BRITISH STANDARD

Methods of testing cement

Part 2. Chemical analysis of cement

The European Standard EN 196-2 : 1994 has the status of a
British Standard

BSi

STANDARDS

196-2 : 1995

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BS EN 196-2 : 1995

Cooperating organizations

The European Committee for Standardization (CEN), under whose supervision this European Standard was prepared, comprises the national standards organizations of the following countries:

Austria	Oesterreichisches Normungsinstitut
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United Kingdom	British Standards Institution

This British Standard, having been prepared under the direction of the Technical Committee B/516, was published under the authority of the Standards Board and comes into effect on 15 March 1995

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Committee reference B/516
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Contents

National foreword

This British Standard has been prepared under the direction of the Technical Committee B/516, Cement and lime. It is the English language version of EN 196-2 : 1994 *Methods of testing cement Part 2: Chemical analysis of cement*, published by the European Committee for Standardization (CEN). EN 196-2 was drawn up by CEN Technical Committee 51, Cement and building limes, as Part 2 of a series on testing cement which was originally accepted by CEN on 15 November 1985 and made available on 12 May 1987. The UK gave a negative vote at the final voting stage and, under the CEN Rules then in force, was not obliged to implement this Part. A second formal vote was taken in November 1992 when the UK again gave a negative vote but, under the CEN Rules now in force, is obliged to implement this Part which supersedes BS 4550 : Part 2 : 1970, which is now withdrawn.

BS 4550 : Part 2 : 1970 included some useful UK methods of analysis which do not appear in EN 196-2. These are included for information in the following national annexes (clause numbers refer to BS 4550 : Part 2 : 1970).

National annex NA Determination of total sulfur (clause **12**)

National annex NB Determination of minor constituents (TiO_2 and P_2O_5) and free lime (clause **14**)

National annex NC Determination of propylene glycol content (clause **18**).

The pozzolanicity test for pozzolanic cements in clause **15** of BS 4550 : Part 2 : 1970 is now published in BS EN 196-5 : 1995. The methods for determining alkali content and chloride content in clauses **16** and **17**, respectively, of BS 4550 : Part 2 : 1970 are now published in BS EN 196-21 : 1992.

Though the methods given in this standard are generally the reference procedures, the great majority of cement analyses at the present time are carried out using X-ray fluorescence spectrometry. A method suitable for the major oxide analysis of cements conforming to BS 12 is given in national annex ND.

There are limiting requirements in BS 7583 and in the European Prestandard specification for cement, ENV 197-1, for methylene blue adsorption and total organic carbon content of limestone used as a main constituent of cement. National annexes NE and NF give appropriate methods for the determination of methylene blue adsorption and of total organic carbon content, respectively.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 196-2

December 1994

ICS 91.100.10

Descriptors: Cement, chemical analysis, determination of content, losses on ignition, sulfates, sulfides, manganese, silicon dioxide, iron oxides, aluminium oxides, calcium oxides, magnesium oxides, evaporation residue, gravimetric analysis, spectrophotometric analysis, EDTA.

English version

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

Méthodes d'essai des ciments —
Partie 2: Analyse chimique des ciments

Prüverfahren für Zement —
Teil 2: Chemische Analyse von Zement

This European Standard was approved by CEN on 1994-12-12. 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 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 the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies 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 de Stassart 36, B-1050 Brussels

Ref. No. EN 196-2 : 1994 E

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Foreword

This European Standard was drawn up by CEN/TC 51, Cement and building limes, the secretariat of which is held by IBN.

The 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

ENV 196-4   Methods of testing cement — Part 4: Quantitative determination of constituents

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 196-21   Methods of testing cement — Part 21: Determination of the chloride, carbon dioxide and alkali content of cement

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 June 1995, and conflicting national standards shall be withdrawn at the latest by June 1995.

This European Standard supersedes EN 196-2 : 1987.

According to the CEN/CENELEC Internal Regulations, 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, United Kingdom.

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1 Scope

This European Standard describes the procedures for the chemical analysis of cement.

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

If other methods are used it is necessary to show that they give results equivalent to those given by the reference methods. In the case of a dispute, only the reference procedures are used.

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

Standard specifications state which methods are to be used.

2 Normative references

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

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

ISO 3534 : 1977   *Statistics — Vocabulary and symbols*

3 General requirements for testing

3.1 Number of tests

The number of tests for the various determinations (clauses **7** to **13**) is fixed at 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 material tested 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 material but tested 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 %[2].

3.3 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0,0001 g and volumes from the burette in millilitres to the nearest 0,05 ml.

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

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

If the difference between two determinations is more than twice the repeatability standard deviation, repeat the test and take the mean of the two closest values.

3.4 Ignitions

Carry out the ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate it slowly in an oxidising atmosphere, without flaming while ensuring complete combustion. Then ignite at the stated temperature. Allow the crucible and its contents 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 0,0005 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 and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (**4.33**). 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.

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[1] Definitions taken from ISO 3534.
[2] The values of the standard deviation for repeatibility and standard deviation for reproducibility given in this standard shall be considered as provisional. These values will subsequently by stipulated according to experience acquired in the laboratories.

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4 Reagents

4.0 General requirements

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

Unless otherwise stated % means % 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
sulfuric acid	1,84
phosphoric acid	1,71 to 1,75
acetic acid	1,05 to 1,06
ammonium hydroxide	0,88 to 0,91
triethanolamine	1,12

The degree of dilution is always given as a volumetric sum, for example: 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.* Add five or six drops of concentrated hydrochloric acid to 2 l water. Control the pH value by means of a pH-meter. Store the solution in a polyethylene flask.

4.10 *Concentrated hydrofluoric acid (HF).*

4.11 *Dilute hydrofluoric acid 1 + 3.*

4.12 *Nitric acid (HNO$_3$).*

4.13 *Concentrated sulfuric acid (H$_2$SO).*

4.14 *Dilute sulfuric acid 1 + 1.*

4.15 *Phosphoric acid (H$_3$PO$_4$).*

4.16 *Boric acid (H$_3$BO$_3$).*

4.17 *Acetic acid (CH$_3$COOH).*

4.18 *Amino-acetic acid (NH$_2$CH$_2$COOH).*

4.19 *Metallic chromium in powder form (Cr).*

4.20 *Concentrated ammonium hydroxide (NH$_4$OH.)*

4.21 *Dilute ammonium hydroxide 1 + 1.*

4.22 *Dilute ammonium hydroxide 1 + 10.*

4.23 *Dilute ammonium hydroxide 1 + 16.*

4.24 *Sodium hydroxide (NaOH).*

4.25 *Sodium hydroxide solution 4 mol/l.* Dissolve 160 g of sodium hydroxide in water and make up to 1000 ml. Store in a polyethylene flask.

4.26 *Sodium hydroxide solution 2 mol/l.* Dissolve 80 g of sodium hydroxide in water and make up to 1000 ml. Store in a polyethylene flask.

4.27 *Ammonium chloride (NH$_4$Cl).*

4.28 *Tin (II) chloride (SnCl$_2$.2H$_2$O).*

4.29 *Potassium periodate (KIO$_4$).*

4.30 *Sodium peroxide in powder form (Na$_2$O$_2$).*

4.31 *Mixture of sodium carbonate and sodium chloride.* Mix 7 g of sodium carbonate (anhydrous Na$_2$CO$_3$) with 1 g sodium chloride (NaCl).

4.32 *Barium chloride solution.* Dissolve 120 g of barium chloride (BaCl$_2$.2H$_2$O) in water and make up to 1000 ml.

4.33 *Silver nitrate solution.* Dissolve 5 g of silver nitrate (AgNO$_3$) in water, add 10 ml of concentrated nitric acid (HNO$_3$) and make up to 1000 ml with water.

4.34 *Sodium carbonate solution.* Dissolve 50 g of sodium carbonate (anhydrous Na$_2$CO$_3$) in water and make up to 1000 ml.

4.35 *Potassium hydroxide solution.* Dissolve 250 g of potassium hydroxide (KOH) in water and make up to 1000 ml.

4.36 *Ammoniacal zinc sulfate solution.* Dissolve 50 g of zinc sulfate (ZnSO$_4$.7H$_2$O) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (NH$_4$OH). Leave to stand for at least 24 h and filter.

4.37 *Lead acetate solution.* Dissolve approximately 0,2 g of lead acetate Pb(CH$_3$COO)$_2$.3H$_2$O in water and make up to 100 ml.

4.38 *Starch solution.* To 1 g of starch (water soluble), add 1 g of potassium iodide (KI), dissolve in water and make up to 100 ml.

4.39 *Polyethylene oxide solution.* Dissolve 0,25 g of polyethylene oxide (-CH$_2$-CH$_2$-O-)$_n$ of average molecular mass 200 000 to 600 000, in 100 ml water while stirring vigorously.

This solution is stable for approximately two weeks.

4.40 *Boric acid solution, saturated.* Dissolve approximately 50 g of boric acid (H$_3$BO$_3$) in water and make up to 1000 ml.

4.41 *Citric acid solution.* Dissolve 10 g of citric acid (C$_6$H$_8$O$_7$.H$_2$O) in water and make up to 100 ml.

4.42 *Ammonium molybdate solution.* Dissolve 10 g of ammonium molybdate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O in water and make up to 100 ml.

Store the solution in a polyethylene flask. This keeps for approximately one week.

4.43 *Copper sulfate solution.* In a 50 ml volumetric flask dissolve 0,45 g of copper sulfate (CuSO$_4$.5H$_2$O) in water and make up to the mark.

4.44 *Ammonium acetate solution.* Dissolve 250 g of ammonium acetate (CH$_3$COONH$_4$) in water and make up to 1000 ml.

4.45 *Triethanolamine N(CH$_2$CH$_2$OH)$_3$ solution* 1 + 4.

4.46 *Reducing solution.* Dissolve successively in water 0,15 g of 1-amino-2-hydroxy naphthalene-4-sulfonic acid (C$_{10}$H$_9$NO$_4$S), 0,7 g of sodium sulfite (anhydrous Na$_2$SO$_3$) and 9,0 g of sodium metabisulfite (Na$_2$S$_2$O$_5$) and make up to 100 ml.

This solution will keep for a maximum of one week.

4.47 *Buffer solution of pH 1,40.* Dissolve 7,505 g of amino-acetic acid (NH$_2$CH$_2$COOH) and 5,850 g of sodium chloride (NaCl) in water and make up to 1000 ml. Dilute 300 ml of this solution to 1000 ml with dilute hydrochloric acid 1 + 99.

4.48 *Standard potassium iodate solution containing approximately 0,0166 mol/l*[3]. Dissolve successively, in freshly boiled and cooled water in a 1000 ml volumetric flask, (3,6 ± 0,1) g of potassium iodate (KIO$_3$, dried at 120 °C), two tablets of sodium hydroxide (NaOH) and 25 g of potassium iodide (KI). Make up to the mark with freshly boiled and cooled water.

The factor F of this solution is calculated from the following formula:

$$F = \frac{m_1}{3,5668} \qquad (1)$$

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

4.49 Sodium thiosulfate solution approximately 0,1 mol/l[3]

4.49.1 *Preparation*

Dissolve 24,82 g of sodium thiosulfate (Na$_2$S$_2$O$_3$.5H$_2$O) in water and make up to 1000 ml. Before each test series, determine the factor f of this solution as described in **4.49.2**.

4.49.2 *Standardization*

4.49.2.1 This standardization is carried out preferably in relation to the standard potassium iodate solution (**4.48**).

For this standardization, pipette 20 ml of the standard potassium iodate solution into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution to a pale yellow colour.

Then add 2 ml of the starch solution (**4.38**) and continue the titration until the colour changes from blue to colourless.

The factor f of this solution is calculated from the formula:

$$f = \frac{20 \times 0,01667 \times 214,01 \times F}{3,5668 \times V_1} = 20 \times \frac{F}{V_1} \qquad (2)$$

where:

F is the factor of the standard potassium iodate solution (**4.48**);

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

3,5668   is the mass of potassium iodate corresponding to a solution with exactly 0,01667 mol/l of potassium iodate, in grams;

214,01   is the molecular mass of KIO$_3$.

4.49.2.2 The standardization may also be carried out in relation to a known quality of potassium iodate.

For this standardization, place in a 500 ml conical flask (0,07 ± 0,005) g (m_2) of potassium iodate and dissolve in approximately 150 ml of water.

Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution until a pale yellow colour is obtained. Then add 2 ml of the starch solution (**4.38**) and titrate until the colour changes from blue to colourless.

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[3] If the sulfide content is low (< 0,1 %), solutions ten times less concentrated should be used. They are prepared by pipetting 100 ml of the solutions **4.48** and **4.49** into 1000 ml volumetric flasks and making up to the mark with water.

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The factor f of this solution is calculated from the formula:

$$f = \frac{1000 \times m_2}{3,5668 \times V_2} = 280,3634 \times \frac{m_2}{V_2} \qquad (3)$$

where:

m_2 is the mass of the portion 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;

3,5668   is the mass of potassium iodate, in grams corresponding to a solution with exactly 0,01667 mol/l of potassium iodate.

4.50 Standard manganese ion solution

4.50.1 *Anhydrous manganese sulfate*

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

4.50.2 *Preparation*

Into a 1000 ml volumetric flask, weigh approximately 2,75 g of anhydrous manganese sulfate (m_3); dissolve in water and make up to the mark. The content G of manganese (II) ions of this solution, expressed in milligrams of Mn^{2+}/ml, is calculated from the formula:

$$G = \frac{m_3}{2,7485} \qquad (4)$$

where:

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

4.50.3 *Construction of the calibration graph*

Into each of two volumetric flasks, respectively 500 ml (No. 1) and 1000 ml (No. 2), pipette 20 ml of the standard manganese ion solution. Make up to the mark with water. Into each of three volumetric flasks, respectively 200 ml (No. 3), 500 ml (No. 4) and 1000 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, 1,5 g of potassium periodate (**4.29**) and 10 ml of phosphoric acid (**4.15**), heat to boiling and boil gently for 30 min.

Cool to 20 °C and transfer the contents of each beaker to a 200 ml volumetric flask. Cool the flasks and their contents to 20 °C and make up to the mark with water. Measure the optical density of the solutions using a photometer (**5.9**) at a wavelength of around 525 nm, against water (use one or more cells (**5.10**) of appropriate sizes). Record the optical density values to three decimal places.

For each cell optical length plot a separate graph of the optical densities of these standard solutions E 1 to E 5 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 **4.50.2** has the value 1,0000. Otherwise, multiply the manganese concentrations in table 1 by G.

Table 1. Concentrations of manganese standard solutions

Standard solution	E 1	E 2	E 3	E 4	E 5
Concentration of manganese in mg of Mn per 200 ml	4,0	2,0	1,0	0,4	0,2

4.51 Standard silica solution

4.51.1 *Silica (SiO_2)*, of purity > 99,9 % after ignition.

4.51.2 *Sodium carbonate*, anhydrous (Na_2CO_3).

4.51.3 *Basic solution*

Weigh 0,2000 g of silica, freshly ignited at (1175 ± 25) °C, in a platinum crucible already containing 2,0 g of sodium carbonate.

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 bottle.

1 ml of solution contains 1 mg of SiO_2.

4.51.4 *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 bottle. 1 ml of the solution contains 0,02 mg silica. This solution will keep for a maximum of one week.

4.51.5 *Compensating solutions*

Prepare the compensating solutions according to the procedure adopted for the 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.

4.51.6 *Construction of the calibration curve*

Add from a burette the volumes of the silica calibration solution 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. Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (**4.40**) into the solution.

Table 2. Composition of the compensation solutions for a volume of 500 ml

		Precipitation by polyethylene oxide (13.3)	Precipitation by double evaporation (13.4)	Decomposition by HCl and NH_4Cl (13.5)
HCl conc.	ml	70	75	15
H_2SO_4 1 + 1	ml	1	1	–
HNO_3 conc.	ml	–	–	1
Polyethylene oxide solution	ml	5	–	–
NH_4Cl	g	–	–	1
Na_2CO_3	g	1,75	1,75	1,75
NaCl	g	0,25	0,25	0,25
Na_2O_2	g	3	3	–

Table 3. Composition of the silica calibration solutions and their silica content

Serial No.	Blank	1	2	3	4	5	6	7	8
Standard SiO_2 solution (ml)	0	2	4	5	6	8	10	15	20
Water (ml)	20	18	16	15	14	12	10	5	0
Silica content (mg SiO_2/100 ml)	0	0,04	0,08	0,10	0,12	0,16	0,20	0,30	0,40

Adjust the pH of the solution to (1,15 ± 0,05) by adding, drop by drop, either the sodium hydroxide solution (**4.25**), or hydrochloric acid 1 + 2. Carry out this operation with the aid of a pH meter calibrated using a buffer (**4.47**) with a neighbouring pH value (e.g. 1,40).

Pipette 5 ml of the ammonium molybdate solution (**4.42**) into the solution (time 0). Adjust the pH of this solution to 1,60 by adding, drop by drop, either the sodium hydroxide solution (**4.25**) or hydrochloric acid 1 + 2. Transfer the solution to a 100 ml volumetric flask rinsing with dilute hydrochloric acid of pH = 1,60 (**4.9**).

After 20 min, pipette 5 ml of the citric acid solution (**4.41**) into the volumetric flask, stir and leave to stand for 5 min.

Then pipette 2 ml of the reducing solution (**4.46**) into the volumetric flask. Make up to the mark with dilute hydrochloric acid pH = 1,60 (**4.9**) and mix thoroughly. Exactly 30 min after introducing the ammonium molybdate (time 0 + 30), measure the optical density with a photometer (**5.9**) using a cell of 1 cm optical length against the blank solution prepared in the same way, using the wavelength of maximum extinction near 815 nm. Construct a graph giving the measured optical densities as function of the corresponding silica contents given in table 3.

The blank solution used in constructing the calibration curve may be used as the blank solution here. The calibration curve enables the silica content in mg SiO_2/100 ml to be determined.

4.52 Standard calcium ion solution, approximately 0,01 mol/l

4.52.1 *Calcium carbonate (CaCO3)*, dried at 200 °C of purity > 99,9 %.

4.52.2 *Standard solution*

Weigh approximately 1 g of calcium carbonate and place it in a 400 ml beaker with approximately 100 ml of water. Cover the beaker with a watch glass and carefully introduce approximately 10 ml of hydrochloric acid 1 + 2. After the reaction is completed, bring to boiling in order to expel the dissolved carbon dioxide. Cool and make up to 1000 ml in a volumetric flask.

4.53 EDTA solution, approximately 0,03 mol/l

4.53.1 *Dihydrated disodium salt of ethylenediaminetetra-acetic acid (EDTA)*

4.53.2 *Preparation*

Dissolve 11,17 g of EDTA in water and make up to 1000 ml. Store in a polyethylene bottle.

4.53.3 *Standardization*

Pipette 50 ml of the standard calcium ion solution (**4.52**) into a beaker suitable for the measuring apparatus (**5.11**). Then dilute with water to a volume suitable for the operation of the apparatus.

Using a pH meter, adjust the pH of this solution to 12,5 with the sodium hydroxide solution or solutions (**4.25** and **4.26**).

Determine the end-point using one of the following two methods.

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a) *Photometric determination of the end-point (reference method)*

Add about 0,1 g of murexide (**4.57**) or of mixed indicator (**4.63**). Place the beaker in the apparatus (**5.11**) set at 620 nm when using murexide or at 520 nm when using the mixed indicator and, while stirring continuously, titrate with 0,03 mol/l EDTA solution. In the vicinity of the indicator colour change, construct a diagram giving the optical density values as a function of the volume of EDTA added. The volume V_3 used is determined from the intersection of the line of greatest slope near the colour change and the line of almost constant optical density after the colour change.

The factor f_D of this solution is calculated from the formula:

$$f_D = \frac{50 \times m_4}{100{,}09 \times 0{,}03 \times V_3} = 16{,}65 \times \frac{m_4}{V_3} \qquad (5)$$

where

m_4 is the mass of the portion of calcium carbonate taken to prepare the standard calcium ion solution (**4.52**), in grams;

V_3 is the volume of the EDTA solution used for the titration, in millilitres.

b) *Visual determination of the end-point (alternative method)*

Add about 0,1 g of the calcon indicator (**4.59**). Stir and titrate with 0,03 mol/l EDTA solution until the colour changes from pink to blue, and one drop in excess does not further increase the intensity of the blue colour. The volume V_3 is used to calculate the standardization factor f_D using the formula (5).

4.54 Copper complexonate solution

Pipette 25 ml of the copper sulfate solution (**4.43**) into a 400 ml beaker and add from a burette an equivalent volume of the 0,03 mol/l EDTA solution (**4.53**). The required volume of EDTA solution is calculated as follows.

Pipette 10 ml of the copper sulfate solution (**4.43**) into a 600 ml beaker. Dilute to approximately 200 ml with water and add 10 ml of concentrated ammonium hydroxide and about 0,1 g of murexide indicator (**4.57**). Titrate with the 0,03 mol/l EDTA solution (**4.53**) until the colour changes from pink to violet.

If V_4 is the volume used, the volume V_5 of the 0,03 mol/l EDTA solution to be added to 25 ml of the copper sulfate solution to obtain copper complexonate is:

$$V_5 = 2{,}5 \; V_4 \qquad (6)$$

4.55 EGTA solution, approximately 0,03 mol/l

4.55.1 *Ethylenebis (oxyethylenenitrilo) tetra-acetic acid (EGTA)*

4.55.2 *Preparation*

Weigh approximately 11,4 g of EGTA into a 600 ml beaker and add about 400 ml of water and 10 ml of the sodium hydroxide solution (**4.26**). Heat the mixture until the EGTA is completely dissolved. Allow to cool to room temperature. Using a pH meter, adjust the pH value of the solution to 7, by adding, drop by drop, dilute hydrochloric acid 1 + 2. Transfer the solution quantitatively to a 1000 ml volumetric flask and make up to the mark with water. Store the solution in a polyethylene bottle.

4.55.3 *Standardization*

Pipette 50 ml of the standard calcium ion solution (**4.52**) into a beaker suitable for the measuring apparatus (**5.11**). Then dilute with water to a volume suitable for the correct operation of the apparatus. Add 25 ml of the triethanolamine 1 + 4 solution (**4.45**).

Using a pH meter, adjust the pH of this solution to 12,5 with the sodium hydroxide solution or solutions (**4.25** and **4.26**).

Add about 0,1 g of murexide (**4.57**) or of calcein indicator (**4.58**). Place the beaker in the apparatus (**5.11**) set at 620 nm when using murexide or at 520 nm when using calcein and, while stirring the solution, titrate using the 0,03 mol/l EGTA solution. In the vicinity of the indicator colour change, construct a diagram giving the optical density values as a function of the volume of EGTA added. The volume V_6 used is determined from the intersection of the line of greatest slope near the colour change and the line of almost constant optical density after the colour change.

The factor f_G is calculated from the formula:

$$f_G = \frac{50 \times m_5}{100{,}09 \times 0{,}03 \times V_6} = 16{,}65 \times \frac{m_5}{V_6} \qquad (7)$$

where:

m_5 is the mass of the portion of calcium carbonate taken to prepare the standard calcium ion solution (**4.52**), in grams;

V_6 is the volume of EGTA solution used to titrate 50 ml of the standard calcium ion solution (**4.52**), in millilitres.

4.56 DCTA solution, approximately 0,01 mol/l

4.56.1 *Cyclohex-1,2-ylenedinitrilotetra-acetic monohydrate (DCTA)*

4.56.2 *Preparation*

Weigh 3,64 g of DCTA into a 600 ml beaker and add about 400 ml of water and 10 ml of sodium hydroxide solution (**4.26**). Heat the mixture until the DCTA is completely dissolved. Allow to cool to room temperature. Using a pH meter, adjust the pH value of the solution to 7 by adding dilute hydrochloric acid 1 + 2, drop by drop. Transfer the solution quantitatively to a 1000 ml volumetric flask and make up to the mark with water. Store this solution in a polyethylene bottle.

4.56.3 *Standardization*

Pipette 50 ml of the standard calcium ion solution (**4.52**) into a beaker appropriate for the measuring apparatus (**5.11**). Then dilute with water to a volume suitable for the correct operation of the apparatus.

Using a pH meter, adjust the pH of this solution to 10,5 with concentrated ammonium hydroxide.

Add approximately 0,1 g of murexide (**4.57**) or of calcein indicator (**4.58**). Place the beaker in the apparatus (**5.11**) set at 620 nm when using murexide or at 520 nm when using calcein and, stirring the solution, titrate with the DCTA solution. In the vicinity of the colour change of the indicator, construct a diagram of the optical density values as a function of the volume of DCTA added. The volume V_7 used is determined by the intersection of the line of greatest slope near the colour change and the line of almost constant optical density after the colour change.

The factor f_c is calculated from the formula:

$$f_c = \frac{50 \times m_6}{100{,}09 \times 0{,}01 \times V_7} = 49{,}955 \times \frac{m_6}{V_7} \qquad (8)$$

where

m_6 is the mass of the portion of calcium carbonate taken for preparing the standard calcium ion solution (**4.52**), in grams;

V_7 is the volume of DCTA solution used for the titration, in millilitres.

4.57 Murexide indicator

Grind 1 g of murexide (ammonium purpurate) with 100 g of sodium chloride (NaCl).

4.58 Calcein indicator

4.58.1 *Calcein*

Bis [(bis (carboxymethyl)-amino-methyl] - 2', 7' -fluorescein.

4.58.2 *Preparation*

Grind 1 g of calcein with 99 g of potassium nitrate (KNO$_3$).

4.59 Calcon indicator

4.59.1 *Calcon*

Sodium 2-hydroxy-4-(2-hydroxy-1-naphthylazo) naphthalene-1-sulfonate.

4.59.2 *Preparation*

Grind 1 g of calcon with 100 g of anhydrous sodium sulfate (Na$_2$SO$_4$).

4.60 Sulfosalicylic acid indicator (sulfo-5-salicylic acid dihydrate)

4.61 PAN indicator

4.61.1 *PAN*

1-(2-pyridylazo)-2-naphthol.

4.61.2 *Preparation*

Dissolve 0,1 g of PAN in 100 ml ethanol (C$_2$H$_5$OH, ρ = 0,79 g/cm^3).

4.62 Methylthymol blue indicator

4.62.1 *Methylthymol blue*

Sodium salt of 3', 3''-bis- [bis (carboxy-methyl)-aminomethyl]- thymolsulfonphthalein.

4.62.2 *Preparation*

Grind 1 g of methylthymol blue with 100 g of potassium nitrate (KNO$_3$).

4.63 Mixed calcein and methylthymol blue indicator

Grind 0,2 g of calcein and 0,1 g of methylthymol blue with 100 g of potassium nitrate (KNO$_3$).

5 Apparatus

5.1 *Balance(s)*, capable of weighing to the nearest 0,0001 g.

5.2 *Porcelain and/or platinum crucible(s)*, 20 ml to 25 ml capacity, fitted with a lid.

5.3 *Fire proof ceramic support(s)*, for preventing overheating of the crucible. It shall be in thermal equilibrium with the furnace at the moment the crucible is introduced.

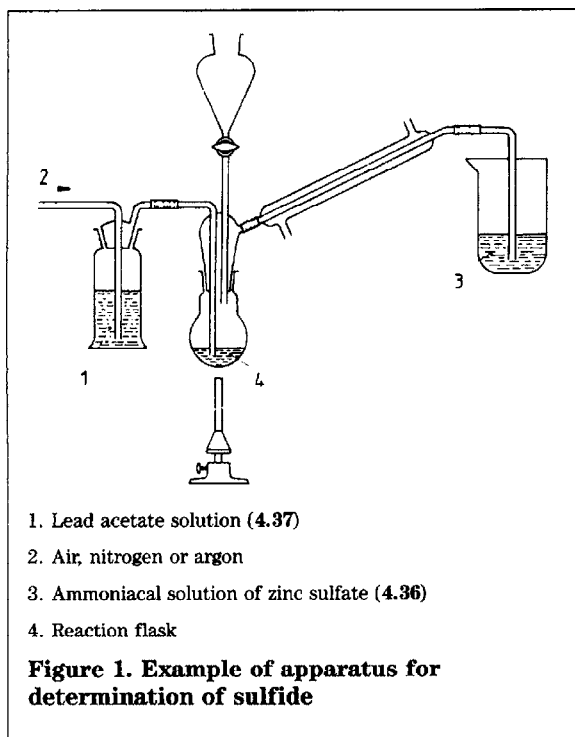**5.4** *Porcelain evaporating dish*, of approximately 200 ml.

5.5 *Electric furnace(s)*, naturally ventilated, capable of being set at the following temperatures: 500 °C, 925 °C, 975 °C and 1175 °C.

5.6 *Desiccator(s)*, containing anhydrous magnesium perchlorate (Mg(ClO$_4$)$_2$).

5.7 *Bulb condenser.*

5.8 *Apparatus for determining sulfides.* A typical apparatus is shown in figure 1.

1. Lead acetate solution (4.37)

2. Air, nitrogen or argon

3. Ammoniacal solution of zinc sulfate (4.36)

4. Reaction flask

Figure 1. Example of apparatus for determination of sulfide

A Woolf bottle may be added for controlling the flow of gas.

The connecting tubes shall be made of a material free from sulfur (polyvinyl chloride, polyethylene, etc.).

5.9 *Photometer(s)*, for measuring the optical density of a solution in the vicinity of 525 nm and 815 nm.

5.10 *Cells*, for the photometer.

5.11 *Apparatus*, for measuring the optical density at 520 nm and at 620 nm of a solution contained in a titration beaker, while stirring the solution with a magnetic stirrer.

5.12 *Magnetic stirrer*, with PTFE covered bar.

5.13 *Evaporation apparatus*, controlled at (105 ± 3) °C.

5.14 *Sand bath or hot plate*, controlled at approximately 400 °C.

5.15 *Filter papers*. The filter papers used shall be ashless.

NOTE. Filter papers with a mean pore diameter of around 2 μm are called fine, those with a mean pore diameter of around 7 μm are called medium and those with a mean pore diameter of around 20 μm are called coarse.

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

6 Preparation of a cement sample

Before chemical analysis, the laboratory sample taken in accordance with EN 196-7 is treated to give a sample for testing.

Take approximately 100 g of the sample by means of a sample divider or by quartering. Sieve this portion on a 150 μm or 125 μm sieve until no more passes through. Remove with a magnet all the metallic iron from the material retained on the sieve. Then grind the iron-free fraction of the retained material so that it completely passes the 150 μm or 125 μm sieve. Transfer the sample to a clean dry flask with an airtight closure and shake vigorously to mix it thoroughly.

The preceding operations are to be carried out as quickly as possible so that the sample is exposed to ambient air for the minimum time.

NOTE. The sample is presented for analysis as marketed. If it contains particles of metallic iron, such as those that may be introduced accidentally during grinding, the complete separation of these iron particles is carried out by means of a magnetic stirrer in a suspension, for example in cyclohexane.

7 Determination of loss on ignition

7.1 Principle

The loss on ignition is determined in an oxidizing atmosphere (air). By igniting in air at (975 ± 25) °C the carbon dioxide and water are driven off and any oxidizable elements present are oxidized. A correction for the influence of this oxidation on the loss on ignition is described.

7.2 Procedure

Weigh (1 ± 0,05) g of cement (m_7) into a crucible which has been previously ignited and tared. Place the covered crucible in the electric furnace (5.5) controlled at (975 ± 25) °C. After heating for 5 min, remove the lid and leave the crucible in the furnace for a further 10 min. Cool the crucible to room temperature in the desiccator. Weigh. Determine constant mass in accordance with 3.5.

NOTE. For cement containing sulfides, a more precise determination of the loss on ignition can be obtained by determining the sulfate contents before and after ignition. The corrections applicable to these cements are given in 7.4.

7.3 Expression of results

The observed loss on ignition is calculated in percent from the formula:

$$\text{Observed loss on ignition} = \frac{m_7 \times m_8}{m_7} \times 100 \quad (9)$$

where

m_7 is the mass of the test portion, in grams;

m_8 is the mass of the ignited test portion, in grams.

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7.4 Errors and corrections

Errors are caused either by the presence of carbon or by oxidation of sulfides of any remaining metallic iron, of bivalent iron and of bivalent manganese. The error resulting from the presence of these different elements may be corrected for, but only the correction due to oxidation of sulfides is to be applied, the others usually being considered to be negligible.

In this case, the correction due to sulfide is $1,996 \times S^{2-}$ and:

the corrected loss on ignition

= observed loss on ignition + $(1,996 \times S^{2-})$

where S^{2-} and the losses on ignition are expressed in percent.

For determination of sulfate present before and after ignition the relation is:

SO_3 (final) – SO_3 (initial) = SO_3 resulting from the oxidation of sulfides i.e. a correction of:

$0,8 \times$ (SO_3 from oxidation of sulfide)

= oxygen taken up

and

corrected loss on ignition = observed loss on ignition + oxygen taken up

where all the values are expressed in percent.

Any corrections applied shall be indicated in the test report.

In the case of dispute, only the correction due to oxidation of sulfide shall be applied.

7.5 Repeatability and reproducibility

The standard deviation for repeatability is 0,04 %.

The standard deviation for reproducibility is 0,08 %.

8 Gravimetric determination of sulfate

8.1 Principle

Sulfate ions, dissolved by decomposing cement with hydrochloric acid, are precipitated at a pH between 1 and 1,5 by a solution of barium chloride. The precipitation is carried out at boiling point:

$SO_4^{2-} + Ba^{2+} = BaSO_4$
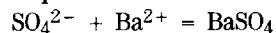
The determination is then completed gravimetrically and expressed as SO_3.

8.2 Procedure

To $(1 \pm 0,05)$ g of cement (m_9), placed in a 250 ml beaker, add 90 ml of cold water. While stirring the mixture vigorously, add 10 ml of concentrated hydrochloric acid. Heat the solution gently and crush the sample with the flattened end of a glass stirring rod until decomposition of the cement is complete. Allow the solution to digest for 15 min at a temperature just below boiling.

Filter the residue through a medium filter paper into a 400 ml beaker. Wash thoroughly with hot water. Check for the disappearance of Cl^- ions by the silver nitrate test (**3.6**).

Adjust the volume to about 250 ml; if necessary, adjust the pH of the solution to between 1 and 1,5 with hydrochloric acid 1 + 11 or ammonium hydroxide 1 + 16.

Bring to the boil and boil for 5 min. Check that the solution is clear; if not, start the test again using a new portion. While stirring vigorously the solution maintained at boiling point, add drop by drop 10 ml of the barium chloride solution (**4.32**) heated to just below boiling. Continue the boiling for 15 min so that the precipitate is properly formed. Allow the solution to stand for 12 h to 24 h below boiling temperature but above 60 °C, taking care to avoid concentration by evaporation.

Filter the precipitate through fine filter paper and wash thoroughly with boiling water until free from Cl^- ions, tested by the silver nitrate test (**3.6**).

Ignite at (925 ± 25) °C (**3.4**) then check for constant mass (**3.5**). In general, an ignition period of 15 min is sufficient for obtaining constant mass.

8.3 Expression of results

The sulfate content, expressed as SO_3, is calculated in percent from the formula:

$$SO_3 = \frac{m_{10} \times 0,343 \times 100}{m_9} = 34,3 \times \frac{m_{10}}{m_9} \qquad (10)$$

where:

m_9 is the mass of the test portion, in grams;

m_{10} is the mass of barium sulfate, in grams.

8.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,07 %.

The standard deviation for reproducibility is 0,08 %.

9 Determination of residue insoluble in hydrochloric acid and sodium carbonate

9.1 Principle

This is a conventional method in which the insoluble residue in cements is obtained by treatment with a dilute hydrochloric acid solution so as to avoid as far as possible the precipitation of soluble silica. The residue from this treatment is treated with a boiling solution of sodium carbonate in order to re-dissolve traces of silica which may have been precipitated. The residue is determined gravimetrically after ignition.

9.2 Procedure

To (1 ± 0.05) g of cement (m_{11}), placed in a 250 ml beaker, add 90 ml of water and, while stirring the mixture vigorously, add 10 ml of concentrated hydrochloric acid.

Heat the solution gently and crush the sample with the flattened end of a glass stirring rod until decomposition of the cement is complete. Allow the solution to digest for 15 min at a temperature just below boiling.

Filter the residue through a medium filter paper and wash thoroughly with almost boiling water. Transfer the filter paper and its contents back to the reaction beaker and add 100 ml of the sodium carbonate solution (**4.34**). Boil for 15 min. Filter on a medium filter paper and wash with almost boiling water, then four times with hot hydrochloric acid 1 + 19 until pH < 2 is obtained and finally at least ten times with almost boiling water until free from Cl$^-$ ions, tested by the silver nitrate test (**3.6**).

Ignite at (975 ± 25) °C (**3.4**) then check for constant mass (**3.5**). In general, an ignition period of 30 min is sufficient for obtaining constant mass.

NOTE. If a cloudy filtrate is observed, filter again on a fine filter paper, wash thoroughly with hot water and combine the two residues on their filter papers to ignite them.

If in spite of this operation the filtrate remains cloudy, its effect on the insoluble residue may be neglected.

9.3 Expression of results

The insoluble residue is calculated in percent from the formula:

$$\text{Insoluble residue} = \frac{m_{12}}{m_{11}} \times 100 \qquad (11)$$

where:

m_{11} is the mass of the test portion, in grams;

m_{12} is the mass of the ignited insoluble residue, in grams.

9.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,04 %. The standard deviation for reproducibility is 0,06 %.

10 Determination of residue insoluble in hydrochloric acid and potassium hydroxide

10.1 Principle

This is a conventional method in which the insoluble residue in cements is obtained by treating with a hydrochloric acid solution. The residue from this treatment is then treated with a boiling solution of potassium hydroxide. The residue is determined gravimetrically after ignition.

10.2 Procedure

To (1 + 0.05) g of cement (m_{13}), placed in a porcelain dish (**5.4**), add 25 ml of cold water and disperse using a glass stirring rod. Add 40 ml of concentrated hydrochloric acid. Heat the solution gently and crush the sample with the flattened end of a glass stirring rod until decomposition of the cement is complete. Evaporate to dryness on a water bath. Repeat the operation twice more with 20 ml concentrated hydrochloric acid.

Treat the residue from the last evaporation with 100 ml of dilute hydrochloric acid 1 + 3. Re-heat, filter through a medium filter paper and wash with almost boiling water at least ten times until free from Cl$^-$ ions, tested by the silver nitrate test (**3.6**).

Transfer the filter and its contents to a 250 ml conical flask fitted with a bulb condenser and add 100 ml of the potassium hydroxide solution (**4.35**). Leave to stand for 16 h at room temperature and then boil the solution under reflux for 4 h.

Filter on a medium filter paper and wash with water then with 100 ml of hydrochloric acid 1 + 9 and finally with almost boiling water until free from Cl$^-$ ions, tested by the silver nitrate test (**3.6**).

Ignite at (975 ± 25) °C (**3.4**) then check for constant mass (**3.5**). In general, an ignition period of 30 min is sufficient for obtaining constant mass.

10.3 Expression of results

The insoluble residue is calculated in percent from the formula:

$$\text{Insoluble residue} = \frac{m_{14}}{m_{13}} \times 100 \qquad (12)$$

where:

m_{13} is the mass of the test portion, in grams;

m_{14} is the mass of the ignited insoluble residue, in grams.

10.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,15 %. The standard deviation for reproducibility is 0,18 %.

11 Determination of sulfide

11.1 Principle

The sample is decomposed by hydrochloric acid under reducing conditions. The sulfides are transformed into hydrogen sulfide, which is carried over by a gaseous stream into an ammoniacal solution of zinc sulfate. The precipitated zinc sulfide is determined by iodometry.

11.2 Procedure

Use the apparatus described in **5.8**. Place (1 ± 0,05) g of the cement (m_{15})[4] in a 250 ml stoppered round bottom flask with a ground glass joint. Add about 2,5 g of tin II chloride (**4.28**) and 0,1 g of chromium (**4.19**)[5]. Disperse in 50 ml of water. Fix the flask to the ground neck of the separating funnel and connect to the condenser the glass outlet tube which dips into the beaker containing 15 ml of ammoniacal zinc sulfate

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[4] If the sulfide content is low (< 0,10 %) the mass of the test sample is increased in proportion.
[5] Chromium contributes to the solution of any pyrites (FeS$_2$) that happens to be present in the cement.

solution (**4.36**) and 285 ml of water. Connect the gas supply (air, nitrogen or argon) and adjust the flow to about 10 ml per min. Stop the flow of gas. Release 50 ml of hydrochloric acid 1 + 1 from the separating funnel ensuring that a small quantity of acid remains in the separating funnel to prevent leakage. Reconnect the gas supply, heat the contents of the flask to boiling and boil for 10 min. Disconnect the outlet tube which will serve as a stirrer during the titration.

Cool the receiver to 20 °C, add exactly 10 ml of potassium iodate solution approximately 0,0166 mol/l (**4.48**) and 25 ml concentrated hydrochloric acid. Titrate with sodium thiosulfate solution (**4.49**) until pale yellow. Then add 2 ml of starch solution (**4.38**) and titrate until the colour changes from blue to colourless.

11.3 Expression of results

The sulfide content is calculated in percent from the formula:

$$S^{2-} = \frac{(V_8 \times F) - (V_9 \times f) \times 1,603 \times 100}{1000 \times m_{15}}$$

$$= 0,1603 \times \frac{(V_8 \times F) - (V_9 \times f)}{m_{15}} \qquad (13)$$

where

V_8	is the volume of potassium iodate solution, in millilitres;
F	is the factor of the potassium iodate solution as in **4.48**;
V_9	is the volume of the sodium thiosulfate solution used for the titration, in millilitres;
f	is the factor of the sodium thiosulfate solution as in **4.49**;
m_{15}	is the mass of the test portion, in grams, as in **11.2**.

11.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,02 %.

The standard deviation for reproducibility is 0,04 %.

12 Photometric determination of manganese

12.1 Principle

The manganese present is oxidized to MnO_4^- by means of potassium periodate. The optical density of the violet solution is measured at 525 nm. The Fe^{3+} ions are complexed with phosphoric acid which also assists the formation of MnO_4 and stabilizes the colour of the solution.

12.2 Procedure

According to the manganese content expected[6], weigh 0,1 g to 1,0 g of cement into a 250 ml beaker. Disperse in about 75 ml of water. Stir, add cautiously 15 ml of concentrated nitric acid and boil until free from any hydrogen sulphide (H_2S) present and all the cement[7] is decomposed.

Filter through a medium filter paper into a 400 ml beaker. Wash the residue with hot water until the volume of the filtrate is 120 ml. To this filtrate, add 10 ml of phosphoric acid (**4.15**), mix and add 1.5 g of potassium periodate (**4.29**). Heat to boiling until the characteristic pink colour of permanganate appears. If it does not appear, reduce the acidity by adding a few drops of concentrated ammonium hydroxide. Once the colour has appeared, continue boiling gently for 30 min. Cool and transfer the contents of the beaker to a 200 ml volumetric flask.

Cool to 20 °C and make up to the mark with water.

Using a photometer, measure the optical density of the solution against water at a wavelength of approximately 525 nm (**5.9** and **5.10**).

Record the optical density value to three decimal places. The optical density read from the calibration graph corresponding to the cell used gives the concentration of manganese, C, in milligrams of Mn per 200 ml. Record the manganese concentration, C, to three decimal places.

12.3 Expression of results

The manganese content is calculated in percent from the formula:

$$Mn = \frac{C \times 100}{1000 \times m_{16}} = 0,1 \times \frac{C}{m_{16}} \qquad (14)$$

where

C	is the manganese concentration of the solution in mg/200 ml;
m_{16}	is the mass of the test portion, in grams, as in **12.2**.

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[6] For contents of the order of 0,01 %, taking a test portion close to 1 g and varying its amount to suit the probable manganese oxide concentration is recommended.

[7] For cements with a high insoluble residue, fusion of a separate sample may be necessary to obtain complete solution. This is carried out by the method of sintering with sodium peroxide as described for the determination of the main constituents (see **13.2**).

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The manganese content may be converted into MnO or Mn_2O_3 by means of the following formulae:

$$MnO = 1,2912 \times Mn \text{ (in \%)} \tag{15}$$

$$Mn_2O_3 = 1,4368 \times Mn \text{ (in \%)} \tag{16}$$

12.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,003 %.

The standard deviation for reproducibility is 0,03 %.

13 Determination of main constituents

13.1 Principle

The analysis is carried out after the sample is completely dissolved.

The cement is decomposed by sintering with sodium peroxide or by treatment with hydrochloric acid in the presence of ammonium chloride. In the first case, after dissolution of the sintered solid in hydrochloric acid, the major part of the silica is precipitated either by hydrochloric acid with coagulation by polyethylene oxide or by double evaporation; in the second case, the major part of the silica is separated by the treatment. The impure silica precipitated is treated with hydrofluoric acid and sulphuric acid to volatilize silica; the residue, treated with a mixture of sodium carbonate and sodium chloride, is dissolved in hydrochloric acid and added to the silica filtrate.

In the case of the treatment with hydrochloric acid in the presence of ammonium chloride, if the residue obtained after volatilization of impure silica by means of hydrofluoric acid and sulfuric acid is greater than 0,5 %, the method is not applicable. The cement shall in this case be decomposed by sodium peroxide.

In the final solution made up to 500 ml, the silica in solution is determined by photometric determination, and iron (III) oxide, aluminium oxide, calcium oxide and magnesium oxide are determined by complexometric methods.

The schematic diagram of the chemical analysis is shown in figure 2.

The scheme given in figure 2 results, as far as the determination of silica is concerned, in the same values for total silica whichever path is chosen.

13.2 Decomposition with sodium peroxide

Weigh $(1 \pm 0,05)$ g of cement (m_{17}) and 2 g of sodium peroxide (4.30) into a platinum crucible (5.2); mix thoroughly with a spatula. Brush back into the mixture any particles adhering to the spatula. Cover the mixture with 1 g of sodium peroxide. Carefully preheat the covered crucible for about 2 min at the opening of the furnace (5.5) before placing it on its support (5.3) in the heated zone controlled at a uniform temperature of (500 ± 10) °C.

After 30 min, remove the crucible from the furnace and allow it to cool to room temperature. The sintered mass should not stick to the sides of the crucible. If it does, then repeat the decomposition at a temperature 10 °C lower than was first used.

Transfer the sintered mass to a 400 ml beaker and rinse the crucible with 150 ml cold water.

Cover the beaker with a watch glass and heat until the solid is completely dissolved. Then add cautiously 50 ml of concentrated hydrochloric acid. The solution obtained shall be perfectly clear. If not, reject it and repeat the decomposition by peroxide at a temperature increased by 10 °C or for double the time in the furnace. Add to the solution 1 ml of sulfuric acid $1 + 1$. Bring the solution to the boil and boil for 30 min.

This solution is ready for use for the precipitation of silica in accordance with 13.3 or 13.4.

13.3 Precipitation and determination of silica – Polyethylene oxide method (reference method)

13.3.1 Procedure

Evaporate to dryness the solution prepared as described in 13.2. Allow the beaker to cool.

Treat the residue with 5 ml of water and 10 ml of concentrated hydrochloric acid. While stirring, add some ashless filter paper pulp to the mixture and then 5 ml of the polyethylene oxide solution (4.39) ensuring that the precipitate and the polyethylene oxide are thoroughly mixed, especially the precipitate adhering to the sides of the beaker. Stir the mixture thoroughly then add 10 ml of water, stirring briefly and leave to stand for 5 min.

Then filter through a medium filter paper into a 500 ml volumetric flask and rinse with hot hydrochloric acid $1 + 19$. Remove any precipitate adhering to the sides of the beaker using a rubber scraper. Wash the filter and precipitate at least five times with hot hydrochloric acid $1 + 19$, then rinse with hot water, ensuring that the residue in the filter is broken up thoroughly during washing, until free from Cl^- ions, tested by the silver nitrate test (3.6).

Collect the washings in the same 500 ml volumetric flask.

Ignite the filter and the precipitate in a platinum crucible (1175 ± 25) °C (3.4). Check for constant mass (3.5). In general, an ignition period of 60 min is sufficient for obtaining constant mass (m_{18}).

Volatilize the decomposed residue as in 13.6. Add the decomposed residue (13.7) to the filtrate and washings in the 500 ml volumetric flask. The combined solution is used for the colorimetric determination of silica remaining in solution (13.8) and also for the complexometric determinations of iron (III) oxide (13.10), aluminium oxide (13.11), calcium oxide (13.12 or 13.14) and magnesium oxide (13.13 or 13.15).

Decomposition of 1 g with Na$_2$O$_2$ (13.2)

or

Direct treatment of 1 g[8] with HCl + NH$_4$Cl (13.5)

Precipitation by HCl in the presence of polyethylene oxide (13.3)

or

Precipitation by double evaporation by HCl (13.4)

Impure SiO$_2$

Volatilization of pure SiO$_2$, (I)[9] by HF + H$_2$SO$_4$ (13.6)

Fusion of residue with Na$_2$CO$_3$ + NaCl and dissolution (13.7)

Filtrate

Final solution 500 ml

or

20 ml — Soluble SiO$_2$ by photometry (II) (13.8)

100 ml — Fe$_2$O$_3$ EDTA (13.10)

25 ml — CaO EGTA (13.12)

50 ml — MgO DCTA (13.13)

50 ml — CaO EDTA (13.14)

50 ml — CaO + MgO EDTA (13.15)

(I + II) Total SiO$_2$ (13.9)

Al$_2$O$_3$ EDTA (13.11)

MgO by difference

[8] If the residue insoluble in hydrochloric acid and sodium carbonate is greater than 1,5 %, it is necessary to use the method by decomposition with sodium peroxide.

[9] When the ammonium chloride method is used, if the residue after volatilization with hydrofluoric acid and sulfuric acid exceeds 0,5 %, the analysis shall be recommenced using the decomposition with sodium peroxide.

Figure 2. Schematic diagram for analysis of the main constituents

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13.3.2 *Expression of results*

The impure silica content is calculated in percent from the formula:

$$\text{Impure SiO}_2 = \frac{m_{18}}{m_{17}} \times 100 \tag{17}$$

where

m_{17} is the mass of the test portion as in **13.2**, in grams;

m_{18} is the mass determined in accordance with **13.3.1**, in grams.

13.4 Precipitation and determination of silica – Double evaporation method (alternative method)

13.4.1 *Procedure*

Evaporate to dryness the solution prepared as described in **13.2** on evaporation apparatus controlled at (105 ± 3) °C (**5.13**). Moisten with several drops of concentrated hydrochloric acid. Leave for 1 h at this temperature.

After cooling to room temperature, treat the residue with 10 ml of concentrated hydrochloric acid. After a few minutes dilute with 50 ml of water, bring to the boil and filter the hot solution through a medium filter paper into a 500 ml volumetric flask. Wash the filter and the residue three times with hot water. Evaporate the filtrate and washings in the same way, treat with 10 ml of concentrated hydrochloric acid and dilute with 50 ml of water. Boil, then pass through the same filter into a 500 ml volumetric flask.

Wash the filter and the residue with hot water until free from Cl^- ions, tested by the silver nitrate test (**3.6**). Collect the washings in the same 500 ml volumetric flask.

Ignite the filter and precipitate in a platinum crucible at (1175 ± 25) °C (**3.4**). Check for constant mass (**3.5**). In general, an ignition period of 60 min is sufficient for obtaining constant mass. Volatilize the decomposed residue as described in **13.6**. Add the decomposed residue (**13.7**) to the filtrate and washings in the 500 ml volumetric flask.

The combined solutions are used for the colorimetric determination of silica remaining in solution (**13.8**) and for the complexometric determinations of iron (III) oxide (**13.10**), aluminium oxide (**13.11**), calcium oxide (**13.12** or **13.14**) and magnesium oxide (**13.13** or **13.15**).

13.4.2 *Expression of results*

The impure silica content is calculated in percent from the formula:

$$\text{Impure SiO}_2 = \frac{m_{19}}{m_{17}} \times 100 \tag{18}$$

where

m_{17} is the mass of the test portion as in **13.2**, in grams;

m_{19} is the mass determined in accordance with **13.4.1**, in grams.

13.5 Decomposition with hydrochloric acid and ammonium chloride and precipitation of silica (alternative method)

13.5.1 *Procedure*

Weigh $(1 \pm 0,05)$ g of cement (m_{20}) and place in a 100 ml beaker. Add about 1 g of ammonium chloride (**4.27**) and mix thoroughly with a glass stirring rod. Cover the beaker with a watch glass and cautiously add 10 ml of concentrated hydrochloric acid taking care to let the acid run down the side of the beaker. When effervescence has stopped, add 10 drops of nitric acid and stir with a glass stirring rod.

Place the beaker and its watch glass on a boiling water bath and leave for 30 min. Filter through a coarse filter paper into a 500 ml volumetric flask: transfer the gelatinous precipitate to the filter as completely as possible without dilution, and allow the solution to drain through the filter. Remove all precipitate adhering to the beaker by using a rubber scraper.

Rinse the beaker and precipitate with hot hydrochloric acid $1 + 99$. Then wash the precipitate and filter 12 times with small amounts of hot water until free from Cl^- ions, tested by the silver nitrate test (**3.6**). Collect the washings in the same 500 ml volumetric flask.

This is used, together with the decomposed residue treated as described in **13.7** for the photometric determination of silica in solution in accordance with **13.8**. Ignite the filter and the precipitate in a platinum crucible at (1175 ± 25) °C (**3.4**). Check for constant mass (**3.5**). In general, an ignition period of 60 min is sufficient for obtaining constant mass. Volatize the decomposed residues as described in **13.6**.

13.5.2 *Expression of results*

The impure silica is calculated in percent from the formula:

$$\text{Impure } SiO_2 = \frac{m_{21}}{m_{20}} \times 100 \qquad (19)$$

where:

m_{20} is the mass of the test portion as in **13.5.1**, in grams;

m_{21} is the mass determined in accordance with **13.5.1**, in grams.

13.6 Determination of pure silica

13.6.1 *Procedure*

Moisten the residue obtained in accordance with **13.3.1** (m_{18}) or **13.4.1** (m_{19}) or **13.5.1** (m_{21}) with about 0,5 ml to 1 ml of water, add approximately 10 ml of hydrofluoric acid then two drops of sulfuric acid. Evaporate in a fume cupboard over a sand bath or hot plate (**5.14**), then continue to heat until free from white sulfuric acid fumes.

Ignite the crucible with the evaporation residue in an electric furnace (1175 ± 25) °C (**5.5**) for 10 min, leave to cool to room temperature in a desiccator and weigh (m_{22}).

The evaporation residue is decomposed as described in **13.7**. If the residue obtained by this method exceeds 0,5 %, the analysis shall be restarted and decomposition with sodium peroxide used (**13.2**).

13.6.2 *Expression of results*

The pure silica content is calculated in percent from the formula:

$$\text{Pure } SiO_2 = \frac{m_{24} - m_{22}}{m_{23}} \times 100 \qquad (20)$$

m_{22} is the mass determined in accordance with **13.6.1**, in grams;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams;

m_{24} is the mass determined in accordance with **13.3.1** (m_{18}), **13.4.1** (m_{19}) or **13.5.1** (m_{21}), in grams.

13.7 Decomposition of the evaporation residue

To the evaporation residue, obtained in accordance with **13.6.1**, add 2 g of the sodium carbonate and sodium chloride mixture (**4.31**) and fuse to a bright red heat using a gas burner. Swirl the melt frequently until the residue is completely dissolved.

Check visually that no part of the residue remains at the base of the crucible. Allow the crucible and its contents to cool, transfer to a 250 ml beaker, add about 100 ml water and acidify with a few millilitres of concentrated hydrochloric acid.

When the decomposed mass is completely dissolved, remove the platinum crucible from the solution and rinse it with water.

The solution shall be perfectly clear. If not, filter through a medium filter paper, wash, burn off the paper, ignite and then repeat the decomposition as above. Transfer the solution to the 500 ml volumetric flask containing the filtrate and washings from the precipitation of silica in accordance with **13.3.1** or **13.4.1** or **13.5.1**. Fill the flask up to the mark with water. After stirring, this solution is ready for use.

It is used in the photometric determination of the silica remaining in solution (**13.8**) and also in the complexometric determinations of iron (III) oxide (**13.10**), aluminium oxide (**13.11**), calcium oxide (**13.12** or **13.14**) and magnesium oxide (**13.13** or **13.15**).

13.8 Determination of soluble silica

13.8.1 *Procedure*

Pipette 20 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a polyethylene beaker already containing a magnetic stirrer bar and add 20 ml water. While stirring with the magnetic stirrer, add 15 drops of hydrofluoric acid 1 + 3. Stir again for at least 1 min. Then pipette 15 ml of the boric acid solution (**4.40**). Adjust the pH of the solution to (1,15 ± 0,05) by adding, drop by drop, sodium hydroxide (**4.25**) or hydrochloric acid 1 + 2, using a pH meter calibrated with a buffer solution of similar pH value (e.g. 1,40, see **4.47**). Add from a pipette 5 ml of the ammonium molybdate solution (**4.42**) to the solution (time 0). Adjust the pH of the solution to 1,60 by adding, drop by drop, the sodium hydroxide solution (**4.25**) or hydrochloric acid 1 + 2. Transfer the solution to a 100 ml volumetric flask and rinse the beaker with hydrochloric acid of pH 1,60 (**4.9**). After 20 min, add from a pipette 5 ml of the citric acid solution (**4.41**), stir and leave to stand for 5 min. Then add from a pipette 2 ml of the reducing solution (**4.46**). Make up to volume with dilute hydrochloric acid of pH 1,60 and mix. At time 0 + 30 min measure the optical density with the photometer (**5.9**) against a blank solution prepared in a similar way and using the same wavelength of a cell of the same optical length as used for the construction of the calibration graph (**4.50.3**). The silica concentration in mg SiO_2/100 ml is read from the calibration graph.

13.8.2 *Expression of results*

The soluble silica content is calculated in percent from the formula:

$$\text{Soluble SiO}_2 = \frac{500 \times m_{25} \times 100}{20 \times 1000 \times m_{23}}$$

$$= 2,5 \times \frac{m_{25}}{m_{23}} \tag{21}$$

where

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams;

m_{25} is the silica content of the solution in accordance with **13.8.1** in mg SiO$_2$/100 ml.

13.9 Total silica

13.9.1 *Expression of results*

The total silica content is equal to the sum of the pure silica content (**13.6**) and the soluble silica content (**13.8**).

13.9.2 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,10 %.

The standard deviation for reproducibility is 0,25 %.

13.10 Determination of iron (III) oxide

13.10.1 *Procedure*

Pipette 100 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a beaker compatible with the measuring apparatus (**5.11**). Then make up with water to a volume suitable for the correct operation of the equipment.

Add 0,5 g amino-acetic acid (**4.18**) and 0,3 g to 0,4 g of sulfosalicylic acid indicator (**4.60**).

Using a pH meter, adjust the pH of this solution to (1,5 ± 0,1) with the ammonium hydroxide 1 + 1 (**4.21**) and 1 + 10 (**4.22**).

Heat to (47,5 ± 2,5) °C. Place the beaker in the apparatus (**5.11**) set at 520 nm and, while stirring the solution, titrate with 0,03 mol/l EDTA solution (**4.53**). In the vicinity of the indicator colour change, construct a diagram of the optical density values as a function of the volume of EDTA added. The volume V_{10} used is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant optical density after the colour change.

During the titration, the temperature of the solution shall not exceed 50 °C. Otherwise the determination shall be repeated.

This titrated solution is retained for the determination of aluminium oxide content in accordance with **13.11.1**. The presence of titanium oxide (TiO$_2$) can disturb the determination of iron oxide (Fe$_2$O$_3$) in the presence of peroxide and the latter shall be completely decomposed.

NOTE. The presence of titanium affects the speed of the titration of iron by EDTA. This cause of error can be overcome by proceeding slowly, for example with the help of an automatic burette. It is equally possible to mask the titanium by adding 2 ml of sulfuric acid 1 + 1 to the solution before titration.

13.10.2 *Expression of results*

The iron (III) oxide content is calculated in percent from the formula:

$$\text{Fe}_2\text{O}_3 = $$
$$\frac{0,03 \times 159,692 \times 500 \times V_{10} \times f_\text{D}}{2 \times 1000 \times 100 \times m_{23}} \times 100$$

$$= 1,1977 \times \frac{V_{10} \times f_\text{D}}{m_{23}} \tag{22}$$

where

V_{10} is the volume of 0,03 mol/l EDTA solution used for the titration, in millilitres;

f_D is the factor of the 0,03 mol/l EDTA solution defined in **4.53**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

13.10.3 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,08 %.

The standard deviation for reproducibility is 0,15 %.

13.11 Determination of aluminium oxide

13.11.1 *Procedure*

Cool the solution retained from **13.10.1** to room temperature. Then add 5 ml of acetic acid (**4.17**) then, drop by drop, the ammonium acetate solution (**4.44**) so as to obtain a pH of (3,05 ± 0,05). This zone shall be strictly adhered to and controlled by means of a pH meter. Under no circumstances is a pH of 3,1 to be exceeded. Bring to the boil, add three drops of the copper complexonate solution (**4.54**) and 10 drops of PAN indicator (**4.61**).

During the titration, the solution shall be kept gently boiling (work in a fume cupboard). Titrate with the 0,03 mol/l EDTA solution (**4.53**) until the colour changes from violet-pink to pale yellow. When the pink colour reappears, add the 0,03 mol/l EDTA drop by drop until the yellow colour persists for at least 1 min.

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13.11.2 *Expression of results*

The aluminium oxide content is calculated in percent from the formula:

$$Al_2O_3 = \frac{0,03 \times 101,961 \times 500 \times V_{11} \times f_D}{2 \times 1000 \times 100 \times m_{23}} \times 100$$

$$= 0,7647 \times \frac{V_{11} \times f_D}{m_{23}} \qquad (23)$$

where

V_{11} is the volume of 0,03 mol/l EDTA solution used for the titration, in millilitres;

f_D is the factor of the 0,03 mol/l EDTA solution defined in **4.53.3**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

13.11.3 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,10 %.

The standard deviation for reproducibility is 0,25 %.

13.12 Determination of calcium oxide by EGTA (reference method)

13.12.1 *Procedure*

Pipette 25 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a beaker compatible with the measuring apparatus (**5.11**) and make up to the same volume as in **4.55.3** with water and then add 25 ml of the triethanolamine solution 1 + 4 (**4.45**). Adjust the pH of this solution to 12,5 (using a pH meter) with a sodium hydroxide solution (**4.25**). Add about 0,1 g of murexide (**4.57**) or calcein indicator (**4.58**). Place the beaker in the apparatus (**5.11**) set at 520 nm when using calcein or at 620 nm when using murexide and, while stirring, titrate with the 0,03 mol/l EGTA solution (**4.55**). In the vicinity of the colour change, construct a diagram of the readings from the measuring apparatus as a function of the volume of EGTA added. The volume V_{12} used is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant optical density after the colour change.

13.12.2 *Expression of results*

The calcium oxide content is calculated in percent from the formula:

$$CaO = \frac{0,03 \times 56,08 \times 500 \times V_{12} \times f_G}{1000 \times 25 \times m_{23}} \times 100$$

$$= 3,3648 \times \frac{V_{12} \times f_G}{m_{23}} \qquad (24)$$

where

V_{12} is the volume of 0,03 mol/l EGTA solution used for titration, in millilitres;

f_G is the factor of the 0,03 mol/l EGTA solution defined in **4.55.3**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

NOTE. Strontium oxide is determined and expressed as calcium oxide.

13.12.3 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,18 %.

The standard deviation for reproducibility is 0,37 %.

13.13 Determination of magnesium oxide by DCTA (reference method)

13.13.1 *Procedure*

Pipette 50 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a beaker compatible with the measuring apparatus (**5.11**), add 50 ml of triethanolamine solution 1 + 4 (**4.45**) and a volume V_{13} of the EGTA solution. The volume V_{13} required is calculated in millilitres from the formula:

$$V_{13} = 2\,V_{12} + 1,5 \qquad (25)$$

where

V_{12} is the volume of the EGTA solution used for titration in accordance with **13.12.1**, in millilitres;

V_{13} is the volume of the EGTA solution, in millilitres.

After addition of the calculated volume of EGTA solution, dilute with water to a volume suitable for the correct operation of the apparatus. Using a pH meter, adjust the pH of this solution to 10,5 with concentrated ammonium hydroxide.

Add about 0,1 g of methylthymol blue indicator (**4.62**).

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Place the beaker in the apparatus (**5.11**) set at 620 nm and, while stirring the solution, titrate with the 0,01 mol/l DCTA solution (**4.56**). In the vicinity of the colour change of the indicator, plot a graph of the optical density values as a function of the volume of DCTA added. The volume V_{14} used is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant optical density after the colour change.

13.13.2 *Expression of results*

The magnesium oxide content is calculated in percent from the formula:

$$MgO = \frac{0,01 \times 40,311 \times 500 \times V_{14} \times f_c}{1000 \times 50 \times m_{23}} \times 100$$

$$= 0,4031 \times \frac{V_{14} \times f_c}{m_{23}} \qquad (26)$$

where

V_{14} is the volume of 0,01 mol/l DCTA solution used for the titration, in millilitres;

f_c is the factor of the 0,01 mol/l solution defined as **4.56.3**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

13.13.3 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,15 %.

The standard deviation for reproducibility is 0,15 %.

13.14 Determination of calcium oxide by EDTA (alternative method)

13.14.1 *Restriction on the method*

This method shall be preceded by the determination of manganese content (see clause **12** and also **13.15.1**).

13.14.2 *Procedure*

Pipette 50 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a beaker compatible with the measuring apparatus (**5.11**). Then dilute with water to a volume suitable for the correct operation of the equipment. Add 50 ml of the triethanolamine solution 1 + 4 (**4.45**).

Using a pH meter, adjust the pH of this solution to 12,5 with the sodium hydroxide solution (**4.25**).

Add about 0,1 g of murexide (**4.57**) or calcein indicator (**4.58**). Place the beaker in the apparatus (**5.11**) set at 620 nm when using murexide or at

520 nm when using calcein and, while stirring the solution, titrate with the 0,03 mol/l EDTA solution (**4.53**). In the vicinity of the colour change of the indicator, plot a graph of the optical density values as a function of the volume of EDTA added. The volume V_{15} used is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant optical density after the colour change.

13.14.3 *Expression of results*

The calcium oxide content is calculated in percent from the formula:

$$CaO = \frac{0,03 \times 56,08 \times 500 \times V_{15} \times f_D}{1000 \times 50 \times m_{23}} \times 100$$

$$= 1,6824 \times \frac{V_{15} \times f_D}{m_{23}} \qquad (27)$$

where

V_{15} is the volume of 0,03 mol/l EDTA solution used for the titration, in millilitres;

f_D is the factor of the 0,03 mol/l EDTA solution defined in **4.53.3**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

NOTE. Strontium oxide is determined and expressed as calcium oxide.

13.14.4 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,15 %.

The standard deviation for reproducibility is 0,43 %

13.15 Determination of magnesium oxide by EDTA (alternative method)

13.15.1 *Restriction on the method*

For the rare particular instances where cements have a manganese oxide (Mn_2O_3) content greater than 0,5 %, the method of determination of magnesium oxide by DCTA (**13.13**) is applicable. Indeed in this case, the alternative method gives high results, or it requires a preliminary separation of hydroxides by precipitation.

13.15.2 *Procedure*

Pipette 50 ml of the solution prepared in accordance with **13.7** from the 500 ml volumetric flask into a beaker compatible with the measuring apparatus (**5.11**). Then dilute with water to a volume suitable for the correct operation of the equipment. Add 50 ml of the triethanolamine solution 1 + 4 (**4.45**).

Using a pH meter, adjust the pH of this solution to 10,5 with dilute ammonium hydroxide 1 + 1.

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Using a burette, add the volume V_{15} of EDTA required for the titration of calcium oxide previously determined in **13.14.2**.

Then add about 0,1 g of methylthymol blue indicator (**4.62**).

Place the beaker in the apparatus (**5.11**) set at 620 nm and, while stirring the solution, titrate with the 0,03 mol/l EDTA solution (**4.53**). In the vicinity of the colour change of the indicator, plot a graph of the optical density values as a function of the volume of EDTA added. The volume V_{16} used is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant optical density after the colour change.

13.15.3 *Expression of results*

The magnesium oxide content is calculated in percent from the formula:

$$MgO = \frac{0,03 \times 40,311 \times 500 \times (V_{16} - V_{15})f_D}{1000 \times 50 \times m_{23}} \times 100$$

$$= 1,2093 \times \frac{(V_{16} - V_{15})}{m_{23}} \qquad (28)$$

where

V_{15} is the volume of EDTA required for the determination of calcium oxide determined in **13.14.2**, in millilitres;

V_{16} is the volume of EDTA required for the determination of calcium oxide and magnesium oxide defined in **13.15.2**, in millilitres;

f_D is the factor of the 0,03 mol/l EDTA solution defined in **4.53.3**;

m_{23} is the mass of the test portion as in **13.2** (m_{17}) or **13.5.1** (m_{20}), in grams.

13.15.4 *Repeatability and reproducibility*

The standard deviation for repeatability is 0,21 %.

The standard deviation for reproducibility is 0,25 %.

13.16 Comments on the visual observation of the titrations for the determinations of calcium oxide and magnesium oxide

The methods described in **13.12**, **13.13**, **13.14** and **13.15** use a photometric determination of the end-points.

It is possible to make visual observations of the titrations but with less precision. The indicators often used for this purpose are as follows:

a) For the determination of calcium oxide by EGTA:

mixed indicator: calcein and methylthymol blue (**4.63**) (colour change from pale green to pink).

This indicator is suitable also for the photometric determination.

b) For the determination of magnesium oxide by DCTA:

methylthymol blue (**4.62**) (colour change from blue to grey).

c) For the determination of calcium oxide by EDTA:

calcon (**4.59**) (colour change from pink to blue).

d) For the determination of magnesium oxide by EDTA:

a dispersion of 1 g of phthalein purple in 100 g of solid NaCl (colour change from violet to pale pink).

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National annex NA (informative)

Determination of total sulfur

NA.1 Procedure

To 1.000 g of cement add 25 ml of saturated bromine water and while stirring vigorously add 5 ml of hydrochloric acid saturated with bromine. If necessary, heat the solution and break up the cement with the flattened end of a glass rod until decomposition is complete. Dilute the solution to 150 ml and heat it to boiling point until all the bromine has been driven off.

Then follow the procedures from the second paragraph of **8.2**.

NA.2 Calculation

Calculate the sulfur content, S, as a percentage from the formula:

$$S = W \times 13.73$$

where

W is the mass of barium sulfate (in g).

National annex NB (informative)

Determination of minor constituents (TiO_2 and P_2O_5) and free lime

NB.1 Colorimetry

An approximate determination can be made by visual comparison with a colorimetric scale corresponding to known quantities of the constituent to be determined.

A more precise determination can be made absorptiometrically. Two kinds of spectrophotometric apparatus are in common use: that employing a prism or grating monochromator capable of selecting a wavelength band of about 1 nm, and that using an optical filter of the ordinary or the interference type, allowing the passage of a band of 5 nm to 20 nm. The narrower the wave band the more accurately does the additivity law apply to the optical densities measured.

NB.2 Colorimetric determination of titanium

NB.2.1 Reagents

NB.2.1.1 *Ammonium nitrate.* Dissolve 20 g of ammonium nitrate in 1 l of water and just neutralize to methyl red with ammonia solution.

NB.2.1.2 *Hydrogen peroxide.* 6 % (20 volumes).

NB.2.1.3 *Standard titanium stock solution.* Boil for 15 min a mixture of 4.435 g of potassium titanium oxalate dihydrate with 8 g of ammonium sulfate and 50 ml of sulfuric acid. Cool, dilute with water to 1 l and mix. One ml contains 1.0 mg TiO_2.

NB.2.1.4 *Standard titanium working solution.* Dilute the stock solution ten times to give a solution of which 1 ml contains 0.10 mg TiO_2.

NB.2.2 *Procedure*

Dilute the filtrate, including the dissolved hydrofluoric acid residue, from a silica separation (**13.5.1**) to 500 ml. Take a 50 ml aliquot (equivalent to 0.1 g of cement), heat to boiling and neutralize with dilute ammonia solution (1 + 1), using methyl red indicator. Filter the precipitated hydroxides on a rapid filter paper[*] and wash with hot ammonium nitrate solution until the washings are chloride-free. Transfer the precipitate to the original beaker, first with water and then with 30 ml of hot dilute sulfuric acid (1 + 4), taking care to dissolve all the precipitate. Filter if necessary to remove paper fibres. Cool and transfer to a 100 ml volumetric flask, add 5 ml of hydrogen peroxide, dilute to 100 ml and mix the contents. Allow 5 min for full colour development before measuring the optical density.

NB.2.3 *Measurement*

The colour can be measured by visual comparison or instrumentally, using a spectrophotometer.

With the monochromator-type instrument, operate at 410 nm; with the filter-type instrument, use a blue filter of which the wavelength band is as near as possible to 410 nm[†].

Prepare a range of standards containing known amounts of titanium. Each standard should contain 30 ml of sulfuric acid (1 + 4) and 5 ml of hydrogen peroxide in 100 ml. Construct a standard curve giving the optical density as a function of concentration. Refer the optical density obtained for the sample solution to this curve and calculate the percentage TiO_2 content.

NB.3 Colorimetric determination of phosphorus

NB.3.1 *Reagents*

NB.3.1.1 *Ammonium vanado molybdate (AVM).* Dissolve 1 g of ammonium vanadate in 300 ml of water, preferably with the help of mechanical stirring. After complete solution, add slowly 140 ml of nitric acid then 400 ml of 10 % ammonium molybdate solution. Make up the mixture to 1 l with water.

NB.3.1.2 *Standard phosphate solution.* Dissolve exactly 0.186 g of dry diammonium phosphate in water and dilute to 1 l. One ml contains 0.1 mg P_2O_5.

NB.3.1.3 *Sodium fluoride solution.* Dissolve 20 g of sodium fluoride in 1 l of water.

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[*] A Whatman No. 541 or similar filter paper is suitable.
[†] An Ilford 601 filter is suitable.

NB.3.2 Procedure

Dilute the filtrate, including the dissolved hydrofluoric acid residue, from a silica separation (**13.5.1**) to 500 ml. Place a 50 ml aliquot (equivalent to 0.1 g of cement) in a 100 ml volumetric flask, add 15 ml of AVM reagent (**NB.3.1.1**) and allow to stand. (If the iron content of the cement exceeds 3 % Fe_2O_3 add 5 ml of sodium fluoride solution after 20 min). Dilute to 100 ml and mix. Measure the optical density 30 min after adding the AVM solution.

NB.3.3 Measurement

The colour can be measured by visual comparison or instrumentally, using a spectrophotometer.

With the monochromator-type instrument, operate at 426 nm; with the filter-type instrument, use a filter of which the wavelength band is as near as possible to 426 nm[†].

Prepare a range of standards containing known amounts of phosphorus and the same amounts of reagents as the sample. Construct a standard curve giving the optical density as a function of concentration. Refer the optical density obtained for the sample solution to this curve and calculate the percentage P_2O_5 content.

NB.4 Estimation of free lime (calcium oxide plus calcium hydroxide)

NB.4.1 Special reagents

NB.4.1.1 *Mixed indicator.* Dissolve 0.05 g of methyl red in about 40 ml of absolute ethyl alcohol, and 0.05 g of bromocresol green in about 40 ml of ethyl alcohol. Mix both solutions and make up to 100 ml with ethyl alcohol.

NB.4.1.2 *Absolute ethyl alcohol.* This liquid readily absorbs moisture from the atmosphere. It should be kept in tightly stoppered bottles fitted with an airtight cap, and opened only for the lapse of time necessary for manipulations.

NB.4.1.3 *Glycol.* (1 : 2 ethane diol). Ensure that this reagent is pure and anhydrous. It absorbs atmospheric moisture and should be treated in the same way as absolute alcohol. Ensure that the glycol does not contain more than 0.5 % of water.

NOTE. Water content in absolute alcohol and glycol can be determined by titration by the Karl Fischer method.

Add to each litre of glycol 5 ml of mixed indicator (**NB.4.1.1**) and adjust if necessary by the addition of alcoholic potassium hydroxide to a green colour.

NB.4.1.4 *Hydrochloric acid.* (0.1 N).

NB.4.1.5 *Calcium oxide standard.* Ignite about 0.20 g of calcium carbonate in a weighed platinum crucible at 1000 °C in an electric furnace. Verify the complete removal of carbon dioxide by re-weighing and record the mass of calcium oxide.

NB.4.2 Procedure

Weigh a 1.000 g sample into a dry conical 200 ml flask, add 1 g to 2 g of dry sand[‡] and about 0.5 g of dry filter paper or pulp. Mix thoroughly. Add 40 ml of glycol, stopper the flask. Shake or stir vigorously. Place the flask for 30 min in a water bath at 65 °C to 70 °C and shake manually every 5 min. Continuous mechanical agitation is even better.

Filter the mixture under suction through a dry filter of suitable porosity to provide a clear filtrate. Unless the filtration is rapid it may be necessary to keep the mouth of the sintered glass filter protected by an apparatus which will remove moisture and carbon dioxide from incoming air (for instance a close fitting rubber cover connected to guard tubes containing soda-lime and magnesium perchlorate).

Wash with three separate 10 ml portions of absolute alcohol or hot glycol, carefully rinsing the conical flask, then remove the filtration flask and titrate with 0.1 N hydrochloric acid until the colour changes (colour changes through brown to orange).

NB.4.3 Standardization

Transfer the weighed calcium oxide obtained in **NB.4.1.5** to a dry conical flask, add 40 ml of glycol, agitate and heat as in **NB.4.2**. The lime should dissolve without residue. Nevertheless, filter and titrate as in **NB.4.2**.

NB.4.4 Calculation

Calculate the free lime content, C_a, as a percentage from the formula:

$$C_a = t \times \frac{100w}{t_s}$$

where

w is the mass of standard calcium oxide (in g);

t_s is the volume of hydrochloric acid used in **NB.4.3** (in ml);

t is the volume of hydrochloric acid used in **NB.4.2** (in ml).

[†] An Ilford 601 filter is suitable.

[‡] It is best to use quartz sand (grains of about 0.5 mm diameter upwards) or glass beads for this purpose. Alternatively, magnetic stirring with a naked magnet may be employed.

National annex NC (informative)

Determination of propylene glycol content

NC.1 Principle

The cement is extracted with industrial methylated spirits containing decanol as an internal standard. After centrifuging, the clear solution is analysed by gas liquid chromatography.

NC.2 Reagents

NC.2.1 *Industrial methylated spirits.*

NC.2.2 *Decanol solution (250 mg/l).* Weigh 0.250 g of decan-l-ol and dilute to 1000 ml in a volumetric flask with the industrial methylated spirits.

NC.2.3 *Propylene glycol solution (500 mg/l).* Weigh 0.100 g of propane-1,2-diol and dilute to 200 ml in a volumetric flask with the industrial methylated spirits.

NC.3 Apparatus

NC.3.1 *Electric centrifuge*[*], complying with BS 4402, capable of whirling two or more filled centrifuge tubes at a speed controlled to give an acceleration of 7000 m/s² at the tips of the tubes calculated from the formula:

$$\text{acceleration} = 11\, n^2 r \times 10^{-6}$$

where

n is the rate of rotation (r/min);

r is the radial distance to the inside of the tips of the tubes when rotating (mm).

NC.3.2 *15 ml glass vials (with caps)*, suitable for use with **NC.3.1**.

NC.3.3 *Graduated pipettes* (10 ml and 1 ml).

NC.3.4 *Gas liquid chromatograph* equipped with flame ionization detector.

NC.4 Method

Weigh 1.000 g of the sample and place into a glass vial. Pipette into the vial 4.0 ml of industrial methylated spirits and 1.0 ml of the decanol solution.

Place the cap on the vial and shake vigorously for 1 min. Centrifuge at an acceleration of 7000 m/s² for 5 min. Decant the clear liquid into a clean vial. Inject 1.0 μl into the chromatograph using the following operational conditions.

a) Column	10 % polyethylene glycol (molecular weight 20 000) on diatomite Grade C, acid-washed 150 μm to 125μm, length 1.5 m, internal diameter 4 mm.
b) Carrier gas	Nitrogen, flow rate 40 ml/min.
c) Column temperature	150 °C.
d) Recorder chart speed	10 mm/min.

The chromatograms of the calibration solutions (see **NC.5**) give peaks due to propylene glycol and decanol at approximately 7 min and 14 min respectively after the sample is injected. If propylene glycol is present in the sample then the chromatogram obtained from the sample containing the internal standard will give peaks with similar retention times. Measure these peak areas either manually or using an integrator. Calculate the ratio:

$$\frac{\text{area for propylene glycol}}{\text{area for decanol}}$$

Read off the proportion of propylene glycol in the cement from the calibration graph, prepared as in **NC.5** and report it as a percentage to the nearest 0.01 %.

NC.5 Preparation of calibration graph

Transfer by means of a pipette 0.5 ml, 1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml and 5.0 ml aliquots of the propylene glycol solution each into one of six glass vials. Add to each vial 1.0 ml of the decanol solution and mix thoroughly.

Analyse each mixture on the chromatograph as in **NC.4**. Plot a graph of the ratio of the peak areas against percentage of propylene glycol in 1 g of cement. (The above aliquots are equivalent to 0.025 %, 0.05 %, 0.10 %, 0.15 %, 0.20 % and 0.25 % propylene glycol in cement respectively.)

NC.6 Normative reference

BS 4402 : 1982 *Specification for safety requirements for laboratory centrifuges*

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[*] For information on the availability of a suitable electric centrifuge, write to Customer Services, Information Services Group, BSI, 389 Chiswick High Road, London, W4 4AL.

National annex ND (informative)

Method of analysis of cements by X-ray fluorescence spectrometry

ND.1 General

The method is intended for the determination of the major oxide contents of Portland cement, conforming to BS 12 : 1991 (see note), within the following compositional ranges.

Oxide	%
SiO_2	18 - 24
Al_2O_3	2.6 - 8
Fe_2O_3	1.5 - 7
CaO	61 - 69
MgO	0.5 - 4
SO_3	0.2 - 4
K_2O	0.2 - 1.0

It is not considered appropriate to apply this method to the determination of Na_2O content in view of the inadequate precision at present obtainable by X-ray fluorescence (XRF) spectrometry using fused beads at the levels normally present in cements.

NOTE. Whilst the method was originally developed for cements conforming to the 1978 and 1989 editions of BS 12, the calibration range has been extended to allow for minor constituents of up to 5 %. It is therefore believed that the method and precision values will be valid for Portland cement conforming to BS 12 : 1991.

ND.2 Principle

The cement is fused with a mixture of lithium tetraborate and lanthanum oxide. The resultant melt is cast to form a glass bead suitable for introduction into an X-ray fluorescence spectrometer. The intensities of the fluorescent X-rays of the required elements are measured and the chemical composition of the cement is determined by reference to previously established calibrations. These have been selected to cover narrow compositional ranges so that, together with the use of lanthanum oxide as a heavy absorber, matrix effects are minimized.

A monitoring scheme is incorporated to compensate for any short-term instrumental drift and thus to avoid the need for full re-calibration with every batch of test samples. The frequency of full re-calibration for each particular instrument is determined by the analyst. An on-going check on the accuracy of the method is made by incorporating beads made with a certified reference cement with each batch of test samples.

ND.3 Symbols

I	Intensity for an element
I_M	Intensity for an element from the single monitor bead
I_H	Intensity for an element from the high monitor bead
I_L	Intensity for an element from the low monitor bead
m	Slope of a calibration line in concentration per unit intensity
k_1, m_1	Intercept (concentration at zero intensity) and slope (concentration per unit intensity ratio) for an element when using the single monitor method
k_2, m_2	Intercept (concentration at zero intensity) and slope (concentration per unit intensity) for an element when using the high/low monitors
$\hat{C}$	Concentration of an oxide in the calibration standards calculated using a calibration line
$\hat{C}_H, \hat{C}_L$	Concentration of an oxide in the high and low monitors calculated using a calibration line at the time of calibration
C	Actual concentration of an oxide in a standard bead, calculated from the masses given in table ND.5
$\overline{C}$	Average concentration of an oxide in the 14 calibration standards, calculated from the masses given in table ND.5
$\hat{C}_{K_2O}$	Concentration of K_2O in the unknowns calculated using the calibration line for K_2O (as used in **ND.11.3**)

C'_{CaO}	Apparent concentration of CaO
$\hat{C}'_{CaO}$	Apparent concentration of CaO calculated using the calibration line for CaO, prior to applying the α-correction for K_2O
$\hat{C}_{CaO}$	Calculated concentration of CaO after applying the α-correction for K_2O
a	Influence coefficient of potassium on calcium
K	Figure of merit
S	Calibration standard deviation

Table ND.1. Ignition conditions for pure standards

	Temp. °C	Time h
Silicon dixoide (SiO_2)	1200	1
Aluminium oxide (Al_2O_3)	1200	1
Iron oxide (Fe_2O_3)	700	1
Calcium carbonate ($CaCO_3$)	220	2
Magnesium oxide (MgO)	1200	1
Calcium sulfate ($CaSO_4.2H_2O$)	500	1
Potassium carbonate (K_2CO_3)	220	2

ND.4 Sample preparation (see ND.7)

Remove a 100 g subsample from the original laboratory sample by repeated riffling, or by use of a rotating sampler, or by spreading the material in a thin layer and taking about 50 evenly spaced spoonfuls.

Separate the subsample into coarse and fine fractions by passing through a 150 µm sieve. Remove with a magnet any iron from the material retained on the sieve and then grind the remainder so that it passes the 150 µm sieve.

Transfer both fractions to a clean, dry, 200 ml bottle with an air-tight closure and thoroughly mix by tumbling, rolling and shaking for at least 2 min, (test portion).

ND.5 Reagents

ND.5.1 *Lithium tetraborate flux (purity not less than 99.99 %).* Ignite the lithium tetraborate at (600 ± 25) °C for a minimum of 2 h and allow to cool over a suitable desiccant immediately prior to weighing.

ND.5.2 *Lanthanum oxide (purity not less than 99.9 %).* Sieve the lanthanum oxide to pass a 150 µm sieve, ignite at (1000 ± 25) °C for a minimum of 1 h and allow to cool over a suitable desiccant immediately prior to weighing.

NOTE. See **ND.8.1e)** for action to be taken after changing the batch of either of the flux components.

ND.5.3 *Chemicals for synthetic calibration standards.* Ignite the high quality purity chemicals at the temperature and for the time specified in table ND.1 and allow to cool over a suitable desiccant immediately prior to weighing. It is necessary for the silicon dioxide and calcium carbonate to have purities of not less than 99.99 %, the aluminium, iron and magnesium oxides to have purities of not less than 99.95 %, and the remaining reagents to be of analytical reagent quality or better.

ND.6 Apparatus

ND.6.1 *General.* Vessels used for the fusion of samples with the flux and for casting the beads, made from a platinum alloy which is not wetted by the melt.

NOTE. Platinum 95 %/gold 5 % is suitable.

ND.6.2 *Fusion dishes*, of sufficient capacity to hold the quantity of unfused sample and flux required by the size of the casting mould.

NOTE. A fusion dish of 50 ml capacity is generally suitable.

ND.6.3 *Casting moulds*, designed to give a circular bead of a diameter within the range 35 mm to 40 mm and of thickness to exceed the critical depth for the element lines used in analysis, with sides set at a suitable angle to the vertical, to ensure that the beads are readily released. The moulds are frequently polished and examined for flatness, unless the top surface is used as in **ND.8.2**, and reforming is carried out if there is any noticeable bowing. Carry out calibration and analysis using the same pattern and size of casting mould throughout.

NOTE. It is usually necessary, especially when using moulds of small size, to place the mould on a heat reservoir, e.g. a small piece of refractory material, so that the bead does not crack as a result of rapid cooling.

ND.6.4 *Fusion mould.* An alternative method is fusion in a dish followed by casting into a mould, for which a combined vessel functioning both as a fusion dish and a casting mould (see figure ND.1) may be used. It is necessary for the capacity of the dish to be sufficient to hold the unfused sample and flux required to fill the mould part of the vessel when fused. The mould part of the vessel has the same specifications as given in **ND.6.3**. However, where such combined vessels are used, only the top surface of the bead is suitable for measurement (see **ND.8.2**).
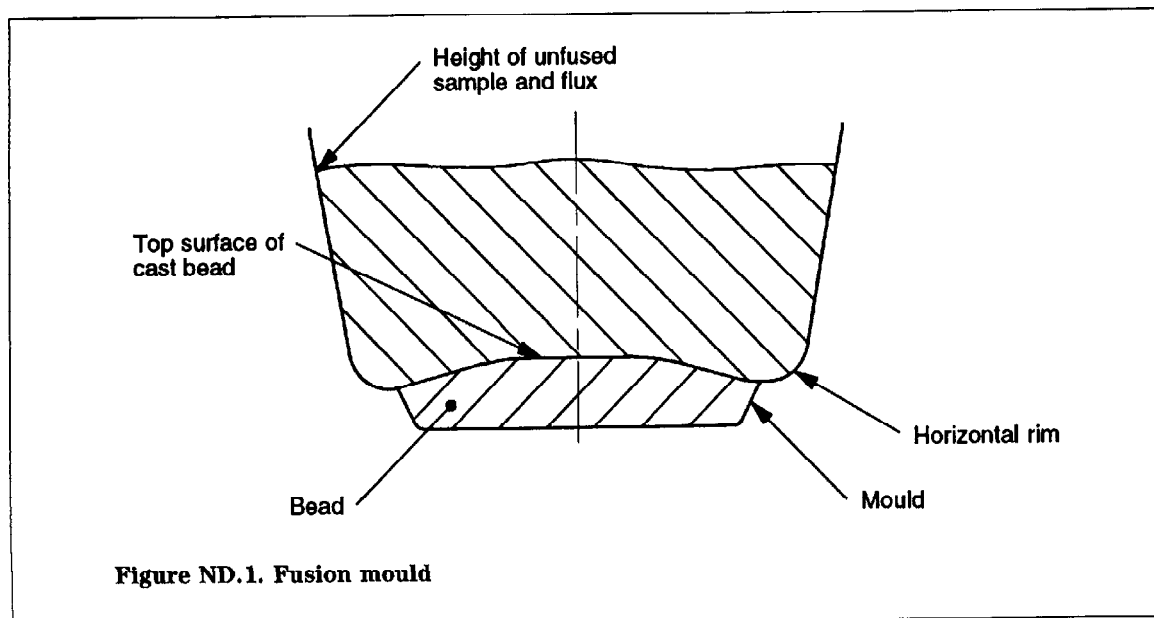
Figure ND.1. Fusion mould

ND.7 Preparation of beads

ND.7.1 *Number of tests*

Carry out all determinations on test samples and calibration standards on duplicate beads.

ND.7.2 *Loss on ignition*

Determine the loss on ignition, L, of the test portion using the method described in clause **7** and calculate the result to two decimal places.
Calculate, to four decimal places, the mass of sample in grams, W_L, required to give 1.0000 g of ignited sample using the equation:

$$W_L = \frac{100}{100 - L}$$

Alternatively, take approximately 1.5 g, carry out a test for loss on ignition in accordance with clause **7** and use the ignited sample for bead preparation.

ND.7.3 *Weighing*

Weigh (9.000 ± 0.001) g of the freshly ignited lithium tetraborate flux, (1.000 ± 0.001) g of the freshly ignited lanthanum oxide and either (W_L ± 0.0001) g of the test portion or (1.0000 ± 0.0001) g of freshly ignited test portion, into a glass container. Stopper the container and mix thoroughly.

NOTE. It is not necessary to stopper the container completely after weighing the two flux components. In practice a small amount of moisture, picked up by the flux, aids the mixing and the transfer to the fusion dish.

ND.7.4 *Fusion*

Transfer the mixture as completely as possible to the fusion dish.

NOTE. If desired, 1.01 ml of 1 % aqueous lithium iodide may be added to aid bead release.

Place the fusion dish in the furnace at (1100 ± 20) °C. After 5 min remove the dish, swirl the melt and return it to the furnace. Place the casting mould (with the refractory reservoir if used, see note to **ND.6.3**) in the furnace. After a total fusion time of 10 min (± 10 s) remove the casting mould and reservoir, swirl the melt and pour into the mould as quickly as possible. Cover with a beaker and allow to cool. Remove the bead from the casting mould; if this is not easily achieved, tapping the casting mould gently onto a firm warm surface will normally release it. Inspect the bead surface to be analysed for blemishes and if these are present reject the bead. Alternative techniques for bead preparation may be used providing the following criteria are satisfied:

    a) the same preparation technique is applied consistently;

    b) the melts produced are homogeneous;

    c) there is no measurable loss of any component from the sample during fusion;

    d) any loss of flux during fusion is reproducible;

    e) the process does not contaminate the sample;

    f) beads produced are free from blemishes on the analytical surface.

ND.8 Measurement

ND.8.1 *Instrument requirements*

Owing to the inherent differences in commercial XRF instruments it is not possible to specify conditions precisely; in consequence the requirements for the instrument to meet the needs of the analysis are as follows.

a) The instrument is used and maintained in accordance with the limitations imposed by the manufacturer.

b) The detector is used within its linear response region.

c) The X-ray line, crystals, collimators, detectors, use of off-peak backgrounds and pulse height analysis are chosen to avoid line overlap wherever possible.

d) The differential detection limit, D, for each element is given by the equation[*]:

$$D = 4m\sqrt{N_{EL}}$$

where

$m = \dfrac{m_1}{N_M}$ or $m = \dfrac{m_2}{t}$ according to the monitor method used (see **ND.9**);

where

N_M is the total number of counts on the single monitor;

t is the counting time (in s);

N_{EL} is the total number of counts at the mean element concentration.

NOTE. For elements where there is no bead containing the mean concentration (SiO_2, CaO, SO_3) N_{EL} is obtained by linear interpolation from the two beads on either side of that concentration.

With the instrumental parameters used, it is necessary for the instrument to satisfy the maximum allowable differential detection limits given in table ND.2. However, operators should strive for the lowest differential detection limits obtainable within practical counting times. It is necessary that the chosen counting time as determined in this clause is used for all measurements.

e) In order to maintain the ongoing accuracy of the method, a bead prepared with the same batch of flux and lanthanum oxide as each batch of test portions, but using a certified reference cement, is presented to the instrument with that batch of test samples. It is necessary that the determined value for each element lies within $\pm D/2$ (see item d)) of the certified value. If this is not the case after repeated measurements, undertake recalibration for that element. If a calibration change has occurred immediately after the use of a new batch of flux component, prepare new calibration standards.

Table ND.2. Maximum allowable differential detection limits	
Oxide	Maximum allowable differential detection limit %
SiO_2	0.30
Al_2O_3	0.15
Fe_2O_3	0.05
CaO	0.25
MgO	0.20
SO_3	0.10
K_2O	0.05

ND.8.2 *Presentation of the bead*

Place the bead in the instrument such that the bottom (flat) surface is presented to the X-ray beam for analysis. The suitability of this method using the top (convex) surface of beads has not been verified, but providing it can be demonstrated that the precision is not inferior, then its use is permitted. In this case additional requirements for the specifications of the casting and fusion moulds are as follows.

There is an adequate horizontal rim to the casting mould or, in the case of fusion moulds, interposed between the top of the mould and the sides of the dish. The mass of melt is sufficient to fill the mould (or mould section in the case of fusion moulds) and give a reproducible convex top surface.

ND.8.3 *Measurement of intensities*

Measure and record, for the appropriate counting time (see **ND.8.1d**)), the intensities of the seven elements in either the single monitor bead (I_M) or the high and low monitor beads (I_H and I_L); (see **ND.9.2** or **ND.9.3**). Then measure and record, for the same counting time, the intensities (I) of the same elements in a maximum of two test sample beads. Repeat this cycle until the batch of test samples is complete.

ND.9 Compensation for instrumental drift

ND.9.1 *General*

This may be achieved by one of two methods, using either a single monitor bead or a pair of high and low monitor beads. Ignition of reagents to use is not necessary in the preparation of monitor beads.

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[*] See Tertian and Claisse. *Principles of quantitative X-ray fluorescence analysis.* Heyden, London 1982, p.349.

ND.9.2 *Single monitor method*

Prepare a bead using the masses of oxides, carbonate, sulfate and flux specified in table ND.3 and following the procedure given in **ND.7.3** and **ND.7.4**.

Table ND.3. Mass of ingredients to be used for single monitor bead

Ingredient	Mass g
SiO_2	0.2
Al_2O_3	0.1
Fe_2O_3	0.1
$CaCO_3$	1.0
MgO	0.1
K_2CO_3	0.1
$CaSO_4$	0.1
La_2O_3	1.0
Flux	8.9

ND.9.3 High and low monitors method

Prepare beads using the masses of oxides, carbonate, sulfate and flux specified in table ND.4 and following the procedure given in **ND.7.3** and **ND.7.4**.

Table ND.4. Mass of ingredients to be used for 'high and low' monitor beads

Ingredient	High g	Low g
SiO_2	0.3	0.1
Al_2O_3	0.1	Nil
Fe_2O_3	0.1	Nil
$CaCO_3$	1.2	1.0
MgO	0.1	Nil
K_2CO_3	0.1	Nil
$CaSO_4$	0.1	Nil
La_2O_3	1.0	1.0
Flux	8.5	9.3

ND.10 Calibration

ND.10.1 *Preparation of standards*

Prepare a series of seven beads in duplicate using the masses given in table ND.5 and following the procedure given in **ND.7.3** and **ND.7.4**. The composition of these beads corresponds to cements with the compositions given in table ND.6.

ND.10.2 *Measurement*

Using the cycle of monitor (single or high and low) and two test samples as in **ND.8.3**, measure and record, for the appropriate counting time (see **ND.8.1e**)), the intensities of the seven elements in the 14 calibration standards (duplicate beads 1 to 7 of table ND.6). The values are designated I and I_M (or I_H and I_L) as appropriate.

a) *Single monitor method*. Using a linear regression procedure, determine for each element, except calcium (see **ND.10.3**), the slope, m_1, and intercept, k_1, of the calibration line of actual concentration, C, (taken from table ND.6) against I/I_M. Determine the calculated value for each element in the calibration standards from the formula:

$$C = k_1 + (m_1 \times I/I_M)$$

b) *High and low monitors method*. Using a linear regression procedure, determine for each element, except calcium (see **ND.10.3**), the slope, m_2, and intercept, k_2, of the calibration line of actual concentration, C, (taken from table ND.6) against I. Then determine the calculated concentration, $\hat{C}_H$ and $\hat{C}_L$, of the high and low monitors from intensities I_H and I_L using the formulae:

$$\hat{C}_H = k_2 + (m_2 \times I_H) \text{ and}$$
$$\hat{C}_L = k_2 + (m_2 \times I_L) \text{ respectively.}$$

Determine the calculated value for each element in the calibration standards from the formula:

$$\hat{C} = \hat{C}_H - \left[\frac{(\hat{C}_H - \hat{C}_L) \times (I_H - I)}{(I_H - I_L)} \right]$$

Table ND.5. Calibration standards: mass of ingredients required for each fusion

Ingredient	Bead number						
	1	2	3	4	5	6	7
	g	g	g	g	g	g	g
SiO_2	0.2400	0.1950	0.2040	0.2230	0.1800	0.1870	0.2140
Al_2O_3	0.0720	0.0810	0.0260	0.0540	0.0450	0.0630	0.0360
Fe_2O_3	0.0150	0.0610	0.0680	0.0420	0.0530	0.0230	0.0340
$CaCO_3$	1.0422	1.0912	1.0960	1.1487	1.1354	1.1886	1.1992
MgO	0.0110	0.0170	0.0400	0.0260	0.0220	0.0320	0.0050
K_2CO_3	0.0147	0.0059	0.0029	0.0117	0.0088	0.0176	—
$CaSO_4$	0.0680	0.0306	0.0459	0.0034	0.0578	0.0170	0.0391
La_2O_3	1.000	1.000	1.000	1.000	1.000	1.000	1.000
$Li_2B_4O_7$	9.000	9.000	9.000	9.000	9.000	9.000	9.000

Table ND.6. Composition of calibration standards

Oxide	Bead number							
	1	2	3	4	5	6	7	Mean
	%	%	%	%	%	%	%	%
SiO_2	24.0	19.5	20.4	22.3	18.0	18.7	21.4	20.6
Al_2O_3	7.2	8.1	2.6	5.4	4.5	6.3	3.6	5.4
Fe_2O_3	1.5	6.1	6.8	4.2	5.3	2.3	3.4	4.2
CaO	61.2	62.4	63.3	64.5	66.0	67.3	68.8	64.8
MgO	1.1	1.7	4.0	2.6	2.2	3.2	0.5	2.2
SO_3	4.0	1.8	2.7	0.2	3.4	1.0	2.3	2.2
K_2O	1.0	0.4	0.2	0.8	0.6	1.2	0.0	0.6

ND.10.3 *Influence of potassium on calcium*

To calibrate for calcium it is necessary to know the influence coefficient (α) of potassium on calcium. This is defined by the equation:

$$C_{CaO} = C'_{CaO}(1 + \alpha C_{K_2O}).$$

NOTE. This equation is based on an alpha coefficient expressed in terms of per cent concentration units. Where α has been calculated from intensity or other units, an appropriate conversion is required.

Hence, for calcium, utilize in **ND.10.2a)** or **ND.10.2b)** the calibration lines of apparent concentration, calculated from:

$$C'_{CaO} = \frac{C_{CaO}}{1 + \alpha C_{K_2O}}$$

The value of α, which will be specific for a particular set of instrumental parameters, may be obtained by one of the following means:

a) from a published theoretical paper;

b) calculated using appropriate computer software;

c) determined using the following method.

Prepare two beads in duplicate using the masses given in table ND.7 and following the procedure given in **ND.7.3** and **ND.7.4**.

Measure the intensities for calcium on each bead using identical measuring conditions to those used in the main calibration, and calculate α for potassium on calcium using the formula:

$$\alpha = \frac{I_1 - I_2}{10 \times I_2}$$

where

I_1 is the intensity for calcium in bead 1;

I_2 is the intensity for calcium in bead 2.

Table ND.7. Composition of beads for determination of a-correction				
Ingredient	Bead 1		Bead 2	
	Mass	Equivalent oxide	Mass	Equivalent oxide
	g	%	g	%
SiO_2	0.3500	35	0.2500	25
$CaCO_3$	1.1600	65	1.1600	65
K_2CO_3	0	0	0.1467	10
La_2O_3	1.000	—	1.000	—
$Li_2B_4O_7$	9.000	—	9.000	—

ND.10.4 *Examination of calibration data*

Examine the data to determine whether linear calibration has been obtained (for calcium after applying the α correction), with K values not exceeding 0.05,

where $K = \dfrac{S}{\sqrt{\overline{C}}}$

$$S = \sqrt{\frac{\sum(\overline{C} - \hat{C})^2}{(n - 2)}}$$

n is the number of standards (7 duplicate beads, i.e. 14).

If higher K values are obtained, examine the calibration data for outliers and, if necessary, re-make the standards.

NOTE. If C differs from $\hat{C}$ by more than $2.6\sqrt{\left(\frac{C - k}{b}\right)}$, where $k = k_1$ or k_2 and $b = I_M/m_1$ or $1/m_2$ as appropriate, then the measurement may be considered to be an outlier rated at the 1 % significance level and excluded.

If difficulty is still encountered in achieving these requirements, check the sensitivity for that element (see **ND.8.1d**)).

ND.11 Measurement of test samples

ND.11.1 *Single monitor method*

Calculate the oxide content of the test sample for all elements except calcium using the equation:

% oxide (as-received basis)

$$= [K_1 + m_1 I/I_M] \times \left[\frac{100 - loss}{100}\right]$$

ND.11.2 *High and low monitors method*

Calculate the oxide content of the test sample for all the elements except calcium using the equation:

% oxide (as-received, basis)

$$= \left[\hat{C}_H - \frac{(\hat{C}_H - C_L)(I_H - I)}{(I_H - I_L)}\right] \times \left[\frac{100 - loss}{100}\right]$$

ND.11.3 *Calculation of calcium oxide content*

Calculate:

a) an apparent calcium oxide content of the test sample

($\hat{C}'_{CaO}$) and the potassium oxide content of the test sample

($\hat{C}_{K_2O}$) using the equation in **ND.10.2a**) or **ND.10.2b**) as appropriate;

b) the corrected calcium oxide content using the equations:

$$\hat{C}_{CaO} = \hat{C}'_{CaO}(1 + a\hat{C}_{K_2O})$$

and % CaO in the test sample $= \hat{C}_{CaO} \times$

$\times \dfrac{[100 - loss]}{100}$ (as-received basis)

ND.12 Precision

ND.12.1 The precision values for SiO_2 and CaO are given in table ND.8.

Table ND.8. Precision values for SiO_2 and CaO				
Oxide	Range	r_1	r_2	R
	%	%	%	%
SiO_2	19.9 to 23.4	0.17	0.28	0.49
CaO	64.2 to 66.4	0.27	0.46	0.63

ND.12.2 The precision value at a particular level of concentration of Al_2O_3, Fe_2O_3, MgO, K_2O and SO_3 is calculated as:

r_1 (or r_2 or R) % $= b \sqrt{c}$

where

b is the multiplier from table ND.9;

c is the level of concentration in %.

Table ND.9. Multipliers for precision values for Al_2O_3, Fe_2O_3, MgO, K_2O and SO_3				
Oxide	**Range** %	r_1 %	r_2 %	R %
Al_2O_3	3.1 to 6.7	0.050	0.065	0.099
Fe_2O_3	2.3 to 5.0	0.029	0.038	0.077
MgO	0.9 to 2.7	0.094	0.097	0.143
K_2O	0.2 to 1.0	0.018	0.025	0.101
SO_3	1.4 to 3.7	0.035	0.077	0.151

ND.12.3 The precision information given here was obtained from an experiment carried out in the period 1986 to 1988, involving 12 laboratories. The experiment was designed, and the data analysed, by following the principles set out in BS 5497 : Part 1. Seven cements were used with the compositions shown in table ND.10. Approximately 5 kg of each of these cements was homogenised and one 100 g sample of each sent to each participant. The participants were required to calibrate their instruments by the procedure described in the method, make two beads from each sample, then do two analyses on each bed one or two weeks apart.

ND.12.4 Each of the values r_1, r_2 and R is a value which should be exceeded on only 1 in 20 occasions by the difference between two test results:

r_1 should be used when the two results are obtained from repeat runs on the same bead (and obtained by the same operator, using the same equipment);

r_2 should be used when the two results are obtained from different beads made from the same cement sample (and obtained by the same operator, using the same equipment);

R should be used when the two results are obtained by different operators, using different equipment, analysing different beads made from the same cement sample.

The precision values were first calculated for each cement separately. For SiO_2 and CaO the ranges of concentrations in the seven cements were numerically small, so values of r_1, r_2 and R were calculated as averages over the seven cements. These values are given in table ND.8.

For the other oxides the precision values varied with the level of concentration of the oxides, so equations of the form given in **ND.12.2** are used to provide a concise summary of the results.

Table ND.10. Composition of cements used in precision experiment								
Cement	**Type**	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %
XP1	RHPC[1]	21.0	4.9	2.8	64.2	1.60	3.7	1.04
XP2	OPC[1]	19.9	5.5	3.3	64.7	2.70	2.6	0.48
XP3	OPC[1]	20.1	6.7	2.3	65.2	1.18	3.1	0.60
XP4	OPC[1]	20.7	5.1	2.9	64.8	2.33	2.6	0.76
XP5	CPA55[2]	23.4	3.1	2.5	66.3	1.17	1.9	0.21
XP6	Ground clinker	21.4	6.1	2.5	66.4	0.96	1.4	0.62
XP7	SRPC[3]	22.3	3.4	5.0	65.0	0.89	2.2	0.70

[1] Conforming to BS 12.
[2] Conforming to NF P 15-301 (identical with DD ENV 197-1).
[3] Conforming to BS 4027.

ND.12.5 The data obtained in the precision experiment were examined for outliers and stragglers using the methods described in BS 5497 : Part 1. All the data for one laboratory were excluded from the calculation of the CaO precision values, all the data from another laboratory were excluded from the calculation of the SO_3 precision values, and all the data from two laboratories were excluded from the calculation of the K_2O precision values. Some other data were also excluded.

ND.13 *Equivalence of X-ray fluorescence spectrometry method*

Tables ND.11 and ND.12 offer supportive evidence for the equivalence of the method to the reference methods as required by clause 1. The precision figures are compared to those obtained from the co-operative XRF CERILH exercise (1986/7). Table ND.12 shows comparisons to wet analysis figures for two of the samples from the precision experiment.

Table ND.11. Comparison of precision values for CERILH interlaboratory test sample (XP5)

Oxide	r_1		R	
	BSI Panel	CERILH	BSI Panel	CERILH
	%	%	%	%
SiO_2	0.17	0.25	0.60	0.56
Al_2O_3	0.09	0.11	0.23	0.25
Fe_2O_3	0.04	0.06	0.11	0.18
CaO	0.27	0.31	0.74	0.74
MgO	0.10	0.08	0.13	0.19
SO_3	0.04	0.06	0.21	0.20

Table ND.12. Accuracy checks against wet analysis figures

Oxide	Sample XP6		Sample XP5	
	BSI (XRF)	Blue Circle (wet)	BSI (XRF)	CERILH (wet)
	%	%	%	%
SiO_2	21.40	21.38	23.40	23.24
Al_2O_3	6.10	5.97	3.10	3.22
Fe_2O_3	2.50	2.56	2.50	2.55
CaO	66.40	66.39	66.30	66.60
MgO	0.96	0.97	1.17	1.16
SO_3	1.40	1.44	1.90	1.79
K_2O	0.62	0.60	0.21	0.21

ND.14 Reporting

Calculate the average of the results from duplicate beads and report SiO_2 and CaO to one decimal place and the other oxides to two decimal places.

ND.15 Informative references

BS 12 : 1991	*Specification for Portland cement*
BS 4027 : 1991	*Specification for sulfate-resisting Portland cement*
BS 5497 :	*Precision of test methods*
BS 5497 : Part 1 : 1987	*Guide for the determination of repeatability and reproducibility for a standard test method by interlaboratory tests*
DD ENV 197-1 : 1994	*Cement. Composition, specifications and conformity criteria* Part 1 *Common cements*

National annex NE (informative)

Methylene blue test

NE.0 Introduction

This annex comprises a translation of the French Experimental Standard P 18-592 *Aggregates. Methylene blue test*, of July 1980, for the determination of the methylene blue adsorption.

Although this French Experimental Standard was revised in December 1990, the earlier version was called up in the June 1989 draft European Prestandard for cement with which the 1991 versions of the British Standard specifications for cements were aligned. Hence, in order to maintain co-ordination in the revised British Standards, the 1980 version of the French Standard has been retained in this national annex.

It should be noted that the object (see **NE.1**) of the French Standard is the determination of the blue value of the fine fraction of a sand, defined elsewhere as particles below 80 µm, and that it is currently under consideration by CEN/TC 154, Aggregates. The details would thus seem to require some modification in order to provide a suitable procedure for the assessment of crushed limestone. In particular, it is necessary to grind the limestone to pass a 90 µm sieve; furthermore, the sample size can be reduced to about 2 g, with corresponding reduction in the addition of the reagent.

The foreword to Experimental Standard P 18-592 : 1980 is as follows.

> AFNOR has prepared this standard and proposes to give it the status of an experimental standard, in view of the need to confirm the validity of the test through experience.
>
> After a maximum period of 3 years, this standard will be subject to a new examination and to a possible modification of its status.

NOTE. The French standards referred to in the text are available from BSI Customer Services, 389 Chiswick High Road, London W4 4AL.

NE.1 Object

The object of the present standard is a description of the method for the determination of the blue value of the fine fraction of a sand[*]. It also describes a rapid method of checking the conformity of a sand with a specified blue value.

NE.2 Field of application

The present standard is applicable to sands of natural or artificial origin, for use in building and public works.

NE.3 Purpose of the test

This test permits the measurement of the capacity of the fine particles of a sand to adsorb methylene blue.

Since methylene blue is adsorbed preferentially by clays, organic substances and iron hydroxides, this capacity takes account of the total surface activity of these elements.

The blue value of the fines is the quantity of methylene blue adsorbed by 100 g of fines.

NE.4 Principle of the test

The test consists of measuring, by titration, the adsorption capacity of the material.

Aliquots of methylene blue solution are injected successively into the water bath containing the test sample. The adsorption of the blue is checked after each addition by making a stain on a filter paper (stain test, see **NE.7.2.1**).

For a simple conformity check, the specified quantity of blue is injected at one time.

NE.5 Apparatus
NE.5.1 *Specific apparatus*

Burette

capacity:	100 cm^3 or 50 cm^3;
graduation:	0.1 cm^3 or 0.2 cm^3.
Filter paper:	analytical, ash-less (< 0.010); weight: 95 g/m^2;
	thickness: 0.20 mm, filtration rate: 75;
	retention: 8 μm.
Glass rod:	length 300 mm; diameter 8 mm.

Blade stirrer, rotating between 400 min^{-1} and 700 min^{-1}.

500 ml beaker (glass or plastics) of diameter about 100 mm.

NE.5.2 *Apparatus for general use*

Balance, the capacity of which is compatible with the mass of the test sample and is accurate to within about 1 %.

Stopclock or stopwatch.

Sampling equipment[†].

NE.5.3 *Materials*

Methylene blue solution of medicinal quality at (10 ± 0.1) g/l.

Demineralized or distilled water.

NE.6 Calculation of the sample size

Knowing the contents of moisture, w, and of fines, f, (see standard NF P 18-597[‡]) calculate the mass of the test sample, to the nearest 1 g, including the water content, by the formula:

$$M_h = f' \frac{(w + 100)}{f}$$

where

f' represents the quantity of fines, in g, which it is desirable to have in the test sample (about 30 g).

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[*] See standard NF P 18-101 *Aggregates — Terminology, definitions, classification*, in preparation.
[†] See standard NF P 18-553 *Preparation of a sample for test*.
[‡] NF P 18-597 *Determination of the property of sands: sand equivalent with 10 % of fines.* (Translator's note: particles below 80 μm).

NE.7 Test method

NE.7.1 *Dispersing the test sample*

Place the test sample into a 500 ml beaker with 200 cm³ of demineralized or distilled water. Stir for one minute at 700 min⁻¹, then continuously at 400 min⁻¹ during the whole duration of the test using the stirrer, the blades being situated at 1 cm above the bottom of the beaker.

NE.7.2 *Determination by titration of the quantity of blue adsorbed*

NE.7.2.1 *Description of the stain test*

Following each injection of blue (see **NE.7.2.2**), this test consists of using the glass rod to pick up a drop of suspension which is deposited on the filter paper. The stain which is formed comprises a central deposit of material, tinted by a generally strong blue colour, surrounded by a colourless wet zone.

The drop taken shall be such that the diameter of the deposit is between 8 mm and 12 mm.

The test is considered to be positive if, in the wet zone, a light blue halo appears around the central deposit. It is considered to be negative if the halo is colourless.

NE.7.2.2 *Titration*

Using the burette, add 5 cm³ of blue solution to the beaker, this addition being followed by the stain test on the filter paper.

Proceed in this way until the test becomes positive. At this stage, allow the adsorption of the blue to take place, while carrying out tests every minute without adding anything.

If the light blue halo disappears from the stain before the fifth minute, proceed with new unit additions of blue, which are:

5 cm³ as before, if the volume of the blue solution already added is more than or equal to 30 cm³, or

2 cm³ if this volume is less than 30 cm³.

Follow each addition by tests carried out every minute. Repeat these operations until the test remains positive for five consecutive minutes; the titration is then considered finished.

NOTE. Clean the apparatus as soon as the tests are finished, the blue deposits being easily removed when they are fresh. The apparatus can easily be cleaned with water. If detergents are used, then a final thorough rinse in water is necessary.

NE.8 Expression of results

The blue value of the fines expressed in grams of blue for 100 g of fines is given by the formula:

$$VB = \frac{V}{f'}$$

where

V is the final volume of solution added (in cm³).

NE.9 Conformity control in relation to a given specification

The specification is expressed as blue value for 100 g of fines; let this value be s.

The volume of the blue solution to be added at one time is therefore:

$$V' = f' \cdot s$$

The stain test is carried out after stirring for 8 min. If it is positive, the sand conforms to the specification; if it is negative, then add a volume of blue solution equal to:

$$\frac{f' \cdot s}{10}$$

If the test is still negative after 5 min, carry out the titration in accordance with **NE.7.2**; if the test is positive, the sand conforms to the specification.

National annex NF (informative)

Determination of total organic carbon

NF.1 Introduction

The following clauses are an extract from the German journal Zement-Kalk-Gips reporting the conclusions of a working party set up by CEN Technical Committee 51[*]. It describes a reference method and two alternative procedures which have been shown to give similar results for the total organic carbon content in naturally occurring limestone.

NF.2 Scope and field of application

The following procedures are suitable for the determination of the total organic carbon content (TOC) in naturally occurring limestone which is intended to be used for the production of fillerized cements. Procedure 1 shall be taken as the reference method. Alternatively the procedures 2 and 3 may be used. All three procedures have been proved by comparative tests to give similar results for the determination of TOC content without statistically apparent deviations of the mean values.

The three procedures only differ in equipment, cost and in analysis time. The reference method 1 requires the least expensive apparatus but takes the longest time. The alternative method 2 is moderate in equipment expense and needs less operation time. The alternative method 3 requires a comparatively expensive, automatic apparatus which can be used advantageously for analysing many samples within a short time, once the decarbonation stage has been completed.

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[*] The article first appeared in *ZKG International* issue 8/1990.

NF.3 General requirements

In general all procedures consist of the following stages:

    decarbonation of the original limestone sample;

    purification of the carrier gas;

    oxidation of the organic carbon matter;

    drying of the CO_2 produced by oxidation;

    measurement of the CO_2 content.

The different steps may be performed by various techniques provided they give the same result.

The number of determinations shall be at least two. The result shall be expressed as the mean of the single determinations. Depending on the size of the raw material a sample of at least 1 kg up to 10 kg shall be taken, crushed, reduced and ground to form a representative laboratory sample for analysis. The laboratory sample should pass the 90 µm ISO sieve.

NF.4 Wet oxidation method (reference method)

NF.4.1 *Principle*

The carbon dioxide in the limestone is first removed by the use of phosphoric acid. The remaining organic carbon is then oxidized to carbon dioxide with a strong oxidizing reagent mixture. The liberated carbon dioxide is absorbed on an inorganic carrier impregnated with sodium hydroxide in a U-tube. The increase in weight is directly proportional to the carbon content in the sample.

NF.4.2 *Apparatus*

The apparatus for TOC determination is illustrated in figure NF.1. A small vacuum pump or an aspirator is used to generate reduced pressure in the apparatus.

The U-tube (8) is filled to approximately two thirds of its volume with the absorbent for carbon dioxide and with magnesium perchlorate. The U-tube is then inserted into the apparatus as shown in figure NF.1 drawing through it about 4 l of carrier gas. At this time the apparatus should be checked for leaks by turning off the drying tower tap whilst keeping the small vacuum pump or the aspirator trap fully open. If leaks are absent, the gas flow through the bubble counter (9) stops completely. After this, check that the taps of the U-tube (8) are turned off, transfer it to a desiccator for 10 min, wipe it with a clean cloth and weigh to the nearest 0.0001 g. Reassemble the apparatus as shown in figure NF.1.

NF.4.3 *Reagents*

Use only reagents of analytical quality and distilled water or water of equal purity for analysis. The densities of concentrated liquid reagents are expressed in g/cm^3. The degree of dilution is expressed as a volumetric sum (i.e. nitric acid 1 + 9 means that 1 volume of concentrated nitric acid has to be mixed with 9 volumes of water).

Phosphoric acid, H_3PO_4, $\rho = 1.71$ to 1.75

Sulfuric acid, H_2SO_4, $\rho = 1.84$

Nitric acid, HNO_3, $\rho = 1.40$ to 1.42

Nitric acid, dilute, 1 + 9

Hydrogen peroxide, H_2O_2, $\rho = 1.11$

Hydrogen peroxide, dilute, 1 + 9

Phosphorus pentoxide, P_2O_5

Potassium dichromate, $K_2Cr_2O_7$

Potassium iodate, KIO_3

Chromium trioxide, CrO_3

Ammonium hydroxide, NH_4OH, $\rho = 0.91$

Lead chromate, $PbCrO_4$

Zinc wool, Zn

Oxidizing mixture. To 85 ml sulfuric acid in a 250 ml beaker add, in order, 15 ml phosphoric acid, 20 g phosphorus pentoxide, 15 g potassium dichromate, and 1 g potassium iodate. Heat the mixture carefully to about 170 °C and keep for 5 min at this temperature with occasional stirring with a thermometer. After cooling, store the mixture in a stoppered bottle.

Chromic acid. Dissolve 5 g of chromium trioxide in 10 ml of water. Add sulfuric acid with stirring, until the chromium trioxide, which initially precipitates, is just redissolved.

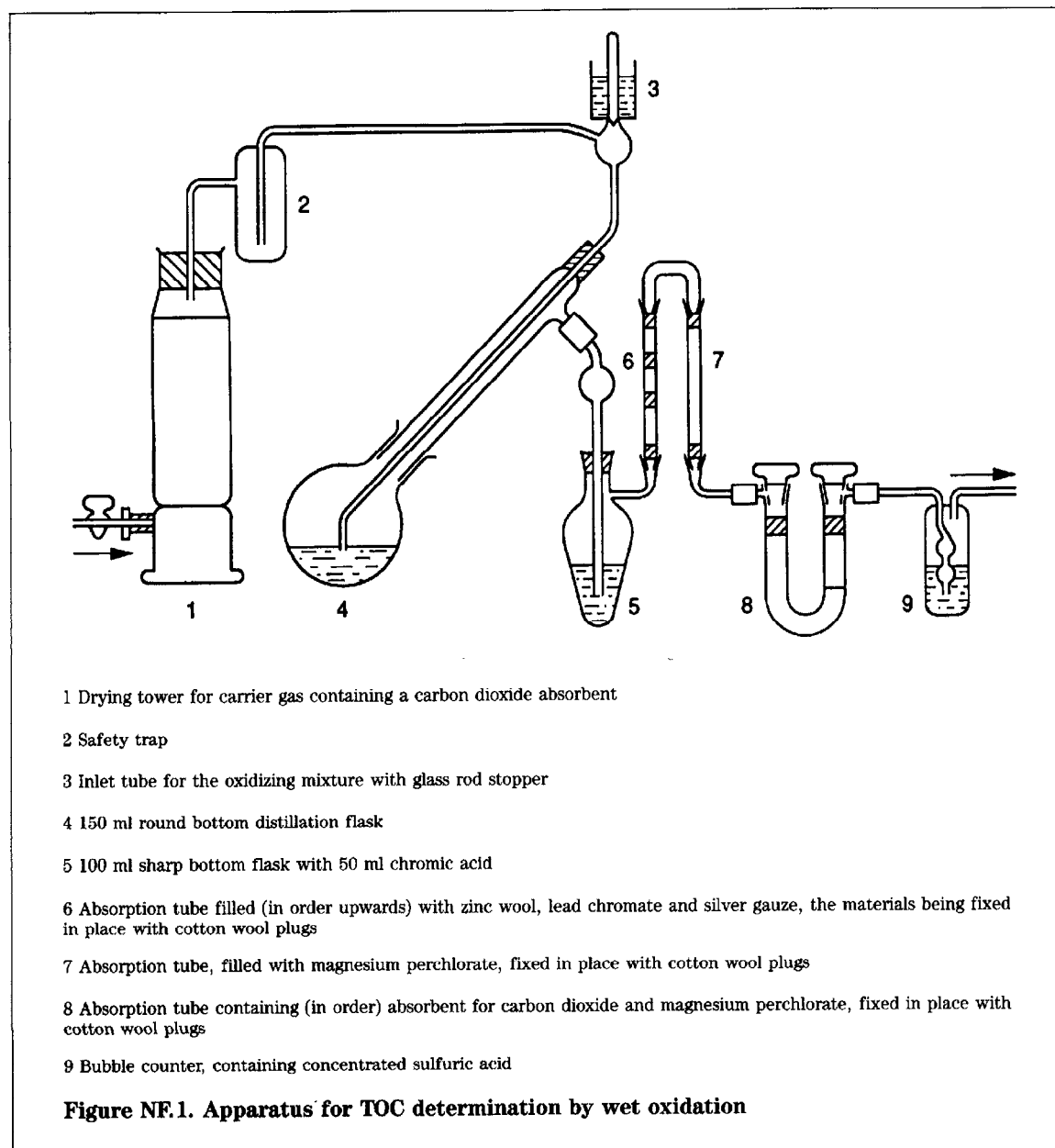Silver gauze, Ag. Wash the silver gauze with ammonium hydroxide, nitric acid 1 + 9 and hydrogen peroxide. Rinse the gauze with water between each washing.

Magnesium perchlorate. $Mg(ClO_4)_2$ with a particle size between 0.6 mm and 1.2 mm.

Absorbent for carbon dioxode. NaOH on an inert inorganic carrier.

Carrier gas. Air (carbon dioxide free), alternatively the use of oxygen, nitrogen or argon is possible.

1 Drying tower for carrier gas containing a carbon dioxide absorbent

2 Safety trap

3 Inlet tube for the oxidizing mixture with glass rod stopper

4 150 ml round bottom distillation flask

5 100 ml sharp bottom flask with 50 ml chromic acid

6 Absorption tube filled (in order upwards) with zinc wool, lead chromate and silver gauze, the materials being fixed in place with cotton wool plugs

7 Absorption tube, filled with magnesium perchlorate, fixed in place with cotton wool plugs

8 Absorption tube containing (in order) absorbent for carbon dioxide and magnesium perchlorate, fixed in place with cotton wool plugs

9 Bubble counter, containing concentrated sulfuric acid

Figure NF.1. Apparatus for TOC determination by wet oxidation

NF.4.4 Procedure

Weigh 1 g of the limestone sample to the nearest 0.0001 g. Transfer to the 150 ml round bottom flask (4), add 2 ml of water and 30 ml phosphoric acid. Heat the mixture and boil gently to expel the carbon dioxide. Cool the mixture and connect the flask to the apparatus. Substitute for the U-tube (8) a glass tube and pass 2 l of carrier gas through the apparatus, to clear the system of any carbon dioxide. Fit the weighed U-tube again to the apparatus and check once more for leaks. Open the taps of the U-tube. Add approximately 30 ml of oxidizing mixture to the flask through the inlet tube (3) by lifting the glass rod stopper. At this stage the flow rate of the carrier gas should be producing about 2 bubbles per second (9). Heat the sample mixture in the round bottom flask gently to boiling and keep at boiling for 4 min. Then remove the heater and whilst cooling pass approximately 3 l of carrier gas through the system. Close the taps of the U-tube. Transfer it to a desiccator, cool for 30 min, wipe with a clean cloth and weigh to the nearest 0.0001 g.

NF.4.5 *Calculation*

Calculate the carbon content as a percentage by mass using the formula:

$$C = \frac{m_{u_2} - m_{u_1}}{m} \times 27.29 \qquad (1)$$

where

m_{u_1} is the mass of the U-tube before absorption of carbon dioxide (in g);

m_{u_2} is the mass of the U-tube after absorption of carbon dioxide (in g);

m is the mass of the sample (in g).

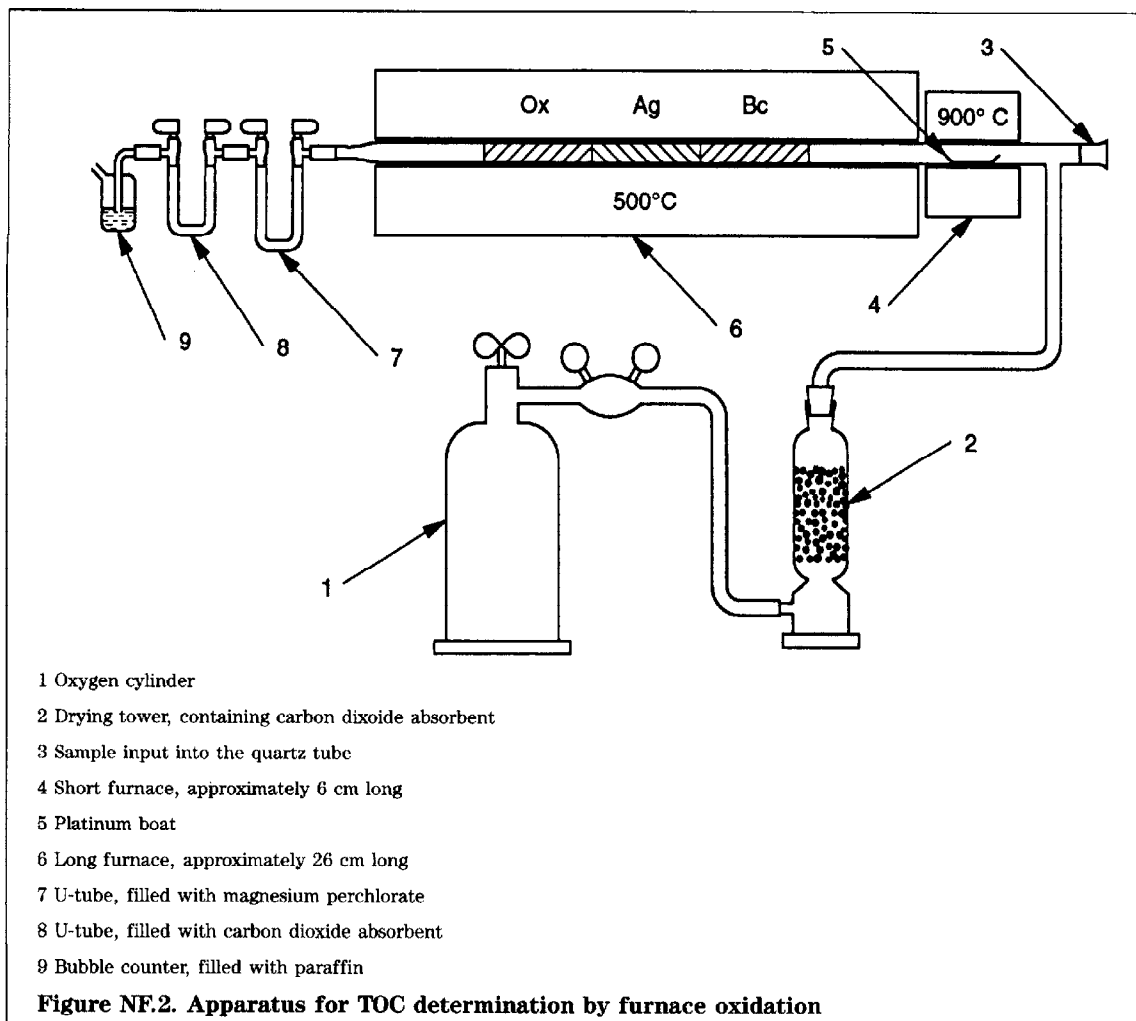Express the result to two decimal places.

NF.5 Furnace oxidation method (alternative method 1)

NF.5.1 *Principle*

The carbon dioxide in the limestone is driven off by the use of hydrochloric acid in a PTFE dish. The insoluble residue is transferred to a platinum boat. The remaining organic carbon is oxidized in an oxygen atmosphere at 900 °C and the liberated carbon dioxide is absorbed on an inorganic carrier impregnated with sodium hydroxide in a U-tube. The increase in weight is directly proportional to the carbon in the sample (2).

NF.5.2 *Apparatus*

The apparatus for the determination of carbon is shown in figure NF.2.

The PTFE dish has a diameter of approximately 8 cm and a height of approximately 3 cm. The dimensions of the platinum boat are 5.0 cm × 0.8 cm × 0.8 cm.

1 Oxygen cylinder

2 Drying tower, containing carbon dixoide absorbent

3 Sample input into the quartz tube

4 Short furnace, approximately 6 cm long

5 Platinum boat

6 Long furnace, approximately 26 cm long

7 U-tube, filled with magnesium perchlorate

8 U-tube, filled with carbon dioxide absorbent

9 Bubble counter, filled with paraffin

Figure NF.2. Apparatus for TOC determination by furnace oxidation

NF.5.3 *Reagents*

Use only reagents of analytical quality and distilled water or water of equal purity during the analysis. The density of concentrated liquid reagents is expressed in g/cm^3.

Oxidation catalyst. Ignited silver permanganate with a composition of approximately AgMnO$_2$.

Silver gauze, Ag

Lead chromate, PbCrO$_4$

Platinum on quartz wool* as carrier

Oxygen, O$_2$

Hydrochloric acid, HCl, ρ = 1.19

Magnesium perchlorate. Mg(ClO$_4$)$_2$ with a particle size of 0.6 mm to 1.2 mm.

Absorbent for carbon dioxide. NaOH on an inert inorganic carrier.

NF.5.4 *Procedure*

NF.5.4.1 *Filling the quartz tube*

Close the left-hand side outlet of the quartz tube in figure NF.2 with a 1 cm quartz wool plug. While holding the quartz tube in a vertical position, fill it with 6 cm of the oxidation catalyst (Ox), 6 cm silver gauze (Ag), and 6.5 cm lead chromate (Bc). Compact the catalyst and the lead chromate by slight vibration while filling the tube. Compact the silver gauze with a glass rod.

Fix the three layers in place with a plug of platinum on quartz wool*. Position the tube in the long furnace (6) as shown in figure NF.2. Heat the long furnace to (500 ± 20) °C, while passing oxygen through the tube. The flow rate of the oxygen should be at least 7 ml/min. After 30 min the equipment is ready for the carbon determination. The catalyst filling in the tube is sufficient for about 15 carbon determinations, after which it has to be renewed.

NF.5.4.2 *Analysis*

Weigh (0.4 ± 0.1) g of the limestone sample to the nearest 0.0001 g in a PTFE dish. Moisten the weighed test sample with 1 or 2 drops of water and then add slowly 10 ml of hydrochloric acid. At the end of the first intensive reaction heat the dish on a hot plate with a furnace temperature of (140 ± 10) °C. Heat the sample to complete dryness. Break up the residue and remove it from the wall of the bowl with a PTFE rod, while still on the hot plate. Transfer the dried residue completely into a platinum boat, which is immediately introduced into the right-hand side inlet of the quartz tube (3), whilst oxygen is still passing through the tube at a flow rate of at least 7 ml/min. Close the inlet with a rubber stopper.

Move the short furnace (4) into position, and heat to (900 ± 25) °C maintaining this temperature for 15 min. Then switch it off, but pass oxygen through the tube for another 20 min. After that close the taps of the U-tube (8). Remove the U-tube, cool in a desiccator, and weigh it to the nearest 0.0001 g.

NF.5.5 *Calculation*

Calculate the carbon content using the formula (1) (see **NF.4.5**). Express the result to two decimal places.

NF.6 Automatic determination method (alternative method 2)
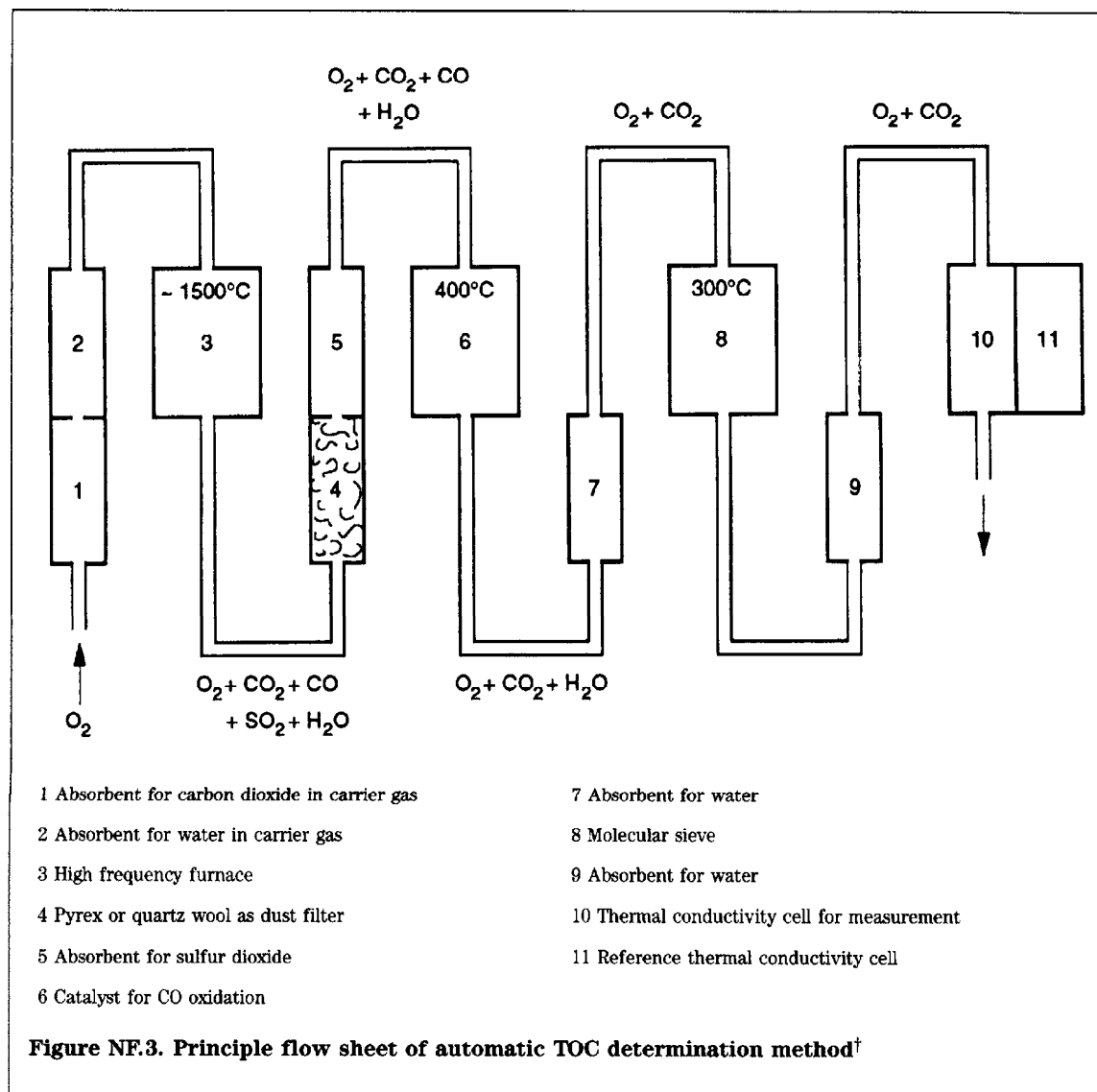
NF.6.1 *Principle*

The carbon dioxide in the limestone is driven off by the use of hydrochloric acid. The carbon content of the residue is oxidized with oxygen in a high frequency furnace in the presence of an accelerator at approximately 1500 °C. The resulting gas mixture which consists of oxygen, carbon dioxide, carbon monoxide, sulfur dioxide and water is treated with manganese dioxide to absorb sulfur dioxide. The carbon monoxide is oxidized by copper oxide to give carbon dioxide. The water is absorbed by magnesium perchlorate. The carbon dioxide is first absorbed on a molecular sieve, then liberated again, and quantitatively determined by a thermal conductivity meter (10).

NF.6.2 *Apparatus*

The apparatus for the automatic determination of carbon is illustrated in a flow sheet in figure NF.3.

After thirty determinations the dust filter (4) and the water traps (7) and (9) have to be changed. At the same time the combustion tube in the furnace (3) has to be cleaned. The SO$_2$ absorbent (5) has to be changed every 500 analyses. The CO$_2$ and water traps (1) and (2) have to be changed once a month and the catalyst (6) once a year.

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* The original document (see **NF.1**) refers to asbestos. However, asbestos is no longer to be used in the UK.

$O_2 + CO_2 + CO + H_2O$

$O_2 + CO_2$

$O_2 + CO_2$

~ 1500°C

400°C

300°C

O_2

$O_2 + CO_2 + CO + SO_2 + H_2O$

$O_2 + CO_2 + H_2O$

1 Absorbent for carbon dioxide in carrier gas
2 Absorbent for water in carrier gas
3 High frequency furnace
4 Pyrex or quartz wool as dust filter
5 Absorbent for sulfur dioxide
6 Catalyst for CO oxidation
7 Absorbent for water
8 Molecular sieve
9 Absorbent for water
10 Thermal conductivity cell for measurement
11 Reference thermal conductivity cell

Figure NF.3. Principle flow sheet of automatic TOC determination method[†]

[†] For information on the availability of automatic equipment, write to Customer Services, Information Services Group, BSI, 389 Chiswick High Road, London, W4 4AL.

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NF.6.3 *Reagents*

Use only reagents of analytical quality and distilled water or water of equal purity for analysis. The densities of concentrated liquid reagents are expressed in g/cm^3. The degree of dilution is expressed as a volumetric sum.

Hydrochloric acid, HCl, $\rho = 1.19$

Hydrochloric acid, dilute, $1 + 5$

Sodium hydroxide, NaOH

Sodium hydroxide solution.

Dissolve 40 g sodium hydroxide in 1000 ml water

Absorbent for carbon dioxide. NaOH on an inert anhydrous inorganic carrier

Absorbent for water. $Mg(ClO_4)_2$ with a particle size of 0.6 mm to 1.2 mm

Absorbent for sulfur dioxide. MnO_2 with a particle size of 0.6 mm to 1.2 mm

Catalyst. CuO with a particle size of 0.6 mm to 1.2 mm

Iron accelerator. Fe, free of carbon

Copper accelerator. Cu, free of carbon

Calibration reagent. Metal, for example iron, with known carbon content

NF.6.4 *Procedure*

NF.6.4.1 *Calibration*

First, several blank determinations are performed to obtain a low and stable reading of the thermal conductivity cell. The apparatus will keep this reading as the blank. Next, several different weights of the calibration reagent are analyzed and the readings are stored in the calculator of the apparatus to give a straight calibration line. This calibration line is used to calculate the result.

NF.6.4.2 *Determination*

Weigh in a 100 ml beaker 0.4 g of the limestone sample to the nearest 0.0001 g. Wet the sample with 2 drops of water. Add gently 10 ml of hydrochloric acid $(1 + 5)$. Swirl the sample and leave it to stand for approximately 16 h (overnight) covered with a watch glass. Heat the mixture to (75 ± 5) °C until the dolomitic parts of the sample are dissolved completely and CO_2 is no longer evolved.

Neutralize the excess of hydrochloric acid with sodium hydroxide solution[‡]. After neutralization leave the beaker to stand until the residue has settled. Decant the supernatant liquid without loss of the residue. Filter the remaining liquid and the residue by suction through the special crucible used with the high frequency furnace. After washing the residue with water dry the crucible and the residue in an oven at (105 ± 5) °C. Add iron and copper accelerators to the crucible, place it in the holder of the high frequency furnace and start the apparatus. The apparatus stops automatically and the meter gives a reading which corresponds to the percentage of carbon present in the sample.

NF.6.5 *Calculation*

Report the TOC content as a percentage by mass. Express the result to two decimal places.

NF.7 Precision of test results

The standard deviation of repeatability (with one exception) was found to be less than 0.07 % by mass and was independent of the method used and the amount of carbon present. Similar results were obtained in different laboratories during comparison tests for the standard deviation of reproducibility.

[‡] This step gives the possibility of calculating the mineral carbon content.

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National annex NG (informative)
Committees responsible

The United Kingdom participation in the preparation of this European Standard was entrusted by the Technical Committee B/516 Cement and lime, to Subcommittee B/516/4, upon which the following bodies were represented:

British Cement Association
British Civil Engineering Test Equipment Manufacturers' Association
British Ready Mixed Concrete Association
Cementitious Slag Makers' Association
Department of the Environment (Building Research Establishment)
Electricity Association
Quality Ash Association
Society of Chemical Industry

National annex NH (informative)
Cross-references

Publication referred to	Corresponding British Standard
EN 196-7 : 1989	BS EN 196-7 : 1992 *Methods of testing cement*
	Part 7 *Methods of taking and preparing samples of cement*
ISO 3534 : 1977	BS 5532 *Statistical terminology*
	Part 1 : 1978 *Glossary of terms relating to probability and general terms relating to statistics*

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**BS EN
196-2 : 1995**

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