.

4.11.4 Magnesium standard solution C, corresponding to 1,0 mg of magnesium per litre.

Transfer 10,00 ml of magnesium standard solution B (4.11.3) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.4). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,001 mg of magnesium.

4.12 Yttrium internal standard solution, corresponding to 100 mg of yttrium per litre.

Calcine several grams of yttrium oxide [purity ≥99,9 % (mass fraction)] in a muffle furnace at 850 °C ± 10 °C for at least 40 min and then cool to room temperature in a desiccator. Weigh 0,127 0 g of the calcined product into a 400 ml beaker, add 10 ml of hydrochloric acid (4.3), cover with a watch-glass, and heat gently until the product is completely dissolved. Cool to room temperature and transfer the solution to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,100 mg of yttrium.

5 Apparatus

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

Ordinary laboratory apparatus and the following shall be used.

5.1 Inductively coupled plasma atomic emission spectrometer

The inductively coupled plasma atomic emission spectrometer used will be satisfactory if, after optimizing according to 7.4, it meets the performance criteria given in 5.1.2 to 5.1.4.

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

5.1.1 Analytical wavelengths

This method does not specify any particular emission line. It is mandatory that each laboratory carefully investigates the wavelengths available on its own equipment to find the most suitable one regarding sensitivity and absence of interferences.

In Table 1, however, several suggestions are given together with possible interferences. These wavelengths have been carefully investigated

The wavelength of the internal standard element chosen shall not interfere with the analytical wavelengths, nor should the internal element wavelength be interfered by elements present in the test solution. It is, however, recommended to use Y 371,03 nm or Y 360,07 nm. This wavelength is free of interferences from the elements.

Table 1 — Analytical wavelengths together with interfering elements

Element	Wavelength nm	Possible interferences
Ca	393,66	none
Mg	279,55	none
Y	371,03	none
	360,07	none

Other elements can be used as internal standards, but they shall not be present in the sample, and shall not interfere with the elements to be determined at the appropriate wavelengths. Likewise, the elements present in the test solution shall not interfere with the internal standard at the wavelength chosen. The excitation requirements of the internal standard should be similar to those of the elements to be determined.

5.1.2 Minimum practical resolution of the spectrometer

Calculate the bandwidth, according to A.1, for the wavelength used. The bandwidth shall be less than 0,030 nm.

5.1.3 Minimum short-term precision

Calculate the short-term precision according to A.2. The relative standard deviation (RSD) shall not exceed 1 % of the mean absolute or ratioed intensities for concentrations 100 to 1 000 times the limit of detection (LOD) (5.1.4). For concentrations that are 10 to 100 times the LOD (5.1.4), the RSD shall not exceed 5 %.

5.1.4 Limit of Detection (LOD) and Limit of Quantification (LOQ)

Calculate the LOD and LOQ, according to A.3, for the analytical wavelengths used. The calculated values shall be below the values given in Table 2.

Table 2 — Limit of Detection (LOD) and Limit of Quantification (LOQ)

Element	Wavelength nm	LOD mg/l	LOQ mg/l
Ca	393,66	0,003 4	0,010
Mg	279,55	0,004 6	0,014

5.1.5 Linearity of the calibration curve

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

5.2 Polytetrafluoroethylene (PTFE) beakers with PTFE cover

NOTE For the determination of magnesium, glass beakers and watch-glass covers can be used.

5.3 Volumetric flask, of capacity 100 ml, made of polypropylene or polyethylene terephthalate (PET).

5.4 Filter, 0,22 µm pore size, 47 mm diameter PTFE, or polycarbonate filter membrane.

5.5 Suction filtration system, including a flask, a filter funnel, and a vacuum filtration device.

6 Sampling

Sampling shall be carried out in accordance with ISO 14284 or with an appropriate national standard for steels and cast irons.

7 Procedure

WARNING — Perchloric acid vapour can cause explosions in the presence of ammonia, nitrous fumes, or organic matter in general.

All glassware and plasticware shall first be washed with hydrochloric acid (4.3), then with water. The quantities of calcium and magnesium in the glassware and plasticware can be checked by measuring the intensity of the emitted light of water poured into glassware and plasticware after washing with acid and rinsing with water. If contamination from calcium and magnesium is present, the glassware and plasticware are unsuitable and should be replaced or cleaned again.

For each set of determinations, all reagents, including water, calibration and test solutions, shall be from the same batch.

7.1 Test portion

Place the sample or the pure iron in a PTFE beaker. Add 10 ml of hydrochloric acid (4.5) and swirl the beaker gently. Discard the hydrochloric acid solution and rinse the sample thoroughly with water. Repeat the rinsing, firstly with anhydrous ethanol and then with acetone. Once dried, weigh 0,50 g of the test sample to the nearest 0,001 g.

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 as for the test portion including pure iron (4.1).

7.3 Determination

7.3.1 Preparation of the test solution

a) Place the test portion into a PTFE beaker.

b) Add 6 ml of hydrochloric acid (4.2) and 3 ml of nitric acid (4.6). Heat gently until the acid action ceases. Add 3 ml of hydrofluoric acid (4.7) and heat at approximately 90 °C for 15 min.

c) Cool the solution and add 5 ml of perchloric acid (4.8). Heat and evaporate until white fumes appear. Cover the beaker with a PTFE cover, and continue heating at a temperature at which a steady reflux of white perchloric acid fumes is maintained along the walls of the beaker. Continue heating until the residual volume is about 1 ml.

NOTE It is recommended to cover the beaker with a PTFE cover only for samples with high carbon content in order to dissolve the free carbon completely during the perchloric acid fuming step.

d) Allow to cool, add 10 ml of the mixture of hydrochloric and nitric acid (4.9), and heat gently to dissolve the salts.

e) Cool the solution to room temperature. Transfer the solution quantitatively into a 100 ml one-mark polypropylene or polyethylene terephthalate volumetric flask (5.3). If the internal standard

technique is used, add 1,0 ml of the yttrium internal standard solution (4.12). Dilute to the mark with water and mix.

If some insoluble residue is present in the test solution, filter the solution as described in 7.3.2. Otherwise, omit the filtration step.

7.3.2 Filtration of the test solution

Place a filter (5.4) in the suction filtration system (5.5), wash it several times with warm hydrochloric acid (4.4) and then with warm water. Filter a portion of the test solution (7.3.1). Discard the washings and filtrate from the flask.

NOTE A filter paper can also be used for filtration, but operators have to pay attention to the blank of calcium in the filter paper. Alternatively, the residue can be allowed to settle before aspiration but the operator should be careful to avoid blockage of the nebuliser.

Take a clean and dry flask to collect the filtrate. Filter a second portion of the test solution (7.3.1) through the same filtration system and collect the filtrate in the flask. Transfer the filtrate into a 100 ml dry one-mark polypropylene or polyethylene terephthalate volumetric flask (5.3). The filtrate will be measured directly by inductively coupled plasma atomic emission spectrometry.

7.3.3 Preparation of the calibration solutions

Place 0,500 g ± 0,005 g of pure iron (4.1) into a series of 200 ml PTFE beakers.

Proceed as specified in 7.3.1 b) to e).

Cool the solutions to room temperature. Transfer the solutions quantitatively into a series of 100 ml one-mark polypropylene or polyethylene terephthalate volumetric flasks (5.3). If the internal standard technique is used, add 1,0 ml of yttrium internal standard solution (4.12) to each of the series of one-mark polypropylene or polyethylene terephthalate volumetric flask.

Add the volumes of calcium standard solutions and magnesium standard solutions, as indicated in Table 3, Table 4, and/or Table 5. The calibration solutions for calcium and magnesium can be prepared in the same volumetric flasks, where appropriate.

Dilute to the mark with water and mix.

Table 3 — Calibration for calcium mass fractions between 0,000 5 % and 0,006 %

Calibration solution label	Volume of calcium standard solution C (4.10.4) ml	Volume of calcium standard solution B (4.10.3) ml	Concentration of calcium in the calibration solution µg/ml	Corresponding calcium mass fraction in the test portion %
S_0	0	0	0	0
$S_{Ca,1}$	2,00	0	0,020	0,000 4
$S_{Ca,2}$	4,00	0	0,040	0,000 8
$S_{Ca,3}$	6,00	0	0,060	0,001 2
$S_{Ca,4}$	10,00	0	0,10	0,002 0
$S_{Ca,5}$	0	2,00	0,20	0,004 0
$S_{Ca,6}$	0	3,00	0,30	0,006 0

Table 4 — Calibration for magnesium mass fractions between 0,000 5 % and 0,010 %

Calibration solution label	Volume of magnesium standard solution C (4.11.4) added ml	Volume of magnesium standard solution B (4.11.3) added ml	Concentration of magnesium added in the calibration solution g/ml	Corresponding magnesium mass fraction in the test portion %
S_0	0	0	0	0
$S_{Mg,1}$	1,00	0	0,010	0,000 2
$S_{Mg,2}$	2,50	0	0,025	0,000 5
$S_{Mg,3}$	5,00	0	0,050	0,001 0
$S_{Mg,4}$	10,00	0	0,10	0,002 0
$S_{Mg,5}$	0	2,50	0,25	0,005 0
$S_{Mg,6}$	0	5,00	0,50	0,010

Table 5 — Calibration for magnesium mass fractions between 0,010 % and 0,20 %

Calibration solution label	Volume of magnesium standard solution B (4.11.3) added ml	Volume of magnesium standard solution A (4.11.2) added ml	Concentration of magnesium added in the calibration solution µg/ml	Corresponding magnesium mass fraction in the test portion %
S_0	0	0	0	0
$S_{Mg,6}$	5,00	0	0,50	0,010
$S_{Mg,7}$	10,00	0	1,00	0,020
$S_{Mg,8}$	0	2,50	2,50	0,050
$S_{Mg,9}$	0	5,00	5,00	0,100
$S_{Mg,10}$	0	10,00	10,00	0,200

7.4 Adjustment of the apparatus

Start the inductively coupled plasma atomic emission spectrometer and let it stabilize in accordance with the manufacturer's instructions before any measurement.

Optimize the instrument according to the manufacturer's instructions.

Prepare the software to measure the intensity, and for the calculation of the mean value and relative standard deviation corresponding to each analytical line.

If an internal standard is used, prepare the software to calculate the ratio between the analyte intensity and the internal standard intensity. The intensity of the internal standard shall be measured simultaneously with the analyte intensity.

Check the instrument performance requirements given in 5.1.2 to 5.1.5.

7.5 Measurement of the calibration solutions

Measure the absolute intensities or the ratioed intensities of the analytical wavelength beginning with the lowest calibration solution S_0 and ending up with the highest calibration solution.

Measure each of the calibration solutions three times and calculate the mean intensities.

Subtract the mean absolute intensity or the mean ratioed intensity ($I_{c\,0}$) of the calibration solution S_0 from the mean absolute intensity or the mean ratioed intensity ($I_{c\,i}$) of each calibration solution, in order to obtain the net absolute intensity or the net ratioed intensity ($I_{c\,N}$).

7.6 Plotting a calibration curve

Calculate the linear regression through the points representing the net intensities or the net ratioed intensities of calcium or magnesium on the *y*-axis and the concentration, expressed in micrograms per millilitre, of calcium or magnesium in the calibration solution on the *x*-axis.

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

7.7 Measurements of the test solution

Measure the absolute intensity or ratioed intensity of the test sample solution three times and calculate the mean intensities.

Subtract the mean absolute intensity or the mean ratioed intensity (I_0) of the blank test from the mean absolute intensity or the mean ratioed intensity (I_i) of each solution in order to obtain the net absolute intensity or the net ratioed intensity (I_N).

8 Expression of results

8.1 Method of calculation

Using the linear regression functions calculated in 7.6 and the net absolute intensity, or the net ratioed intensity of the test solution calculated in 7.7, calculate the concentration of calcium or magnesium in the test solution, expressed in micrograms per millilitre.

The mass fraction of calcium or magnesium, expressed as a percentage, w_i, is given by Formula (1)

$$W_i = \frac{\rho_i \times V \times 10^{-6}}{m} \times 100 \quad (1)$$

where

ρ_i is the concentration of calcium or magnesium in the test solution, in µg/ml;

V is the volume of the test solution, in ml;

m is the mass of the test portion, in g.

8.2 Precision

A planned trial of this method was carried out by 10 laboratories at 6 levels of calcium and 8 levels of magnesium, each laboratory making three determinations for each element 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 Annex B.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2, and ISO 5725-3.

The relationship between the content of each element and the repeatability limit (r) and reproducibility limits (R_w and R) of the test results (see NOTE 3) are summarized in Tables 6 and 7. The graphical representation of the data is shown in Annex C.

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

Table 6 — Calcium — Results for repeatability limit and reproducibility limits

Mass fraction %	Repeatability limit r % (mass fraction)	Reproducibility limits	
		R_w % (mass fraction)	R % (mass fraction)
0,000 5	0,000 16	0,000 25	0,000 49
0,001 0	0,000 23	0,000 33	0,000 67
0,002 0	0,000 33	0,000 43	0,000 92
0,005 0	0,000 53	0,000 60	0,001 40
0,006 0	0,000 58	0,000 65	0,001 52

Table 7 — Magnesium — Results for repeatability limit and reproducibility limits

Mass fraction %	Repeatability limit R % (mass fraction)	Reproducibility limits	
		R_w % (mass fraction)	R % (mass fraction)
0,000 5	0,000 15	0,000 13	0,000 38
0,001 0	0,000 16	0,000 19	0,000 57
0,002 0	0,000 18	0,000 29	0,000 86
0,005 0	0,000 25	0,000 51	0,001 49
0,010 0	0,000 36	0,000 79	0,002 26
0,020 0	0,000 59	0,001 21	0,003 42
0,050	0,001 28	0,002 13	0,005 92
0,100	0,002 4	0,003 3	0,009 0
0,150	0,003 6	0,004 2	0,011 4

9 Test report

The test report shall include the following information:

a) the method used by reference to this International Standard (i.e. ISO 13933:2014);

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

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 might have influenced the results;

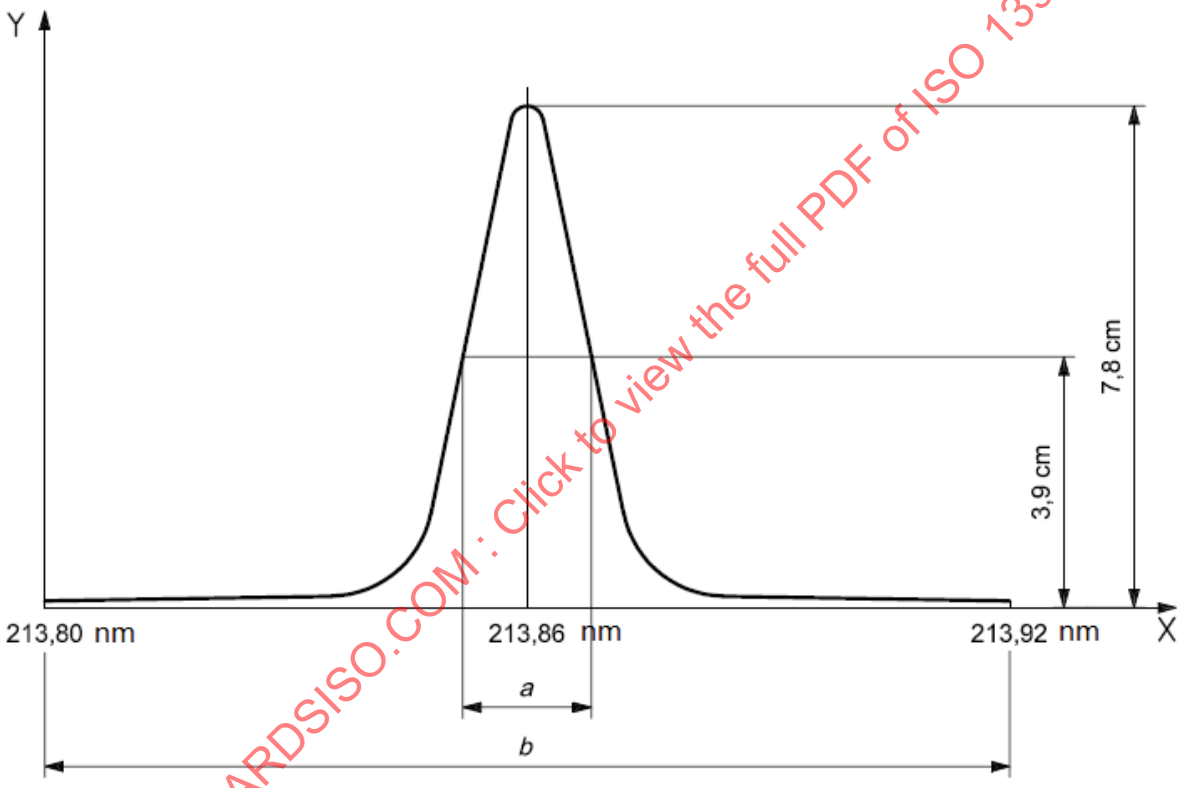
f) signature of the responsible person.

Annex A
(normative)

Procedure for the determination of instrumental criteria

A.1 Practical resolution of the spectrometer

The practical assessment of resolution 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 nanometres. An example is shown in Figure A.1.



$$\text{Resolution} = (213{,}92 - 213{,}80) \times \frac{2}{15} = 0{,}016\ (\text{nm})$$

Key

X wavelength for zinc, nm

Y intensity (arbitrary unit)

a half peak width = 2 cm

b peak window = 15 cm

Figure A.1 — Example of calculation of practical resolution

A.2 Minimum short-term precision

An important parameter for assessing the suitability of an instrument for a given determination is the short-term stability of the emission signal, i.e. the closeness of agreement between the values obtained on the same test sample solution by repeating measurements in rapid succession.

It is expressed as a relative standard deviation (RSD) of the measurement signals.

Make 10 consecutive measurements on the same solution and calculate the RSD.

A.3 Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of detection and limit of quantification represent two of the parameters of an analytical method. Both are derived from the standard deviation of the repeatability.

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

Nebulize the zero test solution for approximately 10 s and then take 10 readings at the pre-set integration time. Thereafter, do the same for the solution containing a concentration of the analyte approximately 10 times the limit of detection (use LOD in Table 2).

From the intensity readings, calculate the mean intensities X_{10}, X_0, and the standard deviation of the zero member s_0.

Calculate the net mean intensity (X_{n10}) for the solution at 10 times the limit of detection using the following formula:

$$X_{n10} = X_{10} - X_0 \tag{A.1}$$

Calculate the limit of detection using Formula (A.2):

$$\mathrm{LOD} = 4{,}65 \times s_0 \times \frac{\rho 10}{X_{n10}} \tag{A.2}$$

where

ρ_{10} is the concentration, expressed in mg/l, of the solution at 10 times the limit of detection.

The limit of quantification is then given as

$$\mathrm{LOQ} = 14{,}1 \times s_0 \times \frac{\rho 10}{X_{n10}} \tag{A.3}$$

Annex B
(informative)

Additional information on international cooperative test

The test samples used are listed in Table B.1. Detailed results for calcium and magnesium obtained in the international cooperative test are shown in Tables B.2 and B.3.

Tables B.2 and B3 were derived from the results of an international analytical trial carried out in 2011 on steel and iron samples in five countries involving 10 laboratories.

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

Table B.1 — Test samples used

ID No. of CRM	Type	Ca % (mass fraction)	Mg % (mass fraction)	Composition
60–1 GBW01131a	Low alloy cast iron	—	0,000 33	C 3,3; Si 0,9; Cr 2,0; Mo 0,8
60–2 GBW01137a	Low alloy cast iron	—	0,001 0	C 1,8; Si 3,4; Ni 1,1; Cu 1,7
60–3 GBW01622	Alloy steel	0,003 2	0,005 3	Cr 14,4; Ni 36,2; W 5,6; Ti 3,0; Mo 2,0; Al 1,9
60–4 GBW01619	Alloy steel	0,004 2	0,008 2	Cr 14,5; Ni 38,0; W 5,6; Ti 2,8; Mo2,0; Al 1,6
60–5 GSB03–1104–1999	Nodular cast iron	—	0,022	C 1,6; Si 1,9
60–6 BH1914–1-1	Nodular cast iron	—	0,090	C 2,2; Si 3,8
60–7 GSB03–1813–2005 (T006–1)	Alloy cast iron	—	0,137	C 2,6; Si 3,4; Cr 2,9; Ni 4,5; Mo 1,9
60–8 BS CA 316–4	316 stainless steel	0,005 6	—	Cr 17,6; Ni 11,0; Mo 2,0; Mn 1,4
60–9 YSBS15327–5-2008 (6G)	Stainless steel	0,000 4	—	Cr 12,67; Ni 15,3; Cu 1,90; Mo 1,51; Nb 0,1
60–10 Euronorm-CRM 481–1	Ductile (Nodular) iron	—	0,050 7	C 3,9; Si 2,3; Ni 1,2
60–11 Euronorm-ZRM 194–1	Low alloy steel	0,002 6	—	Mn 1,2; Cr 0,7
60–12 AISI 1215Bi IARM 233A	Low alloy steel	0,001	—	Mn 0,9; P 0,07; S 0,3; Cr 0,04; Ni 0,04; Cu 0,09; Bi 0,2

Table B.2 — Detailed results obtained in international cooperative test for calcium

No.	Sample	Calcium % (mass fraction)			Precision data % (mass fraction)		
		Certified	Found	Found	Repeatability limit	Reproducibility limits	
			$\bar{w}_{Ca1}$	$\bar{w}_{Ca2}$	r	R_w	R
1	GBW01622	0,003 2	0,003 286	0,003 311	0,000 739	0,000 739	0,001 435
2	GBW01619	0,004 2	0,003 970	0,003 969	0,000 481	0.000 481	0,001 496
3	BS CA 316–4	0,005 6	0,005 588	0,005 551	0,000 298	0,000 742	0,000 990
4	YSBS15327–5-2008 (6G)	0,000 4	0,000 383	0,000 402	0,000 120	0,000 164	0,000 358

$\bar{w}_{Ca1}$: general mean within a day.

$\bar{w}_{Ca2}$: general mean over several days.

Table B.2 *(continued)*

No.	Sample	Calcium % (mass fraction)			Precision data % (mass fraction)		
		Certified	Found	Found	Repeatability limit	Reproducibility limits	
			$\bar{w}_{Ca1}$	$\bar{w}_{Ca2}$	r	R_w	R
5	Euronorm-ZRM 194–1	0,002 6	0,002 524	0,002 534	0,000 479	0,000 479	0,001 137
6	AISI 1215Bi IARM 233A	0,001	0,001 126	0,001 068	0,000 220	0,000 636	0,000 839
$\bar{w}_{Ca1}$: general mean within a day.							
$\bar{w}_{Ca2}$: general mean over several days.							

Table B.3 — Detailed results obtained in international cooperative test for magnesium

No.	Sample	Magnesium % (mass fraction)			Precision data % (mass fraction)		
		Certified	Found	Found	Repeatability limit	Reproducibility limits	
			$\bar{w}_{Mg1}$	$\bar{w}_{Mg2}$	r	R_w	R
1	GBW01131a	0,000 33	0,000 337	0,000 339	0,000 207	0,000 207	0,000 242
2	GBW01137a	0,001 0	0,000 884	0,000 889	0,000 092	0,000 139	0,000 719
3	GBW01622	0,005 3	0,005 168	0,005 128	0,000 173	0,000 208	0,000 989
4	GBW01619	0,008 2	0,007 633	0,007 687	0,000 328	0,000 437	0,004 429
5	GSB03–1104–1999	0,022	0,021 875	0,021 850	0,000 874	0,001 723	0,001 966
6	BH1914–1-1	0,090	0,088 670	0,090 108	0,001 697	0,003 618	0,013 050
7	GSB03–1813–2005 (T006–1)	0,137	0,135 033	0,134 358	0,003 840	0,003 840	0,011 219
8	Euronorm-CRM 481–1	0,050 7	0,051 694	0,051 821	0,001 144	0,0032 2	0,004 131
$\bar{w}_{Mg1}$: general mean within a day.							
$\bar{w}_{Mg2}$: general mean over several days.							