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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

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](http://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](http://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 meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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

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# 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**,  $\rho$  about 1,19 g/ml.

**4.3 Hydrochloric acid**,  $\rho$  about 1,19 g/ml, diluted 1 + 1.

**4.4 Hydrochloric acid**,  $\rho$  about 1,19 g/ml, diluted 1 + 4.

**4.5 Hydrochloric acid**,  $\rho$  about 1,19 g/ml, diluted 1 + 100.

**4.6 Nitric acid**,  $\rho$  about 1,42 g/ml.

**4.7 Hydrofluoric acid**,  $\rho$  about 1,14 g/ml.

**4.8 Perchloric acid**,  $\rho$  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  $\geq 99,9$  % (mass fraction)] in an oven at  $100\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  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  $\geq 99,9$  % (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  $\geq 99,9$  % (mass fraction)] in a muffle furnace at  $850\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  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.

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**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 <sub>0</sub>	0	0	0	0
S <sub>Ca,1</sub>	2,00	0	0,020	0,000 4
S <sub>Ca,2</sub>	4,00	0	0,040	0,000 8
S <sub>Ca,3</sub>	6,00	0	0,060	0,001 2
S <sub>Ca,4</sub>	10,00	0	0,10	0,002 0
S <sub>Ca,5</sub>	0	2,00	0,20	0,004 0
S <sub>Ca,6</sub>	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 <sub>0</sub>	0	0	0	0
S <sub>Mg,1</sub>	1,00	0	0,010	0,000 2
S <sub>Mg,2</sub>	2,50	0	0,025	0,000 5
S <sub>Mg,3</sub>	5,00	0	0,050	0,001 0
S <sub>Mg,4</sub>	10,00	0	0,10	0,002 0
S <sub>Mg,5</sub>	0	2,50	0,25	0,005 0
S <sub>Mg,6</sub>	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 <sub>0</sub>	0	0	0	0
S <sub>Mg,6</sub>	5,00	0	0,50	0,010
S <sub>Mg,7</sub>	10,00	0	1,00	0,020
S <sub>Mg,8</sub>	0	2,50	2,50	0,050
S <sub>Mg,9</sub>	0	5,00	5,00	0,100
S <sub>Mg,10</sub>	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<sub>0</sub> 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 ( $I_{c0}$ ) of the calibration solution S<sub>0</sub> from the mean absolute intensity or the mean ratioed intensity ( $I_{ci}$ ) of each calibration solution, in order to obtain the net absolute intensity or the net ratioed intensity ( $I_{cN}$ ).