

## **Bestämning av halten organiskt kol i kalksten**

## **Determination of total organic carbon in limestone**

Europastandarden EN 13639:2002 gäller som svensk standard. Detta dokument innehåller den officiella engelska versionen av EN 13639:2002 med EN 13639:2002/AC:2004 inarbetad.

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English version

## Determination of total organic carbon in limestone

Détermination du carbone organique total dans le calcaire

Bestimmung des Gesamtgehalts an organischem  
Kohlenstoff in Kalkstein

This European Standard was approved by CEN on 23 December 2001.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
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## Foreword

This document EN 13639:2002 has been prepared by Technical Committee CEN/TC 51 "Cement and building limes", the secretariat of which is held by IBN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2002, and conflicting national standards shall be withdrawn at the latest by October 2002.

The annexes A and B are informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

## 1 Scope

This European Standard specifies methods for the determination of the total organic carbon content (TOC) in limestone.

The standard describes the reference method and alternative methods which can be considered to be equivalent. In the case of a dispute, only the reference method is used.

Any other methods may be used provided they are calibrated, either against the reference method or against internationally accepted reference materials, in order to demonstrate their equivalence.

## 2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

ISO 3310-1, *Test sieves – Technical requirements and testing - Part 1: Test sieves of metal wire cloth*.

ISO 11464, *Soil quality – Pretreatment of samples for physico-chemical analyses*.

## 3 General requirements for testing

### 3.1 Number of tests

Where the analysis is one of the series subject to statistical control, determination of the total organic carbon content by a single test shall be the minimum required.

Where the analysis is not part of a series subject to statistical control, the number of tests for determination of the total organic carbon content shall be two (see also 3.3).

In the case of a dispute, the number of tests for determination of the total organic carbon content shall be two (see also 3.3).

**EN 13639:2002 (E)****3.2 General statistical terms**

**Repeatability standard deviation** - the standard deviation of test results obtained under repeatability conditions where independent test results are obtained with the same method on identical material tested in the same laboratory by the same operator using the same equipment within short intervals of time.

**Reproducibility standard deviation** - the standard deviation of test results obtained under reproducibility conditions where test results are obtained with the same method on identical material tested in different laboratories with different operators using different equipment.

NOTE Definitions based on ISO 3534-1.

The standard deviations of repeatability and reproducibility are expressed in absolute percent.

**Determination limit** - is the content where its relative uncertainty, which is assigned to a fixed probability level, and defined as the quotient of the half of a two-side prognosis interval and the content to be assigned to the determination limit, is equal to a pre-set value.

$$x_{DI} = k \cdot s_{x0} \cdot t_{f,\alpha} \sqrt{\frac{1}{n} + \frac{1}{p} + \frac{(x_{DI} - \bar{x})^2}{Q_x}} \quad (1)$$

where

$\alpha$  is the probability level

$f$  is the variability (number of degrees of freedom)

$\frac{1}{k} = \frac{\Delta x_{DI}}{x_{DI}}$  is the relative uncertainty

$n$  is the number of calibration samples

$$Q_x = \sum_{i=1}^n (x_i - \bar{x})^2$$

$p$  is the number of analyses of each calibration sample

$s_{x0}$  is the standard deviation of the procedure

$t_{f,\alpha}$  is the quantile of the  $t$ -distribution ( $f = n - 2$ )

$x_i$  is the analyzed content assigned to a calibration sample

$\bar{x}$  is the arithmetic mean of the contents assigned to all calibration samples

$x_{DI}$  is the determination limit

$\Delta x_{DI}$  is half width of the two-side prognosis interval

NOTE This determination limit is based on DIN 32645.

**3.3 Expression of masses and results**

Express masses in grams to an accuracy of  $\pm 0,0005$  g.

Express the results, as a percentage to at least two decimal places. If the difference between the individual test results exceeds two times the repeatability standard deviation given in clause 10, the test shall be repeated.

### 3.4 Blank determinations

Carry out a blank determination without a sample following the same procedure and using the same amounts of reagents. Correct the results obtained for the analytical determination.

### 3.5 Sampling and sample preparation

Depending on the size of the raw material, a sample of at least 1 kg up to 10 kg shall be taken by the procedure described in ISO 11464, dried, crushed, reduced and ground to form a representative laboratory sample for analysis. The laboratory sample shall pass a sieve of 90  $\mu\text{m}$  mesh size conforming to ISO 3310-1. The drying process shall be modified, if necessary, to accommodate samples known to contain high contents of volatile organic carbon.

### 3.6 General test principles

In general all procedures consist of the following stages:

- decarbonation of the original limestone sample;
- purification of the carrier gas, if it is not of high purified quality;
- oxidation of the organic carbon matter;
- purifying of the  $\text{CO}_2$  produced by oxidation;
- measurement of the  $\text{CO}_2$  content.

## 4 Reagents

### 4.1 General requirements

Use only reagents of analytical quality. References to water mean distilled water, or water of equal purity.

Unless otherwise stated percent means percent by mass.

The concentrated liquid reagents used in this standard have the following densities ( $\rho$ ) in grams per cubic centimetre at 20 °C.

ammonia solution	0,88 to 0,91
hydrochloric acid	1,18 to 1,19
hydrogen peroxide	1,11
nitric acid	1,40 to 1,42
phosphoric acid	1,71 to 1,75
sulfuric acid	1,84

The degree of dilution is always given as a volumetric sum, for example: dilute hydrochloric acid 1+ 2 means that 1 volume of concentrated hydrochloric acid is to be mixed with 2 volumes of water.

## EN 13639:2002 (E)

- 4.2 Ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ )**
- 4.3 Calcium chloride, anhydrous ( $\text{CaCl}_2$ )**
- 4.4 Calibration reagent.** Metal, for example iron with known carbon content.
- 4.5 Carbon dioxide in oxygen, 0,95 vol.-% and 19 vol.-%**
- 4.6 Carrier gases, depending on application: air, oxygen, nitrogen or argon, free of carbon dioxide and hydrocarbons**
- 4.7 Chromic acid.<sup>1)</sup>** Dissolve 5 g of chromium trioxide (**4.8**) in 10 ml of water. Add sulfuric acid (**4.13**) with stirring, until the chromium trioxide, which initially precipitates, is just redissolved.
- 4.8 Chromium trioxide ( $\text{CrO}_3$ )**
- 4.9 Concentrated hydrochloric acid ( $\text{HCl}$ )**
- 4.10 Concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ )**
- 4.11 Concentrated nitric acid ( $\text{HNO}_3$ )**
- 4.12 Concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ )**
- 4.13 Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ )**
- 4.14 Copper ( $\text{Cu}$ ), free of carbon**
- 4.15 Copper oxide ( $\text{CuO}$ ).** Particle size of 0,6 mm to 1,2 mm.
- 4.16 Dilute hydrochloric acid 1 + 5**
- 4.17 Dilute nitric acid 1 + 9**
- 4.18 Iron ( $\text{Fe}$ ), free of carbon**
- 4.19 Lead chromate ( $\text{PbCrO}_4$ )**
- 4.20 Magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ), anhydrous.** Particle size 0,6 mm to 1,2 mm.
- 4.21 Magnesium sulfate, anhydrous ( $\text{MgSO}_4$ )**
- 4.22 Magnesium turnings according to Grignard ( $\text{Mg}$ )**
- 4.23 Manganese dioxide ( $\text{MnO}_2$ ).** Particle size of 0,6 mm to 1,2 mm.
- 4.24 Oxalic acid dihydrate ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ )**

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1) **Warning:** Chromic acid and its mixtures with sulfuric acid, may cause cancer. Also the vapour phase is dangerous. It is therefore necessary to take special precautions when working with chromic acids. The use of chromic acid resistant fume cupboards and acid resistant gloves is obligatory.

**4.25 Oxidation catalyst.** Ignited silver permanganate with a composition of approximately  $\text{AgMnO}_4$ .

**4.26 Oxidizing mixture<sup>1)</sup>** To 85 ml sulfuric acid (4.13) in a 250 ml beaker add in order 15 ml phosphoric acid (4.12), 20 g phosphorus pentoxide (4.28), 15 g potassium dichromate (4.30), and 1 g potassium iodate (4.31). Carefully heat the mixture to about 170 °C maintaining the temperature for about 5 min and occasionally stirring with a thermometer. Allow the mixture to cool to room temperature and store it in a stoppered bottle.

**4.27 Paraffin**

**4.28 Phosphorus pentoxide ( $\text{P}_2\text{O}_5$ )**

**4.29 Platinum (1 %) on alumina pellets (Pt).** Particle size 3,2 mm, oxidation catalyst.

**4.30 Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )**

**4.31 Potassium iodate ( $\text{KIO}_3$ )**

**4.32 Silver gauze (Ag).** Wash commercially available silver gauze with ammonia solution (4.2), nitric acid 1 + 9 (4.17) and hydrogen peroxide (4.10). Rinse the gauze with water between each washing.

**4.33 Sodium hydroxide (NaOH)**

**4.34 Sodium hydroxide (NaOH) on a high surface dark coloured siliceous carrier**

**4.35 Sodium hydroxide solution.** Dissolve 40 g sodium hydroxide (4.33) in water and make up to 1 000 ml. Store in a polyethylene container.

**4.36 Sodium iodide (NaI)**

**4.37 Sodium iodide solution.** Add 10 ml of hydrochloric acid (4.9) and 150 g of sodium iodide (4.36) into a 1 l volumetric flask and dilute to 1 l with water.

**4.38 Zinc wool (Zn)**

## 5 General apparatus

**5.1 Balances** capable of weighing to an accuracy of  $\pm 0,0005$  g, and of  $\pm 0,00005$  g for alternative method 2, respectively.

**5.2 Laboratory ovens** capable of maintaining at the following temperatures:  $(75 \pm 5)^\circ\text{C}$ ;  $(105 \pm 5)^\circ\text{C}$

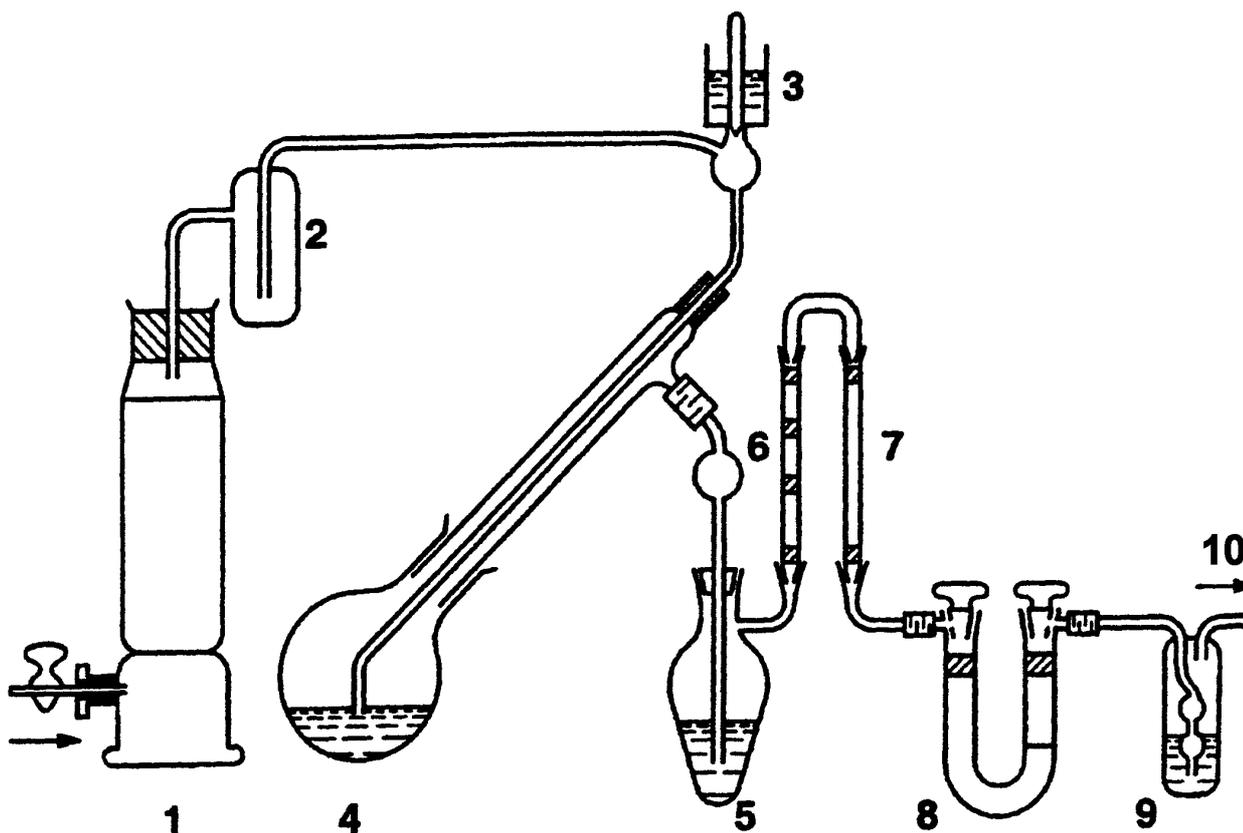
## 6 Wet oxidation method (reference method)

### 6.1 Principle

The carbon dioxide in the limestone is driven off by use of phosphoric acid (4.12). The remaining organic carbon is then oxidized to carbon dioxide with a strong oxidizing reagent mixture (4.26). The liberated carbon dioxide is absorbed on an inorganic carrier impregnated with sodium hydroxide (4.34) in a U-tube. The increase in mass is directly proportional to the organic carbon content in the sample.

## 6.2 Apparatus

The apparatus is illustrated in Figure 1. To generate reduced pressure in the apparatus a small vacuum pump or an aspirator is used. The absorption tube (see Figure 1, no. 8) is filled approximately two thirds of its volume with the absorbent for carbon dioxide (4.34) and with magnesium perchlorate (4.20). The absorption tube is then inserted into the apparatus as shown in Figure 1 drawing through it about 4 l of carrier gas (4.6). At this time the apparatus should be checked for leaks by turning off the drying tower tap whilst keeping the small vacuum pump or the aspirator trap fully open. If leaks are absent the gas flow through the bubble counter stops completely. After checking for leaks, the taps of the absorption tube are to be closed, it is transferred to a desiccator for 10 min, weighed to an accuracy of 0,0005 g ( $m_{ut}$ ), and reassembled as shown in Figure 1.



### Key

- 1 Drying tower for carrier gas containing a carbon dioxide absorbent (4.34)
- 2 Safety trap
- 3 Inlet tube for the oxidizing mixture (4.26) with glass rod stopper
- 4 150 ml round bottom distillation flask
- 5 100 ml sharp bottom flask with 50 ml chromic acid (4.7)
- 6 Absorption tube filled (in order upwards) with zinc wool (4.38), lead chromate (4.19) and silver gauze (4.32). The materials are fixed in place with cotton wool plugs
- 7 Absorption tube, filled with magnesium per-chlorate (4.20), fixed in place with cotton wool
- 8 Absorption tube with a total volume of approximately 11 cm<sup>3</sup> containing, in order, absorbent for carbon dioxide (4.34) and magnesium perchlorate (4.20), fixed in place with cotton wool plugs
- 9 Bubble counter, containing concentrated sulfuric acid (4.13)
- 10 Vacuum

Figure 1 — Apparatus for TOC determination by wet oxidation

The use of acid resistant fume cupboards and acid resistant gloves is obligatory.

### 6.3 Procedure

Weigh to an accuracy of  $\pm 0,0005$  g, ( $1,00 \pm 0,05$ ) g of limestone ( $m_1$ ). Transfer to the 150 ml round flask, add 2 ml of water and 30 ml of phosphoric acid (4.12). Heat the mixture and boil gently for 4 min to expel the carbon dioxide. Cool the mixture and connect the flask to the apparatus. Substitute for the absorption tube (see Figure 1, no. 8) a glass tube and pass 2 l of carrier gas (4.6) through the apparatus to clear the system of any carbon dioxide. Fit the weighed absorption tube again to the apparatus and check once more for leaks. Open the taps of the absorption tube<sup>2</sup>. Add approximately 30 ml of oxidizing mixture (4.26) to the flask through the inlet tube by lifting the glass rod stopper. At this stage the flow rate of the carrier gas (4.6) shall produce about 2 bubbles per second. Heat the sample mixture in the round bottom flask gently to boiling and keep at boiling for 4 min. Then remove the heater and whilst cooling pass approximately 3 l of carrier gas (4.6) through the system. Close the taps of the absorption tube. Transfer it to a desiccator, allow to cool for 30 min and weigh to an accuracy of  $\pm 0,0005$  g ( $m_{u2}$ ).

### 6.4 Calculation

Calculate the total organic carbon content in percent using the formula:

$$\text{TOC} = \frac{m_{u2} - m_{u1}}{m_1} \times 27,29 \quad (2)$$

where

$m_{u1}$  is the mass of the absorption tube before absorption of carbon dioxide in grams;

$m_{u2}$  is the mass of the absorption tube after absorption of carbon dioxide in grams;

$m_1$  is the mass of the sample in grams.

## 7 Gravimetric furnace oxidation method (alternative method 1)

### 7.1 Principle

The carbon dioxide in the limestone is driven off by use of hydrochloric acid (4.9) at approximately 130 °C. The insoluble residue is transferred to a platinum vessel. The remaining organic carbon is then oxidized in an oxygen atmosphere at approximately 900 °C and the liberated carbon dioxide is absorbed on an inorganic carrier impregnated with sodium hydroxide (4.34) in an absorption tube. The increase in mass is directly proportional to the organic carbon content in the sample.

### 7.2 Apparatus

The apparatus is illustrated in Figure 2. A hot plate or sand bath, controlled at 140 °C is also needed.

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<sup>2</sup> When the white colour has extended along the first half of the tube, change the absorbent.