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Metode preskušanja cementa - 2. del: Kemijska analiza cementa

Methods of testing cement - Part 2: Chemical analysis of cement

Prüfverfahren für Zement - Teil 2: Chemische Analyse von Zement

Méthodes d'essais des ciments - Partie 2: Analyse chimique des ciments

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Methods of testing cement - Part 2: Chemical analysis of cement

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Prüfverfahren für Zement - Teil 2: Chemische Analyse von Zement

This European Standard was approved by CEN on 29 December 2004.

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Foreword

This document (EN 196-2:2005) has been prepared by Technical Committee CEN/TC 51 '*Cement and building limes*', the secretariat of which is held by IBN/BIN.

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of an identical text or by endorsement, at the latest by August 2005, and conflicting national standards shall be withdrawn at the latest by August 2005.

This document supersedes EN 196-2:1994 and EN 196-21:1989.

This 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 time and soundness*

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

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.

Another document, ENV 196-4 *Methods of testing cement — Part 4: Quantitative determination of constituents*, has been drafted and will be published as a CEN Technical Report.

This edition introduces the following technical changes based on comments received by the secretariat:

a) EN 196-21 has been consolidated into EN 196-2;

b) calibration against internationally accepted reference materials is permitted;

c) the number of tests to be carried out, when the analysis is part of a series subject to statistical control, has been reduced to one;

d) a requirement for blank determinations has been included;

e) limiting ranges have been set for masses, volumes and temperatures wherever these are significant;

f) the required accuracy of the balance is consistent with that of equipment traditionally used;

g) a specification for a laboratory oven has been included;

h) the calibration procedure for standard silica solution has been simplified;

i) additional indicators have been included for the visual determination of EDTA titrations;

j) an ignition temperature of (950 ± 25) °C has been set for the determination of loss on ignition and the ignition of barium sulfate and insoluble residues;

k) determination of sulfate before and after ignition in the determination of loss on ignition becomes the reference method when correcting for sulfide;

l) determination of silica by the double evaporation method becomes the reference method;

m) in the determination of carbon dioxide by decomposition with sulfuric acid an additional, empty, gas washing bottle is included as a safety precaution against the reverse flow of sulfuric acid should pressure be lost;

n) in the determination of alkali the influence of phosphoric acid on the potassium emission from the calibration solutions is suppressed by the addition of calcium to the calibration solutions. The procedure is adjusted accordingly.

Analytical methods utilising x-ray fluorescence (XRF) were considered during this revision but no published, standardised method was considered sufficiently comprehensive to be included. A new work item has been established by CEN/TC51 in order to prepare a method based on XRF.

XRF and other instrumental methods such as differential thermal analysis for determination of carbon dioxide, atomic absorption spectroscopy, etc. may be used as alternative methods provided they are calibrated against the reference methods, or against internationally accepted reference materials.

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

1 Scope

This document specifies the methods for the chemical analysis of cement.

This document describes the reference methods and, in certain cases, an alternative method which can be considered to be equivalent. In the case of a dispute, only the reference methods are used.

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

This document describes methods which apply principally to cements, but which can also be applied to their constituent materials. They can also be applied to other materials, the standards for which call up these methods.

Standard specifications state which methods are used.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 835-1, *Laboratory glassware — Graduated pipettes — Part 1: General requirements*

3 General requirements for testing

3.1 Number of tests

Analysis of a cement may require the determination of a number of its chemical properties. For each determination one or more tests shall be carried out in which the number of measurements to be taken shall be as specified in the relevant clause of this document.

Where the analysis is one of a series subject to statistical control, determination of each chemical property 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 each chemical property shall be two (see also 3.3).

In the case of a dispute, the number of tests for determination of each chemical property shall be two (see also 3.3).

3.2 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 e.g. absolute percent, grams, etc., according to the property tested.

3.3 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0,000 1 g and volumes from burettes in millilitres to the nearest 0,05 ml.

Express the factors of solutions, given by the mean of three measurements, to three decimal places.

Express the results, where a single test result has been obtained, as a percentage generally to two decimal places.

Express the results, where two test results have been obtained, as the mean of the results, as a percentage generally to two decimal places.

If the two test results differ by more than twice the standard deviation of repeatability, repeat the test and take the mean of the two closest test results.

The results of all individual tests shall be recorded.

3.4 Ignitions

Carry out ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate slowly in an oxidising atmosphere in order to avoid immediate flaming, while ensuring complete combustion. Ignite the crucible and its contents at the stated temperature then allow to cool to the laboratory temperature in a desiccator. Weigh the crucible and its contents.

3.5 Determination of constant mass

Determine constant mass by making successive 15 min ignitions followed each time by cooling and then weighing. Constant mass is reached when the difference between two successive weighings is less than 0,000 5 g.

3.6 Check for absence of chloride ions (silver nitrate test)

After generally five to six washes of a precipitate, rinse the base of the filter stem with a few drops of water. Wash the filter paper and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (4.43). Check the absence of turbidity or precipitate in the solution. If present, continue washing while carrying out periodic checks until the silver nitrate test is negative.

3.7 Blank determinations

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

4 Reagents

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

Unless otherwise stated percent means percent by mass.

Unless otherwise stated the concentrated liquid reagents used in this document have the following densities (ρ) (in g/cm^3 at 20 °C):

hydrochloric acid	1,18 to 1,19	acetic acid	1,05 to 1,06
nitric acid	1,40 to 1,42	phosphoric acid	1,71 to 1,75
perchloric acid	1,60 to 1,67	ammonium hydroxide	0,88 to 0,91

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.

4.1 Concentrated hydrochloric acid (HCl)

4.2 Dilute hydrochloric acid 1 + 1

4.3 Dilute hydrochloric acid 1 + 2

4.4 Dilute hydrochloric acid 1 + 3

4.5 Dilute hydrochloric acid 1 + 9

4.6 Dilute hydrochloric acid 1 + 11

4.7 Dilute hydrochloric acid 1 + 19

4.8 Dilute hydrochloric acid 1 + 99

4.9 Dilute hydrochloric acid of pH (1,60 ± 0,05). Prepare by adjusting the pH of two litres of water to (1,60 ± 0,05) by adding five or six drops of concentrated hydrochloric acid. Control using the pH meter (5.18.1). Store the solution in a polyethylene container.

4.10 Concentrated hydrofluoric acid (> 40 %) (HF)

4.11 Dilute hydrofluoric acid 1 + 3

4.12 Concentrated nitric acid (HNO_3)

4.13 Dilute nitric acid 1 + 2

4.14 Dilute nitric acid 1 + 100

4.15 Concentrated sulfuric acid (>98 %) (H_2SO_4)

4.16 Dilute sulfuric acid 1 + 1

4.17 Dilute sulfuric acid 1 + 4

4.18 Concentrated perchloric acid ($HClO_4$)

4.19 Concentrated phosphoric acid (H_3PO_4)

4.20 Dilute phosphoric acid 1 + 19; store this solution in a polyethylene container.

4.21 Boric acid (H_3BO_3)

4.22 Concentrated acetic acid (CH_3COOH)

4.23 Amino-acetic acid (NH_2CH_2COOH)

4.24 Metallic chromium (Cr), in powder form

4.25 Concentrated ammonium hydroxide (NH_4OH)

4.26 Dilute ammonium hydroxide 1 + 1

4.27 Dilute ammonium hydroxide 1 + 10

4.28 Dilute ammonium hydroxide 1 + 16

4.29 Sodium hydroxide (NaOH)

4.30 Sodium hydroxide solution 4 mol/l. Dissolve 160 g of sodium hydroxide (4.29) in water and make up to 1 000 ml. Store in a polyethylene container.

4.31 Sodium hydroxide solution 2 mol/l. Dissolve 80 g of sodium hydroxide (4.29) in water and make up to 1 000 ml. Store in a polyethylene container.

4.32 Ammonium chloride (NH_4Cl)

4.33 Tin (II) chloride ($SnCl_2.2H_2O$)

4.34 Potassium iodate (KIO_3), dried to constant mass at (120 ± 5) °C.

4.35 Potassium periodate (KIO_4)

4.36 Sodium peroxide (Na_2O_2), in powder form.

4.37 Sodium chloride (NaCl), dried to constant mass at (110 ± 5) °C.

4.38 Potassium chloride (KCl), dried to constant mass at (110 ± 5) °C.

4.39 Sodium carbonate (Na_2CO_3), dried to constant mass at (250 ± 10) °C.

4.40 Mixture of sodium carbonate and sodium chloride. Mix 7 g of sodium carbonate (4.39) with 1 g sodium chloride (NaCl) (4.37).

4.41 Barium chloride solution. Dissolve 120 g of barium chloride ($BaCl_2.2H_2O$) in water and make up to 1 000 ml.

4.42 Silver nitrate ($AgNO_3$), dried to constant mass at (150 ± 5) °C.

4.43 Silver nitrate solution. Dissolve 5 g of silver nitrate ($AgNO_3$) (4.42) in water, add 10 ml of concentrated nitric acid (HNO_3) (4.12) and make up to 1 000 ml with water.

4.44 Silver nitrate solution 0,05 mol/l. Dissolve (8,494 0 ± 0,000 5) g of silver nitrate ($AgNO_3$) (4.42) in water in a 1 000 ml volumetric flask and make up to the mark. Store in a brown glass container and protect from the light.

4.45 Sodium carbonate solution. Dissolve 50 g of anhydrous sodium carbonate (4.39) in water and make up to 1 000 ml.

4.46 Potassium hydroxide solution. Dissolve 250 g of potassium hydroxide (KOH) in water and make up to 1 000 ml. Store in a polyethylene container.

4.47 Ammoniacal zinc sulfate solution. Dissolve 50 g of zinc sulfate ($ZnSO_4.7H_2O$) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (4.25). Leave to stand for at least 24 h and filter.

4.48 Lead acetate solution. Dissolve approximately 0,2 g of lead acetate ($Pb(CH_3COO)_2.3H_2O$) in water and make up to 100 ml.

4.49 Starch solution. To 1 g of starch (water soluble), add 1g of potassium iodide (KI), dissolve in water and make up to 100 ml. Use within two weeks.

4.50 Polyethylene oxide solution. Dissolve 0,25 g of polyethylene oxide ($(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_n$) of average molecular mass 200 000 to 600 000, in 100 ml water while stirring vigorously. Use within two weeks.

4.51 Boric acid solution, saturated. Dissolve approximately 50 g of boric acid (H_3BO_3) in water and make up to 1 000 ml.

4.52 Citric acid solution. Dissolve 10 g of citric acid ($C_6H_8O_7.H_2O$) in water and make up to 100 ml.

4.53 Calcium carbonate ($CaCO_3$), dried to constant mass at (200 ± 10) °C (of purity > 99,9 %).

4.54 Ammonium molybdate solution. Dissolve 10 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and make up to 100 ml. Store the solution in a polyethylene flask. Use within one week.

4.55 Copper sulfate solution. Dissolve 0,45 g of copper sulfate ($CuSO_4.5H_2O$) in water and make up to 50 ml in a volumetric flask.

4.56 Ammonium acetate solution. Dissolve 250 g of ammonium acetate (CH_3COONH_4) in water and make up to 1 000 ml.

4.57 Triethanolamine $N(CH_2CH_2OH)_3$ (>99 %) diluted to 1 + 4 solution.

4.58 Reducing solution. Dissolve 1 g of tin (II) chloride ($SnCl_2.2H_2O$) (4.33) in water to which has been added 1 ml of concentrated hydrochloric acid (4.1). Make up to 100 ml with water. Use within one day.

4.59 Buffer solution of pH 1,40. Dissolve (7,505 ± 0,001) g of amino-acetic acid (4.23) and (5,850 ± 0,001) g of sodium chloride (NaCl) (4.37) in water and make up to 1 000 ml. Dilute 300 ml of this solution to 1 000 ml with hydrochloric acid 1 + 99 (4.8).

4.60 Standard potassium iodate solution, approximately 0,016 6 mol/l. Weigh, to ± 0,000 5 g, (3,6 ± 0,1) g, of potassium iodate (KIO_3) (4.34) (m_1) and place in a 1000 ml volumetric flask. Add 0,2 g of sodium hydroxide (4.29), 25 g of potassium iodide (KI), dissolve all the solids in freshly boiled and cooled water and make up to the mark using the same water.

Calculate the factor F of the potassium iodate solution from the following formula:

$$F = \frac{m_1}{3{,}566\,8} \qquad (1)$$

where m_1 is the mass of the portion of potassium iodate, in grams.

4.61 Sodium thiosulfate solution approximately 0,1 mol/l

4.61.1 Preparation

Dissolve (24,82 ± 0,01) g of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in water and make up to 1 000 ml. Before each test series, determine the factor *f* of this solution as described in 4.61.2.

4.61.2 Standardization

4.61.2.1 This standardization is carried out preferably using the standard potassium iodate solution (4.60).

For this standardization, pipette 20 ml of the standard potassium iodate solution (4.60) into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1+1 (4.2) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (4.61.1) to a pale yellow colour. Add 2 ml of the starch solution (4.49) and continue the titration until the colour changes from blue to colourless.

Calculate the factor *f* of the sodium thiosulfate solution from the formula:

$$f = \frac{20 \times 0{,}016\,67 \times 214{,}01 \times F}{3{,}566\,8 \times V_1} = 20 \times \frac{F}{V_1} \qquad (2)$$

where

F is the factor of the standard potassium iodate solution (4.60);

V_1 is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration, in millilitres;

3,566 8 is the mass of potassium iodate corresponding to a solution with exactly 0,016 67 mol/l of potassium iodate, in grams;

214,01 is the molecular mass of KIO_3, in grams.

4.61.2.2 The standardization may alternatively be carried out using a known quantity of potassium iodate.

For this standardization, weigh, to ± 0,000 5 g, (0,070 ± 0,005) g of potassium iodate (4.34) (m_2) and place in a 500 ml conical flask. Dissolve in approximately 150 ml of water. Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1+1 (4.2) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (4.61.1) until a pale yellow colour is obtained. Then add 2 ml of the starch solution (4.49) and titrate until the colour changes from blue to colourless.

Calculate the factor *f* of the sodium thiosulfate solution from the formula:

$$f = \frac{1000 \times m_2}{3{,}566\,8 \times V_2} = 280{,}363\,4 \times \frac{m_2}{V_2} \qquad (3)$$

where

m_2 is the mass of potassium iodate, in grams;

V_2 is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration, in millilitres;

3,566 8 is the mass of potassium iodate corresponding to a solution with exactly 0,016 67 mol/l of potassium iodate, in grams.

4.62 Standard manganese solution

4.62.1 Anhydrous manganese sulfate

Dry hydrated manganese sulfate ($MnSO_4.xH_2O$) to constant mass at (250 ± 10) °C. The composition of the product obtained corresponds to the formula $MnSO_4$.

4.62.2 Preparation

Into a 1 000 ml volumetric flask, weigh, to ± 0,000 5 g, (2,75 ± 0,05) g of anhydrous manganese sulfate (m_3); dissolve in water and make up to the mark. Calculate the content G of manganese (II) ions of this solution, expressed in milligrams of Mn^{2+} per millilitre, from the formula:

$$G = \frac{m_3}{2{,}748\,5} \qquad (4)$$

where m_3 is the mass of anhydrous manganese sulfate, in grams.

4.62.3 Construction of the calibration curve

Into each of two volumetric flasks, respectively 500 ml (No. 1) and 1 000 ml (No. 2), pipette 20 ml of the standard manganese solution. Make up to the mark with water. Into each of three volumetric flasks, respectively 200 ml (No. 3), 500 ml (No. 4) and 1 000 ml (No. 5) pipette 100 ml of the solution from flask No. 2 and make up to the mark with water.

Take 100 ml of each solution from flasks 1 to 5 and pipette each portion into a 400 ml beaker. Add 20 ml of concentrated nitric acid (4.12), 1,5 g of potassium periodate (4.35) and 10 ml of phosphoric acid (4.19), heat to boiling and boil gently for 30 min.

Allow to cool to room temperature and transfer the contents of each beaker to a 200 ml volumetric flask and make up to the mark with water. Measure the absorbance of the solutions using a photometer (5.10) at a wavelength of around 525 nm, against water (use one or more cells (5.11) of appropriate sizes). Record the absorbance values to three decimal places.

For each cell optical length construct a separate curve of the absorbance of these calibration solutions E1 to E5 as a function of the corresponding manganese concentrations in milligrams of Mn per 200 ml. The corresponding manganese concentrations are given in Table 1. They can be used as given if the content G obtained in accordance with 4.62.2 has the value 1,000 0. Otherwise, multiply the manganese concentrations in Table 1 by the value of G calculated from equation (4).

Table 1 — Concentrations of manganese calibration solutions

Calibration solution	E1	E2	E3	E4	E5
Concentration of manganese in mg of Mn per 200 ml	4,0	2,0	1,0	0,4	0,2

4.63 Standard silica solution

4.63.1 Silica (SiO_2), of purity >99,9 % after ignition to constant mass at (1 175 ± 25) °C.

4.63.2 Basic solution

Weigh (0,200 0 ± 0,000 5) g of freshly ignited silica (4.63.1),in a platinum crucible already containing (2,0 ± 0,1) g of anhydrous sodium carbonate (4.39).

Heat the mixture and fuse it at a bright-red heat for at least 15 min. After cooling to room temperature, place the fused solid in a polyethylene beaker and dissolve it in water, then transfer the solution quantitatively to a 200 ml volumetric flask and make up to the mark with water.

Store the solution in a polyethylene container.

This solution contains 1 mg of SiO_2 per millilitre.

4.63.3 Standard solution

Pipette 5 ml of the basic solution into a 250 ml volumetric flask and make up to the mark with water. Store the solution in a polyethylene container. This solution contains 0,02 mg silica per millilitre. Use within one week.

4.63.4 Compensating solutions

Prepare the compensating solutions according to the procedure adopted in the determination of silica content (13.3 to 13.5) by dissolving the amounts of the reagents given in Table 2 in water and making up to 500 ml.

4.63.5 Construction of the calibration curve

Add from a burette the volumes of the silica calibration solutions given in Table 3 into 100 ml polyethylene beakers each containing a magnetic stirrer bar. Add 20 ml of the compensating solution by pipette and make up to 40 ml with water from a burette. The volumes required for this are also given in Table 3. While stirring with a magnetic stirrer, add 15 drops of hydrofluoric acid 1+3 (4.11). Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (4.51) into the solution.