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**Kemična analiza železovih zlitin - Določanje kalcija v jeklih - Metoda s plamensko atomsko absorpcijsko spektrometrijo**

Chemical analysis of ferrous materials - Determination of calcium in steels - Flame atomic absorption spectrometric method

Chemische Analyse von Eisenwerkstoffen - Bestimmung von Calcium in Stahl -  
Flammenatomabsorptionsspektrometrisches Verfahren

Analyse chimique des matériaux sidérurgiques - Dosage du calcium dans les aciers -  
Méthode par spectrométrie d'absorption atomique dans la flamme

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Chemical analysis of metals

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**English version**

Chemical analysis of ferrous materials  
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Analyse chimique des matériaux  
 sidérurgiques - Dosage du calcium  
 dans les aciers - Méthode  
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European Committee for Standardization  
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### Brief History

This European Standard takes over the content of Euronorm 177-85 "Chemical analysis of ferrous materials - Determination of calcium in steels - Flame atomic absorption spectrometric method", prepared by ECIS/TC 20 "Methods of chemical analysis"; the Secretariat of which is allocated to the Dansk Standardiseringsrad (DS).

It has been submitted to the CEN Formal Vote following the decision of the Coordinating Commission (COCOR) of the European Committee for Iron and Steel Standardization on 1987-11-24/25.

It has been adopted and ratified by CEN BT on 1988-11-05.

According to the Common CEN/CENELEC Rules, following countries are bound to implement this European Standard:

Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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Note in clauses 1 and 9 Euronorm shall read EUROPEAN STANDARD.

# Chemical analysis of ferrous materials

## Determination of calcium in steels

### Flame atomic absorption spectrometric method

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#### 1. SCOPE AND FIELD OF APPLICATION

This EURONORM specifies a method for the determination of calcium in steels by means of flame atomic absorption spectrometry. The method is applicable to non-alloy and low alloy steels with calcium contents greater than 0.0002% (m/m).

NOTE – The method has also been successfully applied to a highly alloyed steel with appropriate modification of the calibration solutions to contain the principal alloying elements in concentrations similar to those in the sample to be analysed (see Annex).

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#### 2. REFERENCE

EURONORM 18 – Selection and preparation of samples and test pieces for steel and iron and steel products.

General guidelines for the application of flame atomic absorption spectrometric methods are in course of preparation.

#### 3. PRINCIPLE

Dissolution of a test portion with hydrochloric acid followed by oxidation with nitric acid.

Addition of potassium chloride solution and spraying of the solution into an acetylene-nitrous oxide flame.

Determination of the calcium by means of the spectrometric measurement of the atomic absorption of the 422.67 nm line emitted by a calcium hollow cathode lamp.

NOTE – Potassium chloride is added to suppress ionization of calcium and the instrument is calibrated by addition of a calcium standard solution to a similar matrix to that of the test solution.

#### 4. REAGENTS

During the analysis use only reagents of recognized analytical reagent quality and having a very low calcium content, and only distilled water or water of equivalent purity.

Carefully check the calcium content of all reagents.

If possible, use only freshly prepared distilled or deionized water.

**4.1 Iron, of high purity, free from calcium****4.2 Hydrochloric acid,  $\rho$  1.19 g/ml approximately, diluted 1 + 1 (V/V) (6 mol/l approximately)****4.3 Nitric acid,  $\rho$  1.40 g/ml approximately, diluted 4 + 6 (V/V) (5.6 mol/l approximately)****4.4 Potassium chloride, 190 g/l solution****4.5 Calcium stock solution corresponding to 1 mg of calcium per ml**

Weigh 2.500 g of pure calcium carbonate, dried at 105 °C, and transfer to a 250 ml beaker. Add 20 ml of water and then,

slowly, 20 ml of hydrochloric acid (4.2). When dissolved, dilute to 100 ml approximately and transfer to a 1 000 ml volumetric flask, dilute to the mark and mix.

**4.6 Calcium reference solution I, corresponding to 20  $\mu$ g of calcium per ml**

Using a burette or pipette, transfer 20.0 ml of the calcium stock solution (4.5) to a 1 000 ml volumetric flask, dilute to the mark and mix.

**4.7 Calcium reference solution II, corresponding to 2  $\mu$ g of calcium per ml**

Using a burette or pipette, transfer 20.0 ml of the calcium reference solution I (4.6) to a 200 ml volumetric flask, dilute to the mark and mix.

**5. APPARATUS**

Ordinary laboratory equipment and

**5.1 Atomic absorption spectrometer; a calcium hollow cathode lamp; supplies of nitrous oxide and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from calcium**

For example, if the top and bottom calibration solutions represent 0.0060% and 0.0010% calcium in the sample, the precision called for (as two standard deviations) would be 0.00036% and 0.00012% calcium respectively, assuming curve linearity.

**5.1.2 Additional performance requirements**

The atomic absorption spectrometer used will be satisfactory if after optimization according to 7.3.4 the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the following performance requirements.

It is also desirable that the instrument should conform to the following additional performance requirements.

**5.1.1 Minimum precision**

The standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution shall not exceed 3% of the mean absorbance.

The standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero calibration solution) shall not exceed 1% of the mean absorbance of the most concentrated calibration solution.

(a) **Characteristic concentration** — The characteristic concentration for calcium in a matrix similar to the final test portion solution shall be better than 0.05  $\mu$ g/ml.

(b) **Limit of detection** — The limit of detection of calcium in a matrix similar to the final sample test solution shall be better than 0.025  $\mu$ g/ml.

**5.2 Ancillary equipment**

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.1 and for all subsequent measurements.

**6. SAMPLING**

Sampling shall be carried out in accordance with EURO-NORM 18.

Degrease the chips with ethyl ether, avoiding contamination of the sample when handling.

**NOTE** — Calcium is liable to non-uniform distribution throughout the steel and it is recommended that the analysis sample should contain not less than 25 g of chips, from which the test portion (7.1) shall be drawn.

**7. PROCEDURE**

**NOTE** — All glassware shall first be washed in dilute hydrochloric acid and then in water. The quantity of calcium present in the beakers and the flasks can be checked by

measuring the absorption of the distilled water introduced into the glassware after the acid wash.

## 7.1 Test portion

Weigh the mass ( $m$ ) indicated below to the nearest 0.001 g:

$$m = 2 \text{ g} \pm 1\%.$$

## 7.2 Blank test

With each analytical run, carry out an analysis on a reagent blank in parallel with the test portion analysis, using identical reagents, conditions, analytical procedures and dilutions throughout.

## 7.3 Determination

### 7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 400 ml beaker. Add 20 ml of hydrochloric acid (4.2). Heat gently until the reaction ceases. Oxidize with 5 ml nitric acid (4.3).

Boil the solution for 5 minutes to remove oxides of nitrogen. Cool, transfer the solution to a 100 ml volumetric flask. Do not filter unless absolutely necessary. If unavoidable, use only filters known to be free of calcium. Add 0.5 ml of potassium chloride solution (4.4), dilute to the mark with water and mix.

For test solutions giving a calcium absorbance in excess of about 0.6, the solution must be diluted (dilution factor  $D$ ) and compared with calibration solutions prepared and diluted with the same iron and reagent concentrations. These more dilute solutions should also be employed if problems with burner blockage are encountered.

### 7.3.2 Preparation of the calibration solutions

Place 10 g of iron (4.1) in an 800 ml beaker and add 100 ml of hydrochloric acid (4.2). Heat gently until the reaction ceases. Oxidize with 25 ml of nitric acid (4.3).

Boil the solution for 5 minutes to remove oxides of nitrogen. Transfer to a 200 ml volumetric flask, add 2.5 ml of potassium chloride solution (4.4), dilute to the mark with water and mix.

Transfer a series of 20.0 ml aliquots to 50 ml volumetric flasks. For a calibration graph to cover the range up to 0.006% calcium add to each flask from a burette or pipette 0, 5.0, 10.0, 15.0, 20.0, 25.0; and 30.0 ml of calcium reference solution II (4.7), dilute to the mark with water and mix.

For calcium levels above 0.006% suitable aliquots of calcium reference solutions I (4.6) and II (4.7) should be used to give a range of calibration solutions with the highest level of calcium approximately twice that of the sample.

NOTE — 1 ml of calcium reference solution I (4.6) is equivalent to 0.002% calcium in the sample.

### 7.3.3 Adjustment of atomic absorption spectrometer (5.1)

Type of lamp:	Calcium hollow cathode.
Wavelength:	422.67 nm.
Flame:	Nitrous oxide/acetylene fuel-lean flame adjusted for maximum calcium response.

Lamp current —	
Slit width:	Follow manufacturer's recommendations.

NOTE — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

- the explosive nature of acetylene and regulations concerning its use;
- the need to shield the eyes of the operator from UV radiation by means of tinted glass;
- the need to keep the burner head clear of deposits. A badly clogged burner may cause a flashback;
- make sure the liquid trap is filled with water.

### 7.3.4 Optimization of 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. Choose a damping setting or integration time to give a signal steady enough to fulfil the precision requirements (5.1.1).

Adjust the flame to be fuel-lean and the burner height to about 1 cm below the light path. Spraying, alternately, the high and zero calibration solutions, adjust the gas flow and the burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum.

Evaluate the criteria of 5.1.1 to ensure that the instrument is suitable for the determination.

### 7.3.5 Atomic absorption measurements

Set the scale expansion so that the top calibration solution gives nearly full-scale deflection. Aspirate the calibration solutions in ascending order repetitively until each gives acceptable precision (see 5.1.1), thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test solution and one just higher. Aspirate 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. Aspirate the complete range of calibration solutions again.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two 'sandwiching' solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Obtain the net mean absorbance of each calibration solution by subtracting the mean absorbance of the zero calibration solution.

Obtain the mean absorbance of the test solution and the mean absorbance of the reagent blank solution.

Convert the mean absorbances of the test solution and of the reagent blank solution to micrograms of calcium per millilitre by means of the calibration graph (7.4).

## 7.4 Establishment of the calibration graph

It is necessary to draw up a new calibration graph for each series of determinations, and for the range of calcium contents expected.

Prepare a calibration graph by plotting the net mean absorbance values of the calibration solutions against micrograms of calcium per millilitre. Refer the net absorbances of the two adjacent calibration solutions to the graph. If these two

calibration readings do not deviate from the graph by more than the permitted precision criteria then the test solution readings are acceptable.

## 8. EXPRESSION OF RESULTS

The percentage by mass of calcium (Ca) is given by the expression

$$\text{Ca \% (m/m)} = \frac{(b - c) \cdot D \cdot 100}{10^6} \cdot \frac{100}{m} = \frac{(b - c) \cdot D}{100 m}$$

where:

*b* is the concentration of calcium in the test solution expressed in  $\mu\text{g/ml}$

*c* is the concentration of calcium in the reagent blank solution expressed in  $\mu\text{g/ml}$

*D* is the dilution factor applied in Section 7.3.1

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

## 9. TEST REPORT

The test report shall contain the following particulars:

- (a) the method of analysis used by reference to this Euronorm;
- (b) the results obtained, as well as the form in which they are expressed;
- (c) any particular details which may have been noted during the determination;

- (d) any operations not specified in this Euronorm or any optional operations which could have had an influence on the results;

- (e) all indications necessary for the identification of the sample;

- (f) the laboratory and the date of analysis.

## ANNEX

### Precision data

Planned trials of this method were carried out by 3 analysts from different laboratories; 10 determinations were carried

out by each analyst on each of 3 samples. From the results obtained the 95% (2s) confidence limits have been calculated in accordance with ISO 5725, and are tabulated as follows:

Alloy Type	Calcium % (m/m)	Repeatability <i>r</i>	Reproducibility <i>R</i>
0.33% C free-cutting	0.00030	0.00017	0.00025
0.36% C steels with	0.00125	0.00020	0.00023
0.43% C 1.4% Mn, 0.25% S	0.00326	0.00025	0.00048

In addition, the method was also tested by 13 laboratories on Euronorm CRM 252-1, a high chromium-nickel-molybdenum stainless steel, with results varying from 0.0015% to 0.0020%, and with a repeatability of 0.0001% within each laboratory.

than once in 20 cases in the normal and correct operation of the method.

### Repeatability

The difference between two single results found on identical material by one analyst using the same apparatus within a short time interval will exceed the repeatability, *r*, not more

### Reproducibility

The difference between two single and independent results found by two operators working in different laboratories on identical test material will exceed the reproducibility, *R*, on average not more than once in 20 cases in the normal and correct operation of the method.