SLOVENSKI STANDARD

SIST-TP CEN/TR 196-4:2008

01-marec-2008

Nadomeġļa:

SIST ENV 196-4:1995

Metode preskuġanja cementa - 4. del: Kvantitativno doloļanje sestavin

Methods of testing cement - Part 4: Quantitative determination of constituents

Prüfverfahren für Zement - Teil 4: Quantitative Bestimmung der Bestandteile

Méthodes d'essais des ciments - Partie 4 : Détermination quantitative des constituants

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Ta slovenski standard je istoveten z: **CEN/TR 196-4:2007**

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ICS:

91.100.30

SIST-TP CEN/TR 196-4:2008 **en,de**

2003-01.Slovenski inštitut za standardizacijo. Razmnoževanje celote ali delov tega standarda ni dovoljeno.

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TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 196-4

September 2007

ICS 91.100.30

Supersedes ENV 196-4:1993

English Version

Methods of testing cement - Part 4: Quantitative determination of constituents

Méthodes d'essais des ciments - Partie 4 : Détermination quantitative des constituants

Prüfverfahren für Zement - Teil 4: Quantitative Bestimmung der Bestandteile

This Technical Report was approved by CEN on 14 April 2007. It has been drawn up by the Technical Committee CEN/TC 51.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Ref. No. CEN/TR 196-4:2007: E

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Foreword

This document (CEN/TR 196-4:2007) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

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

This document supersedes ENV 196-4:1993.

This European Technical Report was drawn up by Technical Committee CEN/TC 51 "*Cement and building limes*" the Secretariat of which is held by NBN. It is based on a revision of the European Pre-standard ENV 196-4 of July 1993.

The main aim of this document is to quantitatively verify the compositions (analysis of the constituents) of all the cements included in EN 197-1:2000 (Cements – Part1: composition, specifications and conformity criteria for common cements) as set out in Table 1 “The 27 products in the family of common cements”.

Further to this objective, original methods of analysis were devised, firstly, for cements with 3 constituents and then a reference method for cements with more constituents. Following the progress of work on EN 197-1, cements with blastfurnace slag, siliceous fly ash and natural pozzolans have been successively studied. As a result the first draft of ENV 196-4 was published in December 1989, followed by the ENV 196-4 in July 1993.

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The main aim of the revision of the Pre-standard was to adapt the reference method in such a way that it would be qualitative and quantitative whatever the constituent materials, including blastfurnace slag (which had not been included in the 1989 draft ENV 196-4). This entailed revising the analytical procedure and the calculation of the constituents.

The opportunity was taken at the same time to unify the presentation of the different methods, reference and alternative, endeavoring to standardize the notational symbols to eliminate all ambiguities in the interpretation of the formulae for calculations.

Table 1 of ENV 197-1:1992 introduced further new constituent materials. One of them, silica fume, could be routinely determined by the reference method, while calcareous fly ash and burnt shale, being composites of several minerals, react partially like other constituents capable of being determined by the reference method. Where these materials are constituents it has proved not to be possible to determine the mass composition of the cement but only to obtain an overall bulk analysis.

Almost all of the cements manufactured in Europe can be correctly characterized and quantified by the reference method. However, for cements containing burnt shale (CEM II/A-T and B-T) or calcareous fly ash (CEM II/A-W and B-W) it would be necessary to undertake further research in order to obtain an acceptable reference method.

For cements having constituents that can be analyzed by the current reference method as defined in section 1 “Scope” the method will be adequate. Where other constituents are known, or suspected, to be included it will be necessary to develop additional methods for the quantitative determination of those particular constituents.

The European Standard on the methods of testing cement comprises the following Parts:

EN 196-1 *Methods of testing cement — Part 1: Determination of strength*

EN 196-2 *Methods of testing cement — Part 2: Chemical analysis of cement*

EN 196-3 *Methods of testing cement — Part 3: Determination of setting times and soundness*

EN 196-5 *Methods of testing cement — Part 5: Pozzolanicity test for pozzolanic cement*

EN 196-6 *Methods of testing cement — Part 6: Determination of fineness*

EN 196-7 *Methods of testing cement — Part 7: Methods of taking and preparing samples of cement*

EN 196-8 *Methods of testing cement — Part 8: Heat of hydration — Solution method*

EN 196-9 *Methods of testing cement — Part 9: Heat of hydration — Semi-adiabatic method.*

NOTE A previous Part, EN 196- 21: Methods of testing cement — Part 21: Determination of the chloride, carbon dioxide and alkali content of cement, has been revised and incorporated into EN 196-2

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1 Scope

This European Technical Report describes procedures for determining the contents of most of the constituents of the cements that fall within the scope of EN 197-1.

In principle, the method described in Clause 6 applies to all cements, whatever the number and nature of their constituents, but in practice is limited to the cements identified in Table 1.

The method in clause 6 should be considered to be the method of choice and is based on a sequential selective dissolution of the cement's constituents, generally of an unknown number, where they are not available separately for analysis at the same time as the cement.

The method of choice enables the quantitative determination (by mass) of: Portland cement clinker, blastfurnace slag, siliceous fly ash, natural pozzolans, limestone, silica fume and set regulators in cements of the types identified in Table 1. Table 1 is derived from Table 1 of EN 197-1.

Table 1 — Common cement types specified in EN 197-1

Type of cement	Designation	Notation	Excluding (1)
CEM I	Portland cement	I	
CEM II	Portland-slag cement (with blastfurnace slag)	II/A-S II/B-S	
	Portland-silica fume cement	II/A-D	
	Portland pozzolana cement (with natural pozzolana)	II/A-P II/B-P	
	Portland-fly ash cement (with siliceous fly ash)	II/A-V II/B-V	
	Portland-limestone cement	II/A-L or LL* II/B-L or LL*	
	Portland-composite cement	II/A-M II/B-M	limestone Burnt shale
CEM III	Blastfurnace cement	III/A III/B III/C	
CEM IV	Pozzolanic cement	IV/A IV/B	
CEM V	Composite cement	V/A V/B	

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*The method is incapable of distinguishing between limestones of type L and LL

NOTE 1 Where cements contain calcareous fly ash, burnt shale and/or constituents that partly contain mineral phases, similar to those of clinker, further investigation into the characteristics of those constituents will be necessary before the method can be applied.

The method of choice has limitations, as indicated earlier, and cannot be considered to be a means by which clinker content can simply be determined in isolation from any other constituent. Clinker content is determined 'by difference' and other constituents contain, in part, mineral phases similar to those present in clinker and can cause interferences that lead to difficulties in interpretation of the results.

Where apparently anomalous results are obtained, it is recommended that further investigations are undertaken in accordance with the procedure given in Section 6.2.5.4.

Any other method with the same objectives, and intended for use where the constituents are unavailable for separate analysis, can be considered to be an alternative to the method of choice when it is shown that, with appropriate statistical validity, it gives equivalent results.

In individual cases, where the laboratory has been formally advised that:

— the cement contains only two constituents, the method is greatly simplified because it is sufficient to determine the set regulator content (R) in order to be able to calculate the clinker content by difference;

— the cement contains only three constituents, i.e. a set regulator, clinker and one of the following three: slag, pozzolana or siliceous fly ash. Some of the methods in clause 7 are variations on the method of choice whereas others are based on physical separation of constituents and different analytical principles.

NOTE 2 This European Technical Report adopts the following use of terms for major constituents:

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— 'Portland cement clinker' as defined in EN 197-1 is referred to as 'clinker';

— 'granulated blastfurnace slag' as defined in EN 197-1 is referred to as 'slag';

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— 'natural pozzolans' as defined in EN 197-1 is referred to as 'pozzolans';

— 'siliceous fly ash' as defined in EN 197-1 is referred to as 'fly ash';

— 'calcium sulfate' as defined in EN 197-1 is referred to as 'set regulator'.

2 Normative references

This European Technical Report 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 Technical Report only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 196-2, *Methods of testing cement — Part 2: Chemical analysis of cements*

EN 196-7, *Methods of testing cement — Part 7: Methods of taking and preparing samples of cement*

EN 197-1, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*

ISO 3534, *Statistics — Vocabulary and symbols*

3 General requirements for testing

3.1 Number of tests

To carry out the calculation for the contents of the cement constituents, two tests shall be made for each. The following analytes are determined:

— for the method of choice by selective dissolution (clause 6):
sulfuric anhydride and carbon dioxide contents, residues after EDTA and nitric acid dissolution and sulfide contents in the cement and in the EDTA residue;

— for the methods of analysis for cements with three constituents (clause 7):
sulfuric anhydride and carbon dioxide contents, loss on ignition, calcium oxide, magnesium oxide and manganese oxide contents, sulfide contents and insoluble residues. Depending on the method used, only some of these analytes can be determined.

If, for each analyte, the difference between the two values obtained is less than twice the standard deviation for repeatability for this analyte, the value to take for further calculations is the arithmetic mean of the two values. If the difference between the two values is greater than twice the standard deviation for repeatability, a third test shall be carried out and the value to be taken for further calculations shall be the arithmetic mean of the two closest values.

Hence, for the method of choice by selective dissolution, only one calculation will need to be carried out for the quantitative determination of constituents, in particular for clinker.

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Likewise, for the methods of analysis for cements with three constituents, a single calculation will enable the content of hydraulic or pozzolanic constituent to be determined.

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The standard deviations for repeatability of the various analytes to be considered, most of which can be found in EN 196-2: 2005, are as follows:

Analyte	**Standard deviation for repeatability (s_r in % by mass)**
SO_3	0,07
CO_2	0,07
a (EDTA residue)	0,50
b (HNO_3 residue)	0,11
S^{2-}	0,02
CaO	0,18
MgO	0,15
MnO	0,003
insoluble residue	0,10
loss on ignition	0,04

3.2 Determination of constant mass

Constant mass shall be determined by making successive 15 min ignitions, followed each time by cooling and then by weighing. Constant mass is reached when the difference between two successive weighing is less than 0,0005 g.

3.3 Expression of masses and results

Express masses in grams to the nearest 0,0001 g.

Express the values for the analytes, given by the mean of two determinations (see 3.1) as the contents of constituents calculated in percentages, to one decimal place.

3.4 Repeatability and reproducibility

Repeatability - Precision under repeatability conditions where independent test results are obtained with the same method on identical test items (material) in the same laboratory by the same operator using the same equipment within short intervals of time.

Reproducibility - Precision under reproducibility conditions where test results are obtained with the same method on identical test items (material) in different laboratories with different operators using different equipment.

Repeatability and reproducibility in this document are expressed as repeatability standard deviation(s) and reproducibility standard deviation(s) in absolute percent and relate to clinker contents for the general method of determination of the constituents by selective dissolution and to hydraulic and pozzolanic contents for the methods of analysis of cement with three constituents

4 Preparation of a cement sample

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Before analysis, the laboratory sample taken in accordance with the provisions of EN 196-7 shall be treated to obtain a test sample.

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The details of this treatment of the sample differs according to the methods used and is specified at the start of each procedure (see 6.2.4.1, 7.2.1.4.1, 7.2.2.3.1, 7.3.1.4.1, 7.4.1.4.1 and 7.4.2.4.1).

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5 Reagents

Use only reagents of analytical quality. References to water mean distilled water or de-ionised water having an electrical conductivity ≤ 0,5 mS/m.

Unless otherwise specified, “%” means “% by mass”

The density "ρ" of liquids is given at 20 °C. The densities of concentrated liquid reagents are expressed in g/cm^3.

The degree of dilution is always given in the form of a volumetric sum, for example, nitric acid (1+2) means that 1 volume of concentrated nitric acid has to be mixed with 2 volumes of water.

6 Determination of the contents of cement constituents

6.1 General

This method applies to cements with several constituents, i.e.:

— clinker;

— hydraulic, pozzolanic or inert constituents;

— set regulator(s).

The constituents determined by this method are classified as follows:

— set regulator;

— clinker;

— slag;

— (undifferentiated) calcareous constituents (i.e. combinations of any limestone, chalk, or materials derived from the clinker production process, etc);

— (undifferentiated) siliceous constituents (i.e. combinations of any flint, natural pozzolana, siliceous fly ash, silica fume, etc).

Their number is therefore five in principle, but

— some constituents, mainly calcareous or siliceous, can contain one or more components of the same nature although it may not be possible to identify them separately.

— these same (undifferentiated) calcareous or siliceous constituents, could contain one or more of each type, e.g. chalk can contain flint inclusions; some siliceous fly ashes and pozzolans have compositions similar to calcareous fly ashes. It is therefore not possible, using the method in this clause, to precisely identify the constituents of cement because of the possibility of the content of each type being modified by the other.

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Should there be a need to determine (differentiate) the nature of the calcareous or siliceous constituents more precisely, further enquiries should involve the manufacturer of the cement as described in 6.2.5.4.

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The results obtained from the application of this method are quantitatively valid, whatever the relative importance of the constituents identified.

6.2 Selective dissolution method

6.2.1 Principle

Following preparation, one fraction of the cement sample is treated with a solution containing triethanolamine (TEA), diethylamine (DEA) and EDTA.

Another fraction is treated with dilute nitric acid (see Table 2).

The results from these two selective dissolutions and the additional determinations of the sulfuric anhydride and carbon dioxide contents of the cement together with the sulfide contents of the cement and the residue from the dissolution in the EDTA solution enable the contents of the various constituents to be calculated.

Table 2 — Reagents and their effects

Reagent	Soluble	Insoluble
EDTA solution	Set regulator(s) Clinker Calcareous constituent(s)	Slag Pozzolana Fly ash Siliceous constituent(s) Silica fumes
Dilute nitric acid	Set regulator(s) Clinker Calcareous constituent(s) Slag	Pozzolana Fly ash Siliceous constituent(s) Silica fumes

6.2.2 Reagents

a) Triethanolamine (TEA) : $N(CH_2CH_2OH)_3$
[p = 1,12 g/cm^3]

b) EDTA: dihydrate of the disodium salt of ethylene-diamine-tetracetic acid
$C_{10}H_{14}N_2Na_2O_8.2H_2O$

c) Diethylamine (DEA): $(C_2H_5)_2NH$

d) Ethanol: C_2H_5OH (ethyl alcohol)

e) Concentrated nitric acid: HNO_3
[p (1,40 to 1,42) g/cm^3]

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6.2.3 Apparatus

a) *Balance*, capable of weighing to the nearest 0,0001 g.

b) *Drying oven*, controlled at (105 ± 5) °C.

c) Apparatus, to check the *temperature at (20 ± 0,5) °C.*

d) *Electrically controlled stirrer*, fitted with a glass propeller.

e) *Glass microflbre filter papers,* with a porosity of the order of 1 µm to 2 µm and a maximum diameter of 9 cm that fits the funnel of the filtration system. Insert above and below the filter a ring of polytetrafluoroethylene (PTFE) obtained from the supplier in order to improve the collection of particles on the filter. The filter shall be resistant to alcohol and alkalis and shall be dried to constant mass at 105 °C.

f) *Filter paper*, capable of retaining particles between 4 µm and 12 µm to use in case of particularly fine filtration. If necessary, two superimposed glass microfibre filters can be used.

g) *Vacuum filtration system,* capable of being used with glass microfibre filter papers.

h) *Desiccator,* containing anhydrous magnesium perchlorate.

i) *Volumetric glassware*, of analytical accuracy,
i.e. class A as defined in ISO 385-1 and ISO 835-1.