EUROPEAN STANDARD

NORME EUROPEENNE

EUROPAISCHE NORM

EN 196
Part 21

December 1989

UDC 666.94:691.54:620.1:543.84

Key words: Cements, tests, chemical analysis, determination of content, chlorides, carbon dioxide, alkali

English version

Methods of testing cement; Determination of the chloride, carbon dioxide and alkali content of cement.

Méthodes d'essais des ciments; Détermination de la teneur en chlorures, en dioxide de carbone et en alcalis dans les ciments.

Prüfverfahren für Zement; Bestimmung des Chlorid-, Kohlenstoffdioxid- und Alkalianteils von Zement.

This European Standard was accepted by CEN on 1989-06-16. CEN members are bound to comply with the requirements of the CEN/CENELEC Common Rules 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 Central Secretariat 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 CEN Central Secretariat has the same status as the official versions.

CEN members are the national standards organizations of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue Bréderode 2, B-1000 Brussels

(c) CEN 1989 Copyright reserved to all CEN members

Ref. No. EN 196-21:1989 E

Copyright by the European Committee For Standardization
Mon Feb 28 14:30:41 2005

azmanco.com

BRIEF HISTORY

This European Standard was prepared by Technical Committee CEN/TC 51 'Cement', the Secretariat of which is held by IBN.

It is intended, in a revision of European Standard EN 196: Part 2, to adopt the methods of test presented for final vote in this draft standard into EN 196: Part 2, so that this standard will then contain all methods of test required for the chemical analysis of cement.

In accordance with the Common CEN/CENELEC Rules, the 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

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:01 2005

azmanco.com

Foreword

The standard EN 196 on methods of testing cement consists of the following parts:

Part 1. Determination of strength

Part 2. Chemical analysis of cement

Part 3. Determination of setting time and soundness

Part 4. Quantative determination of constituents

Part 5. Pozzolanicity test for pozzolanic cements

Part 6. Determination of fineness

Part 7. Methods of taking and preparing samples of cement

Part 21. Determination of the chloride, carbon dioxide and alkali content of cement.

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:10 2005

azmanco.com

Contents

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:21 2005

azmanco.com

1 Object and field of application

This European Standard lays down the methods for the determination of the chloride, carbon dioxide and alkali content of cement.

The standard describes the reference methods and, in certain cases, an alternative method which can be considered as giving equivalent results.

If other methods are used, their results shall be shown to be equivalent to the results given by the reference methods. In the case of a dispute, only the reference methods are applicable.

This standard applies to cements and also to their constituent materials, such as clinker and blastfurnace slag.

2 References

EN 196-2	Methods of testing cement - Chemical analysis of cement
EN 196-7	Methods of testing cement - Methods of taking and preparing samples of cement
ISO 3534-1977	Statistics - Vocabulary and symbols

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:32 2005

azmanco.com

3 General requirements for testing

3.1 Number of tests

The number of tests for the various determinations (clauses 4 to 8) shall be two (see also 3.3).

3.2 Repeatability and reproducibility

The standard deviation of repeatability gives the closeness of agreement between successive results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and short time interval[1)]).

The standard deviation of reproducibility gives the closeness of agreement between individual results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or different times[1)]).

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

3.3 Expression of masses, volumes and results

State masses in grams to the nearest 0,0001 g and volumes from burettes in millilitres to the nearest 0,05 mL.

Express the results, given by the mean of two determinations, as a percentage generally to two decimal places.

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

3.4 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 0,0005 g.

---

1) As defined in ISO 3534.

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:44 2005

azmanco.com

3.5 Preparation of the cement sample

Before starting the determinations, treat the laboratory sample, taken in accordance with EN 196-7 , as follows to obtain a sample for testing.

Take approximately 100 g of the sample using a sample divider or by quartering. Sieve this portion on a 150 µm or 125 µm sieve until the residue remains constant. Remove the metallic iron from the material retained on the sieve by means of a magnet. Then grind the iron free fraction of the retained material so that it completely passes the 150 µm or 125 µm sieve. If this sample contains particles of metallic iron such as those that may be introduced accidentally during grinding, remove these iron particles completely using a magnetic stirrer in a suspension, for example in cyclohexane. Transfer the sample to a clean dry flask with an airtight closure and shake vigorously to mix it thoroughly.

Carry out all operations as quickly as possible to ensure that the sample is exposed to ambient air only for the minimum time.

3.6 Reagents

Use only reagents of analytical quality and distilled water, or water of equal purity, during the analysis.

Unless otherwise stated % means percent by mass.

The concentrated liquid reagents used in this standard have the following densities (ρ) (in g/cm^3 at 20 °C):

hydrochloric acid	1,18 to 1,19
hydrofluoric acid	1,13
nitric acid	1,40 to 1,42
perchloric acid	1,60 to 1,67
phosphoric acid	1,71 to 1,75
sulphuric 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.

3.7 Volumetric glassware

The volumetric glassware shall be of analytical accuracy, i.e. class A as defined in the ISO standards on laboratory glassware.

Copyright by the European Committee For Standardization
Mon Feb 28 14:31:55 2005

azmanco.com

4 Determination of the chloride content

4.1 Principle

This method gives the total halogen content except for fluoride and expresses the result as Cl^-. The cement sample is decomposed with boiling dilute nitric acid. Sulphides are oxidized into sulphates and do not interfere. The dissolved chloride is precipitated using a known volume of a standard silver nitrate solution. After boiling, the precipitate is washed with dilute nitric acid and discarded. The filtrate and washings are cooled to less than 25 °C and the residual silver nitrate is titrated with a standard ammonium thiocyanate solution using an iron (III) salt as indicator.

4.2 Reagents

4.2.1 ***Concentrated nitric acid*** (HNO_3).

4.2.2 ***Dilute nitric acid*** 1 + 2.

4.2.3 ***Dilute nitric acid*** 1 + 100.

4.2.4 ***Silver nitrate*** ($AgNO_3$), dried at 150 °C.

4.2.5 ***Silver nitrate solution 0,05 mol/L***

Dissolve 8,494 g of silver nitrate in water in a 1000 mL volumetric flask and make up to the mark. Store the solution in a brown glass flask and protect it from the light.

4.2.6 ***Ammonium thiocyanate*** (NH_4SCN).

4.2.7 ***Ammonium thiocyantate solution, approximately 0,05 mol/L***

Dissolve 3,8 g of ammonium thiocyanate in water and make up to 1000 mL.

4.2.8 ***Ammonium iron (III) sulphate*** ($NH_4Fe(SO_4)_2.12H_2O$).

Copyright by the European Committee For Standardization
Mon Feb 28 14:32:07 2005

azmanco.com

4.2.9 *Indicator solution*

Add 10 mL of dilute nitric acid 1 + 2 to 100 mL of a cold saturated solution of ammonium iron (III) sulphate in water.

4.3 Apparatus

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

4.3.2 *10 mL burette*, graduated to 0,1 mL.

4.3.3 *Desiccator*, containing anhydrous magnesium perchlorate ($Mg(ClO_4)_2$).

4.3.4 *Filter paper*, coarse (pore diameter approximately 20 µm).

4.3.5 *5 mL pipette*.

4.4 Procedure

Weigh 5 ± 0,05 g of cement and place in a 250 mL beaker, add 50 mL of water and, while stirring with a glass rod, 50 mL of dilute nitric acid 1 + 2 (4.2.2). Heat the mixture to boiling, stirring occasionally, and boil for 1 min. Add 5 mL of silver nitrate solution (4.2.5) by pipette (4.3.5) into the boiling solution. Then boil for a maximum of 1 min and filter through a filter paper (4.3.4) washed before use with dilute nitric acid 1 + 100 (4.2.3) into a 500 mL flask. Wash the beaker, glass rod and filter paper with dilute nitric acid 1 + 100 until the volume of the filtrate and the washings is 200 mL. Cool the filtrate and washings to below 25 °C.

Add 5 mL indicator solution (4.2.9) and titrate with the ammonium thiocyanate solution (4.2.7) shaking vigorously until a drop of this solution produces a faint reddish-brown colouration which no longer disappears on shaking. Record the volume V_1.

If the chloride content of cement exceeds 0,17 %, it will be necessary to start the test again with a smaller quantity of cement.

Carry out the same procedure with no cement sample and record the volume, V_2, of ammonium thiocycanate solution used in the blank titration.

Copyright by the European Committee For Standardization
Mon Feb 28 14:32:19 2005

azmanco.com

4.5 Expression of results

Calculate the chloride content (in %) from the formula:

$$Cl^- = \frac{1,773}{1000} \times (V_2 - V_1) \times \frac{100}{m_1} = 0,1773 \times \frac{(V_2 - V_1)}{m_1} \quad (1)$$

where

m_1 is the mass of the cement test portion

V_1 is the volume of the ammonium thiocyanate solution used for the titration of the test solution

V_2 is the volume of the ammonium thiocyanate solution used for the titration of the blank solution.

The mean of the two results shall be rounded to the nearest 0,01 %.

4.6 Repeatability and reproducibility

The standard deviation of repeatability is 0,005 %.
The standard deviation of reproducibility is 0,010 %.

5 Determination of the carbon dioxide content (reference method)

5.1 Principle

The cement sample is treated with phosphoric acid to decompose the carbonate present. The carbon dioxide liberated is entrained in a current of carbon dioxide-free gas or air through a series of absorption tubes. The first two remove hydrogen sulphide and water and the following then absorb carbon dioxide. Two absorption tubes, each containing a granular absorbent for carbon dioxide and anhydrous magnesium perchlorate to retain the water formed during the absorption reaction are weighed to determine the mass of carbon dioxide released.

5.2 Reagents

5.2.1 *Copper sulphate* ($CuSO_4.5\ H_2O$).

5.2.2 *Copper sulphate solution, saturated*

Copyright by the European Committee For Standardization
Mon Feb 28 14:32:34 2005

azmanco.com

5.2.3 *Absorbent for hydrogen sulphide*

Place a weighed quantity of dried pumice stone with a grain size between 1,2 mm and 2,4 mm into a flat dish and cover with a volume of saturated copper sulphate solution so the mass of the copper sulphate solution is approximately half that of the pumice stone. Evaporate the mixture to dryness, while stirring frequently with a glass rod. Dry the contents of the dish for at least 5 h in an oven at a temperature of 155 ± 5 °C. Allow the solid mixture to cool in a desiccator and store in an airtight bottle.

5.2.4 *Absorbent for water*, anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) with a particle size between 0,6 mm and 1,2 mm.

5.2.5 *Absorbent for carbon dioxide*, synthetic silicates with a particle size between 0,6 mm to 1,2 mm[2)] impregnated with sodium hydroxide (NaOH).

5.2.6 *Concentrated phosphoric acid* (H_3PO_4).

5.2.7 *Concentrated sulphuric acid* (H_2SO_4).

---

2) The absorbent can be obtained ready for use.

Copyright by the European Committee For Standardization
Mon Feb 28 14:32:48 2005

azmanco.com

5.3 Apparatus

5.3.1 *Apparatus for the determination of the carbon dioxide content*

Figure 1 shows a typical piece of apparatus which can be fitted with either a cylindrical pressure container, a small electrical compressor or a suitable suction pump which will ensure an even flow of gas or air.

The gas (air or nitrogen) entering the apparatus has previously had its carbon dioxide removed by first being passed through an absorbent tube or tower containing the carbon dioxide absorbent (5.2.5). The apparatus consists of a 100 mL reaction flask (A) fitted with a three neck adaptor. Neck B_1 is connected to a dropping funnel (O), neck B_2 to a connecting tube and neck C to a water cooled condenser. The funnel onto B_1 and the connecting tube onto B_2 are joined together by means of a Y-piece (P), so that the carbon dioxide-free air can flow either through the connecting tube or the funnel by means of a Mohr clip (N). After the condenser (L), the gas is passed through concentrated sulphuric acid (D), then through absorption tubes containing the absorbent for hydrogen sulphide (5.2.3) (E) and for water (5.2.4) (F) and subsequently through two absorption tubes (G,H) which can be weighed and which are three-quarters filled with the absorbent for carbon dioxide (5.2.5) and a quarter with the absorbent for water (5.2.4). The absorbent for carbon dioxide (5.2.5) is placed upstream of the absorbent for water (5.2.4) with respect to the gas flow. Absorption tube H is followed by an additional absorption tube (I), which also contains the absorbent for carbon dioxide and water, which is fitted in order to protect absorption tube H against penetration by carbon dioxide and water from the air.

The absorption tubes G and H which are to be weighed may have, for example, the following sizes:

External distance between branches	45 mm
Internal diameter	20 mm
Distance between the lower part of the tube and the upper part of the ground section	75 mm
Tube wall thickness	1,5 mm

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

5.3.3 ***Electric oven***, which can be set at 105 ± 5 °C and at 155 ± 5 °C.

5.3.4 ***Desiccator***, containing anhydrous magnesium perchlorate ($Mg(ClO_4)_2$).

Copyright by the European Committee For Standardization
Mon Feb 28 14:33:04 2005

azmanco.com

5.4 Procedure

Weigh 1 ± 0,05 g of cement and place it in a dry 100 mL distillation flask. Connect the flask to the apparatus (5.3.1) as shown in figure 1, but without the two absorption tubes G and H. Pass a current of carbon dioxide-free gas through the apparatus for 15 min at approximately 3 bubbles per second (bubble counter) via the connecting tube onto B_2 (branch onto B_1, Mohr clip closed). Release the Mohr clip and remove the gas supply from the funnel O. Add 30 mL concentrated phosphoric acid into the dropping funnel and reconnect the gas supply to fill the funnel O.

Condition the closed absorption tubes G and H for 15 min in the balance case in order to achieve temperature equilibrium. Then weigh each tube separately. Shut off the flow of gas and attach the tubes to the apparatus as shown in figure 1.

Wear protective gloves when carrying out this operation.

Then reopen the gas flow. After 10 min close absorption tubes G and H, remove them, place them in the balance case for 15 min and then weigh them separately. Repeat the passage of gas, removal and weighing of absorption tubes G and H for as long as is required for the results of two successive weighings of a tube not to differ by more than 0,0005 g.

If the change in mass of the absorption tubes G and H remains greater than 0,0005 g, renew the absorbents in tubes E and F.

Attach the weighed absorption tubes G and H to the apparatus, as shown in figure 1.

Open the funnel tap and allow the phosphoric acid to drop into the distillation flask A. After the reaction has ceased, heat the contents of the flask to boiling and boil gently for 5 min. Maintain the gas flow through the apparatus until the flask has cooled to room temperature.

Close absorption tubes G and H, remove them and place them in the balance case for 15 min and then weigh them separately. The increase in mass of each tube is used for the calculation of the carbon dioxide content (see 5.5).

The carbon dioxide is practically completely absorbed by tube G. If the increase in mass of tube H exceeds 0,0005 g, renew the absorbent in tube G and start the test again.

Copyright by the European Committee For Standardization
Mon Feb 28 14:33:18 2005

azmanco.com

5.5 Expression of results

Calculate the carbon dioxide content (in %) of the cement from the formula:

$$CO_2 = \frac{m_3 + m_4}{m_2} \times 100 \qquad (2)$$

where

m_2 is the mass of cement test portion

m_3 is the increase in mass of tube G after absorption

m_4 is the increase in mass of tube H after absorption.

The mean of the two results shall be rounded to the nearest 0,01 %.

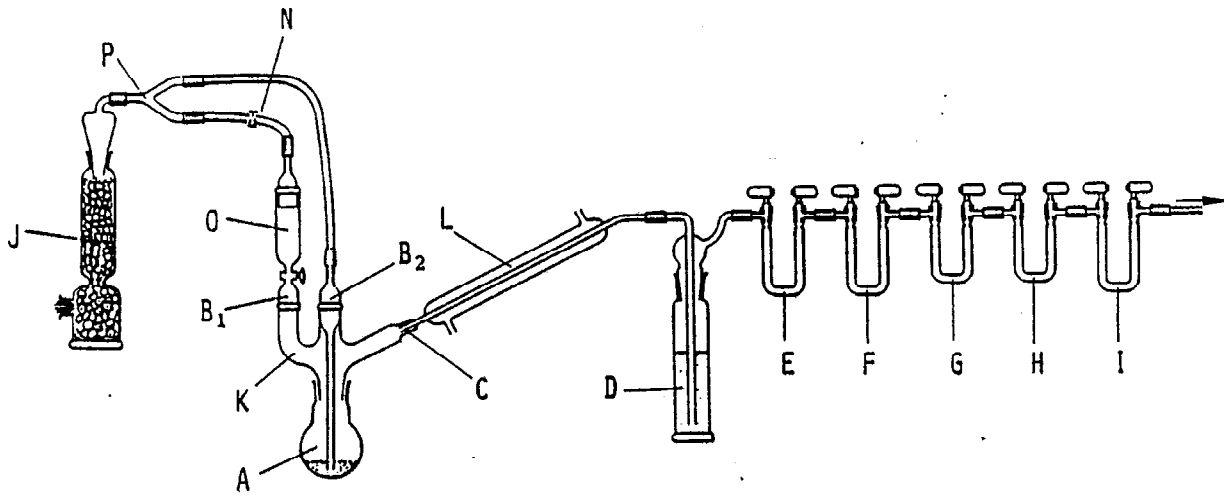
If the carbon dioxide content calculated from equation (2) is less than 0,5 %, repeat the determination with a cement sample weighing 2 g.

5.6 Repeatability and reproducibility

The standard deviation of repeatability is 0,07 %.
The standard deviation of reproducibility is 0,10 %.

Copyright by the European Committee For Standardization
Mon Feb 28 14:33:34 2005

azmanco.com



Key

A	100 *mL* distillation flask
B_1	Dropping funnel connector
B_2	Connecting tube connector
C	Condenser connector
D	Wash bottle with concentrated sulphuric acid (5.2.7)
E	Absorption tube with absorbent for hydrogen sulphide (5.2.3)
F	Absorption tube with magnesium perchlorate absorbent for water (5.2.4)
G, H and I	Absorption tubes with absorbents for carbon dioxide (5.2.5) and for water (5.2.4)
J	Absorption tower containing carbon dioxide absorbent (5.2.5)
K	Three-armed still head
L	Condenser
N	Mohr clip
O	Dropping funnel
P	Y-piece

Figure 1. Apparatus for the determination of the carbon dioxide content (reference method)

Copyright by the European Committee For Standardization
Mon Feb 28 14:33:47 2005

azmanco.com

6 Determination of the carbon dioxide content (alternative method)

6.1 Principle

The carbon dioxide is driven off by means of sulphuric acid, absorbed by sodium hydroxide and determined gravimetrically. Any hydrogen sulphide present which may distort the results is absorbed by mercuric (II) chloride.

6.2 Reagents

6.2.1 ***Mercuric (II) chloride*** ($HgCl_2$).

6.2.2 ***Absorbent for carbon dioxide***, synthetic silicates with a particle size between 0,6 mm and 1,2 mm[3)] impregnated with sodium hydroxide, (NaOH).

6.2.3 ***Concentrated sulphuric acid*** (H_2SO_4).

6.2.4 ***Dilute sulphuric acid*** 1 + 4.

6.2.5 ***Absorbent for water***, anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) with a partide size between 0,6 mm and 1,2 mm.

6.3 Apparatus

6.3.1 ***Apparatus for the determination of the carbon dioxide content***

The apparatus is shown in figure 2. A small vacuum pump is used to generate reduced pressure in the apparatus.

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

---

3) See page 11.

Copyright by the European Committee For Standardization
Mon Feb 28 14:34:04 2005

azmanco.com

6.4 Procedure

Place 1 ± 0,05 g of cement into the 100 mL distillation flask A of the apparatus (6.3.1). Mix this cement with a small (about 50 mg) amount of mercuric (II) chloride (6.2.1) using a spatula and then add enough water to form a slurry. Connect the flask to the ground joint of the dropping funnel O. Then draw air for 15 min through the apparatus, passing the air through an absorption tower J filled with absorbent (6.2.2) to remove the carbon dioxide before the air passes into the flask.

After stopping the flow of air add 25 mL to 30 mL of sulphuric acid (6.2.4) from the dropping funnel (O) into the flask. Take care to ensure that some of the acid remains in the dropping funnel as a seal.

Turn the vacuum pump on again, so that the current of air carries the liberated carbon dioxide through the condenser (L) and the first two absorption tubes F, filled with magnesium perchlorate (6.2.5) for the purposes of drying the air, to the two previously weighed absorption tubes G filled with absorbent (6.2.2). An absorption tube I filled with magnesium perchlorate (6.2.5) and absorbent (6.2.2) is fitted after these tubes in order to prevent penetration by the ambient air. A gas washing bottle D filled with sulphuric acid (6.2.3) is connected to this as a bubble counter.

After about 10 min heat the contents of the flask to boiling and boil gently for 5 min. Maintain the air flow through the apparatus until the flask has cooled to room temperature. Close the taps and remove the absorption tubes G, place them in the balance case for 15 min in order to achieve temperature equilibrium and then weigh them.

6.5 Expression of results

Calculate the carbon dioxide content (in %) from the formula:

$$CO_2 = \frac{m_g \times 100}{m_s} \qquad (3)$$

where

m_s is the mass of the cement test portion

m_g is the increase in mass of the absorption tubes G after absorption

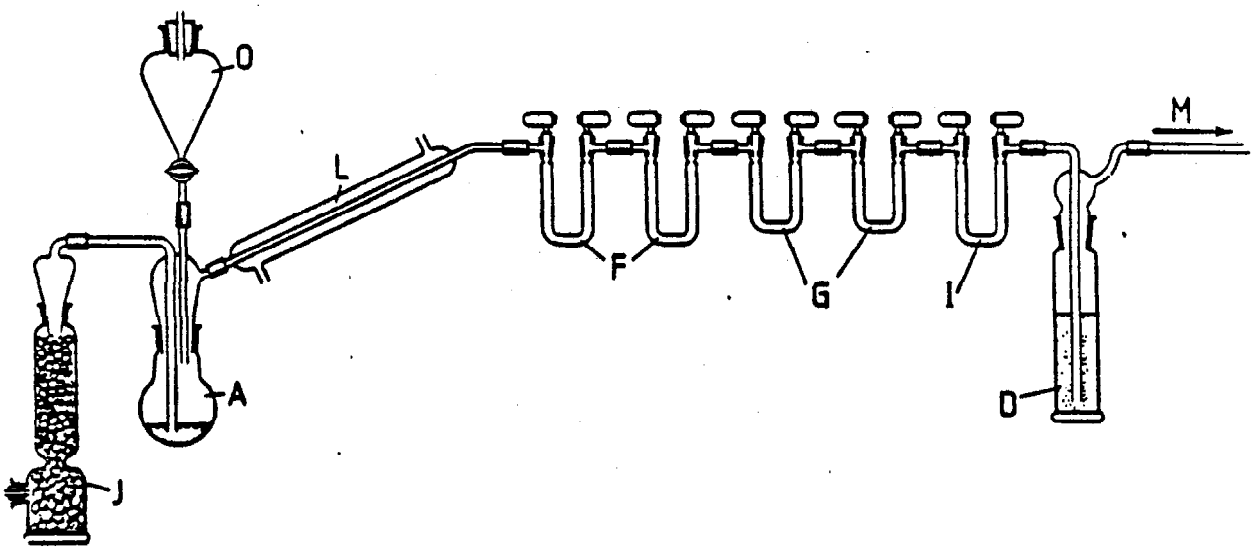
The mean of the two results shall be rounded to the nearest 0,01 %.

6.6 Repeatability and reproducibility

The standard deviation of repeatability is 0,07 %.
The standard deviation of reproduciblity is 0,10 %.

Copyright by the European Committee For Standardization
Mon Feb 28 14:34:18 2005

azmanco.com



A 100 mL distillation flask
D Washing bottle containing concentrated sulphuric acid (6.2.3)
F Absorption tubes containing magnesium perchlorate (6.2.5)
G Absorption tubes containing absorbent for carbon dioxide (6.2.2)
I Absorption tube containing carbon dioxide absorbent (6.2.2) and magnesium perchlorate (6.2.5)
J Absorption tower containing carbon dioxide absorbent (6.2.2)
L Condenser
M To the vacuum pump
O Dropping funnel for sulphuric acid (6.2.3)

Figure 2. Apparatus for the determination of the carbon dioxide content (alternative method)

Copyright by the European Committee For Standardization
Mon Feb 28 14:34:36 2005

azmanco.com

7 Determination of the alkali content (reference method)

7.1 Principle

A butane or propane flame is used to excite the alkalis to emit their characteristic spectrum in the visible range. The emission is proportional to the alkali content at low concentrations. The influence of large quantities of calcium on the sodium determination is suppressed by means of phosphoric acid.

7.2 Reagents

7.2.1 *General requirements*

References to water mean distilled water or water of the same degree of purity with an electrical conductivity of approximately 2 µS/cm. Use reagents of analytical quality (see also 3.6); their alkali content shall be tested by means of this method. If the alkali content of a reagent exceeds 0,01 %, the batch concerned is unsuitable and shall therefore be replaced by another which shall be tested in the same way.

7.2.2 ***Concentrated hydrochloric acid*** (HCl).

7.2.3 ***Dilute hydrochloric acid*** 1 + 19.

7.2.4 ***Concentrated phosphoric acid*** (H_3PO_4).

7.2.5 ***Dilute phosphoric acid*** 1 + 19; store this solution in a polyethylene flask.

7.2.6 ***Concentrated nitric acid*** (HNO_3).

7.2.7 ***Concentrated perchloric acid*** ($HClO_4$).

7.2.8 ***Concentrated hydrofluoric acid*** (HF).

7.2.9 ***Sodium chloride*** (NaCl), dried at 105 °C to constant mass.

Copyright by the European Committee For Standardization
Mon Feb 28 14:34:51 2005

azmanco.com

7.2.10 ***Potassium chloride*** (KCl), dried at 105 °C to constant mass.

7.2.11 ***Alkali stock solution***

Weigh about 0,566 g of sodium chloride and about 0,475 g of potassium chloride, transfer them to a 1000 mL volumetric flask, add 100 mL each of dilute hydrochloric acid 1 + 19 and dilute phosphoric acid 1 + 19, dissolve and make up to the mark with water. This solution contains approximately 0,300 g each of Na_2O and K_2O. The actual contents can be determined from the original quantities from the following formulae:

$$K_2O \text{ (in g/L)} = 0{,}6318 \times \text{actual mass of potassium chloride in g} \quad (4)$$

$$Na_2O \text{ (in g/L)} = 0{,}5303 \times \text{actual mass of sodium chloride in g} \quad (5)$$

7.3 Apparatus

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

7.3.2 ***Calibrated burettes***

7.3.3 ***Flame photometer***, with which the intensities of the sodium line at 589 nm and the potassium line at 768 nm can be measured: a sufficiently stable apparatus shall be used.

7.3.4 ***Platinum dish***

7.3.5 ***Filter paper***, medium pore size (pore diameter approximately 7 µm).

7.3.6 ***Platinum stirrer***.

7.4 Preparation of calibration solutions and calibration graphs

Prepare the calibration solutions using the volumes of alkali stock solution, dilute hydrochloric acid 1 + 19 and dilute phosphoric acid 1 + 19 listed in table 1. The volumes listed in lines 1 to 8 shall be made up to 1000 mL with water. Store these calibration solutions in polyethylene bottles.

Spray the calibration solutions into the flame of the flame photometer (7.3.3). Spray the blank solution (table 1, line 1) first and set the indication on the apparatus to 0. Then spray the other calibration solutions in the order of increasing concentration (lines 2 to 8). Measure the intensities for Na_2O at 589 mm and for K_2O at 768 nm.

Plot graphs of the measured intensities against the corresponding concentrations of sodium oxide and potassium oxide in the calibration solutions.

Copyright by the European Committee For Standardization
Mon Feb 28 14:35:10 2005

azmanco.com

Table 1. Volumes of solutions for the preparation of calibration solutions and their sodium oxide and potassium oxide concentrations

Line	Alkali stock solution (7.2.11) mL	Dilute hydrochloric acid 1 + 19 mL	Dilute phosphoric acid 1 + 19 mL	Na_2O and K_2O concentrations mg/L
1	-	100,0	100,0	Blank solution
2	3,3	99,6	99,6	1,0
3	8,3	99,1	99,1	2,5
4	16,7	98,3	98,3	5,0
5	25,0	97,5	97,5	7,5
6	33,3	96,6	96,6	10,0
7	41,7	95,8	95,8	12,5
8	50,0	95,0	95,0	15,0

7.5 Dissolution of the test portion

7.5.1 *Cements completely soluble in acid* (content of insoluble residue < 3 %)

Weigh 0,1 g cement into a 50 mL beaker, make into a slurry with 10 mL of water and add 10 mL of dilute hydrochloric acid 1 + 19. Warm the mixture until the cement has dissolved, breaking any lumps down with a glass rod. Filter the suspension through the filter paper (7.3.5) into a 100 mL volumetric flask washing through with boiling water. Wash the filter paper and residue with boiling water until there is a quantity of approximately 80 mL in the 100 mL volumetric flask. Then allow the filtrate and washing water to cool to ambient temperature. Add 10 mL of dilute phosphoric acid 1 + 19 to the solution, make up to the mark and mix thoroughly.

7.5.2 *Cements not completely soluble in acid*

Use the method described below where the content of insoluble residue, determined in accordance with clause 9 of EN 196-2, exceeds 3 %.

Copyright by the European Committee For Standardization
Mon Feb 28 14:35:28 2005

azmanco.com

Weigh 0,2 g of cement into a platinum dish and add 5 mL of concentrated nitric acid (7.2.6). Heat the mixture, for example, on a hot-plate, and evaporate to dryness. Disperse the residue from evaporation in 5 mL of water, add 2 mL of concentrated perchloric acid[4] (7.2.7) and then add 10 mL of concentrated hydrofluoric acid (7.2.8). Heat the mixture and evaporate to dryness. Prevent overheating by frequent agitation by means of the platinum stirrer (7.3.6). Add 40 mL of water and 20 mL of dilute hydrochloric acid 1 + 19 to the residue from evaporation and heat until the residue has dissolved. Filter the suspension through the filter paper (7.3.5) into a 200 mL volumetric flask washing through with hot water. Wash the filter paper and residue with hot water until the 200 mL volumetric flask contains a volume of approximately 150 mL. Then allow the filtrate and washing water to cool to ambient temperature. Add 20 mL of dilute phosphoric acid 1 + 19 to the solution, make up to the mark with water and mix thoroughly.

7.6 Procedure

Spray the measuring solution produced as described in 7.5.1 or 7.5.2 into the flame of the flame photometer (7.3.3). Measure the intensity of the sodium line at 589 nm and the potassium line at 768 nm. Obtain the sodium oxide or potassium oxide concentration in the solution respectively by means of a linear interpolation from the intensities and the associated concentrations of the calibration solutions measured as described in 7.4.

Use the graphs plotted as in 7.4 to obtain the sodium oxide and potassium oxide concentrations of the solution in mg/L or use the intensities and the associated concentrations of the calibration solutions with the next higher and the next lower intensity for the calculation as follows.

---

[4] Perchloric acid vapours form explosive mixtures with organic materials. It is therefore necessary to take special precautionary measures when working with perchloric acid: the use of fume cupboards flushed with water and a general ban on the use of organic substances in the same fume cupboard.

Copyright by the European Committee For Standardization
Mon Feb 28 14:35:44 2005

azmanco.com

Calculate the sodium oxide (C_{Na_2O}) or potassium oxide (C_{K_2O}) concentration of the sample from the intensities I_{Na_2O} or I_{K_2O} respectively using the following formulae:

$$C_{Na_2O} = C_{Bn} + (C_{Bh} - C_{Bn}) \times \frac{I_{Na_2O} - I_{Bn}}{I_{Bh} - I_{Bn}} \quad (6)$$

$$C_{K_2O} = C_{Bn} + (C_{Bh} - C_{Bn}) \times \frac{I_{K_2O} - I_{Bn}}{I_{Bh} - I_{Bn}} \quad (7)$$

where

C_{Bn} is the concentration of the sodium oxide or potassium oxide respectively in the calibration solution having a lower concentration than the measuring solution in mg/L

C_{Bh} is the concentration of the sodium oxide or potassium oxide respectively in the calibration solution having a higher concentration than the measuring solution in mg/L

I_{Bn} is the intensity of the calibration solution having a lower concentration than the measured solution

I_{Bh} is the intensity of the calibration solution having a higher concentration than the measuring solution.

7.7 Expression of results

Calculate the contents of sodium oxide or potassium oxide as percentages in the cement from the following equations using the corresponding concentrations as determined in accordance with 7.6.

$$Na_2O = 0,1\ C_{Na_2O} \quad (8)$$

$$K_2O = 0,1\ C_{K_2O} \quad (9)$$

where

C_{Na_2O} is the sodium oxide concentration of the measuring solution as calculated by formula (6) (in mg/L)

C_{K_2O} is the potassium oxide concentration of the measuring solution as calculated by formula (7) (in mg/L)

The mean of the two results for each oxide shall be rounded to the nearest 0,01 %.

Copyright by the European Committee For Standardization
Mon Feb 28 14:36:01 2005

azmanco.com

The total alkali content, A, is obtained by converting the potassium oxide content to equivalent sodium oxide from the formula:

$$A = Na_2O + 0,658K_2O \qquad (10)$$

7.8 Repeatability and reproducibility

The standard deviation of repeatability is

0,01 % for the determination of Na_2O
0,02 % for the determination of K_2O

The standard deviation of reproducibility is

0,02 % for the determination of Na_2O
0,03 % for the determination of K_2O

8 Determination of the alkali content (alternative method)

8.1 Principle

Cements which are completely soluble are treated with hydrochloric acid. Cements which are incompletely soluble are first evaporated with hydrofluoric acid/sulphuric acid. The alkali contents of the solutions are determined by means of flame photometry.

8.2 Reagents

8.2.1 *Concentrated hydrochloric acid* (HCl).

8.2.2 *Dilute hydrochloric acid* 1 + 9.

8.2.3 *Concentrated hydrofluoric acid* (HF).

Copyright by the European Committee For Standardization
Mon Feb 28 14:36:18 2005

azmanco.com

8.2.4 ***Concentrated sulphuric acid*** (H_2SO_4).

8.2.5 ***Lithium chloride*** (LiCl); dried at 120 °C.

8.2.6 ***Sodium chloride*** (NaCl); dried at 105 °C to constant mass.

8.2.7 ***Potassium chloride*** (KCl); dried at 105 °C to constant mass.

8.2.8 ***Stock solution***[5)]

Dissolve 0,610 g of lithium chloride, 0,2542 g of sodium chloride and 0,1907 g of potassium chloride in water in a 1000 mL volumetric flask and make up to the mark.

8.2.9 ***Caesium chloride*** (CsCl).

8.2.10 ***Aluminium nitrate*** ($Al(NO_3)_3.9H_2O$).

8.2.11 ***Buffer solution***[5)]

Dissolve 50 g of caesium chloride and 250 g of aluminium nitrate in water and make up to 1000 mL.

---

5) These solutions can also be obtained made up ready for use.

Copyright by the European Committee For Standardization
Mon Feb 28 14:36:33 2005

azmanco.com

8.3 Apparatus

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

8.3.2 *Electric oven*, which can be set at 105 ± 5 °C and at 120 ± 5 °C.

8.3.3 *Flame photometer*, capable of measuring the intensities of the sodium line at 589 nm and the potassium line at 768 nm. The flame photometer shall be operated with a propane-air flame at a relatively low temperature in order to avoid distortion of the determination by alkaline earths.

8.3.4 *Filter paper*, medium porosity (pore diameter approximately 7 µm).

8.3.5 *Platinum dish*

8.3.6 *Heating lamp*

8.3.7 *Calibrated burette*

8.4 Plotting the calibration curve

In the case of cements which are completely soluble in hydrochloric acid, evaporate 20 mL of hydrochloric acid 1 + 9 to dryness, and, in the case of cements not completely soluble in acid, evaporate 15 mL of hydrofluoric acid (8.2.3) and 5 mL of sulphuric acid (8.2.4) to dryness for the purposes of preparing the calibration solutions for each calibration point.

In both cases dissolve the residue from evaporation with 2 mL of hydrochloric acid 1 + 9 and 3 mL of water. Transfer the solution to a 100 mL volumetric flask and add 10 mL of buffer solution (8.2.11). Add the following quantities of the stock solution (8.2.8) to the individual volumetric flasks using the calibrated burette (8.3.7).

Volumetric flasks	1	2	3	4	5	6	7
Stock solution (mL)	0	1	3	5	10	20	30

Then make up the volumetric flasks to the mark with distilled water.

Copyright by the European Committee For Standardization
Mon Feb 28 14:36:49 2005

azmanco.com

With an original quantity of sample of 0,2000 g, the values measured for flasks 1 to 7 correspond to a K_2O and Na_2O content of:

Volumetric flasks	1	2	3	4	5	6	7
Na_2O content (%)	0	0,07	0,20	0,34	0,67	1,35	2,02
K_2O content (%)	0	0,06	0,18	0,30	0,60	1,20	1,81

Spray the calibration solutions into the flame of the flame photometer (8.3.3). Spray the blank solution 1 first and set the indication on the apparatus to 0. Then spray the other calibration solutions in order of increasing concentration (2 to 7). Measure the intensities for Na_2O at 589 nm and for K_2O at 768 nm. Plot graphs of the measured intensities against the corresponding concentrations of sodium oxide and potassium oxide in the calibration solutions.

If a sufficiently stable photometer is used, it is only necessary to establish the calibration curves from time to time. However, the values measured for flasks 1 and 7 shall be checked for each analysis.

8.5 Procedure

8.5.1 ***Cements completely soluble in acid*** (content of insoluble residue < 3 %)

Weigh 0,2 g cement into the platinum dish (8.3.5), make into a slurry with 3 mL of water and evaporate to dryness after adding 20 mL of dilute hydrochloric acid 1 + 9. Add hot water and 2 mL of dilute hydrochloric acid 1 + 9 to the residue and filter through the filter paper (8.3.4) into a 100 mL volumetric flask which already contains 10 mL of the buffer solution (8.2.11). Wash the residue with hot water until the volumetric flask is almost filled to the mark. Then cool to 20 °C and make up to the mark with water.

Measure the solution in the flame photometer (8.3.3). The scale values read off in conjunction with the calibration curves (8.4) give the concentrations of K_2O and Na_2O in mg/L respectively.

8.5.2 ***Cements not completely soluble in acid***

Weigh 0,2 g cement into the platinum dish (8.3.5). Make into a slurry with 3 mL of water and evaporate after adding 5 mL of concentrated sulphuric acid (8.2.4) and 15 mL of concentrated hydrofluoric acid (8.2.3). Evaporate to dryness under the heating lamp (8.3.6). Mix the residue with hot water and 2 mL of hydrochloric acid 1 + 9 and continue the procedure as described in 8.5.1.

Copyright by the European Committee For Standardization
Mon Feb 28 14:37:06 2005

azmanco.com

8.6 Expression of results

Calculate the content of alkali as a percentage for an original sample weight of 0,2000 g.

The mean of the two results for each oxide shall be rounded to the nearest 0,01 %.

Convert the potassium oxide content to the equivalent sodium oxide content using formula (10). State the sum of the sodium oxide values as the total alkali content A.

8.7 Repeatability and reproducibility

The standard deviation of repeatability is

0,01 % for the determination of Na_2O
0,02 % for the determination of K_2O

The standard deviation of reproducibility is

0,02 % for the determination of Na_2O
0,03 % for the determination of K_2O

Copyright by the European Committee For Standardization
Mon Feb 28 14:37:26 2005

azmanco.com