INTERNATIONAL STANDARD

ISO
29581-1

First edition
2009-03-15

Cement — Test methods —

Part 1:
Analysis by wet chemistry

Ciments — Méthodes d'essai —

Partie 1: Analyse chimique par voie humide

Reference number
ISO 29581-1:2009(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 29581-1 was prepared by Technical Committee ISO/TC 74, *Cement and lime*.

This first edition of ISO 29581 cancels and replaces ISO 680:1990, which has been technically revised as follows, based on comments received by the secretariat.

a) The scope of the analyses has been extended to include determination of chloride, carbon dioxide and alkali.

b) Calibration against internationally accepted reference materials is permitted.

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

d) A requirement for blank determinations has been included.

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

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

g) A specification for a laboratory oven has been included.

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

i) Additional indicators have been included for the visual determination of EDTA titrations.

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

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

l) Determination of silica by the double evaporation method becomes the reference method.

m) Alternative ignition temperatures during the analysis for silica are permitted, where validated by the laboratory.

n) An alternative method for the determination of chloride by potentiometric titration is included.

o) An alternative method for the determination of acid-soluble alkali by atomic absorption spectroscopy is included.

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

NOTE   Analytical methods utilizing x-ray fluorescence (XRF) were considered during this revision but no published standardized method was considered sufficiently comprehensive to be included. A new Part 2 to ISO 29581 is under development in order to prepare a method based on XRF.

ISO 29581 consists of the following parts, under the general title *Cement — Test methods*:

⎯ *Part 1: Analysis by wet chemistry*

⎯ *Part 2: Analysis by x-ray fluorescence*

Cement — Test methods —

Part 1:
Analysis by wet chemistry

1   Scope

This part of ISO 29581 specifies the methods for the analysis of cement by wet chemistry.

This part of ISO 29581 gives the reference methods and, in certain cases, an alternative method that can be considered to be equivalent. In the case of a dispute, only the reference methods are used.

It is permitted to use other methods provided they are calibrated, either against the reference methods or against internationally accepted reference materials, in order to demonstrate their equivalence. In case of dispute, only the reference methods are used.

This part of ISO 29581 describes methods that apply principally to cements, but which can also be applied to their constituent materials. They can also be applied to other materials, the standards for which call up these methods.

Standard specifications state which methods are used.

2   Normative references

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

ISO 385, *Laboratory glassware — Burettes*

ISO 835, *Laboratory glassware — Graduated pipettes*

3   General requirements for testing

3.1   Number of tests

Analysis of a cement can require the determination of a number of its chemical properties. For each determination, one or more tests shall be carried out in which the number of measurements taken shall be as specified in the relevant clause of this part of ISO 29581.

Where the analysis is one of a series subject to statistical control, determination of each chemical property by a single test shall be the minimum required.

Where the analysis is not part of a series subject to statistical control, the number of tests for determination of each chemical property shall be two (see also 3.3).

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

3.2 Repeatability and reproducibility

3.2.1 General

Repeatability and reproducibility in this part of ISO 29581 are expressed as repeatability standard deviation(s) and reproducibility standard deviation(s) in, for example, absolute percent, grams, etc., according to the property tested.

3.2.2 Repeatability

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

3.2.3 Reproducibility

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

3.3 Expression of masses, volumes, factors and results

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

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

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

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

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

The results of all individual tests shall be recorded.

3.4 Ignition

Carry out ignition as follows.

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

3.5 Determination of constant mass

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

3.6 Check for absence of chloride ions — Silver nitrate test

After generally five to six washes of a precipitate, rinse the base of the filter stem with a few drops of water. Wash the filter paper and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (4.2.43). Check the absence of turbidity or precipitate in the solution. If present, continue washing while carrying out periodic checks until the silver nitrate test is negative.

3.7 Blank determinations

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

4 Reagents

4.1 General

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

Unless otherwise stated, percent means percent mass fraction.

Unless otherwise stated, the concentrated liquid reagents used in this part of ISO 29581 have the following densities, ρ, at 20 °C, expressed in grams per cubic centimetre:

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

The degree of dilution is always given as a volumetric sum, for example: dilute hydrochloric acid $1 + 2$ means that 1 volume of concentrated hydrochloric acid is mixed with 2 volumes of water.

4.2 Products used

4.2.1 Hydrochloric acid (HCl), concentrated,

4.2.2 Hydrochloric acid, dilute, $1 + 1$.

4.2.3 Hydrochloric acid, dilute, $1 + 2$.

4.2.4 Hydrochloric acid, dilute, $1 + 3$.

4.2.5 Hydrochloric acid, dilute, $1 + 9$.

4.2.6 Hydrochloric acid, dilute, $1 + 11$.

4.2.7 Hydrochloric acid, dilute, $1 + 19$.

4.2.8 Hydrochloric acid, dilute, $1 + 99$.

4.2.9   Hydrochloric acid, dilute, pH 1,60 + 0,05.

Prepare by adjusting the pH of 2 l of water to $1,60 \pm 0,05$ by adding five or six drops of concentrated hydrochloric acid (HCl) (4.2.1). Control using the pH meter (5.18.1). Store the solution in a polyethylene container.

4.2.10   Hydrofluoric acid, (HF), concentrated, $> 40\ \%$.

4.2.11   Hydrofluoric acid, dilute, $1 + 3$.

4.2.12   Nitric acid (HNO_3), concentrated.

4.2.13   Nitric acid, dilute, $1 + 2$.

4.2.14   Nitric acid, dilute, $1 + 100$.

4.2.15   Sulfuric acid, concentrated, ($> 98\ \%$) (H_2SO_4).

4.2.16   Sulfuric acid, dilute, $1 + 1$.

4.2.17   Sulfuric acid, dilute, $1 + 4$.

4.2.18   Perchloric acid ($HClO_4$), concentrated.

4.2.19   Phosphoric acid (H_3PO_4), concentrated.

4.2.20   Phosphoric acid, dilute, $1 + 19$.

Store this solution in a polyethylene container.

4.2.21   Boric acid (H_3BO_3).

4.2.22   Acetic acid (CH_3COOH), concentrated.

4.2.23   Aminoacetic acid (NH_2CH_2COOH).

4.2.24   Chromium (Cr), metallic, in powder form.

4.2.25   Ammonium hydroxide (NH_4OH), concentrated.

4.2.26   Ammonium hydroxide, dilute, $1 + 1$.

4.2.27   Ammonium hydroxide, dilute, $1 + 10$.

4.2.28   Ammonium hydroxide, dilute, $1 + 16$.

4.2.29   Sodium hydroxide (NaOH).

4.2.30   Sodium hydroxide solution, 4 mol/l.

Dissolve 160 g of sodium hydroxide (NaOH) (4.2.29) in water and make up to 1 000 ml. Store in a polyethylene container.

4.2.31   Sodium hydroxide solution, 2 mol/l.

Dissolve 80 g of sodium hydroxide (NaOH) (4.2.29) in water and make up to 1 000 ml. Store in a polyethylene container.

4.2.32 **Ammonium chloride** (NH_4Cl).

4.2.33 **Tin(II) chloride** ($SnCl_2 \cdot 2H_2O$).

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

4.2.35 **Potassium periodate** (KIO_4).

4.2.36 **Sodium peroxide** (Na_2O_2), in powder form.

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

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

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

4.2.40 **Sodium carbonate** and **sodium chloride**, mixture.

Mix 7 g of sodium carbonate (Na_2CO_3) (4.2.39) with 1 g sodium chloride (NaCl) (4.2.37).

4.2.41 **Barium chloride solution**.

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

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

4.2.43 **Silver nitrate solution**.

Dissolve 5 g of silver nitrate ($AgNO_3$) (4.2.42) in water, add 10 ml of concentrated nitric acid (HNO_3) (4.2.12) and make up to 1 000 ml with water.

4.2.44 **Silver nitrate solution**, 0,05 mol/l.

Dissolve $(8,494\ 0 \pm 0,000\ 5)$ g of silver nitrate ($AgNO_3$) (4.2.42) in water in a 1 000 ml volumetric flask and make up to the mark. Store in a brown glass container and protect from the light.

4.2.45 **Sodium carbonate solution**.

Dissolve 50 g of anhydrous sodium carbonate (4.2.39) in water and make up to 1 000 ml.

4.2.46 **Potassium hydroxide solution**.

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

4.2.47 **Ammoniacal zinc sulfate solution**.

Dissolve 50 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (4.2.25). Leave to stand for at least 24 h and filter.

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

4.2.49 **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. Use within two weeks.

4.2.50 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. Use within two weeks.

4.2.51 Boric acid solution, saturated.

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

4.2.52 Citric acid solution.

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

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

4.2.54 Ammonium molybdate solution.

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

4.2.55 Copper sulfate solution.

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

4.2.56 Ammonium acetate solution.

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

4.2.57 Triethanolamine $[N(CH_2CH_2OH)_3]$, of purity > 99 %, diluted to $1 + 4$ solution.

4.2.58 Reducing solution.

Dissolve 1 g of tin(II) chloride $(SnCl_2 \cdot 2H_2O)$ (4.2.33) in water to which has been added 1 ml of concentrated hydrochloric acid (4.2.1). Make up to 100 ml with water. Use within one day.

4.2.59 Buffer solution, pH 1,40.

Dissolve $(7,505 \pm 0,001)$ g of amino-acetic acid (4.2.23) and $(5,850 \pm 0,001)$ g of sodium chloride (NaCl) (4.2.37) in water and make up to 1 000 ml. Dilute 300 ml of this solution to 1 000 ml with hydrochloric acid $1 + 99$ (4.2.8).

4.2.60 Standard potassium iodate solution, approximately 0,016 6 mol/l.

Weigh, to $\pm 0,000 5$ g, $(3,6 \pm 0,1)$ g, of potassium iodate (KIO_3) (4.2.34), record as m_1, and place in a 1 000 ml volumetric flask. Add 0,2 g of sodium hydroxide (4.2.29), 25 g of potassium iodide (KI), dissolve all the solids in freshly boiled and cooled water and make up to the mark using the same water.

Calculate the factor, F, of the potassium iodate solution from Equation (1):

$$F = \frac{m_1}{3,566\,8} \tag{1}$$

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

4.2.61 Sodium thiosulfate solution, approximately 0,1 mol/l.

4.2.61.1 Preparation

Dissolve (24,82 ± 0,01) g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in water and make up to 1 000 ml. Before each test series, determine the factor, f_S, of this solution from Equation (2).

4.2.61.2 Standardization

4.2.61.2.1 This standardization is carried out preferably using the standard potassium iodate solution (4.2.60).

For this standardization, pipette 20 ml of the standard potassium iodate solution (4.2.60) into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1 + 1 (4.2.2) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (4.2.61) to a pale yellow colour. Add 2 ml of the starch solution (4.2.49) and continue the titration until the colour changes from blue to colourless.

Calculate the factor, f_S, of the sodium thiosulfate solution from Equation (2):

$$f_S = \frac{20 \times 0,01667 \times 214,01 \times F}{3,5668 \times V_1}$$
$$= 20 \times \frac{F}{V_1}$$

(2)

where

F is the factor of the standard potassium iodate solution (4.2.60);

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

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

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

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

For this standardization, weigh, to ± 0,000 5 g, (0,070 ± 0,005) g of potassium iodate (4.2.34), record as m_2, and place in a 500 ml conical flask. Dissolve in approximately 150 ml of water. Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1 + 1 (4.2.2) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (4.2.61) until a pale yellow colour is obtained. Then add 2 ml of the starch solution (4.2.49) and titrate until the colour changes from blue to colourless.

Calculate the factor, f_S, of the sodium thiosulfate solution from Equation (3):

$$f_S = \frac{1000 \times m_2}{3,5668 \times V_2} = 280,3634 \times \frac{m_2}{V_2}$$

(3)

where

m_2 is the mass of potassium iodate, expressed in grams;

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

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

4.2.62 Manganese

4.2.62.1 Anhydrous manganese sulfate.

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

4.2.62.2 Standard manganese solution.

4.2.62.2.1 Preparation

Into a 1 000 ml volumetric flask, weigh, to $\pm 0,000\,5$ g, $(2,75 \pm 0,05)$ g of anhydrous manganese sulfate, record as m_3, dissolve in water and make up to the mark. Calculate the concentration, $c_{Mn(II)}$, of manganese(II) ions of this solution, expressed in milligrams of Mn^{2+} per millilitre, from Equation (4):

$$c_{Mn(II)} = \frac{m_3}{2,748\,5} \tag{4}$$

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

4.2.62.2.2 Construction of the calibration curve

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

Take 100 ml of each solution from flasks 1 to 5 and pipette each portion into a 400 ml beaker. Add 20 ml of concentrated nitric acid (4.2.12), 1,5 g of potassium periodate (4.2.35) and 10 ml of phosphoric acid (4.2.19), heat to boiling and boil gently for 30 min.

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

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

Table 1 — Concentrations of manganese calibration solutions

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

4.2.63 Standard silica solution.

4.2.63.1   **Silica** (SiO_2), of purity $> 99,9$ % after ignition to constant mass at $(1\,175 \pm 25)$ °C.

4.2.63.2   Basic solution.

Weigh $(0,200\,0 \pm 0,000\,5)$ g of freshly ignited silica (4.2.63.1), in a platinum crucible already containing $(2,0 \pm 0,1)$ g of anhydrous sodium carbonate (4.2.39).

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

Store the solution in a polyethylene container.

This solution contains 1 mg of SiO_2 per millilitre.

4.2.63.3   Standard solution.

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

4.2.63.4   Compensating solutions.

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

4.2.63.5   Construction of the calibration curve

Add from a burette the volumes of the silica calibration solutions given in Table 3 into 100 ml polyethylene beakers each containing a magnetic stirrer bar. Add 20 ml of the compensating solution by pipette and make up to 40 ml with water from a burette. The volumes required for this are also given in Table 3. While stirring with a magnetic stirrer, add 15 drops of hydrofluoric acid $1 + 3$ (4.2.11). Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (4.2.51) into the solution.

Table 2 — Composition of the compensating solutions for a volume of 500 ml

Component and unit	Precipitation by double evaporation (see 13.3)	Precipitation by polyethylene oxide (see 13.4)	Decomposition by HCl and NH_4Cl (see13.5)
HCl, concentrated, millilitres	75	70	15
H_2SO_4 $1 + 1$, millilitres	1	1	—
HNO_3, concentrated, millilitres	—	—	1
Polyethylene oxide solution, millilitres	—	5	-
NH_4Cl, grams	—	—	1
Na_2CO_3, grams	1,75	1,75	1,75
NaCl, grams	0,25	0,25	0,25
Na_2O_2, grams	3	3	—

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

Serial No.	Blank	1	2	3	4
Standard SiO_2 **solution**, millilitres	0	2	5	10	20
Water, millilitres	20	18	15	10	0
Silica content, mg SiO_2/100 ml	0	0,04	0,10	0,20	0,40

Add, from a pipette, 5 ml of the ammonium molybdate solution (4.2.54). Adjust the pH of this solution to $1,60 \pm 0,05$ by adding, drop by drop, sodium hydroxide solution (4.2.30) or hydrochloric acid $1 + 2$ (4.2.3) using the pH meter (5.18.1) calibrated with a buffer solution of similar pH (e.g. 1,40; see 4.2.59). Transfer the solution to a 100 ml volumetric flask and rinse the beaker with dilute hydrochloric acid (4.2.9). After 20 min, add, from a pipette, 5 ml of the citric acid solution (4.2.52), stir and leave to stand for 5 min. Then add, from a pipette, 2 ml of the reducing solution (4.2.58). Consider this as time 0.

Make up to the mark with dilute hydrochloric acid (4.2.9) and mix. At time $(0 + 30)$ min measure the absorbance with the photometer (5.10) using a cell (5.11) of 1 cm optical length against the blank solution prepared in the same way, using the wavelength 815 nm. Construct a curve giving the measured absorbance as a 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 a determination of the silica content in mg SiO_2/100 ml.

4.2.64   Standard calcium ion solution, approximately 0,01 mol/l.

Weigh, to $\pm 0,000\ 5$ g, $(1,00 \pm 0,01)$ g of calcium carbonate (4.2.53), record as m_4 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 $1 + 2$ (4.2.3). Stir with a glass rod and ensure that dissolution is complete; bring to the boil in order to expel the dissolved carbon dioxide. Cool to room temperature, transfer to a 1 000 ml volumetric flask, washing the beaker and watch glass carefully, and make up to the mark with water.

4.2.65   EDTA solution, approximately 0,03 mol/l.

4.2.65.1   Ethylenediaminetetra-acetic acid disodium salt dihydrate (EDTA).

4.2.65.2   Preparation

Dissolve $(11,17 \pm 0,01)$ g of EDTA in water and make up to 1 000 ml. Store in a polyethylene container.

4.2.65.3 Standardization

Pipette 50 ml of the standard calcium ion solution (4.2.64) into a beaker suitable for the measuring apparatus (5.12). Then dilute with water to a volume suitable for the operation of the apparatus.

Using the pH meter (5.18.1), adjust the pH of this solution to $12,5 \pm 0,2$ with either of the sodium hydroxide solutions (4.2.30 or 4.2.31).

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

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

Add, without weighing, about 0,1 g of murexide (4.2.69) or of mixed calcein and methylthymol blue indicator (4.2.75). Place the beaker in the apparatus (5.12) set at 620 nm when using murexide or at 520 nm when using the mixed indicator and, while stirring continuously, titrate with the approximately 0,03 mol/l EDTA solution. In the vicinity of the indicator colour change, construct a curve giving the absorbance 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 absorbance after the colour change.

Calculate the factor, f_D, of the EDTA solution from Equation (5):

$$f_D = \frac{50 \times m_4}{100,09 \times 0,03 \times V_3} = 16,652 \times \frac{m_4}{V_3} \tag{5}$$

where

m_4 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (4.2.64), expressed in grams;

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

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

Add, without weighing, about 0,1 g of either the calcon indicator (4.2.71) or the Patton and Reeders indicator (4.2.76). Stir and titrate with the approximately 0,03 mol/l EDTA solution (4.2.65) until the colour changes from pink to blue (calcon) or purple to blue (Patton and Reeders), volume V_3, and one drop in excess does not further increase the intensity of the blue colour. Calculate the standardization factor, f_D, of the EDTA solution using Equation (5).

4.2.66 Copper complexonate solution.

Pipette 25 ml of the copper sulfate solution (4.2.55) into a 400 ml beaker and add from a burette an equivalent volume, V_5, of the approximately 0,03 mol/l EDTA solution (4.2.65). Determine the required volume, V_5, of EDTA solution as follows.

Pipette 10 ml of the copper sulfate solution (4.2.55) into a 600 ml beaker. Dilute to approximately 200 ml with water and add 10 ml of concentrated ammonium hydroxide (4.2.25) and, without weighing, about 0,1 g of murexide indicator (4.2.69). Titrate with the approximately 0,03 mol/l EDTA solution (4.2.65) until the colour changes from pink to violet; record this volume as V_4.

Calculate the volume, V_5, of the approximately 0,03 mol/l EDTA solution that is necessary to add to 25 ml of the copper sulfate solution to obtain the copper complexonate from Equation (6):

$$V_5 = 2,5 \times V_4 \tag{6}$$

where V_4 is the volume of the approximately 0,03 mol/l EDTA solution for the titration, expressed in millilitres.

4.2.67 Ethyleneglycol-bis (aminoethylether) tetra-acetic acid (EGTA) solution, approximately 0,03 mol/l.

4.2.67.1 Preparation

Dissolve $(11,4 \pm 0,01)$ g of EGTA in 400 ml of water and 30 ml of the sodium hydroxide solution (4.2.31) in a 600 ml beaker. Heat the mixture until the EGTA is completely dissolved. Allow to cool to room temperature. Using the pH meter (5.18.1), adjust the pH to $7,0 \pm 0,5$, by adding, drop by drop, hydrochloric acid $1 + 2$ (4.2.3). Transfer the solution quantitatively to a 1 000 ml volumetric flask and make up to the mark with water. Store the solution in a polyethylene container.

4.2.67.2 Standardization

Pipette 50 ml of the standard calcium ion solution (4.2.64) into a beaker suitable for the measuring apparatus (5.12). Then dilute with water to a volume suitable for the correct operation of the apparatus. Add 25 ml of the triethanolamine $1 + 4$ solution (4.2.57).

Using the pH meter (5.18.1), adjust the pH of this solution to $12,5 \pm 0,2$ with either of the sodium hydroxide solutions (4.2.30 or 4.2.31).

Add, without weighing, about 0,1 g of murexide (4.2.69) or of calcein indicator (4.2.70). Place the beaker in the apparatus (5.12) set at 620 nm when using murexide or at 520 nm when using calcein and, while stirring continuously, titrate with the approximately 0,03 mol/l EGTA solution. In the vicinity of the indicator colour change, record the absorbance values and the correspondent volumes of EGTA added and construct a curve of absorbance versus volume of titrant. 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 absorbance after the colour change.

Calculate the factor, f_G, of the EGTA solution from Equation (7):

$$\begin{aligned} f_G &= \frac{50 \times m_5}{100,09 \times 0,03 \times V_6} \\ &= 16,652 \times \frac{m_5}{V_6} \end{aligned} \tag{7}$$

where

m_5 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (4.2.64), expressed in grams;

V_6 is the volume of the EGTA solution used for the titration, expressed in millilitres.

4.2.68 1,2-diaminocyclohexane tetra-acetic acid monohydrate (DCTA) solution, approximately 0,01 mol/l

4.2.68.1 Preparation

Dissolve (3,64 ± 0,01) g of DCTA in about 400 ml of water and 10 ml of sodium hydroxide solution (4.2.31) in a 600 ml beaker. Heat the mixture until the DCTA is completely dissolved. Allow to cool to room temperature. Using the pH meter (5.18.1), adjust the pH to 7,0 ± 0,5 by adding hydrochloric acid 1 + 2 (4.2.3), drop by drop. Transfer the solution quantitatively to a 1 000 ml volumetric flask and make up to the mark with water. Store this solution in a polyethylene container.

4.2.68.2 Standardization

Pipette 50 ml of the standard calcium ion solution (4.2.64) into a beaker appropriate for the measuring apparatus (5.12). Then dilute with water to a volume suitable for the correct operation of the apparatus.

Using the pH meter (5.18.1), adjust the pH of this solution to 10,5 ± 0,2 with concentrated ammonium hydroxide (4.2.25).

Add, without weighing, about 0,1 g of murexide (4.2.69) or of calcein indicator (4.2.70). Place the beaker in the apparatus (5.12) set at 620 nm when using murexide or at 520 nm when using calcein and, while continuously stirring the solution, titrate with the approximately 0,01 mol/l DCTA solution. In the vicinity of the colour change of the indicator, record the absorbance values and the correspondent volumes of DCTA added and construct a curve of absorbance versus volume of titrant. 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 absorbance after the colour change.

Calculate the factor, f_C, of the DCTA solution from Equation (8):

$$\begin{aligned} f_C &= \frac{50 \times m_6}{100,09 \times 0,01 \times V_7} \\ &= 49,955 \times \frac{m_6}{V_7} \end{aligned} \tag{8}$$

where

m_6 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (4.2.64), expressed in grams;

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

4.2.69   Murexide indicator.

Prepare by grinding $(1,0 \pm 0,1)$ g of murexide (ammonium purpurate, $C_8H_4N_5O_6NH_4$) with (100 ± 1) g of sodium chloride (NaCl).

4.2.70   Calcein indicator.

Prepare by grinding $(1,0 \pm 0,1)$ g of calcein {bis [(bis (carboxymethyl)-amino-methyl)] -2′, 7′-fluorescein; $C_{30}H_{26}N_2O_{13}$} with (100 ± 1) g of potassium nitrate (KNO_3).

4.2.71   Calcon indicator.

Prepare by grinding $(1,0 \pm 0,1)$ g of calcon [sodium 2-hydroxy-4-(2-hydroxy-1-naphthylazo) naphthalene-1-sulfonate; $C_{20}H_{13}N_2NaO_5S$; EriochromeBlue-Black R] with (100 ± 1) g of anhydrous sodium sulfate (Na_2SO_4).

4.2.72   Sulfosalicylic acid indicator (5-sulfosalicylic acid dihydrate).

4.2.73   PAN indicator.

Prepare by dissolving $(0,10 \pm 0,01)$ g of PAN (1-[2-pyridylazo]-2-naphthol; $C_{15}H_{11}N_3O$) in (100 ± 1) ml of ethanol (C_2H_5OH, $\rho = 0,79$).

4.2.74   Methylthymol blue indicator.

Prepare by grinding $(1,0 \pm 0,1)$ g of methylthymol blue {sodium salt of 3′, 3′′-bis- [bis (carboxy-methyl)-aminomethyl]-thymolsulfophthalein; $C_{37}H_{41}N_2O_{13}SNa_3$} with (100 ± 1) g of potassium nitrate (KNO_3).

4.2.75   Mixed calcein and methylthymol blue indicator.

Prepare by grinding $(0,20 \pm 0,02)$ g of calcein (4.2.70) and $(0,10 \pm 0,01)$ g of methylthymol blue (4.2.74) with (100 ± 1) g of potassium nitrate (KNO_3).

4.2.76   Patton and Reeders reagent.

Prepare by mixing $(1,0 \pm 0,1)$ g of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-napthylazo)-3-napthoic acid ($C_{21}H_{14}N_2O_7S$) with (100 ± 1) g of anhydrous sodium sulfate (Na_2SO_4).

4.2.77   Mixed indicator.

Prepare by mixing $(0,10 \pm 0,01)$ g o-cresophthalein complexone [o-cresolphthaleindi-(methyliminodi-acetic acid); $C_{32}H_{32}N_2O_{12}$]; $(0,020 \pm 0,001)$ g methyl red indicator (o-carboxybenzene-azodimethyl-aniline; $C_{15}H_{14}N_3NaO_2$); and $(0,030 \pm 0,001)$ g naphthol green B ($C_{30}H_{15}FeN_3Na_3O_{15}S_3$) with $(10,0 \pm 0,1)$ g of sodium chloride (4.2.37).

4.2.78   Ammonium thiocyanate (NH_4SCN).

4.2.79   Ammonium thiocyanate solution, approximately 0,05 mol/l.

Prepare by dissolving $(3,8 \pm 0,1)$ g of ammonium thiocyanate (4.2.78) in water and making up to 1 000 ml.

4.2.80   Ammonium iron(III) sulfate, ($NH_4Fe(SO_4)_2 \cdot 12H_2O$).

4.2.81   Indicator solution.

Prepare by adding 10 ml of nitric acid 1 + 2 (4.2.13) to 100 ml of a cold, saturated water solution of ammonium iron(III) sulfate (4.2.80).

4.2.82   Copper sulfate ($CuSO_4 \cdot 5H_2O$).

4.2.83   Copper sulfate solution, aqueous, saturated.

4.2.84   Absorbent for hydrogen sulfide.

Place a weighed quantity of dried pumice stone with a grain size between 1,2 mm and 2,4 mm into a flat dish and cover with a volume of saturated copper sulfate solution (4.2.83) so that the mass of the copper sulfate solution is approximately half of that of the pumice stone. Evaporate the mixture to dryness, while stirring frequently with a glass rod. Dry the contents of the dish for at least 5 h in an oven at a temperature of (150 ± 5) °C. Allow the solid mixture to cool in a desiccator and store in an airtight bottle.

4.2.85   Absorbent for water.

Anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] with a particle size between 0,6 mm and 1,2 mm.

4.2.86   Absorbent for carbon dioxide.

Synthetic silicates with a particle size between 0,6 mm to 1,2 mm impregnated with sodium hydroxide (NaOH) (4.2.29).

NOTE   This absorbent can be obtained ready for use.

4.2.87   Mercuric(II) chloride ($HgCl_2$).

WARNING — Mercuric chloride is extremely toxic. Avoid all contact by carrying out operations in a fume cupboard, wearing protective gloves, face shield and protective clothing. It is toxic to aquatic organisms and disposal shall be by authorised contractors.

4.2.88   Alkali stock solution.

Weigh $(0,566\ 0 \pm 0,000\ 5)$ g of sodium chloride (4.2.37) and $(0,475\ 0 \pm 0,000\ 5)$ g of potassium chloride (4.2.38) and place in a 600 ml beaker. Add approximately 150 ml of water and allow the salts to dissolve. Transfer the solution quantitatively, rinsing the beaker with water, to a 1 000 ml volumetric flask and make up to the mark with water. Mix the contents of the flask thoroughly. This solution contains 0,300 g each of sodium oxide (Na_2O) and potassium oxide (K_2O).

4.2.89   Acid stock solution, HCl/H_3PO_4.

To approximately 500 ml of water, placed in a 1 000 ml volumetric flask, add 50 ml of concentrated hydrochloric acid (4.2.1) and 50 ml of concentrated phosphoric acid (4.2.19). Allow to cool then make up to the mark with water and mix thoroughly.

4.2.90   Calcium stock solution.

Weigh $(11,25 \pm 0,01)$ g of calcium carbonate (4.2.53) into a 600 ml beaker. Add 100 ml of water and dissolve the calcium carbonate by cautiously adding 25 ml of concentrated hydrochloric acid (4.2.1). After the reaction is completed, bring slowly to boiling in order to expel the dissolved carbon dioxide and then cool. Transfer the solution, rinsing the beaker with water, into a 1 000 ml volumetric flask, make up to the mark with water and mix thoroughly.

4.2.91   Alkali stock solution (alternative method).

Dissolve (0,254 2 ± 0,000 5) g of sodium chloride (4.2.37) and (0,190 7 ± 0,000 5) g of potassium chloride (4.2.38) in water in a 1 000 ml volumetric flask and make up to the mark.

NOTE   This solution can be obtained made up ready for use.

4.2.92   Caesium chloride (CsCl).

4.2.93   Aluminium nitrate [Al(NO$_3$)$_3$·9H$_2$O].

4.2.94   Buffer solution.

Dissolve 50 g of caesium chloride (4.2.92) and 250 g of aluminium nitrate (4.2.93) in water and make up to 1 000 ml.

NOTE   This solution can be obtained made up ready for use.

4.2.95   Nitric acid (4.2.12).

4.2.96   Nitric acid, dilute, approximately 2 mol/l.

Dilute 145 ml of nitric acid (4.2.95) to 1 000 ml with water.

4.2.97   Hydrogen peroxide solution, approximately 30 %.

4.2.98   Standard chloride solution.

4.2.98.1   Sodium chloride (4.2.37).

Before use, ignite sodium chloride at (600 ± 50) °C for approximately 50 min and cool in a desiccator.

4.2.98.2   Standard chloride solution, 0,005 mol/l.

Dissolve 0,292 g of sodium chloride (4.2.98.1) in an appropriate amount of water, transfer the solution to a 1 000 ml volumetric flask, and make up to the mark with water.

4.2.99   Standard silver nitrate solution, 0,005 mol/l.

4.2.99.1   Preparation

Dissolve 0,85 g of silver nitrate (4.2.42) in an appropriate amount of water, transfer the solution to a 1 000 ml volumetric flask, and make up to the mark with water.

4.2.99.2   Standardization

Transfer 10 ml of the standard chloride solution (4.2.98.2) to a 200 ml beaker using a pipette, add water to the solution to approximately 100 ml. Add 5 ml of nitric acid (4.2.96) to the solution. Set the beaker in the potentiometric titration apparatus (5.26) and titrate with the standard silver nitrate solution. Calculate the factor, f_{Ag}, expressed in percent mass fraction, for the standard silver nitrate solution from Equation (9), and round off the result to four decimal places:

$$f_{Ag} = \frac{10}{V_{Ag}} \qquad\qquad (9)$$

where V_{Ag} is the volume of the standard silver nitrate solution required for titration of the standard chloride solution (4.2.98.2), expressed in millilitres.

4.2.100 Alkali stock solution.

Weigh (0,566 0 ± 0,000 5) g of sodium chloride (4.2.37) and (0,475 0 ± 0,000 5) g of potassium chloride (4.2.38) and place in a 500 ml beaker. Add approximately 150 ml of water and allow the salts to dissolve. Transfer the solution quantitatively, rinsing the beaker, to a 1 000 ml volumetric flask and make up to the mark with water. Mix the contents of the flask thoroughly. This solution contains 0,300 g each of sodium oxide and potassium oxide.

4.2.101 Calcium stock solution.

Weigh (11,25 ± 0,01) g of calcium carbonate (4.2.53) into 500 ml beaker. Add 100 ml of water and dissolve the calcium carbonate by cautiously adding 75 ml of hydrochloric acid (4.2.7). After the reaction is completed, bring slowly to boiling in order to expel the dissolved carbon dioxide and then cool. Transfer the solution, rinsing the beaker with water, into a 1 000 ml volumetric flask, make up to the mark with water and mix thoroughly.

5   Apparatus

5.1   Balance(s), capable of weighing to an accuracy of ± 0,000 5 g.

5.2   Crucibles

5.2.1   Crucibles, porcelain and/or platinum, 20 ml to 25 ml capacity.

NOTE   The methods specify where it is necessary to use platinum crucibles. Unless platinum is specified, porcelain crucibles can be used.

5.2.2   Lids, suitable lids to be fitted to crucibles (5.2.1), where required.

5.3   Ceramic support(s), fire-proof, for preventing overheating of the crucible.

It shall be in thermal equilibrium with the furnace at the moment the crucible is introduced.

5.4   Evaporating dish, porcelain, with approximate 200 ml capacity.

5.5   Electric furnace(s), naturally ventilated, capable of being set at the following temperatures: (500 ± 10) °C, (950 ± 25) °C and (1 175 ± 25) °C.

5.6   Oven(s), laboratory, capable of being set at the following temperatures: (110 ± 5) °C, (120 ± 5) °C, (150 ± 5) °C, (200 ± 10) °C and (250 ± 10) °C.

5.7   Desiccator(s), containing anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] or silica gel.
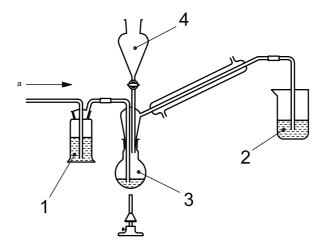
NOTE   Where self-indicating silica gel is used, a non-toxic indicator is recommended.

5.8   Bulb condenser.

5.9   Apparatus for determining sulfide.

A typical apparatus is shown in Figure 1. A Woolf bottle may be added to control the flow of gas.

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

5.10   Photometer(s), for measuring the absorbance of a solution in the vicinity of 525 nm and 815 nm.

5.11   Cells, for the photometer.

Key

1   lead acetate solution (4.2.48)

2   ammoniacal solution of zinc sulfate (4.2.47)

3   reaction flask

4   dropping funnel

a   air, nitrogen or argon

Figure 1 — Typical apparatus for the determination of sulfide
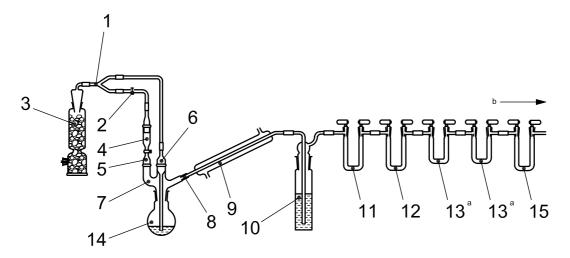
5.12   Apparatus for measuring the absorbance, at 520 nm and 620 nm of a solution contained in a titration beaker, while stirring.

5.13   Stirrer, e.g. magnetic stirrer, with inert, e.g. PTFE, covered bar.

5.14   Evaporation apparatus, controlled at (105 ± 5) °C, e.g. water bath or hot plate.

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

5.16   Filter paper, ashless.

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

5.17   Volumetric glassware, of analytical accuracy, i.e. class A as defined in ISO 385 and ISO 835.

5.18   pH measuring equipment.

5.18.1   pH meter, capable of measuring to an accuracy of $\pm 0,05$.

5.18.2   pH indicator paper(s), capable of measuring pH in the 0 to 14 range.

5.19   Apparatus for the determination of the carbon dioxide content, reference method.

A typical apparatus is shown in Figure 2, which can be fitted with either a cylindrical pressure container, a small electrical compressor or a suitable suction pump that ensures an even flow of gas or air. The gas (air or nitrogen) entering the apparatus has previously had its carbon dioxide removed by first being passed through an absorbent tube or tower containing the carbon dioxide absorbent (4.2.86). The apparatus consists of a 100 ml distillation flask fitted with a three neck adaptor. Neck (key item 5) is connected to a dropping funnel, neck (key item 6) to a connecting tube and neck (key item 8) to a water cooled condenser. The funnel onto (key item 5) and the connecting tube onto (key item 6) are joined together by means of a Y-piece, so that the carbon dioxide-free air can flow either through the connecting tube or the funnel by means of a Mohr clip.

After the condenser, the gas is passed through concentrated sulfuric acid (4.2.15), then through absorption tubes containing the absorbent for hydrogen sulfide (4.2.84) and for water (4.2.85) and subsequently through two absorption tubes, which can be weighed and which are three-quarters filled with the absorbent for carbon dioxide (4.2.86) and a quarter with the absorbent for water (4.2.85). The absorbent for carbon dioxide (4.2.86) is placed upstream of the absorbent for water (4.2.85) with respect to the gas flow. Absorption tubes are followed by an additional absorption tube, which also contains the absorbent for carbon dioxide and water, which is fitted in order to protect the second absorption tube against penetration by carbon dioxide and water from the air.

Key
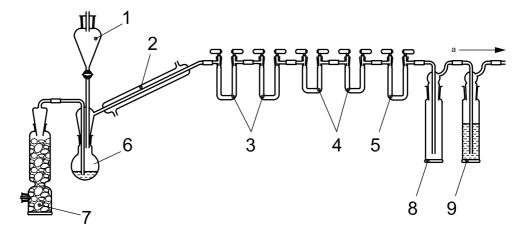
1 Y-piece
2 Mohr clip
3 absorption tower containing carbon dioxide absorbent (4.2.86)
4 dropping funnel
5 dropping funnel connector
6 connecting tube connector
7 three-armed still head
8 condenser connector

9 condenser
10 wash bottle with concentrated sulfuric acid (4.2.15)
11 absorption tube with absorbent for hydrogen sulfide (4.2.84)
12 absorption tube with absorbent for water (4.2.85)
13 absorption tubes with absorbents for carbon dioxide (4.2.86) and water (4.2.85)
14 100 ml distillation flask
15 absorption tubes with absorbents for carbon dioxide (4.2.86) and water (4.2.85)

[a] The absorption tubes, which are weighed, may have, for example, the following approximate sizes.
— external distance between branches: 45 mm;
— internal diameter: 20 mm;
— distance between the lower part of the tube and the upper part of the ground section: 75 mm;
— tube wall thickness: 1,5 mm.
[b] To the vacuum pump.

Figure 2 — Typical apparatus for the determination of carbon dioxide (reference method)

5.20 Apparatus for the determination of the carbon dioxide content, alternative method.

A typical apparatus is shown in Figure 3. A small vacuum pump is used to generate reduced pressure in the apparatus.

Key

1   dropping funnel for sulfuric acid (4.2.17)

2   condenser

3   absorption tubes containing absorbent for water (4.2.85)

4   absorption tubes containing absorbent for carbon dioxide (4.2.86) and water (4.2.85)

5   absorption tube with absorbents for carbon dioxide (4.2.86) and water (4.2.85)

6   100 ml distillation flask

7   absorption tower containing absorbent for carbon dioxide (4.2.86)

8   washing bottle (empty)

9   washing bottle, which may contain either concentrated sulfuric acid (4.2.15) or paraffin as this bottle only serves as a bubble counter

a   To the vacuum pump.

Figure 3 — Typical apparatus for the determination of carbon dioxide (alternative method)

5.21   Flame photometer, of sufficient stability and capable to measure the intensities of the sodium line at 589 nm and the potassium line at 768 nm.

In order to avoid any interference of the determination by alkaline earths, the flame photometer shall be operated at a relatively low temperature by using a propane-air or butane-air flame.

5.22   Platinum dish.

5.23   Filter paper, medium filter paper (5.16), pre-washed with hot water.

5.24   Stirrer, resistant to hydrofluoric acid, e.g. platinum.

5.25   Heating lamp, capable of evaporating to dryness samples in aqueous solution.

5.26   Apparatus for potentiometric titration, capable of measuring the potential difference of a solution, while stirring.

5.27   Magnetic stirrer.

5.28   Atomic absorption spectrophotometer, capable of sufficient stability to enable the measurement of the absorbances of the sodium at 589 nm and the potassium at 768 nm.

6   Preparation of a test sample of cement

Before chemical analysis, treat the laboratory sample as follows to obtain a homogeneous test sample.

Take approximately 100 g of the laboratory sample by means of a sample divider or by quartering. Sieve this portion on a 150 µm or 125 µm sieve until the residue remains constant. Remove metallic iron from the material retained on the sieve by means of a magnet (see Note). 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 container with an airtight closure and shake vigorously to mix it thoroughly.

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

NOTE   Where the analysis is one of a series subject to statistical control and the level of the metallic iron content has been shown to be insignificant in relation to the chemical properties being determined, then it is not necessary to remove metallic iron.

7   Determination of loss on ignition

7.1   Principle

The loss on ignition is determined in an oxidizing atmosphere. By igniting the sample in air at (950 ± 25) °C, the carbon dioxide and water are driven off and any oxidizable elements present are oxidized to some extent. A correction for the influence of this oxidation on the loss on ignition is described. The error resulting from the oxidation of metallic iron, bivalent iron or bivalent manganese is usually considered negligible and only the correction for the extent of oxidation of any sulfides is applied (see 7.4).

7.2   Procedure

Weigh, to $\pm 0,000\ 5$ g, $(1,00 \pm 0,05)$ g of cement into a crucible that has been previously ignited and tared and record as m_7. Place the covered crucible in the electric furnace (5.5) controlled at (950 ± 25) °C. After heating for 5 min, remove the lid and leave the crucible in the furnace for a further 10 min. Allow the crucible to cool to room temperature in the desiccator. Determine the constant mass, m_8, in accordance with 3.5.

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

7.3   Calculation and expression of results

Calculate the observed mass-fraction loss on ignition, w_L, expressed in percent, from Equation (10):

$$w_L = \frac{m_7 - m_8}{m_7} \times 100 \qquad\qquad (10)$$

where

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

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

7.4 Correction for oxidation of sulfides

Calculate the mass, $m_{SO_3\text{-}O}$, of oxygen added by oxidation of sulfides that occurs during the determination of loss on ignition from the masses of sulfate, as SO_3, before ignition and after ignition, $m_{SO_3,i}$ and $m_{SO_3,f}$, respectively, from Equation (11):

$$m_{SO_3-O} = 0,80\left(m_{SO_3,f} - m_{SO_3,i}\right)$$
(11)

The corrected mass-fraction loss, $w_{L\text{-}C}$, taking into account the mass, $m_{SO_3\text{-}O}$, of the additional oxygen, can be calculated from Equation (12):

$$w_{L\text{-}C} = \frac{m_7 - m_8 + m_{SO_3-O}}{m_7} \times 100$$
(12)

NOTE   While "sulfate" is the term conventionally employed, the species used for the calculations is actually the sulfite, SO_3.

Any corrections applied shall be indicated in the test report.

7.5 Repeatability and reproducibility

The standard deviation for repeatability is 0,04 %.

The standard deviation for reproducibility is 0,08 %.

8 Determination of sulfate

8.1 Principle

Sulfate ions, produced by the decomposition of cement with hydrochloric acid, are precipitated at a pH between 1,0 and 1,5 by a solution of barium chloride. The precipitation of barium sulfate is carried out at the boiling point.

The determination is then completed gravimetrically and sulfate expressed as SO_3.

NOTE   While "sulfate" is the term conventionally employed, the species used for the calculations is actually the sulfite, SO_3.

8.2 Procedure

Weigh, to $\pm\,0{,}000\,5$ g, $(1{,}00 \pm 0{,}05)$ g of cement, record as m_9, place in a 250 ml beaker, and add 90 ml of water. While stirring the mixture vigorously, add 10 ml of concentrated hydrochloric acid (4.2.1). Heat the solution gently and crush the sample with the flattened end of a glass stirring rod until decomposition is complete. Allow the solution to digest for 15 min at a temperature just below boiling.

Filter the residue on a medium filter paper (5.16) into a 400 ml beaker. Wash thoroughly with hot water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Adjust the volume to about 250 ml; if necessary, adjust the pH of the solution to between 1,0 and 1,5 with hydrochloric acid 1 + 11 (4.2.6) or ammonium hydroxide 1 + 16 (4.2.28).

Bring to the boil and boil for 5 min. Check that the solution is clear; if not, start the determination again using a new test portion. While stirring vigorously, maintain the solution at boiling point and add drop by drop 10 ml of the barium chloride solution (4.2.41) heated to just below boiling. Maintain the solution at just below boiling point for at least 30 min, ensuring that the volume is kept between 225 ml and 250 ml, and then allow the covered beaker to stand at room temperature for 12 h to 24 h before filtration.

Filter the precipitate on a fine filter paper (5.16) and wash with boiling water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Ignite (see 3.4) at (950 ± 25) °C to constant mass (see 3.5) and record as m_{10}.

NOTE   In general, an ignition period of 15 min is sufficient to achieve constant mass.

8.3   Calculation and expression of results

Calculate the sulfate content, w_{SO_3}, as SO_3, expressed in percent mass fraction, from Equation (13):

$$w_{SO_3} = \frac{m_{10} \times 0{,}343 \times 100}{m_9}$$

$$= 34{,}3 \times \frac{m_{10}}{m_9}$$

(13)

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 method in which the insoluble residue in cement is obtained by treatment with dilute hydrochloric acid in order to minimize 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 that can have been precipitated. After ignition the residue is determined gravimetrically.

9.2   Procedure

Weigh, to $\pm 0{,}000\,5$ g, $(1{,}00 \pm 0{,}05)$ g of cement, record as m_{11} and place in a 250 ml beaker, add 90 ml of water and, while stirring the mixture vigorously, add 10 ml of concentrated hydrochloric acid (4.2.1).

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

Filter the residue on a medium filter paper (5.16) 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 (4.2.45). Boil for approximately 30 min. Filter on a medium filter paper and wash with almost boiling water, then four times with hot hydrochloric acid 1 + 19 (4.2.7) until pH < 2 by indicator paper (5.18.2) is obtained and with almost boiling water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Ignite (see 3.4) at (950 ± 25) °C to constant mass (see 3.5) and record as m_{12}.

NOTE   In general, an ignition period of 30 min is sufficient to achieve constant mass.

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 Calculation and expression of results

Calculate the insoluble residue, w_{ins}, in percent mass fraction, from Equation (14):

$$w_{ins} = \frac{m_{12}}{m_{11}} \times 100 \qquad (14)$$

where

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

m_{12} is the mass of the ignited insoluble residue, expressed 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 method in which the insoluble residue in cement is obtained initially by treatment with a hydrochloric acid solution. The residue from this treatment is then treated with a boiling solution of potassium hydroxide. After ignition the residue is determined gravimetrically.

10.2 Procedure

Weigh, to ± 0,000 5 g, (1,00 ± 0,05) g of cement, record as m_{13} and place in a porcelain dish (5.4), add 25 ml of water and disperse using a glass stirring rod. Add 40 ml of concentrated hydrochloric acid (4.2.1). Heat the solution gently and crush the sample with the flattened end of a glass stirring rod until decomposition is complete. Evaporate to dryness on a water bath (5.14). Repeat the operation twice more with 20 ml concentrated hydrochloric acid (4.2.1).

Treat the residue from the third evaporation with 100 ml of hydrochloric acid 1 + 3 (4.2.4). Re-heat, filter on a medium filter paper (5.16) and wash with almost boiling water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Transfer the filter paper and its contents to a 250 ml conical flask fitted with a bulb condenser (5.8) and add 100 ml of the potassium hydroxide solution (4.2.46). 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 (5.16) and wash with water then with 100 ml of hydrochloric acid 1 + 9 (4.2.5) and finally with almost boiling water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Ignite (see 3.4) at (950 ± 25) °C to constant mass (see 3.5) and record as m_{14}.

NOTE   In general, an ignition period of 30 min is sufficient to achieve constant mass.

10.3 Calculation and expression of results

Calculate the insoluble residue, w_{ins}, expressed in percent mass fraction, from Equation (15):

$$w_{ins} = \frac{m_{14}}{m_{13}} \times 100 \tag{15}$$

where

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

m_{14} is the mass of the ignited insoluble residue, expressed 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 cement 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 amount of precipitated zinc sulfide is determined by iodometry.

11.2 Procedure

Use the apparatus described in 5.9. Weigh, to $\pm\,0,000\,5$ g, $(1,00 \pm 0,05)$ g of cement, record as m_{15}. [If the sulfide content is low ($< 0,10$ %), the mass of the test portion should be increased in proportion.] Place in a 250 ml stoppered round bottom flask with a ground glass joint. Add about 2,5 g of tin(II) chloride (4.2.33) and 0,1 g of chromium (4.2.24) (see Note). Disperse in 50 ml of water. Fix the flask to the ground neck of the dropping funnel and connect to the condenser the glass outlet tube which dips into the beaker containing 15 ml of ammoniacal zinc sulfate solution (4.2.47) and 285 ml of water. Connect the gas supply (air, nitrogen or argon) and adjust the flow to about 10 ml/min. Stop the flow of gas. Release 50 ml of hydrochloric acid $1 + 1$ (4.2.2) from the dropping funnel ensuring that a small quantity of acid remains in the dropping funnel to provide a seal. Reconnect the gas supply, heat the contents of the flask to boiling and boil for 10 min. Disconnect the outlet tube, which can serve as a stirrer during the titration.

Cool to room temperature, add 10 ml of potassium iodate solution, approximately 0,016 6 mol/l (4.2.60), by pipette and 25 ml of concentrated hydrochloric acid (4.2.1). Titrate with sodium thiosulfate solution (4.2.61) until pale yellow. Then add 2 ml of starch solution (4.2.49) and titrate until the colour changes from blue to colourless.

NOTE   Chromium assists in the decomposition of any pyrites (FeS_2) present in the cement.

11.3 Calculation and expression of results

Calculate the sulfide content, $w_{S^{2-}}$, expressed in percent mass fraction, from Equation (16):

$$w_{S^{2-}} = \frac{[(V_8 \times F) - (V_9 \times f_S)] \times 1,603 \times 100}{1\,000 \times m_{15}}$$

$$= 0,160\,3 \times \frac{[(V_8 \times F) - (V_9 \times f_S)]}{m_{15}}$$

(16)

where

V_8 is the volume of the potassium iodate solution, expressed in millilitres;

F is the factor of the potassium iodate solution;

V_9 is the volume of the sodium thiosulfate solution used for the titration, expressed in millilitres;

f_S is the factor of the sodium thiosulfate solution;

m_{15} is the mass of the test portion, expressed in grams.

11.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,02 %.

The standard deviation for reproducibility is 0,04 %.

12 Determination of manganese by photometry

12.1 Principle

The manganese present is oxidized to permanganate, MnO_4^-, by means of potassium periodate. The absorbance of the violet solution is measured at 525 nm. The ferric, 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

Weigh, to ± 0,000 5 g, (0,1 to 1,0) g of cement into a 250 ml beaker and record as m_{16}. (For manganese contents on the order of 0,01 %, taking a test portion close to 1 g and varying its amount to suit the probable manganese concentration is recommended.) Add about 75 ml of water. Stir, add cautiously 15 ml of nitric acid (4.2.12) and boil in a fume cupboard until free from any hydrogen sulfide (H_2S) present and all the cement is decomposed. For cements with a high insoluble residue, fusion of a separate test portion can 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).

Filter through a medium filter paper (5.16) 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 (4.2.19), mix and add 1,5 g of potassium periodate (4.2.35). 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 (4.2.25). 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 room temperature and make up to the mark with water.

Using a photometer and cells (5.10 and 5.11), measure the absorbance of the solution against water at a wavelength of approximately 525 nm.

Record the absorbance value to three decimal places. The absorbance read from the calibration curve (4.2.62.2.2) corresponding to the cell used gives the concentration of manganese, c_{Mn}, in milligrams of manganese per 200 ml. Record the manganese concentration, c_{Mn}, to three decimal places.

12.3 Calculation of results

Calculate the manganese content, w_{Mn}, expressed in percent mass fraction, from Equation (17):

$$w_{Mn} = \frac{c_{Mn} \times 100}{1\,000 \times m_{16}}$$
$$= 0,1 \times \frac{c_{Mn}}{m_{16}} \tag{17}$$

where

c_{Mn} is the manganese (Mn) concentration of the solution, expressed in milligrams per 200 ml;

m_{16} is the mass of the test portion, expressed in grams.

12.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,003 %.

The standard deviation for reproducibility is 0,03 %.

12.5 Expression of results

The manganese content is normally expressed as percent mass fraction MnO, equal to w_{MnO} as given by Equation (18) or percent mass fraction Mn_2O_3, equal to $w_{Mn_2O_3}$ as given by Equation (19)

$$w_{MnO} = 1,29 \times w_{Mn} \tag{18}$$

$$w_{Mn_2O_3} = 1,44 \times w_{Mn} \tag{19}$$

13 Determination of major elements

13.1 Principle

The analysis is carried out after the cement is completely dissolved. The decomposition with hydrochloric acid and ammonium chloride (alternative method) may be used for cement with an insoluble residue (as determined in accordance with Clause 9) not exceeding 1,5 %.

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 double evaporation or by hydrochloric acid with coagulation by polyethylene oxide; 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 sulfuric 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. In this case, it is necessary to decompose the cement by sodium peroxide.

In the final solution, the soluble (residual) silica 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 4.

The relative amounts of impure, pure and soluble (residual) silica may vary depending on the procedure used, but the same result for the total silica is obtained whichever path in Figure 4 is chosen.

13.2 Decomposition with sodium peroxide

Weigh, to $\pm$ 0,000 5 g, (1,00 $\pm$ 0,05) g of cement, record as m_{17} and place, with about 2 g of sodium peroxide (4.2.36), into a platinum crucible (5.2.1); mix thoroughly with a spatula. Brush back into the mixture any particles adhering to the spatula. Cover the mixture with about 1 g of sodium peroxide. Carefully preheat the crucible fitted with a lid (5.2.2) 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 $\pm$ 10) °C.

After 30 min, remove the crucible from the furnace and allow it to cool to room temperature. The sintered, solid mass shall 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, solid mass to a 400 ml beaker and rinse the crucible with 150 ml of cold water.

Cover the beaker with a watch glass and heat until the solid is completely dispersed. Then add cautiously 50 ml of concentrated hydrochloric acid (4.2.1). 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 (4.2.16). 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 — Double evaporation method (reference method)

13.3.1 Procedure
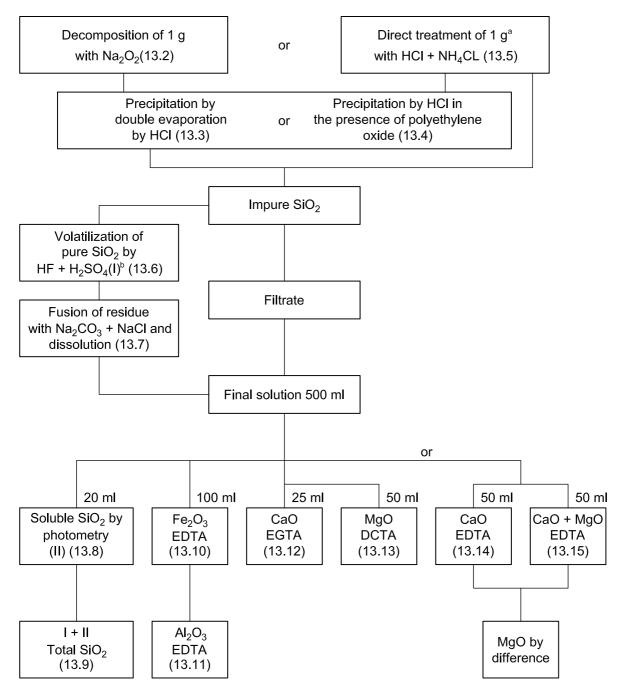
Evaporate to dryness the solution prepared as described in 13.2 with an evaporation apparatus controlled at (105 $\pm$ 5) °C (5.14). Moisten with several drops of concentrated hydrochloric acid (4.2.1). Leave for 1 h at this temperature.

After cooling to room temperature, treat the residue with 10 ml of concentrated hydrochloric acid (4.2.1). After a few minutes dilute with 50 ml of water, bring to the boil and filter the hot solution through a medium filter paper (5.16) 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 (4.2.1) and dilute with 50 ml of water. Boil, then pass through the same filter into a 500 ml volumetric flask. Where filtration is difficult, a second filter paper may be used, in which case the following procedure shall be applied to both filter papers and precipitated residue.

Wash the filter and precipitate with hot water until free from chloride ions, tested by the silver nitrate test (see 3.6). Collect the washings in the same 500 ml volumetric flask.

Ignite (see 3.4) the filter and precipitate, to constant mass (see 3.5) in a platinum crucible at (1 175 $\pm$ 25) °C and record as m_{18}. Other ignition temperatures within the range 1 050 °C to 1 175 °C may be used, provided that results have been demonstrated as equivalent to results using the reference temperature (1 175 $\pm$ 25) °C.

NOTE   In general, an ignition period of 60 min is sufficient to obtain constant mass.

Figure 4 — Schematic diagram for analysis of the major elements

Volatilize the ignited precipitate as described in 13.6. Add the decomposed evaporation residue solution (13.7) to the filtrate and washings in the 500 ml volumetric flask. The combined solutions are used for the colorimetric determination of soluble silica (i.e. the residual silica 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).

a   If the residue insoluble in hydrochloric acid and sodium carbonate (see Clause 9) is greater than 1,5 %, it is necessary to use the method of decomposition by sodium peroxide.

b   When the ammonium chloride method is used, if the residue after volatilization with hydrofluoric acid and sulfuric acid exceeds 0,5 %, it is necessary to recommence the analysis using the decomposition by sodium peroxide.

13.3.2 Calculation and expression of results

Calculate the impure silica content, $w_{SiO_2,imp}$, expressed in percent mass fraction, from Equation (20):

$$w_{SiO_2,imp} = \frac{m_{18}}{m_{17}} \times 100 \qquad (20)$$

where

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

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

13.4 Precipitation and determination of silica — Polyethylene oxide method (alternative method)

13.4.1 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 (4.2.1). While stirring, add some ashless filter paper pulp to the mixture and then 5 ml of the polyethylene oxide solution (4.2.50) 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.

Filter through a medium filter paper (5.16) into a 500 ml volumetric flask and rinse with hot hydrochloric acid 1 + 19 (4.2.7). Remove any precipitate adhering to the sides of the beaker using a rubber or plastic 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 chloride ions, tested by the silver nitrate test (see 3.6).

Collect the washings in the same 500 ml volumetric flask.

Ignite (see 3.4) the filter and the precipitate, to constant mass (see 3.5), in a platinum crucible at $(1\ 175 \pm 25)$ °C and record as m_{19}. Other ignition temperatures within the range 1 050 °C to 1 175 °C may be used, provided that results have been demonstrated as equivalent to results using the reference temperature $(1\ 175 \pm 25)$ °C.

NOTE   In general, an ignition period of 60 min is sufficient to obtain constant mass.

Volatilize the ignited precipitate as described in 13.6. Add the decomposed evaporation residue (13.7) to the filtrate and washings in the 500 ml volumetric flask. The combined solution is used for the colorimetric determination of soluble silica (i.e. the residual silica 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 Calculation and expression of results

Calculate the impure silica content, $w_{SiO_2,imp}$, expressed in percent mass fraction, from Equation (21):

$$w_{SiO_2,imp} = \frac{m_{19}}{m_{17}} \times 100 \qquad (21)$$

where

m_{17} is the mass of the test portion used in 13.2, expressed in grams;

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

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

NOTE   This method is used only where the insoluble residue, as determined in Clause 9, does not exceed 1,5 %.

13.5.1 Procedure

Weigh, to $\pm$ 0,000 5 g, (1,00 $\pm$ 0,05) g of cement, record as m_{20} and place in a 100 ml beaker. Add about 1 g of ammonium chloride (4.2.32) and mix thoroughly with a glass stirring rod. Cover the beaker with a watch glass and cautiously add 10 ml of concentrated hydrochloric acid (4.2.1) taking care to let the acid run down the side of the beaker. When effervescence has stopped, add 10 drops of nitric acid (4.2.12) and stir with a glass stirring rod crushing any lumps.

Place the beaker and its watch glass on a boiling water bath and leave for 30 min. Dilute the contents of the beaker with a small quantity of hot water and filter through a coarse filter paper (5.16) 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 or plastics scraper.

Rinse the beaker and precipitate with hot hydrochloric acid 1 + 99 (4.2.8). Then wash the precipitate and filter with small amounts of hot water until free from chloride ions, tested by the silver nitrate test (see 3.6).

Collect the washings in the same 500 ml volumetric flask.

This is used, together with the evaporation residue decomposed as described in 13.7, for the photometric determination of soluble silica (i.e. residual silica in solution) in accordance with 13.8.

Ignite (see 3.4) the filter and the precipitate, to constant mass (see 3.5), in a platinum crucible at (1 175 $\pm$ 25) °C and record as m_{21}. Other ignition temperatures within the range 1 050 °C to 1 175 °C may be used, provided that results have been demonstrated as equivalent to results using the reference temperature (1 175 $\pm$ 25) °C.

NOTE   In general, an ignition period of 60 min is sufficient to obtain constant mass.

Volatilize the ignited precipitate as described in 13.6.

13.5.2 Calculation and expression of results

Calculate the impure silica, $w_{SiO_2,imp}$, expressed in percent mass fraction, from Equation (22):

$$w_{SiO_2,imp} = \frac{m_{21}}{m_{20}} \times 100 \qquad\qquad (22)$$

where

   m_{20} is the mass of the test portion used in 13.5.1, expressed in grams;

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

13.6 Determination of pure silica

13.6.1 Procedure

Moisten the precipitate, obtained in accordance with 13.3.1 or 13.4.1 or 13.5.1, with about 0,5 ml to 1 ml of water, add approximately 10 ml of hydrofluoric acid (4.2.10) then two drops of sulfuric acid (4.2.15). Evaporate in a fume cupboard over a sand bath or hot plate (5.15), then continue to heat until free from white sulfuric acid fumes.

Ignite the crucible with the evaporation residue in an electric furnace (5.5) at (1 175 ± 25) °C for 10 min, leave to cool to room temperature in a desiccator; weigh and record as m_{22}. Other ignition temperatures within the range 1 050 °C to 1 175 °C may be used, provided that results have been demonstrated as equivalent to results using the reference temperature (1 175 ± 25) °C.

Decompose the evaporation residue as described in 13.7. If the residue obtained by this method exceeds 0,5 %, restart the analysis using the method of decomposition with sodium peroxide (13.2).

13.6.2 Calculation and expression of results

Calculate the pure silica content, $w_{SiO_2,p}$, expressed in percent mass fraction, from Equation (23):

$$w_{SiO_2,p} = \frac{m_{24} - m_{22}}{m_{23}} \times 100 \tag{23}$$

where

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

m_{23} is the mass of the test portion used in 13.2 (equivalent to m_{17}) or in 13.5.1 (equivalent to m_{20}), expressed in grams;

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

13.7 Decomposition of the evaporation residue

To the evaporation residue, obtained in accordance with 13.6.1, add about 2 g of the sodium carbonate and sodium chloride mixture (4.2.40) and fuse to a bright red heat, e.g. 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 (4.2.1). When the decomposed mass is completely dissolved, remove the platinum crucible from the solution and rinse it with water.

Check that the solution is clear. If not, filter through a medium filter paper (5.16), 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; make up to the mark with water.

After shaking the flask vigorously, this solution is ready to be used in the photometric determination of the soluble silica (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 by photometry

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 (5.13) and add 20 ml water. While stirring with the magnetic stirrer (5.13), add 15 drops of hydrofluoric acid 1 + 3 (4.2.11). Stir again for at least 1 min. Then pipette 15 ml of the boric acid solution (4.2.51). Add from a pipette 5 ml of the ammonium molybdate solution (4.2.54) to the solution. Adjust the pH of the solution to 1,60 ± 0,05 by adding, drop by drop, sodium hydroxide (4.2.30) or hydrochloric acid 1 + 2 (4.2.3), using a pH meter (5.18.1) calibrated with a buffer solution of similar pH value (e.g. 1,40; see 4.2.59).

Transfer the solution to a 100 ml volumetric flask and rinse the beaker with hydrochloric acid of pH 1,60 (4.2.9). After 20 min, add from a pipette 5 ml of the citric acid solution (4.2.52), stir and leave to stand for 5 min. Then add from a pipette 2 ml of the reducing solution (4.2.58). (Consider this as time 0).

Make up to volume with dilute hydrochloric acid of pH 1,60 (4.2.9) and mix. At time (0 + 30) min, measure the absorbance with the photometer (5.10) against a blank solution prepared in a similar way and using the same wavelength and a cell (5.11) of the same optical length as used for the construction of the calibration curve (4.2.63.5). The silica concentration, c_{25}, expressed in milligrams SiO_2 per 100 ml is read from the calibration curve.

13.8.2 Calculation and expression of results

Calculate the soluble silica content, $w_{SiO_2,sol}$, expressed in percent mass fraction, from Equation (24):

$$w_{SiO_2,sol} = \frac{500 \times c_{25} \times 100}{20 \times 1\,000 \times m_{23}}$$
$$= 2,5 \times \frac{c_{25}}{m_{23}}$$

(24)

where

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed in grams;

c_{25} is the silica concentration of the solution in accordance with 13.8.1, expressed in milligrams per 100 ml.

13.9 Determination of total silica

13.9.1 Calculation and expression of results

The total silica content, expressed in percent mass fraction, is 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

NOTE 1   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 (4.2.16) to the solution before titration.

NOTE 2   This method uses photometric determination of the end-point. It is also possible to make visual observation of the titration although with less precision. Sulfosalicylic acid (4.2.72) is a suitable indicator (colour changes from violet to clear yellow).

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 (5.12). Then make up with water to a volume suitable for the correct operation of the equipment.

Add 0,5 g amino-acetic acid (4.2.23) and 0,3 g to 0,4 g of sulfosalicylic acid indicator (4.2.72).

Using a pH meter (5.18.1), adjust the pH of this solution to $1,5 \pm 0,1$ with the ammonium hydroxide $1 + 1$ (4.2.26) and $1 + 10$ (4.2.27).

Heat to $(47,5 \pm 2,5)$ °C. Place the beaker in the apparatus (5.12) set at 520 nm and, while stirring the solution, titrate with the approximately 0,03 mol/l EDTA solution (4.2.65). In the vicinity of the indicator colour change, construct a curve of the readings from the measuring apparatus as a function of the volume of EDTA solution added. Record the total volume, V_{tot}, of EDTA solution added. The volume at the end point, V_{10}, is determined from the intersection of the line of greatest slope in the region of the colour change and the line of almost constant absorbance after the colour change. The excess volume, V_{ex}, of EDTA solution added is determined as volume V_{tot} less volume V_{10}.

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.

13.10.2 Calculation and expression of results

Calculate the iron(III) oxide content, $w_{Fe_2O_3}$, expressed in percent mass fraction, from Equation (25):

$$
\begin{aligned}
w_{Fe_2O_3} &= \frac{0,03 \times 159,692 \times 500 \times V_{10} \times f_D}{2 \times 1\,000 \times 100 \times m_{23}} \times 100 \\
&= 1,197\,7 \times \frac{V_{10} \times f_D}{m_{23}}
\end{aligned}
\tag{25}
$$

where

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

$\quad f_D$ is the factor of the approximately 0,03 mol/l EDTA solution determined in accordance with 4.2.65;

$\quad m_{23}$ is the mass of the test portion used in 13.2 or 13.5.1, expressed 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 (4.2.22) then, drop by drop, the ammonium acetate solution (4.2.56) so as to obtain a pH of $3,05 \pm 0,05$. This range shall be strictly observed and controlled by means of the pH meter (5.18.1). The pH shall not exceed 3,10. Bring to the boil and add three drops of the copper complexonate solution (4.2.66) and 2 ml of PAN indicator (4.2.73).

During the titration, keep the solution gently boiling (work in a fume cupboard). Titrate with the approximately 0,03 mol/l EDTA solution (4.2.65) until the colour changes from violet-pink to pale yellow. When the pink colour reappears, add the EDTA solution drop by drop until the yellow colour persists for at least 1 min.

13.11.2 Calculation and expression of results

Calculate the aluminium oxide content, $w_{Al_2O_3}$, expressed in percent mass fraction, from Equation (26):

$$w_{Al_2O_3} = \frac{0,03 \times 101,961 \times 500 \times V_{11} \times f_D}{2 \times 1\,000 \times 100 \times m_{23}} \times 100$$

$$= 0,764\,7 \times \frac{V_{11} \times f_D}{m_{23}}$$

(26)

where

V_{11} is the volume of the approximately 0,03 mol/l EDTA solution used for the titration plus the excess volume, V_{ex} (see 13.10.1), expressed in millilitres;

f_D is the factor of the 0,03 mol/l EDTA solution determined in accordance with 4.2.65.3;

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed 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

NOTE 1   This method uses photometric determination of the end-point. It is possible to make visual observations of the titration, although with less precision. The mixed calcein and methylthymol blue indicator (4.2.75) is suitable (colour change from pale green to pink) for both photometric and visual methods.

NOTE 2   In this method, any strontium oxide is determined and expressed as calcium oxide.

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 (5.12) and make up to the same volume as in 4.2.67.2 with water and then add 25 ml of the triethanolamine solution $1 + 4$ (4.2.57). Using the pH meter (5.18.1), adjust the pH of this solution to $12,5 \pm 0,5$ with sodium hydroxide solution (4.2.30). Add, without weighing, about 0,1 g of murexide (4.2.69) or calcein indicator (4.2.70). Place the beaker in the apparatus (5.12) set at 520 nm when using calcein or at 620 nm when using murexide and, while stirring, titrate with the approximately 0,03 mol/l EGTA solution (4.2.67).

In the vicinity of the colour change, construct a curve of the readings from the measuring apparatus as a function of the volume of EGTA solution 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 absorbance after the colour change.

13.12.2 Calculation and expression of results

Calculate the calcium oxide content, w_{CaO}, expressed in percent mass fraction, from Equation (27):

$$w_{CaO} = \frac{0,03 \times 56,08 \times 500 \times V_{12} \times f_G}{1\,000 \times 25 \times m_{23}} \times 100$$

$$= 3,364\,8 \times \frac{V_{12} \times f_G}{m_{23}}$$

(27)

where

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

f_G is the factor of the approximately 0,03 mol/l EGTA solution determined in accordance with 4.2.67.2;

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed 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

NOTE   This method uses photometric determination of the end-point. It is possible to make visual observations of the titration, although with less precision. Methylthymol blue (4.2.74) is a suitable indicator (colour change from blue to grey).

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 (5.12), add 50 ml of triethanolamine solution $1 + 4$ (4.2.57) and a volume, V_{13}, of the EGTA solution (4.2.67).

Calculate the volume required, V_{13}, expressed in millilitres, from Equation (28):

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

(28)

where V_{12} is the volume of the EGTA solution used for titration in accordance with 13.12.1, expressed in millilitres.

After the addition of the calculated volume of EGTA solution, dilute with water to a volume suitable for the correct operation of the apparatus. Using the pH meter (5.18.1), adjust the pH of this solution to $10,5 \pm 0,5$ with concentrated ammonium hydroxide (4.2.25).

Add, without weighing, about 0,1 g of methylthymol blue indicator (4.2.74).

Place the beaker in the apparatus (5.12) set at 620 nm and, while stirring the solution, titrate with the approximately 0,01 mol/l DCTA solution (4.2.68). In the vicinity of the colour change of the indicator, construct a curve of the absorbance values as a function of the volume of DCTA solution 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 absorbance after the colour change.

13.13.2 Calculation and expression of results

Calculate the magnesium oxide content, w_{MgO}, expressed in percent mass fraction, from Equation (29):

$$w_{MgO} = \frac{0,01 \times 40,311 \times 500 \times V_{14} \times f_C}{1\,000 \times 50 \times m_{23}} \times 100$$

$$= 0,403\,1 \times \frac{V_{14} \times f_C}{m_{23}}$$

(29)

where

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

f_C is the factor of the approximately 0,01 mol/l DCTA solution determined in accordance with 4.2.68.2;

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed 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

NOTE 1   This method uses photometric determination of the end-point. It is possible to determine the end-point of the titration visually. In this case, Calcon (4.2.71) (colour change from pink to blue), mixed methyl calcein and methylthymol blue indicator (4.2.75) (colour change pink to yellow) or Patton and Reeders reagent (4.2.76) (colour change from purple to clear blue) are suitable indicators.

NOTE 2   In this method, any strontium oxide is determined and expressed as calcium oxide.

This method can be used for determination of calcium oxide in the presence of manganese. Where the method is used in conjunction with the method of determination of magnesium oxide by EDTA (see 13.15), it shall be preceded by the determination of manganese content (see Clause 12) for comparison with the limit given in 13.15.1 for manganese oxide.

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 (5.12). Then, dilute with water to a volume suitable for the correct operation of the equipment. Add 50 ml of the triethanolamine solution 1 + 4 (4.2.57).

Using the pH meter (5.18.1), adjust the pH of this solution to $12,5 \pm 0,5$ with sodium hydroxide solution (4.2.30).

Add, without weighing, about 0,1 g of murexide (4.2.69), calcein indicator (4.2.70) or mixed methyl calcein and methylthymol blue indicator (4.2.75). Place the beaker in the apparatus (5.12) set at 620 nm when using murexide or at 520 nm when using calcein and, while stirring the solution, titrate with the approximately 0,03 mol/l EDTA solution (4.2.65). In the vicinity of the colour change of the indicator, construct a curve of the absorbance 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 absorbance after the colour change.

13.14.3 Calculation and expression of results

Calculate the calcium oxide content, w_{CaO}, expressed in percent mass fraction, from Equation (30):

$$w_{CaO} = \frac{0,03 \times 56,08 \times 500 \times V_{15} \times f_D}{1\,000 \times 50 \times m_{23}} \times 100$$

$$= 1,682\,4 \times \frac{V_{15} \times f_D}{m_{23}} \tag{30}$$

where

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

f_D is the factor of the approximately 0,03 mol/l EDTA solution determined in accordance with 4.2.65.3;

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed 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

NOTE   This method uses photometric determination of the end-point. It is possible to determine the end-point of the titration visually. In this case, a mixed calcein and methylthymol blue indicator (4.2.75) (colour change from pink to colourless) or a mixed indicator (4.2.77) (colour change from pink to colourless) or a dispersion of 1 g of phthalein purple in 100 g of solid NaCl (colour change from violet to pale pink) are suitable indicators.

In the rare case where a cement has a manganese oxide (Mn_2O_3) content greater than 0,5 %, only the method of determination of magnesium oxide by DCTA (13.13) is applicable.

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 (5.12). Then dilute with water to a volume suitable for the correct operation of the equipment. Add 50 ml of the triethanolamine solution 1 + 4 (4.2.57).

Using the pH meter (5.18.1), adjust the pH of this solution to $10,5 \pm 0,5$ with ammonium hydroxide 1 + 1 (4.2.26).

Using a burette, add the volume, V_{15}, of EDTA solution (4.2.65) required for the titration of calcium oxide previously determined in 13.14.2.

Then add, without weighing, about 0,1 g of methylthymol blue (4.2.74), mixed calcein and methylthymol blue indicator (4.2.75) or mixed indicator (4.2.77).

Place the beaker in the apparatus (5.12) set at 620 nm and, while stirring the solution, titrate with the approximately 0,03 mol/l EDTA solution (4.2.65). In the vicinity of the colour change of the indicator, construct a curve of the absorbance values as a function of the volume of EDTA solution 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 absorbance after the colour change.

13.15.3 Calculation and expression of results

Calculate the magnesium oxide content, w_{MgO}, expressed in percent mass fraction, from Equation (31):

$$w_{MgO} = \frac{0,03 \times 40,311 \times 500 \times (V_{16} - V_{15}) \times f_D}{1\,000 \times 50 \times m_{23}} \times 100$$

$$= 1,209\,3 \times \frac{(V_{16} - V_{15}) \times f_D}{m_{23}}$$

(31)

where

V_{15} is the volume of EDTA solution required for the determination of calcium oxide as in 13.14.2, expressed in millilitres;

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

f_D is the factor of the approximately 0,03 mol/l EDTA solution determined in accordance with 4.2.65.3;

m_{23} is the mass of the test portion used in 13.2 or 13.5.1, expressed in grams.

13.15.4 Repeatability and reproducibility

The standard deviation for repeatability is 0,21 %.

The standard deviation for reproducibility is 0,25 %.

14 Determination of chloride

14.1 Determination of chloride by titration (reference method)

14.1.1 Principle

This method gives the total chloride plus bromide content and expresses the result as chloride ion (Cl^-). Cement is treated with boiling dilute nitric acid to decompose it and to remove sulfides. The dissolved chloride is precipitated using a known volume of a standard silver nitrate solution. After boiling, the precipitate is washed with dilute nitric acid and discarded. The filtrate and washings are cooled to below 25 °C and the residual silver nitrate is titrated with a standardized ammonium thiocyanate solution using an iron(III) salt as indicator.

14.1.2 Procedure

Weigh, to $\pm\,0,000\,5$ g, $(5,00 \pm 0,05)$ g of cement, record as m_{26} and place in a 400 ml tall form beaker, add 50 ml of water and, while stirring with a glass rod, 50 ml of nitric acid 1 + 2 (4.2.13). Heat the mixture to boiling (in a fume cupboard for samples containing sulfide), stirring occasionally, and boil for 1 min to 2 min avoiding loss of liquid. Remove from the source of heat and add 5 ml of silver nitrate solution (4.2.44) by pipette (5.17) into the solution. Then boil for not less than 1 min and not more than 2 min and filter through a coarse filter paper (5.16), washed before use with nitric acid 1 + 100 (4.2.14), into a 500 ml conical flask. Wash the beaker, glass rod and filter paper with nitric acid 1 + 100 until the volume of the filtrate and the washings is approximately 200 ml. Cool the filtrate and washings to below 25 °C in subdued light or in the dark.

Add up to 5 ml indicator solution (4.2.81) and titrate with the ammonium thiocyanate solution (4.2.79) shaking vigorously until a drop of this solution produces a faint pink colouration that does not disappear on shaking. Record the volume, V_{17}, of ammonium thiocyanate used in the titration. If V_{17} is less than 0,5 ml, repeat the procedure with half the sample mass.

Carry out the same procedure with no cement sample and record the volume, V_{18}, of ammonium thiocyanate solution used in the blank titration.

14.1.3 Calculation and expression of results

Calculate the chloride content, w_{Cl^-}, expressed in percent mass fraction, from Equation (32):

$$
\begin{aligned}
w_{Cl^-} &= \frac{1,773 \times 5(V_{18} - V_{17})}{1\,000 \times V_{18} \times m_{26}} \times 100 \\
&= 0,886\,5 \times \frac{(V_{18} - V_{17})}{V_{18} \times m_{26}}
\end{aligned}
\tag{32}
$$

where

m_{26} is the mass of the test portion, expressed in grams;

V_{17} is the volume of the ammonium thiocyanate solution used for the titration of the test solution, expressed in millilitres;

V_{18} is the volume of the ammonium thiocyanate solution used for the titration of the blank solution, expressed in millilitres.

14.2 Determination of chloride by potentiometric titration (alternative method)

14.2.1 Principle

Dissolve the sample in nitric acid, add the chloride ion standard solution to increase the detection sensibility, then add aqueous hydrogen peroxide to oxidize coexisting interfering components and heat the solution. After cooling to room temperature, titrate the solution with a potential-difference-measuring apparatus having a chloride-ion-selective electrode. Subtract the value obtained from a blank test performed in the same manner as above from the titration value.

14.2.2 Procedure

Weigh 5,000 g of the sample into a dried 200 ml beaker, add 20 ml of water and add 12 ml of nitric acid (4.2.95) while stirring the solution with a glass rod to disperse the sample. Dissolve the sample by heating, if necessary. Add warm water to the solution to 100 ml and add 2,00 ml of the standard chloride solution (4.2.98.2) and 2 ml of hydrogen peroxide (4.2.97). Cover the beaker with a watch glass and heat gently for 1 min to 2 min to boil the solution. After cooling the solution to room temperature, wash the watch glass and the glass rod with water and remove them from the beaker.

NOTE   In the case of a blast-furnace slag or the like which is high in silica content, gel-like matters can precipitate in the solution. This precipitate, however, does not affect the results of measurement.

The dilution of the sample may be varied to match the sensitivity of the apparatus or the concentration of chloride in the sample.

Set the beaker in the apparatus (5.26), and titrate with the standard silver nitrate solution (4.2.99). Record the potential difference, E, and the volume, V_{Ag}, of the standard silver nitrate solution added, and calculate the change, ΔE, of potential difference against the standard silver nitrate solution added. Continue the titration until ΔE decreases clearly. The end-point is determined from the maximum of the ratio $\Delta E/V_{Ag}$.

14.2.3 Blank test

Put 2,00 ml of the standard chloride solution (4.2.98.2) in a 200 ml beaker, add warm water to 100 ml, and further add 5 ml of nitric acid (4.2.96) and hydrogen peroxide (4.2.97) to the solution. Cover the beaker with a watch glass and heat gently for 1 min to 2 min to boil the solution. After cooling the solution to room temperature, wash the watch glass and the glass rod with water and remove them from the beaker. According to 14.2.2, titrate with the standard silver nitrate solution.

14.2.4 Calculation and expression of results

Calculate the content of the chloride, w_{Cl^-}, expressed in percent mass fraction, from Equation (33):

$$w_{Cl^-} = \frac{(V_{19} - V_{20}) \times f_{Ag} \times 0{,}000\ 177\ 3}{m_{25}} \times 100 \tag{33}$$

where

m_{25} is the mass of the test portion, expressed in grams;

V_{19} is the volume of the standard silver nitrate solution (4.2.99) used in titration (14.2.2), expressed in millilitres;

V_{20} is the volume of the standard silver nitrate solution (4.2.99) used in blank test (14.2.3), expressed in millilitres;

f_{Ag} is the factor of the standard silver nitrate solution (4.2.99).

14.3 Repeatability and reproducibility

The standard deviation of repeatability is 0,005 %.

The standard deviation of reproducibility is 0,010 %.

15 Determination of carbon dioxide (reference method)

15.1 Principle

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

15.2 Procedure

Weigh, to $\pm$ 0,000 5 g, (1,00 $\pm$ 0,05) g of cement, record as m_{27} and place it in a dry 100 ml distillation flask. Connect the flask to the apparatus (5.19) as shown in Figure 2, but without the two absorption tubes. Pass a current of carbon dioxide-free gas through the apparatus for 15 min at approximately 3 bubbles per second (bubble counter) via the connecting tube onto the connecting tube connector (branch onto the dropping funnel connector, with the Mohr clip closed). Release the Mohr clip and remove the gas supply from the funnel. Add 30 ml concentrated phosphoric acid (4.2.19) into the dropping funnel and reconnect the gas supply to fill the funnel.

Condition the closed absorption tubes for 15 min in the balance case in order to achieve temperature equilibrium. Then weigh each tube separately and record the masses as m_{28} and m_{29}. Shut off the flow of gas and attach the tubes to the apparatus as shown in Figure 2.

CAUTION — Care should be taken when handling the tubes to avoid affecting their mass, causing damage or sustaining injury. It is advisable to wear protective gloves when carrying out this operation.

Reopen the gas flow. After 10 min close absorption tubes, shown as key item 13 in Figure 2, remove them, place them in the balance case for 15 min and then weigh them separately and record the masses as m_{28} and m_{29}. Repeat the passage of gas, removal and weighing of absorption tubes for as long as is required for the results of two successive weighings of a tube not to differ by more than 0,000 5 g.

If the change in mass of the absorption tubes, shown as key item 13 in Figure 2, remains greater than 0,000 5 g, renew the absorbents in the tubes.

Attach the weighed absorption tubes to the apparatus, as shown in Figure 2.

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

Close absorption tubes, remove them and place them in the balance case for 15 min; then weigh them separately and record as m_{30} and m_{31}. The increase in mass of each tube, $(m_{30} - m_{28})$ and $(m_{31} - m_{29})$ is used for the calculation of the carbon dioxide content (see 15.3).

The carbon dioxide is practically completely absorbed by the first tube. If the increase in mass of the second tube exceeds 0,000 5 g, renew the absorbent in the first tube and start the test again.

15.3 Calculation and expression of results

Calculate the carbon dioxide content, w_{CO_2}, expressed in percent mass fraction, from Equation (34):

$$w_{CO_2} = \frac{(m_{30} - m_{28}) + (m_{31} - m_{29})}{m_{27}} \times 100 \tag{34}$$

where

m_{27} is the mass of the test portion, expressed in grams;

$m_{30} - m_{28}$ is the increase in mass of the first tube, shown as key item 13 in Figure 2, after absorption, expressed in grams;

$m_{31} - m_{29}$ is the increase in mass of the first tube, shown as key item 13 in Figure 2, after absorption, expressed in grams.

If the carbon dioxide content calculated from Equation (34) is less than 0,5 %, repeat the determination with $(2,00 \pm 0,05)$ g of cement, weighed to $\pm$ 0,000 5 g. Alternatively, where the cement contains a high proportion of carbonate the size of the sample should be decreased appropriately.

15.4 Repeatability and reproducibility

The standard deviation of repeatability is 0,07 %.

The standard deviation of reproducibility is 0,10 %.

16 Determination of carbon dioxide (alternative method)

16.1 Principle

The carbon dioxide is driven off by treatment with sulfuric acid, absorbed by sodium hydroxide and determined gravimetrically. Any hydrogen sulfide present which may affect the results is absorbed by mercuric(II) chloride.

WARNING — Mercuric chloride is extremely toxic. Avoid all contact by carrying out operations in a fume cupboard, wearing protective gloves, face shield and protective clothing. It is toxic to aquatic organisms and disposal shall be by authorised contractors.

DANGER — Mercuric chloride is extremely toxic and should be handled only by trained personnel. Proper safety precautions shall be taken.

16.2 Procedure

Weigh, to $\pm\,0{,}000\,5$ g, $(1{,}00 \pm 0{,}05)$ g of cement into the 100 ml distillation flask of the apparatus (5.20) and record as m_{32}. Mix this cement with a small (about 50 mg) amount of mercuric(II) chloride (4.2.87) using a spatula and then add enough water to form a slurry.

Connect the flask to the ground joint of the dropping funnel. Then draw air for 15 min through the apparatus, passing the air through an absorption tower filled with absorbent (4.2.86) to remove the carbon dioxide before the air passes into the flask.

Condition the closed absorption tubes, shown as key item 4 in Figure 3, for 15 min in the balance case in order to achieve temperature equilibrium. Then weigh each tube separately and record as m_{33} and m_{34}. Shut off the flow of gas and attach the tubes to the apparatus as shown in Figure 3.

CAUTION — Care should be taken when handling the tubes to avoid affecting their mass, causing damage or sustaining injury. It is advisable to wear protective gloves when carrying out this operation.

Add 25 ml to 30 ml of sulfuric acid $1 + 4$ (4.2.17) from the dropping funnel (key item 1) into the flask. Take care to ensure that some of the acid remains in the dropping funnel as a seal.

Turn the vacuum pump on again, so that the current of air carries the liberated carbon dioxide through the condenser and the first two absorption tubes, filled with magnesium perchlorate (4.2.85) for the purposes of drying the air, to the two previously weighed absorption tubes filled with absorbents (4.2.85 and 4.2.86). An absorption tube filled with magnesium perchlorate (4.2.85) and absorbent (4.2.86) is fitted after these tubes in order to prevent penetration by the ambient air. An empty gas-washing bottle and one filled with concentrated sulfuric acid (4.2.15) or paraffin are connected as a bubble counter.

After about 10 min, heat the contents of the flask to boiling and boil gently for 5 min. Maintain the air flow through the apparatus until the flask has cooled to room temperature. Close the taps, remove the absorption tubes and place them in the balance case for 15 min in order to achieve temperature equilibrium; then weigh them and record the masses as m_{35} and m_{36}.

16.3 Calculation and expression of results

Calculate the carbon dioxide content, w_{CO_2}, expressed in percent mass fraction, from Equation (35):

$$w_{CO_2} = \frac{(m_{35} - m_{33}) + (m_{36} - m_{34})}{m_{32}} \times 100 \tag{35}$$

where

m_{32} is the mass of the test portion, expressed in grams;

$m_{35} - m_{33}$ is the increase in mass of the first absorption tube, shown as key item 4 in Figure 3, after absorption, expressed in grams.

$m_{36} - m_{34}$ is the increase in mass of the second absorption tube, shown as key item 4 in Figure 3, after absorption, expressed in grams.

If the carbon dioxide content calculated from Equation (35) is less than 0,5 %, repeat the determination with $(2,00 \pm 0,05)$ g of cement, weighed to $\pm 0,000\,5$ g. Alternatively, where the cement contains a high proportion of carbonate, the size of the sample should be decreased appropriately.

16.4 Repeatability and reproducibility

The standard deviation of repeatability is 0,07 %.

The standard deviation of reproducibility is 0,10 %.

17 Determination of alkali by flame photometry (reference method)

17.1 Principle

A butane, propane or acetylene flame is used to excite the alkali metals to emit their characteristic spectrum in the visible range. The emission is proportional to the alkali content at low concentrations. The influence of large quantities of calcium in the sample on the sodium determination is suppressed by means of phosphoric acid. The influence of phosphoric acid on the potassium emission from the calibration solutions is suppressed by adding calcium to the calibration solutions.

17.2 Preparation of calibration solutions and calibration curves

Whenever a new batch of any reagent is used, determine the alkali content by means of this method. If the alkali content of a reagent exceeds 0,01 %, either replace the batch with a new one, which shall be verified in the same way, or prepare new calibration solutions.

Prepare the calibration solutions using the volumes of alkali stock solution, acid stock solution and calcium stock solution listed in Table 4. Make up the volumes listed for solutions S1 to S7 to 1 000 ml with water and mix thoroughly. Store these calibration solutions in polyethylene bottles. Aspirate the calibration solutions into the flame of the flame photometer (5.21). Aspirate the blank solution (see Table 4) first and set the indication on the apparatus to zero. Aspirate the solution of greatest concentration, S7, and set the indication on the apparatus to maximum intensity. Aspirate the other calibration solutions in the order of increasing concentration, S2 to S6. Measure the intensities for Na_2O at 589 nm and for K_2O at 768 nm.

Construct curves of the measured intensities against the corresponding concentrations of Na_2O and K_2O in the calibration solutions.

Table 4 — Volumes of solutions for the preparation of calibration solutions and their sodium oxide and potassium oxide concentrations

Number of the calibration solution	Alkali stock solution (4.88)	Acid stock solution (4.89)	Calcium stock solution (4.90)	Na_2O and K_2O concentrations
	ml	ml	ml	mg/l
S1	—	100	100	0,0
S2	5	100	100	1,5
S3	10	100	100	3,0
S4	20	100	100	6,0
S5	30	100	100	9,0
S6	40	100	100	12,0
S7	50	100	100	15,0

17.3 Dissolution of the test portion

17.3.1 Cements with an insoluble residue not exceeding 3 %

The method in this subclause is applicable to cements that have an insoluble residue content, determined in accordance with Clause 9, not exceeding 3 %.

Weigh (0,500 0 ± 0,000 5) g of cement into a 250 ml beaker, make into a slurry with 50 ml of water and add 50 ml of hydrochloric acid 1 + 19 (4.2.7). Warm the mixture until the cement has decomposed, crushing any lumps with a glass rod. Then allow the suspension to cool to ambient temperature. Transfer the contents of the beaker, rinsing the beaker with water, into a 500 ml volumetric flask. Add 50 ml of phosphoric acid 1 + 19 (4.2.20), make up to the mark with water and mix thoroughly. Filter, without washing, sufficient solution through the filter paper (5.23) into a clean, dry beaker, before aspirating solution into the flame.

17.3.2 Cements with an insoluble residue exceeding 3 %

DANGER — Perchloric acid vapours form explosive mixtures with organic materials; it is, therefore, necessary to take special precautionary measures when working with perchloric acid (4.2.18), e.g. the use of fume cupboards flushed with water and a general ban on the use of organic substances in the same fume cupboard.

Carry out the following evaporation procedures in an appropriate fume cupboard because the vapours from nitric acid (4.2.12), perchloric acid (4.2.18) and hydrofluoric acid (4.2.10) are hazardous. In addition, wear eye protection and suitable rubber or plastics gloves when handling or agitating these acids or their mixtures.

The method in this subclause is applicable to cements that have an insoluble residue content, as determined in accordance with Clause 9, exceeding 3 %.

Weigh (0,500 0 ± 0,000 5) g of cement into a platinum dish (5.22) and add 15 ml of nitric acid (4.2.12). Heat the mixture, e.g. on a hot-plate, and evaporate to dryness. Disperse the residue from evaporation in 15 ml of water, add 5 ml of perchloric acid (4.2.18) and then add 25 ml of hydrofluoric acid (4.2.10).

Heat the mixture and evaporate to dryness. Prevent overheating by frequent agitation by means of the HF-resistant stirrer (5.24). Add 10 ml of water and 50 ml of hydrochloric acid 1 + 19 (4.2.7) to the residue from evaporation and heat until the residue has dissolved. Allow the suspension to cool to room temperature. Transfer the contents of the platinum dish, rinsing the dish with water, into a 500 ml volumetric flask. Add 50 ml of phosphoric acid 1 + 19 (4.2.20) to the solution, make up to the mark with water and mix thoroughly. Filter, without washing, sufficient solution through the filter paper (5.23) into a clean, dry beaker, before aspirating the solution into the flame.

17.4 Procedure

Aspirate the sample solution produced as described in 17.3.1 or 17.3.2 into the flame of the flame photometer (5.21). Measure the intensity of the sodium line at 589 nm and the potassium line at 768 nm. Obtain the sodium oxide or potassium oxide concentration in the solution respectively by means of a linear interpolation from the intensities and the associated concentrations of the calibration solutions measured as described in 17.2.

Use the curves constructed in accordance with 17.2 to obtain the sodium oxide and potassium oxide concentrations of the solution, expressed in milligrams per litre, or use the intensities and the associated concentrations of the calibration solutions with the next higher and the next lower intensity for the calculation as follows.

Calculate the concentration of sodium oxide, c_{Na_2O}, or potassium oxide, c_{K_2O}, expressed in milligrams per litre, of the solution from the intensities I_{Na_2O} or I_{K_2O}, respectively, using Equations (36) and (37), respectively:

$$c_{Na_2O} = c_{Bn} + \left(c_{Bh} - c_{Bn}\right) \times \frac{I_{c_{Na_2O}} - I_{Bn}}{I_{Bh} - I_{Bn}} \qquad (36)$$

$$c_{K_2O} = c_{Bn} + \left(c_{Bh} - c_{Bn}\right) \times \frac{I_{K_2O} - I_{Bn}}{I_{Bh} - I_{Bn}} \qquad (37)$$

where

c_{Bn} is the concentration of the sodium oxide or potassium oxide, respectively, in the calibration solution having a concentration lower than the sample solution, expressed in milligrams per litre;

c_{Bh} is the concentration of the sodium oxide or potassium oxide, respectively, in the calibration solution having a concentration higher than the sample solution expressed in milligrams per litre;

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

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

17.5 Calculation and expression of results

17.5.1 Sodium oxide and potassium oxide content

Calculate the sodium oxide, w_{Na_2O}, or potassium oxide, w_{K_2O}, in percent mass fraction, from Equations (38) and (39), respectively, using the concentrations in milligrams per litre as determined in Equations (36) and (37), respectively:

$$w_{Na_2O} = 0{,}1 \times c_{Na_2O} \qquad (38)$$

$$w_{Ka_2O} = 0{,}1 \times c_{Ka_2O} \qquad (39)$$

17.5.2 Sodium oxide equivalent

Calculate the sodium oxide equivalent content, w_{eqNa_2O}, expressed in percent mass fraction, by converting the potassium oxide content to the equivalent sodium oxide content and adding the measured sodium oxide content using Equation (40):

$$w_{eqNa_2O} = w_{Na_2O} + 0{,}658 w_{K_2O} \qquad (40)$$

NOTE   The sodium oxide equivalent, determined in accordance with this part of ISO 29581, is sometimes referred to as the acid-soluble alkali content to differentiate it from determinations carried out using other extraction methods, e.g. water-soluble alkali content.

17.6 Repeatability and reproducibility

The standard deviation of repeatability is

—   0,01 % for the determination of Na_2O,

—   0,02 % for the determination of K_2O.

The standard deviation of reproducibility is

—   0,02 % for the determination of Na_2O,

—   0,03 % for the determination of K_2O.

18 Determination of alkali (alternative methods)

18.1 Determination of alkali by flame photometry (alternative method)

18.1.1 Principle

Cements, with an insoluble residue not exceeding 3 %, determined in accordance with Clause 9, are treated with hydrochloric acid. Cements, with an insoluble residue greater than 3 %, are first evaporated with hydrofluoric acid/sulfuric acid. The alkali contents of the solutions are determined by means of flame photometry.

18.1.2 Construction of the calibration curves

Whenever a new batch of any reagent is used, determine the alkali content by means of this method. If the alkali content of a reagent exceeds 0,01 % either replace the batch with a new one that shall be verified in the same way or prepare new calibration solutions.

In the case of cements with an insoluble residue not exceeding 3 %, evaporate 20 ml of hydrochloric acid $1 + 9$ (4.2.5) to dryness, and, in the case of cements with an insoluble residue greater than 3 %, evaporate 15 ml of hydrofluoric acid (4.2.10) and 5 ml of sulfuric acid (4.2.15) to dryness for the purposes of preparing the calibration solutions for each calibration point.

In both cases, dissolve the residue from evaporation with 2 ml of hydrochloric acid $1 + 9$ (4.2.5) and 3 ml of water. Transfer the solution to a 100 ml volumetric flask and add 10 ml of buffer solution (4.2.94). Add the quantities of the alkali stock solution (4.2.91) to the individual volumetric flasks shown in Table 5 using a burette (5.17).

Table 5 — Quantities of stock solution added to the flasks

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

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

For an original test portion of 0,200 0 g, the values measured for flasks 1 to 7 correspond to the Na_2O and K_2O percent mass fractions shown in Table 6.

Table 6 — Alkali contents of stock solutions in flasks

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

Aspirate the calibration solutions into the flame of the flame photometer (5.21). Aspirate the blank solution in flask 1 first and set the indication on the apparatus to zero.

Then aspirate the other calibration solutions in order of increasing alkali content (in flasks 2 to 7). Measure the intensities for Na_2O at 589 nm and for K_2O at 768 nm. Construct curves of the measured intensities against the corresponding contents of sodium oxide and potassium oxide in the calibration solutions.

18.1.3 Procedure

18.1.3.1 Cements with an insoluble residue not exceeding 3 %

The procedure in this subclause is applicable to cements that have an insoluble residue content, determined in accordance with Clause 9, not exceeding 3 %.

Weigh, to ± 0,000 5 g, (0,200 ± 0,005) g of cement into the platinum dish (5.22), make into a slurry with 3 ml of water and evaporate to dryness after adding 20 ml of hydrochloric acid 1 + 9 (4.2.5). Add hot water and 2 ml of hydrochloric acid 1 + 9 to the residue and filter through the filter paper (5.23) into a 100 ml volumetric flask that already contains 10 ml of the buffer solution (4.2.94). Wash the residue with hot water until the volumetric flask is almost filled to the mark. Then cool to room temperature and make up to the mark with water.

Measure the solution in the flame photometer (5.21). The scale values read off in conjunction with the calibration curves (18.1.2) give the contents of Na_2O and K_2O, respectively, in percent, uncorrected in the case where a test portion with a mass other than 0,200 g has been taken (see 18.1.2 and 18.1.4).

18.1.3.2 Cements with an insoluble residue exceeding 3 %

WARNING — Carry out the following evaporation procedures in an appropriate fume cupboard because the vapours from sulfuric acid (4.2.15) and hydrofluoric acid (4.2.10) are hazardous. In addition, wear eye protection and suitable rubber or plastics gloves when handling or agitating these acids or their mixtures.

The procedure in this subclause is applicable to cements that have an insoluble residue content, determined in accordance with Clause 9, exceeding 3 %.

Weigh, to ± 0,000 5 g, (0,200 ± 0,005) g of cement into the platinum dish (5.22). Make into a slurry with 3 ml of water and evaporate after adding 5 ml of sulfuric acid (4.2.15) and 15 ml of hydrofluoric acid (4.2.10). Evaporate to dryness under the heating lamp (5.25). Mix the residue with hot water and 2 ml of hydrochloric acid 1 + 9 (4.2.5) and continue the procedure, from the filtering operation onwards, as described in 18.1.3.1.

18.1.4 Calculation and expression of results

Calculate the content of each alkali oxide as a percentage for an original test portion of 0,200 0 g by dividing each value obtained by the method in 18.1.3.1 or 18.1.3.2, expressed in percent, by the actual mass of the test portion and multiplying by 0,2.

Express the result as described in 17.5.

18.2 Determination of acid-soluble alkalis by atomic absorption spectroscopy (alternative method)

18.2.1 Principle

The concentrations of sodium oxide and potassium oxide in sample solution are determined by an atomic absorption spectrophotometer. This method may be applied for all types of cement.

18.2.2 Preparation of calibration solutions and calibration curves

Whenever a new batch of any reagent is used, determine the alkali content by means of this method. If the alkali content of a reagent exceeds 0,01 % either replace the batch with a new one, which shall be verified in the same way or prepare new calibration solutions.

Prepare the calibration solutions using the volumes of alkali stock solution (4.2.100) and calcium stock solution (4.2.101) listed in Table 7. Make up the volumes for solutions S1 to S7 to 1 000 ml with water. Store these calibration solutions in polyethylene bottles.

Aspirate the calibration solutions into the atomic absorption spectrophotometer (5.28). Aspirate the blank solution (Table 7, S1) first and set the indication on the apparatus to zero. Aspirate the solution of greatest concentration (Table 7, S7) and set the indication on the apparatus to maximum absorbance. Aspirate the other calibration solutions in the order of increasing concentration (Table 7, S2 to S6). Measure the absorbances for Na_2O at 589 nm and for K_2O at 767 nm.

Construct calibration curves of the measured absorbances against the corresponding concentrations of Na_2O and K_2O in the calibration solutions.

Table 7 — Volumes of solutions for the preparation of calibration solutions and their sodium oxide and potassium oxide concentrations

Calibration solution	Alkali stock solution (4.2.100) ml	Calcium stock solution (4.2.101) ml	Na_2O and K_2O concentrations mg/l
S1	—	100	Blank solution
S2	5	100	1,5
S3	10	100	3,0
S4	20	100	6,0
S5	30	100	9,0
S6	40	100	12,0
S7	50	100	15,0

18.2.3 Dissolution of the test portion

Weigh $(0{,}500\,0 \pm 0{,}000\,5)$ g of cement into a 200 ml beaker, make into a slurry with 50 ml of water and add 50 ml of hydrochloric acid $1 + 19$ (4.2.7). Warm the mixture until the cement has decomposed, crushing any lumps with a glass rod. After cooling the solution to room temperature, filter the contents of the beaker using medium filter paper (5.23), rinsing the beaker with water, into a 500 ml volumetric flask. Make up to the mark with water and mix thoroughly.

18.2.4 Procedure

Aspirate the sample solution produced as described in 18.2.3 into the flame of the atomic absorption spectrophotometer (5.28). Measure the absorbances of the sodium line at 589 nm and the potassium line at 768 nm. Obtain the sodium oxide or potassium oxide concentration in the solution respectively by means of a linear interpolation from the absorbances and the associated concentrations of the calibration solutions measured as described in 18.2.2.

Use the curves constructed in accordance with 18.2.2 to obtain the sodium oxide and potassium oxide concentrations of the solution in milligrams per litre or use the absorbances and the associated concentrations of the calibration solutions with the next higher and the next lower absorbance for the calculation as follows.

Calculate the concentration of sodium oxide, c_{Na_2O}, or potassium oxide, c_{K_2O}, expressed in milligrams per litre, of the sample from the absorbances, I_{Na_2O} or I_{K_2O}, respectively, using Equations (36) and (37).

18.2.5 Calculation and expression of results

18.2.5.1 Sodium oxide and potassium oxide content

Calculate the sodium oxide, w_{Na_2O}, or potassium oxide, w_{K_2O}, in percent mass fraction, from Equations (38) and (39), respectively, using the concentrations in milligrams per litre as determined in Equations (36) and (37), respectively.

18.2.5.2 Sodium oxide equivalent

Calculate the sodium oxide equivalent content, w_{eqNa_2O}, expressed in percent mass fraction, by converting the potassium oxide content to the equivalent sodium oxide content and adding the measured sodium oxide content using Equation (40).

NOTE   The sodium oxide equivalent, determined in accordance with this part of ISO 29581, is sometimes referred to as the acid-soluble alkali content to differentiate it from determinations carried out using other extraction methods, e.g. water-soluble alkali content.

18.3 Repeatability and reproducibility

18.3.1   The standard deviation of repeatability is

— 0,01 % for the determination of Na_2O;

— 0,02 % for the determination of K_2O.

18.3.2   The standard deviation of reproducibility is

— 0,02 % for the determination of Na_2O;

— 0,03 % for the determination of K_2O.

ICS 91.100.10

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