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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 spectrométrique d'émission atomique avec plasma induit*

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## Foreword

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ISO 13933 was prepared by Technical Committee 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 draft specifies a method for determination of calcium and magnesium contents in iron, cast iron, steel and alloyed steel by inductively coupled plasma atomic emission spectrometry.

The method is applicable to the determination of calcium and magnesium in content range (mass fraction) from 0,000 5 % to 0.006 % and from 0,000 5 % to 0,20 %, respectively.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, Laboratory glassware – Burettes

ISO 648, Laboratory glassware -- Single-volume pipettes

ISO 1042, Laboratory glassware – One mark volumetric flasks

ISO 3696, Water for analytical laboratory use – Specification and test methods

ISO 14284, Steel and iron -- Sampling and preparation of samples for the determination of chemical composition

## 3 Principle

A test portion is dissolved in hydrochloric, nitric and hydrofluoric acid mixture and fumed with perchloric acid. Hydrochloric 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, and nebulized into an ICP and the intensity of the emitted light from each element is measured simultaneously with the intensity of the light emitted by the internal standard element.

Iron is used as matrix in the calibration solution, the quantities of iron being the same as that of the test portion.

## 4 Reagents

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

**4.1 Pure iron**, containing less than 0,000 1 % (mass fraction) 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 Nitric acid**,  $\rho$  about 1,42 g/ml.

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

**4.7 Perchloric acid**,  $\rho$  about 1,67 g/ml.

**4.8 Acid mixture**

Mix two volumes of hydrochloric acid (4.2), one volume of nitric acid (4.5) and three volumes of water.

**4.9 Calcium standard solution**

**4.9.1 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 0,0001 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.

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

Transfer, with a calibrated pipette, 10,00 ml of calcium stock solution (4.9.1) into a calibrated 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.

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

Transfer, with a calibrated pipette, 10,00 ml of calcium standard solution A (4.9.2) into a calibrated 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.

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

Transfer, with a calibrated pipette, 10,00 ml of calcium standard solution A (4.9.3) into a calibrated 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.

#### 4.10 Magnesium standard solution

**4.10.1 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, and add hydrochloric acid (4.3) drop by drop whilst swirling until the acid action ceases, and continue adding hydrochloric acid (4.3) to 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.

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

Transfer, with a calibrated pipette, 10,00 ml of magnesium stock solution (4.10.1) into a calibrated 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.

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

Transfer, with a calibrated pipette, 10,00 ml of magnesium standard solution A (4.10.2) into a calibrated 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.

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

Transfer, with a calibrated pipette, 10,00 ml of magnesium standard solution A (4.10.3) into a calibrated 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.

**4.11 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 stock solution contains 0,100 mg of yttrium.

## 5 Apparatus

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

Ordinary laboratory apparatus and

### 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 the simultaneous or the sequential type. 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 can not be used and an alternative technique without internal standard shall be applied.

**5.1.1 Analytical lines**

This method does not specify any particular emission line. It is mandatory that each laboratory carefully investigate the lines 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 lines have been carefully investigated (see Annex B).

The line 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. This line is free of interferences from the elements given in Annex B.

**Table 1 — Analytical lines together with interfering elements**

Element	Wavelength nm	Possible interferences
Ca	393,66	none
Mg	279,55	none
Y	371,03	none
	360,0	none

NOTE Other element can be used as internal standard, but it shall not be present in the sample, and shall not interfere with the analytical wavelengths, nor should elements present in the test solution interfere with the internal element wavelength. The exciting conditions of the internal standard element shall be similar to that of the analytical elements.

**5.1.2 Minimum practical resolution of the spectrometer**

Calculate the bandwidth, according to the Annex A, Clause 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 the Annex A, Clause 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 LOD (5.1.4). For concentrations 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 the Annex A, Clause A.3, for the analytical line used. The values shall be below the values in Table 2.



Table 2 — Limit of detection (LOD) and limit of quantification (LOQ)

Element	Analytical line	LOD	LOQ
	nm	mg/l	mg/l
Ca	393,66	0,002 2	0,011
Mg	279,55	0,003 0	0,015

### 5.1.5 Graph linearity

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

### 5.2 Polytetrafluoroethylene (PTFE) beakers with PTFE cover

NOTE Glass beakers and glass watch covers can also be used for determination of magnesium.

### 5.3 100 ml polypropylene or polyethylene terephthalate (PET) volumetric flask

NOTE Before the determination, namely that of low concentration of Ca and Mg, it is necessary to clean the beakers and flasks thoroughly with the hydrochloric acid (4.3).

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

**5.5 Suction filter**, including a clean suction flask and vacuum filtration device.

## 6 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

## 7 Procedure

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

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

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

### 7.1 Test portion

Weigh, to the nearest 0,000 1 g, 0,500 g of the test sample.

Note: If necessary, the sample for calcium determination shall be washed according to the following procedure:

Place the sample (included pure iron) to a PTFE beaker. Add 10ml of HCl (1+100) and stir the test portion for about 30 seconds by swinging the beaker gently. Discard the HCl solution and rinse the sample sufficiently with water. Then rinse the sample with anhydrous ethyl alcohol and acetone. After drying the sample, weigh, to the nearest 0,000 1g, 0,500 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 as for the test portion including pure iron (4.1).

## 7.3 Determination

### 7.3.1 Preparation of the test solution

**7.3.1.1** Place the test portion to a PTFE beaker.

**7.3.1.2** Add 6 ml of hydrochloric acid (4.2) and 3 ml of nitric acid (4.5). Heat gently until the acid action ceases. Add 3 ml of hydrofluoric acid (4.6) and heat at approximate 90 °C for 15 min.

**7.3.1.3** Cool the solution and add 5 ml of perchloric acid (4.7). Heat and evaporate until white fumes appear. Cover the beaker with a PTFE cover, continue heating at a temperature at which a steady reflux of white perchloric acid fumes is maintained along on the walls of the beaker. Continue heating until a residual volume of about 1 ml.

**NOTE** It was recommended to cover the beaker with a PTFE cover only for the samples with high content of carbon to dissolve the carbonide completely while continue heating to fume perchloric acid.

**7.3.1.4** Allow to cool, add 10 ml of the mixture of hydrochloric and nitric acid (4.8) and heat gently to dissolve the salts.

**7.3.1.5** Cool the solution to room temperature. Transfer the solution quantitatively into a 100 ml one-mark polypropylene or polyethylene volumetric flask (5.3). If the internal standard technique is used, using a pipette, add 1,00 ml of the yttrium internal standard solution (4.11). Dilute to the mark with water and mix.

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

### 7.3.2 Filtration of the test solution

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

Take a clean and dry flask to collect the filtrate. Filter a new portion of the test solution (7.3.1) through the filter medium (5.4) using the suction filter (5.5) and collect the filtrate in the flask. Transfer the filtrate into a 100 ml dry one-mark polypropylene or polyethylene volumetric flask (5.3). The filtrate will be measured directly by inductively coupled plasma atomic emission spectrometer.

**NOTE** If the filter paper has a very low blank value of calcium which is in accordance with the requirement of determination, it can also be used. As an alternative the residues can also be settled down but operator should be more careful about the nebulizer clotting.

### 7.3.3 Preparation of the calibration solutions

Place  $0,500 \pm 0,005$  g of pure Iron (4.1) in a series of seven 200 ml PTFE beakers.

Proceed as specified in 7.3.1.2 to 7.3.1.5.

Cool the solutions to room temperature. Transfer the solutions quantitatively into seven 100 ml one-mark polypropylene or polyethylene volumetric flasks (5.3), respectively. If the internal standard technique is used, using a burettes or pipette, add 1,0 ml of yttrium internal standard solution (4.11) into each of the series of one-mark polypropylene or polyethylene volumetric flask.