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Steel — Determination of calcium content by flame atomic absorption spectrometry —

Part 1:

Determination of acid-soluble calcium content

*Aciers — Dosage du calcium par spectrométrie d'absorption atomique
dans la flamme —*

Partie 1: Dosage du calcium soluble dans l'acide

ISO 10697-1:1992

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Foreword

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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 10697-1 was prepared by Technical Committee ISO/TC 17, *Steel*, Sub-Committee SC 1, *Methods of determination of chemical composition*.

ISO 10697 consists of the following parts, under the general title *Steel — Determination of calcium content by flame atomic absorption spectrometry*:

- *Part 1: Determination of acid-soluble calcium content*
- *Part 2: Determination of total calcium content*

Annex A forms an integral part of this part of ISO 10697. Annexes B and C are for information only.

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Steel — Determination of calcium content by flame atomic absorption spectrometry —

Part 1:

Determination of acid-soluble calcium content

1 Scope

This part of ISO 10697 specifies a flame atomic absorption spectrometric method for the determination of acid-soluble calcium content in steel.

The method is applicable to calcium contents between 0,000 5 % (*m/m*) and 0,003 % (*m/m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10697. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10697 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 Definition

For the purposes of this part of ISO 10697, the following definition applies.

3.1 Acid-soluble calcium: Calcium dissolved in the acids specified in 8.3.1.

4 Principle

Dissolution of a test portion in hydrochloric and nitric acids.

Addition of potassium chloride/lanthanum nitrate solution as a spectrochemical buffer.

Spraying of the solution into a dinitrogen monoxide-acetylene flame.

Spectrometric measurement of the atomic absorption of the 422,7 nm spectral line emitted by a calcium hollow cathode lamp.

5 Reagents

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

5.1 Pure iron, containing less than 0,000 1% (*m/m*) calcium.

5.2 Suitable solvent, for example acetone or dichloromethane.

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

5.4 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 2.

5.5 Nitric acid, ρ about 1,40 g/ml.

5.6 Potassium chloride/lanthanum nitrate, solution.

Dissolve 95,34 g of potassium chloride (KCl) and 62,35 g of lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ in water, dilute to 1 000 ml and mix.

5.7 Calcium, standard solutions.

5.7.1 Stock solution, corresponding to 100 mg of Ca per litre.

Dry several grams of calcium carbonate [purity $\geq 99,5\%$ (m/m)] in an air oven at 100 °C for at least 1 h and cool to room temperature in a desiccator. Weigh 0,249 7 g of the dried product into a 400 ml beaker, cover with a watch-glass and add 5 ml of hydrochloric acid (5.3) to dissolve. Cool 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 100 μg of Ca.

5.7.2 Standard solution, corresponding to 10 mg of Ca per litre.

Transfer 10,0 ml of the stock solution (5.7.1) into a 100 ml one-mark volumetric flask and add 5 ml of hydrochloric acid (ρ about 1,19 g/ml, diluted 1 + 10). Dilute to the mark with water and mix.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 10 μg of Ca.

6 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

6.1 Filter media, 0,22 μm pore size, 47 mm diameter cellulose-acetate filter.

6.2 Suction apparatus, i.e. a clean empty flask placed between the suction device and filtering flask to prevent any back suction and contamination.

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

The atomic absorption spectrometer used will be satisfactory if after optimization according to 8.3.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 6.3.1 to 6.3.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 6.3.4.

6.3.1 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.

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.

6.3.2 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 calcium in a matrix similar to the final test portion solution shall be better than 0,02 μg of Ca per millilitre.

6.3.3 Graph linearity (see A.3)

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.

6.3.4 Characteristic concentration (see A.4)

The characteristic concentration of calcium in a matrix similar to the final test portion solution shall be better than 0,05 μg of Ca per millilitre.

6.4 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 6.3 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 simply dividing the signal obtained.

7 Sampling

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

8 Procedure

All glassware shall first be washed in hydrochloric acid (5.3), then in water. The quantity of calcium present in the glassware can be checked by measuring the absorption of water introduced into the glassware after washing with acid.

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

8.1 Test portion

Wash the test sample in a suitable solvent (5.2) and dry.

Weigh, to the nearest 0,001 g, approximately 2,0 g of the test sample.

8.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents used for the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

Place the test portion (8.1) in a 250 ml beaker. Add 20 ml of hydrochloric acid (5.3), cover the beaker with a watch-glass and heat gently until solvent action ceases. Add 2 ml of nitric acid (5.5). Simmer the solution for 5 min to remove oxides of nitrogen.

8.3.2 Filtration of the test solution

After placing a filter (6.1) in the suction apparatus (6.2) and flask, wash several times with warm hydrochloric acid (5.4) and then warm water. Discard the washings from the flask prior to filtration.

Filter the warm solution (below about 75 °C) through the filter (6.1) using the suction apparatus (6.2) and collect the filtrate in a clean flask. Rinse the beaker with a small volume of water. Remove adherent particles with a clean rubber-tipped rod and transfer through the filter by rinsing with small volumes of water. Wash the beaker and filter several times with a small volume of water.

Cool and transfer the filtrate at room temperature into a 100 ml one-mark volumetric flask. Add 10,0 ml of potassium chloride/lanthanum nitrate solution (5.6). Dilute to the mark with water and mix.

8.3.3 Preparation of the calibration solutions

Place 2,00 g \pm 0,01 g of the pure iron (5.1) in a series of seven 250 ml beakers. Add 20 ml of hydrochloric acid (5.3) to each beaker, cover each with a watch-glass and heat until solvent action ceases. Add 2 ml of nitric acid (5.5). Simmer the solution for 5 min to remove oxides of nitrogen.

Using the burette, add the volumes of calcium standard solution (5.7.2) as indicated in table 1.

Proceed as specified in 8.3.2.

8.3.4 Adjustment of atomic absorption spectrometer

See table 2.

Table 1

Volume of calcium standard solution (5.7.2) ml	Corresponding concentration of calcium in final test solution $\mu\text{g/ml}$	Corresponding content of calcium in test sample % (m/m)
0 ¹⁾	0	0
1,0	0,1	0,000 5
2,0	0,2	0,001 0
4,0	0,4	0,002 0
6,0	0,6	0,003 0
8,0	0,8	0,004 0
10,0	1,0	0,005 0
1) Zero member		

Table 2

Element	Characteristic
Type of lamp	Calcium hollow cathode
Wavelength	422,7 nm
Flame	Dinitrogen monoxide-acetylene red-feather flame The height of the red-feather flame shall be 10 mm to 20 mm adjusted for maximum calcium response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations. If no recommendation is given, a bandwidth between 0,3 nm and 1,0 nm is suggested
Background correction	If the zero member gives an absorbance comparable with the precision of the least concentrated calibration solution, background correction may be required
<p>WARNING — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:</p> <p>a) the explosive nature of acetylene, and regulations concerning its use;</p> <p>b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;</p> <p>c) the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;</p> <p>d) the need to ensure that the liquid trap is filled with water;</p> <p>e) always spray water between the test solutions, blank solution and/or calibration solutions.</p>	

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8.3.5 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 to zero using water.

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria of 6.3.1 to 6.3.3.

Adjust the flame to be non-luminous and oxidizing with an approximate 10 mm to 20 mm of red feather. Spraying alternately the calibration solution of highest concentration and the zero member (see table 1), adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration

solution is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 6.3.1 to 6.3.3 and the additional performance requirement of 6.3.4, to ensure that the instrument is suitable for the determination.

8.3.6 Spectrometric measurements

Set the scale expansion so that the calibration solution of 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.