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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

# Methods of testing cement — Chemical analysis of cement

[Revision of first edition (ISO 680:1990)]

*Méthodes d'essai des ciments — Analyses chimiques des ciments*

ICS 91.100.10

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### ISO/CEN PARALLEL ENQUIRY

This draft International Standard is a draft European Standard developed within the European Committee for Standardization (CEN) and processed under the CEN-lead mode of collaboration as defined in the Vienna Agreement. The document has been transmitted by CEN to ISO for circulation for ISO member body voting in parallel with CEN enquiry. Comments received from ISO member bodies, including those from non-CEN members, will be considered by the appropriate CEN technical body. **Accordingly, ISO member bodies who are not CEN members are requested to send a copy of their comments on this DIS directly to CEN/TC 51 (IBN/BIN, Avenue de la Brabançonne/laan, 29, B-1000 Bruxelles) as well as returning their vote and comments in the normal way to the ISO Central Secretariat.** Should this DIS be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month FDIS vote in ISO and formal vote in CEN.

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ICS

English version

**Methods of testing cement - Chemical analysis of cement  
(ISO/DIS 680:2002)**

Méthodes d'essais des ciments - Analyses chimiques des  
ciments (ISO/DIS 680:2002)

Prüfverfahren für Zement - Chemische Analyse von  
Zement (ISO/DIS 680:2002)

This draft European Standard is submitted to CEN members for parallel enquiry. It has been drawn up by the Technical Committee CEN/TC 51.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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## Foreword

This document (prEN ISO 680) has been prepared by Technical Committee CEN/TC 51 "Cement and building limes", the secretariat of which is held by national standard body, in collaboration with Technical Committee ISO/TC 74 "Cement and lime".

This document is currently submitted to the parallel Enquiry.

This European Standard has been prepared by Technical Committee CEN/TC 51, '*Cement and building limes*', the Secretariat of which is held by IBN.

This European Standard shall be given the status of a National Standard, either by publication of an identical text or by endorsement, at the latest day by xxxx 200y, and conflicting national standards shall be withdrawn at the latest by xxxx 200y.

This European Standard supersedes EN 196-2:1994 and EN 196-21:1989 which are withdrawn.

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

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- a) EN 196: Part 21 has been consolidated into prEN ISO 680;
  - b) Calibration against internationally accepted reference materials is permitted;
  - c) The number of tests to be carried out, when the analysis is part of a series subject to statistical control, has been reduced to one;
  - d) A requirement for blank determinations has been included;
  - e) Limiting ranges have been set for masses, volumes and temperatures wherever these are significant;
  - f) The required accuracy of the balance is consistent with that of equipment traditionally used;
  - g) A specification for a laboratory oven has been included;
  - h) The calibration procedure for standard silica solution has been simplified;
  - i) Additional indicators have been included for the visual determination of EDTA titrations;
  - j) An ignition temperature of  $(950 \pm 25)$  °C has been set for the determination of loss on ignition and the ignition of barium sulfate and insoluble residues;
  - k) Determination of sulfate before and after ignition in the determination of loss on ignition becomes the reference method when correcting for sulfide;
  - l) Determination of silica by the double evaporation method becomes the reference method;
  - m) In the determination of carbon dioxide by decomposition with sulfuric acid an additional, empty, gas washing bottle is included as a safety precaution against the reverse flow of sulfuric acid should pressure be lost;

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

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

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

According to the CEN/CENELEC Internal Regulations, the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom.

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## 1 Scope

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

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

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

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

Standard specifications state which methods are to be used.

## 2 Normative references

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

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

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements*

ISO 3534-1:1993, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms.*

## 3 General requirements for testing

### 3.1 Number of tests

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

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

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

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

### 3.2 Repeatability and reproducibility

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

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

Repeatability and reproducibility in this European standard are expressed as repeatability standard deviation(s) and reproducibility standard deviation(s) in e.g. absolute percent, grams, etc., according to the property tested.

NOTE Definitions based on ISO 3534:1993.

### 3.3 Expression of masses, volumes, factors and results

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

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

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

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

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

The results of all individual tests shall be recorded.

### 3.4 Ignitions

Carry out ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate slowly in an oxidising atmosphere, without 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 0,0005 g.

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

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

### 3.7 Blank determinations

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

## 4 Reagents

### 4.0 General requirements

Use only reagents of analytical quality. References to water mean distilled water, or water of equal purity with an electrical conductivity of approximately 2  $\mu\text{S}/\text{cm}$ .

Unless otherwise stated percent means percent by mass.

Unless otherwise stated the concentrated liquid reagents used in this standard have the following densities ( $\rho$ ) (in  $\text{g}/\text{cm}^3$  at 20 °C):

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

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

#### 4.1 Concentrated hydrochloric acid (HCl)

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#### 4.2 Dilute hydrochloric acid 1 + 1

#### 4.3 Dilute hydrochloric acid 1 + 2

#### 4.4 Dilute hydrochloric acid 1 + 3

#### 4.5 Dilute hydrochloric acid 1 + 9

#### 4.6 Dilute hydrochloric acid 1 + 11

#### 4.7 Dilute hydrochloric acid 1 + 19

#### 4.8 Dilute hydrochloric acid 1 + 99

**4.9 Dilute hydrochloric acid of pH (1,60  $\pm$  0,05).** Prepare by adjusting the pH of two litres of water to (1,60  $\pm$  0,05) by adding five or six drops of concentrated hydrochloric acid. Control using the pH meter (5.18). Store the solution in a polyethylene container.

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

#### 4.11 Dilute hydrofluoric acid 1 + 3

#### 4.12 Concentrated nitric acid (HNO<sub>3</sub>)

#### 4.13 Dilute nitric acid 1 + 2

#### 4.14 Dilute nitric acid 1 + 100

- 4.15 **Concentrated sulfuric acid (>98 %)** ( $\text{H}_2\text{SO}_4$ )
- 4.16 **Dilute sulfuric acid 1 + 1**
- 4.17 **Dilute sulfuric acid 1 + 4**
- 4.18 **Concentrated perchloric acid** ( $\text{HClO}_4$ )
- 4.19 **Concentrated phosphoric acid** ( $\text{H}_3\text{PO}_4$ )
- 4.20 **Dilute phosphoric acid 1 + 19**; store this solution in a polyethylene container.
- 4.21 **Boric acid** ( $\text{H}_3\text{BO}_3$ )
- 4.22 **Concentrated acetic acid** ( $\text{CH}_3\text{COOH}$ )
- 4.23 **Amino-acetic acid** ( $\text{NH}_2\text{CH}_2\text{COOH}$ )
- 4.24 **Metallic chromium** (Cr), in powder form
- 4.25 **Concentrated ammonium hydroxide** ( $\text{NH}_4\text{OH}$ )
- 4.26 **Dilute ammonium hydroxide 1 + 1**
- 4.27 **Dilute ammonium hydroxide 1 + 10**
- 4.28 **Dilute ammonium hydroxide 1 + 16**
- 4.29 **Sodium hydroxide** (NaOH)
- 4.30 **Sodium hydroxide solution 4 mol/l**. Dissolve 160 g of sodium hydroxide (4.29) in water and make up to 1000 ml. Store in a polyethylene container.
- 4.31 **Sodium hydroxide solution 2 mol/l**. Dissolve 80 g of sodium hydroxide (4.29) in water and make up to 1000 ml. Store in a polyethylene container.
- 4.32 **Ammonium chloride** ( $\text{NH}_4\text{Cl}$ )
- 4.33 **Tin (II) chloride** ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ )
- 4.34 **Potassium iodate** ( $\text{KIO}_3$ ), dried to constant mass at  $(120 \pm 5)^\circ\text{C}$ .
- 4.35 **Potassium periodate** ( $\text{KIO}_4$ )
- 4.36 **Sodium peroxide** ( $\text{Na}_2\text{O}_2$ ), in powder form.
- 4.37 **Sodium chloride** (NaCl), dried to constant mass at  $(110 \pm 5)^\circ\text{C}$ .
- 4.38 **Potassium chloride** (KCl), dried to constant mass at  $(110 \pm 5)^\circ\text{C}$ .
- 4.39 **Sodium carbonate** ( $\text{Na}_2\text{CO}_3$ ), dried to constant mass at  $(250 \pm 10)^\circ\text{C}$ .
- 4.40 **Mixture of sodium carbonate and sodium chloride**. Mix 7 g of sodium carbonate (4.39) with 1 g sodium chloride (NaCl) (4.37).
- 4.41 **Barium chloride solution**. Dissolve 120 g of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in water and make up to 1000 ml.

**4.42 Silver nitrate** ( $\text{AgNO}_3$ ), dried to constant mass at  $(150 \pm 5)^\circ\text{C}$ .

**4.43 Silver nitrate solution.** Dissolve 5 g of silver nitrate ( $\text{AgNO}_3$ ) (4.42) in water, add 10 ml of concentrated nitric acid ( $\text{HNO}_3$ ) (4.12) and make up to 1000 ml with water.

**4.44 Silver nitrate solution 0,05 mol/l.** Dissolve  $(8,4940 \pm 0,0005)$  g of silver nitrate ( $\text{AgNO}_3$ ) (4.42) in water in a 1000 ml volumetric flask and make up to the mark. Store in a brown glass container and protect from the light.

**4.45 Sodium carbonate solution.** Dissolve 50 g of anhydrous sodium carbonate (4.39) in water and make up to 1000 ml.

**4.46 Potassium hydroxide solution.** Dissolve 250 g of potassium hydroxide ( $\text{KOH}$ ) in water and make up to 1000 ml. Store in a polyethylene container.

**4.47 Ammoniacal zinc sulfate solution.** Dissolve 50 g of zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (4.25). Leave to stand for at least 24 h and filter.

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

**4.49 Starch solution.** To 1 g of starch (water soluble), add 1g of potassium iodide ( $\text{KI}$ ), dissolve in water and make up to 100 ml.

**4.50 Polyethylene oxide solution.** Dissolve 0,25 g of polyethylene oxide  $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$  of average molecular mass 200 000 to 600 000, in 100 ml water while stirring vigorously. Use within two weeks.

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

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

**4.53 Calcium carbonate** ( $\text{CaCO}_3$ ), dried to constant mass at  $(200 \pm 10)^\circ\text{C}$  (of purity  $> 99,9\%$ ).

**4.54 Ammonium molybdate solution.** Dissolve 10 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) in water and make up to 100 ml. Store the solution in a polyethylene flask. Use within one week.

**4.55 Copper sulfate solution.** Dissolve 0,45 g of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in water and make up to 50 ml in a volumetric flask.

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

**4.57 Triethanolamine**  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$  ( $>99\%$ ) diluted to 1 + 4 solution.

**4.58 Reducing solution.** Dissolve 1 g of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in water to which has been added 1 ml of concentrated hydrochloric acid (4.1). Make up to 100 ml with water. Use within one day.

**4.59 Buffer solution of pH 1,40.** Dissolve  $(7,505 \pm 0,001)$  g of amino-acetic acid (4.23) and  $(5,850 \pm 0,001)$  g of sodium chloride ( $\text{NaCl}$ ) (4.37) in water and make up to 1000 ml. Dilute 300 ml of this solution to 1000 ml with hydrochloric acid 1 + 99 (4.8).

**4.60 Standard potassium iodate solution containing approximately 0,0166 mol/l.** Weigh, to  $\pm 0,0005$  g,  $(3,6 \pm 0,1)$  g, of potassium iodate ( $\text{KIO}_3$ ) (4.34) ( $m_1$ ) and place in a 1000 ml volumetric flask. Add 0,2 g of sodium hydroxide (4.29), 25 g of potassium iodide ( $\text{KI}$ ), dissolve all the solids in freshly boiled and cooled water and make up to the mark using the same water.

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

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

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

#### 4.61 Sodium thiosulfate solution approximately 0,1 mol/l

##### 4.61.1 Preparation

Dissolve  $(24,82 \pm 0,01)$  g of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in water and make up to 1000 ml. Before each test series, determine the factor  $f$  of this solution as described in 4.61.2.

##### 4.61.2 Standardization

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

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

Calculate the factor  $f$  of the sodium thiosulfate solution from the formula.

$$f = \frac{20,0042 \times 0,01667 \times 214,01 \times F}{3,5668 \times V_1} = 20 \times \frac{F}{V_1} \quad (2)$$

where

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

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

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

214,01 is the molecular mass of  $\text{KIO}_3$ .

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

For this standardization, weigh, to  $\pm 0,0005$  g,  $(0,070 \pm 0,005)$  g of potassium iodate (4.34) ( $m_2$ ) and place in a 500 ml conical flask. Dissolve in approximately 150 ml of water. Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1+1 (4.2) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution until a pale yellow colour is obtained. Then add 2 ml of the starch solution (4.49) and titrate until the colour changes from blue to colourless.

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

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

where

- $m_2$  is the mass of potassium iodate, in grams;
- $V_2$  is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration, in millilitres;
- 3,5668 is the mass of potassium iodate corresponding to a solution with exactly 0,01667 mol/l of potassium iodate, in grams.

#### 4.62 Standard manganese ion solution

##### 4.62.1 Anhydrous manganese sulfate

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

##### 4.62.2 Preparation

Into a 1000 ml volumetric flask, weigh, to  $\pm 0,0005$  g,  $(2,75 \pm 0,05)$  g of anhydrous manganese sulfate ( $m_3$ ); dissolve in water and make up to the mark. Calculate the content  $G$  of manganese (II) ions of this solution, expressed in milligrams of  $Mn^{2+}$  per millilitre, from the formula:

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

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

##### 4.62.3 Construction of the calibration curve

Into each of two volumetric flasks, respectively 500 ml (No. 1) and 1000 ml (No. 2), pipette 20 ml of the standard manganese ion solution. Make up to the mark with water. Into each of three volumetric flasks, respectively 200 ml (No. 3), 500 ml (No. 4) and 1000 ml (No. 5) pipette 100 ml of the solution from flask No. 2 and make up to the mark with water.

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

Allow to cool to room temperature and transfer the contents of each beaker to a 200 ml volumetric flask and make up to the mark with water. Measure the optical density 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 optical density values to three decimal places.

For each cell optical length construct a separate curve of the optical densities of these calibration solutions E1 to E5 as a function of the corresponding manganese concentrations in milligrams of Mn per 200 ml. The corresponding manganese concentrations are given in Table 1. They can be used as given if the content  $G$  obtained in accordance with 4.62.2 has the value 1,0000. Otherwise, multiply the manganese concentrations in Table 1 by the value of  $G$  calculated from equation (4).

**Table 1 — Concentrations of manganese calibration solutions**

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

#### 4.63 Standard silica solution

**4.63.1 Silica (SiO<sub>2</sub>)**, of purity >99,9 % after ignition to constant mass at (1175 ± 25) °C.

##### 4.63.2 Basic solution

Weigh (0,2000 ± 0,0005) g of freshly ignited silica (4.63.1), in a platinum crucible already containing (2,0 ± 0,1) g of anhydrous sodium carbonate (4.39).

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

Store the solution in a polyethylene container.

This solution contains 1 mg of SiO<sub>2</sub> per millilitre.

##### 4.63.3 Standard solution

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

##### 4.63.4 Compensating solutions

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

##### 4.63.5 Construction of the calibration curve

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

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

		Precipitation by double evaporation (13.3)	Precipitation by polyethylene oxide (13.4)	Decomposition by HCl and NH <sub>4</sub> Cl (13.5)
HCl conc.	ml	75	70	15
H <sub>2</sub> SO <sub>4</sub> 1 + 1	ml	1	1	-
HNO <sub>3</sub> conc.	ml	-	-	1
Polyethylene oxide solution	ml	-	5	-
NH <sub>4</sub> Cl	g	-	-	1
Na <sub>2</sub> CO <sub>3</sub>	g	1,75	1,75	1,75
NaCl	g	0,25	0,25	0,25
Na <sub>2</sub> O <sub>2</sub>	g	3	3	-

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

Serial No.	Blank	1	2	3	4
Standard SiO <sub>2</sub> solution (ml)	0	2	5	10	20
Water (ml)	20	18	15	10	0
Silica content (mg SiO <sub>2</sub> /100 ml)	0	0,04	0,10	0,20	0,40

Add from a pipette 5 ml of the ammonium molybdate solution (4.54). Adjust the pH of this solution to  $(1,60 \pm 0,05)$  by adding, drop by drop, sodium hydroxide solution (4.30) or hydrochloric acid 1 + 2 (4.3) using the pH meter (5.18) calibrated with a buffer solution of similar pH (e.g. 1,40 see 4.59). Transfer the solution to a 100 ml volumetric flask and rinse the beaker with dilute hydrochloric acid (4.9). After 20 min, add from a pipette 5 ml of the citric acid solution (4.52), stir and leave to stand for 5 min. Then add from a pipette 2 ml of the reducing solution (4.58). (Time 0).

Make up to the mark with dilute hydrochloric acid (4.9) and mix. At time  $(0 + 30)$  min measure the optical density 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 of maximum extinction near 815 nm. Construct a curve giving the measured optical densities 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 the silica content in mg SiO<sub>2</sub>/100 ml to be determined.

#### 4.64 Standard calcium ion solution, approximately 0,01 mol/l

Weigh, to  $\pm 0,0005$  g,  $(1,00 \pm 0,01)$  g of calcium carbonate (4.53) ( $m_4$ ) 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 (4.3). 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,