SLOVENSKI STANDARD
SIST EN 13639:2017

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Določevanje celotnega organskega ogljika v apnencu

Determination of total organic carbon in limestone

Bestimmung des Gesamtgehalts an organischem Kohlenstoff in Kalkstein

Determination du carbone organique total dans le calcaire

Ta slovenski standard je istoveten z: **EN 13639:2017**

ICS:

91.100.10	Cement. Mavec. Apno. Malta	Cement. Gypsum. Lime. Mortar

SIST EN 13639:2017 **en**

EUROPEAN STANDARD

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English Version

Determination of total organic carbon in limestone

Determination du carbone organique total dans le calcaire

Bestimmung des Gesamtgehalts an organischem Kohlenstoff in Kalkstein

This European Standard was approved by CEN on 26 June 2017.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (EN 13639:2017) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

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of an identical text or by endorsement, at the latest by March 2018, and conflicting national standards shall be withdrawn at the latest by March 2018.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 13639:2002.

In comparison to EN 13639:2002, the following change has been made:

In Clause 10 a new alternative method, *Alternative method No. 4*, developed in Sweden, has been included.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

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

NOTE This method covers the determination of TOC in < 1 %.

The standard describes the reference method and alternative methods that can be considered to be equivalent.

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 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 analysis*

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 case of dispute, only the reference method is used.

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

Any other method may be used provided it is calibrated, either against the reference method or against internationally accepted reference materials, in order to demonstrate its equivalence.

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 are based on ISO 3534-1 [1].

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

Determination limit (Formula (1)) - 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.

$$x_{Dl} = k \times s_{xD} \times t_{f\alpha} \sqrt{\frac{1}{n} + \frac{1}{p} + \frac{(x_{Dl} - \bar{x})^2}{Q_x}} \quad (1)$$

where:

α is the probability level

f is the variability (number of degrees of freedom)

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

$Q_x = \sum_{i=1}^{n} (x_i - \bar{x})^2$ is the number of calibration samples

n number of test results

p is the number of analyses of each calibration sample

s_{xD} is the standard deviation of the procedure

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

x_i is the analysed content assigned to a calibration sample

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

x_{Dl} is the determination limit

Δx_{Dl} is half width of the two-side prognosis interval

NOTE This determination limit is based on DIN 32645 [2].

3.3 Expression of masses and results

Express masses in grams to an accuracy of ± 0,000 5 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 sampling 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 µm 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 the methods consist of the following procedures:

a) decarbonation of the original limestone sample;

b) purification of the carrier gas, if it is not of high purified quality;

c) oxidation of the organic carbon matter;

d) purifying of the CO_2 produced by oxidation;

e) measurement of the CO_2 content.

4 Reagents

4.1 General requirements

Application of this standard involves the use of hazardous substances.

There are national and European regulations and provisions on requirements for occupational health and safety.

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 (ρ) 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.

4.2 Ammonia solution ($NH_3 \times H_2O$)

4.3 Calcium chloride, anhydrous ($CaCl_2$)

4.4 Calibration reagent, metal

For example iron with known carbon content.

4.5 Carbon dioxide in oxygen

Concentrations, 0,95 vol.% and 19 vol.%

4.6 Carrier gases

Air, oxygen, nitrogen or argon, free of carbon dioxide and hydrocarbons, depending on application.

4.7 Chromic acid

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 re-dissolved.

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.

4.8 Chromium trioxide (CrO_3)

4.9 Concentrated hydrochloric acid (HCl)

4.10 Concentrated hydrogen peroxide (H_2O_2)

4.11 Concentrated nitric acid (HNO_3)

4.12 Concentrated phosphoric acid (H_3PO_4)

4.13 Concentrated sulfuric acid (H_2SO_4)

4.14 Copper (Cu), free of carbon

4.15 Copper oxide (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 (Fe), free of carbon

4.19 Lead chromate ($PbCrO_4$) [1]

4.20 Magnesium perchlorate ($Mg(ClO_4)_2$), anhydrous

Particle size 0,6 mm to 1,2 mm.

4.21 Magnesium sulfate, anhydrous ($MgSO_4$)

4.22 Magnesium turnings according to Grignard (Mg)

4.23 Manganese dioxide (MnO_2)

Particle size of 0,6 mm to 1,2 mm.

4.24 Oxalic acid dihydrate ($C_2H_2O_4 \times 2H_2O$)

4.25 Oxidation catalyst

Ignited silver permanganate with a composition of approximately ($AgMnO_4$).

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[1] Where substances are listed in REACH Regulation Annex XIV *List of substances subject to authorisation*, Article 56(3) of REACH provides a generic exemption from authorisation for listed substances for use in scientific research and development. Scientific research and development includes use of listed substances as reagents for analysis and quality control purposes as long as use is carried out under controlled conditions and the amount does not exceed one tonne per year, per legal entity. See FAQ [585] on ECHA's website.

4.26 Oxidizing mixture

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.

WARNING — Chromic acid, formed from mixtures of potassium dichromate and sulfuric acid, may cause cancer. Also the vapour phase is dangerous. It is therefore necessary to take special precautions when working with chromic acids.

4.27 Paraffin

4.28 Phosphorus pentoxide (P_2O_5)

4.29 Platinum (1 %) on alumina pellets (Pt), oxidation catalyst

Particle size 3,2 mm.

4.30 Potassium dichromate ($K_2Cr_20_7$) [1)]

4.31 Potassium iodate (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 litre with water.

4.38 Zinc wool (Zn)

5 General apparatus

5.1 Balances

Capable of weighing to an accuracy of ± 0,000 5 g and of ± 0,000 05 g for alternative methods 2 and 4, respectively.

5.2 Laboratory ovens

Capable of being maintained at the following temperatures: (75 ± 5) °C and (105 ± 5) °C.