



BSI Standards Publication

Methods of testing cement

Part 2: Chemical analysis of cement

National foreword

This British Standard is the UK implementation of EN 196-2:2025. It supersedes BS EN 196-2:2013, which is withdrawn.

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A list of organizations represented on this committee can be obtained on request to its committee manager.

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

Prüfverfahren für Zement - Teil 2: Chemische Analyse von Zement

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European foreword

This document (EN 196-2:2025) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by May 2026, and conflicting national standards shall be withdrawn at the latest by May 2026.

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

This document supersedes EN 196-2:2013.

EN 196-2:2025 includes the following significant technical changes with respect to EN 196-2:2013:

- redefinition of the introduction;
- introduction of concept;
- determination of reactive silica;
- introduction of the concept of determination of total carbonate content instead of determination of CO₂;
- determination of chloride by potentiometric titration as alternative method;
- determination of total carbonate content by gas volumetric method as alternative method;
- determination of total carbonate content by infrared detection system (method A and B) as alternative method;
- determination of SO₃ by inductively coupled plasma optical emission spectroscopy as alternative method.

This European Standard series, under the general title *Methods of testing cement*, comprises the following parts:

- *Part 1: Determination of strength;*
- *Part 2: Chemical analysis of cement;*
- *Part 3: Determination of setting times and soundness;*
- *Part 5: Pozzolanicity test for pozzolanic cement;*
- *Part 6: Determination of fineness;*
- *Part 7: Methods of taking and preparing samples of cement;*
- *Part 8: Heat of hydration — Solution method;*
- *Part 9: Heat of hydration — Semi-adiabatic method;*

- *Part 10: Determination of the water-soluble chromium (VI) content of cement;*
- *Part 11: Heat of hydration — Isothermal conduction calorimetry method.*

NOTE Another document, CEN/TR 196-4 Methods of testing cement — Part 4: Quantitative determination of constituents, has been published as a CEN Technical Report.

Any feedback and questions on this document should be directed to the users' national standards body. A complete listing of these bodies can be found on the CEN website.

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Introduction

In this document, the elemental chemical analysis of a clinker or cement, as of any natural or artificial mineral material (volcanic pozzolan, blast furnace slag, fly ash, etc.) is expressed in a conventional manner in the form of the mass proportions of the common oxides corresponding to the most frequent and stable degree of oxidation (Si: SiO_2 ; Al: Al_2O_3 , etc.). This expression of the chemical analysis does not indicate how these elements are combined into minerals such as silicates, oxides, carbonates, sulphates or sulphides.

This means that the presence of SiO_2 in a chemical analysis sheet does not necessarily imply the presence of crystalline silica e.g. quartz or cristobalite, but most likely silicates. Moreover, even if quartz is detected in the material, this does not necessarily imply an inhalation hazard if the particle size is larger than the inhalable fraction. Similarly, the presence of TiO_2 in a chemical analysis report does not necessarily imply the presence of the mineralogical phase(s) corresponding to this formula (rutile, anatase, brookite), although the presence of the mineralogical phase(s) does not necessarily imply an inhalation hazard if the particle size is larger than the inhalable fraction. In the same way, determination of total carbonate content (TCC) can be done by dosing CO_2 induced by acid attack, which does not mean, in any case, that the material contains CO_2 .

The only way to identify mineralogical phases in a powdered mineral material is by X-ray diffraction, which is the only analytical technique that is sensitive to the crystalline character of minerals. For an accurate quantification of inhalable fractions, it is advisable to be necessary to perform a quantitative particle size selection (e.g. by aerosolization technique) in order to eliminate coarse fractions that could reduce the quantitative character of the X-ray diffraction analysis.

Standardization to 100 made it possible to know if no constituent element had been left out. Hence the expression “percentage by mass of oxides” in the chemical analysis.

1 Scope

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

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

An alternative performance-based method using X-ray fluorescence (XRF) is described for SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, SO₃, K₂O, Na₂O, TiO₂, P₂O₅, Mn₂O₃, SrO, Cl and Br. This method is based on beads of fused sample and analytical validation using certified reference materials, together with performance criteria. A method based on pressed pellets of un-fused sample can be considered as equivalent, providing that the analytical performance satisfies the same criteria.

An alternative performance-based method using inductively coupled plasma optical emission spectroscopy (ICP-OES) is described for SO₃.

When correctly calibrated according to the specified procedures and reference materials, XRF and ICP-OES provides methods equivalent to the reference methods but has not been validated for use yet as a reference procedure for conformity and dispute purposes. They can be applied to other relevant elements when adequate calibrations have been established.

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

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN 13656, *Soil, treated biowaste, sludge and waste — Digestion with a hydrochloric (HCl), nitric (HNO₃) and tetrafluoroboric (HBF₄) or hydrofluoric (HF) acid mixture for subsequent determination of elements*

EN ISO 385, *Laboratory glassware — Burettes (ISO 385)*

EN ISO 835, *Laboratory glassware — Graduated pipettes (ISO 835)*

ISO 33401, *Reference materials — Contents of certificates, labels and accompanying documentation*

ISO Guide 30, *Reference materials — Selected terms and definitions*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp/>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1**analyte**

element to be determined

3.2**calibration solution**

solution used (at least two) to calibrate the instrument, prepared from stock solutions by adding acids, buffer, reference element and salts as needed

3.3**stock solution**

solution with accurately known analyte concentration(s), prepared from pure chemicals

Note 1 to entry: Certified commercial standard solutions can be used.

Note 2 to entry: Stock solutions are reference materials within the meaning of ISO Guide 30.

3.4**blank test solution**

solution prepared in the same way as the test sample solution but omitting the test portion

4 General requirements for testing**4.1 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 to be taken shall be as specified in the relevant clause of this document.

Where the analysis is one of a series subject to statistical control, the 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 4.3 and 6.8).

In the case of a dispute, the number of tests for determination of each chemical property shall be two (see also 4.3 and 6.8).

4.2 Repeatability and reproducibility

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

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

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

4.3 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.

5 Analysis by wet chemistry

5.1 General

5.1.1 Ignitions

Carry out ignitions as follows.

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

5.1.2 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.

5.1.3 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 ashless filter paper and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (5.2.44). 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.

5.1.4 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.

5.1.5 Preparation of a test sample of cement

Before chemical analysis, treat the laboratory sample, taken in accordance with EN 196-7, 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.

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 to be determined then it is not necessary to remove metallic iron.

Then grind the iron-free fraction of the retained material so that it completely passes the 150 μm or 125 μm sieve.

Where the sample is to be used for XRF analysis and it contains quartz, it advisable be necessary to grind the sample to pass a 90 µm sieve in order to obtain a satisfactory fusion (see 6.6). The time and temperature required to obtain a satisfactory fusion is affected by the fineness of the sample.

Where the sample is to be used for XRF analysis using pressed pellets, accuracy can be improved by grinding the sample more finely.

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.

5.2 Reagents

5.2.1 General

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

Unless otherwise stated, percent means percent by mass.

Unless otherwise stated, the concentrated liquid reagents used in this document have the following densities (ρ) (in g/cm³ 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.

5.2.2 Concentrated hydrochloric acid (HCl)

5.2.3 Dilute hydrochloric acid (1 + 1)

5.2.4 Dilute hydrochloric acid (1 + 2)

5.2.5 Dilute hydrochloric acid (1 + 3)

5.2.6 Dilute hydrochloric acid (1 + 9)

5.2.7 Dilute hydrochloric acid (1 + 11)

5.2.8 Dilute hydrochloric acid (1 + 19)

5.2.9 Dilute hydrochloric acid (1 + 99)

5.2.10 Dilute hydrochloric acid of pH (1,60 ± 0,05)

Prepare by adjusting the pH of two litres of water to (1,60 ± 0,05) by adding five or six drops of concentrated hydrochloric acid (5.2.2). Control using the pH meter (5.3.18.1). Store the solution in a polyethylene container.

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

5.2.12 Dilute hydrofluoric acid (1 + 3)

5.2.13 Concentrated nitric acid (HNO₃)

5.2.14 Dilute nitric acid (1 + 2)

5.2.15 Dilute nitric acid (1 + 100)

5.2.16 Concentrated sulfuric acid (>98 %) (H₂SO₄)

5.2.17 Dilute sulfuric acid (1 + 1)

5.2.18 Dilute sulfuric acid (1 + 4)

5.2.19 Concentrated perchloric acid (HClO₄)

5.2.20 Concentrated phosphoric acid (H₃PO₄)

5.2.21 Dilute phosphoric acid (1 + 19)

Store this solution in a polyethylene container.

5.2.22 Boric acid (H₃BO₃)

5.2.23 Concentrated acetic acid (CH₃COOH)

5.2.24 Amino-acetic acid (NH₂CH₂COOH)

5.2.25 Metallic chromium (Cr), in powder form

5.2.26 Concentrated ammonium hydroxide (NH₄OH)

5.2.27 Dilute ammonium hydroxide (1 + 1)

5.2.28 Dilute ammonium hydroxide (1 + 10)

5.2.29 Dilute ammonium hydroxide (1 + 16)

5.2.30 Sodium hydroxide (NaOH)

5.2.31 Sodium hydroxide solution (4 mol/l)

Dissolve 160 g of sodium hydroxide (5.2.30) in water and make up to 1 000 ml. Store in a polyethylene container.

5.2.32 Sodium hydroxide solution (2 mol/l)

Dissolve 80 g of sodium hydroxide (5.2.30) in water and make up to 1 000 ml. Store in a polyethylene container.

5.2.33 Ammonium chloride (NH_4Cl)**5.2.34 Tin (II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)****5.2.35 Potassium iodate (KIO_3) dried to constant mass at $(120 \pm 5)^\circ\text{C}$** **5.2.36 Potassium periodate (KIO_4)****5.2.37 Sodium peroxide (Na_2O_2) in powder form****5.2.38 Sodium chloride (NaCl) dried to constant mass at $(110 \pm 5)^\circ\text{C}$** **5.2.39 Potassium chloride (KCl) dried to constant mass at $(110 \pm 5)^\circ\text{C}$** **5.2.40 Sodium carbonate (Na_2CO_3) dried to constant mass at $(250 \pm 10)^\circ\text{C}$** **5.2.41 Mixture of sodium carbonate and sodium chloride**

Mix 7 g of sodium carbonate (5.2.40) with 1 g sodium chloride (NaCl) (5.2.38).

5.2.42 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 1 000 ml.

5.2.43 Silver nitrate (AgNO_3) dried to constant mass at $(150 \pm 5)^\circ\text{C}$ **5.2.44 Silver nitrate solution**

Dissolve 5 g of silver nitrate (AgNO_3) (5.2.43) in water, add 10 ml of concentrated nitric acid (HNO_3) (5.2.13) and make up to 1 000 ml with water.

5.2.45 Silver nitrate solution (0,05 mol/l)

Dissolve $(8,494\ 0 \pm 0,000\ 5)$ g of silver nitrate (AgNO_3) (5.2.43) 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.

5.2.46 Sodium carbonate solution

Dissolve 50 g of anhydrous sodium carbonate (5.2.40) in water and make up to 1 000 ml.

5.2.47 Potassium hydroxide solution

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

5.2.48 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 (5.2.26). Leave to stand for at least 24 h and filter.

5.2.49 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.

5.2.50 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.

The starch solution needs to boil the solution briefly (about 5 min) to make the blue coloration rich and visible.

5.2.51 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.

5.2.52 Boric acid solution, saturated

Dissolve approximately 50 g of boric acid (H_3BO_3) (5.2.22) in water and make up to 1 000 ml.

5.2.53 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.

5.2.54 Calcium carbonate (CaCO_3) dried to constant mass at $(200 \pm 10)^\circ\text{C}$ (of purity > 99,9 %)

5.2.55 Ammonium molybdate solution

5.2.55.1 Ammonium molybdate: solution a)

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.

5.2.55.2 Ammonium molybdate: solution b)

Dissolve 63 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 500 ml. Prepare 500 ml of sulphuric acid 1+4 (5.2.18) and add the 500 ml of the molybdate solution.

5.2.56 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.

5.2.57 Ammonium acetate solution

Dissolve 250 g of ammonium acetate $(\text{CH}_3\text{COONH}_4)$ in water and make up to 1 000 ml.

5.2.58 Triethanolamine $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]$, (>99 %) diluted to (1 + 4) solution

5.2.59 Reducing solution

Dissolve 1 g of tin (II) chloride $(\text{SnCl}_2 \cdot 2\text{H}_2\text{O})$ (5.2.34) in water to which has been added 1 ml of concentrated hydrochloric acid (5.2.2). Make up to 100 ml with water. Use within one day.

5.2.60 Buffer solution of pH 1,40

Dissolve $(7,505 \pm 0,001)$ g of amino-acetic acid (5.2.24) and $(5,850 \pm 0,001)$ g of sodium chloride (NaCl) (5.2.38) in water and make up to 1 000 ml. Dilute 300 ml of this solution to 1 000 ml with hydrochloric acid 1 + 99 (5.2.9).

5.2.61 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) (5.2.35) (m1) and place in a 1 000 ml volumetric flask. Add 0,2 g of sodium hydroxide (5.2.30), 25 g of potassium iodide (KI), dissolve all the solids in freshly boiled and cooled water and make up to the mark using the same water.

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

$$F = \frac{m_1}{35668} \quad (1)$$

where

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

5.2.62 Sodium thiosulfate solution, approximately 0,1 mol/l

5.2.62.1 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 1 000 ml. Before each test series, determine the factor f of this solution as described in 5.2.62.2.

5.2.62.2 Standardization

5.2.62.2.1 Standardization using potassium iodate solution

This standardization is carried out preferably using the standard potassium iodate solution (5.2.61). For this standardization, pipette 20 ml of the standard potassium iodate solution (5.2.61) into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1+1 (5.2.3) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (5.2.62.1) to a pale-yellow colour. Add 2 ml of the starch solution (5.2.50) and continue the titration until the colour changes from blue to colourless.

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

$$f = \frac{20 \times 0,1667 \times 214,01 \times F}{3,5668 \times V_1} = 20 \times \frac{F}{V_1} \quad (2)$$

where

F is the factor of the standard potassium iodate solution (5.2.61);

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

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

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

5.2.62.2.2 Standardization using a known quantity of potassium iodate

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 (5.2.35) (m_2) and place in a 500 ml conical flask. Dissolve in approximately 150 ml of water. Add about 1 g of potassium iodide (KI), acidify with 25 ml of hydrochloric acid (1+1) (5.2.3) and titrate with the approximately 0,1 mol/l sodium thiosulfate solution (5.2.62.1) until a pale-yellow colour is obtained. Then add 2 ml of the starch solution (5.2.50) 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;
- 3,566 8 is the mass of potassium iodate corresponding to a solution with exactly 0,016 67 mol/l of potassium iodate, in grams.

5.2.63 Standard manganese solution

5.2.63.1 Anhydrous manganese sulfate

Dry hydrated manganese sulfate ($\text{MnSO}_4 \cdot n\text{H}_2\text{O}$) to constant mass at $(250 \pm 10)^\circ\text{C}$. The composition of the product obtained corresponds to the formula MnSO_4 .

5.2.63.2 Preparation

Into a 1 000 ml volumetric flask, weigh, to $\pm 0,000\ 5\ \text{g}$, $(2,75 \pm 0,05)\ \text{g}$ 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.

5.2.63.3 Construction of the calibration curve

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

Take 100 ml of each solution from flasks 1 to 5 and pipette each portion into a 400 ml beaker. Add 20 ml of concentrated nitric acid (5.2.13), 1,5 g of potassium periodate (5.2.36) and 10 ml of phosphoric acid (5.2.20), 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 (5.3.10) at a wavelength of around 525 nm, against water (use one or more cells (5.3.11) of appropriate sizes). Record the absorbance values to three decimal places.

For each cell optical length, construct a separate curve of the absorbance of these calibration solutions E1 to E5 as a function of the corresponding manganese concentrations in milligrams of Mn per 200 ml. The corresponding manganese concentrations are given in Table 1. They can be used as given if the content G obtained in accordance with 5.2.63.2 has the value 1,000 0. Otherwise, multiply the manganese concentrations in Table 1 by the value of G calculated from Formula (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

5.2.64 Standard silica solution

5.2.64.1 Silica (SiO₂), of purity > 99,9 % after ignition to constant mass at $(1\,175 \pm 25)^\circ\text{C}$

5.2.64.2 Basic solution

Weigh $(0,200\,0 \pm 0,000\,5)$ g of freshly ignited silica (5.2.64.1), in a platinum crucible (5.3.2.1) already containing $(2,0 \pm 0,1)$ g of anhydrous sodium carbonate (5.2.40).

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 SiO₂ per millilitre.

Alternatively use a commercially available silica stock solution with a concentration of 1 mg of SiO₂ per millilitre.

5.2.64.3 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.

5.2.64.4 Compensating solutions

Prepare the compensating solutions according to the procedure adopted in the determination of silica content (5.5.3 to 5.5.5) by dissolving the amounts of the reagents given in Table 2 in water and making up to 500 ml.

5.2.64.5 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 dilute hydrofluoric acid 1+3 (5.2.12). Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (5.2.52) into the solution.

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

		Precipitation by double evaporation (5.5.3)	Precipitation by polyethylene oxide (5.5.4)	Decomposition by HCl and NH ₄ Cl (5.5.5)
HCl conc.	ml	75	70	15
H ₂ SO ₄ 1 + 1	ml	1	1	-
HNO ₃ conc.	ml	-	-	1
Polyethylene oxide solution	ml	-	5	-
NH ₄ Cl	g	-	-	1
Na ₂ CO ₃	g	1,75	1,75	1,75
NaCl	g	0,25	0,25	0,25
Na ₂ O ₂	g	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 (ml)	0	2	5	10	20
Water (ml)	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 (5.2.55). Adjust the pH of this solution to $(1,60 \pm 0,05)$ by adding, drop by drop, sodium hydroxide solution (4 mol/l) (5.2.31) or dilute hydrochloric acid (1 + 2) (5.2.4) using the pH meter (5.3.18.1) calibrated with a buffer solution of similar pH (e.g. 1,40 see 5.2.60). Transfer the solution to a 100 ml volumetric flask and rinse the beaker with dilute hydrochloric acid of pH $(1,60 \pm 0,05)$ (5.2.10). After 20 min, add from a pipette 5 ml of the citric acid solution (5.2.53), stir and leave to stand for 5 min. Then add from a pipette 2 ml of the reducing solution (5.2.59). (Time 0).

Make up to the mark with dilute hydrochloric acid of pH $(1,60 \pm 0,05)$ (5.2.10) and mix. At time $(0 + 30)$ min, measure the absorbance with the photometer (5.3.10) using a cell (5.3.11) 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 the silica content in mg SiO₂/100 ml to be determined.

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

Weigh, to $\pm 0,0005$ g, $(1,00 \pm 0,01)$ g of calcium carbonate (5.2.54) (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 dilute hydrochloric acid (1 + 2) (5.2.4). 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.

5.2.66 EDTA solution, approximately 0,03 mol/l

5.2.66.1 Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA)

5.2.66.2 Preparation

Dissolve $(11,17 \pm 0,01)$ g of EDTA (5.2.66.1) in water and make up to 1 000 ml. Store in a polyethylene container.

5.2.66.3 Standardization

5.2.66.3.1 General

Pipette 50 ml of the standard calcium ion solution (5.2.65) into a beaker suitable for the measuring apparatus for measuring the absorbance (5.3.12). Then dilute with water to a volume suitable for the operation of the apparatus.

Using the pH meter (5.3.18.1), adjust the pH of this solution to $(12,5 \pm 0,2)$ with either of the sodium hydroxide solutions (5.2.31 or 5.2.32).

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

5.2.66.3.2 Photometric determination of the end point (reference method)

Add, without weighing, about 0,1 g of murexide indicator (5.2.70) or of mixed calcein and methylthymol blue indicator (5.2.76). Place the beaker in the apparatus for measuring the absorbance (5.3.12), set at 620 nm when using murexide indicator (5.2.70) or at 520 nm when using the mixed indicator (5.2.76) and, while stirring continuously, titrate with the approximately 0,03 mol/l EDTA solution (5.2.66.2). 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 the formula:

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

where

m_4 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (5.2.65), in grams;

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

5.2.66.3.3 Visual determination of the end point (alternative method)

Add, without weighing, about 0,1 g of either the Calcon indicator (5.2.72) or the Patton and Reeder's indicator (5.2.77). Stir and titrate with the approximately 0,03 mol/l EDTA solution (5.2.66.2) until the colour changes from pink to blue (Calcon) or purple to blue (Patton and Reeder's), 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 Formula (5).

5.2.67 Copper EDTA solution

Pipette 25 ml of the copper sulfate solution (5.2.56) into a 400 ml beaker and add from a burette an equivalent volume V_5 of the approximately 0,03 mol/l EDTA solution (5.2.66). Determine the required volume V_5 of EDTA solution as follows.

Pipette 10 ml of the copper sulfate solution (5.2.56) into a 600 ml beaker. Dilute to approximately 200 ml with water and add 10 ml of concentrated ammonium hydroxide (5.2.26) and, without weighing, about 0,1 g of murexide indicator (5.2.70). Titrate with the approximately 0,03 mol/l EDTA solution (5.2.66) until the colour changes from pink to violet (V_4).

Calculate the volume V_5 of the approximately 0,03 mol/l EDTA solution to be added to 25 ml of the copper sulfate solution to obtain copper EDTA from the formula:

$$V_5 = 2,5 \times V_4 \quad (6)$$

where

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

5.2.68 EGTA solution, approximately 0,03 mol/l

5.2.68.1 Ethylene glycol-bis(2-aminoethylether)-N,N,N,N-tetraacetic acid (EGTA)

5.2.68.2 Preparation

Dissolve $(11,4 \pm 0,01)$ g of EGTA (5.2.68.1) in 400 ml of water and 30 ml of the sodium hydroxide solution (2 mol/l) (5.2.32) in a 600 ml beaker. Heat the mixture until the EGTA is completely dissolved. Allow to cool to room temperature. Using the pH meter (5.3.18.1), adjust the pH to $(7,0 \pm 0,5)$, by adding, drop by

drop, dilute hydrochloric acid (1 + 2) (5.2.4). 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.

5.2.68.3 Standardization

Pipette 50 ml of the standard calcium ion solution (5.2.65) into a beaker suitable for the measuring apparatus (5.3.12). Then dilute with water to a volume suitable for the correct operation of the apparatus. Add 25 ml of the triethanolamine (1 + 4) solution (5.2.58).

Using the pH meter (5.3.18.1), adjust the pH of this solution to $(12,5 \pm 0,2)$ with either of the sodium hydroxide solutions (5.2.31 or 5.2.32).

Add, without weighing, about 0,1 g of murexide indicator (5.2.70) or of calcein indicator (5.2.71). Place the beaker in the apparatus for measuring the absorbance (5.3.12) set at 620 nm when using murexide indicator 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, take note of 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 the formula:

$$f_G = \frac{50 \times m_5}{100,09 \times 0,03 \times V_6} = 16,652 \times \frac{m_5}{V_6} \quad (7)$$

where

m_5 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (5.2.65), in grams;

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

5.2.69 DCTA solution, approximately 0,01 mol/l

5.2.69.1 trans-1,2-Diaminocyclohexane-N,N,N,N-tetraacetic acid monohydrate (DCTA)

5.2.69.2 Preparation

Dissolve $(3,64 \pm 0,01)$ g of DCTA (5.2.69.1) in about 400 ml of water and 10 ml of sodium hydroxide solution (2 mol/l) (5.2.32) in a 600 ml beaker. Heat the mixture until the DCTA is completely dissolved. Allow to cool to room temperature. Using the pH meter (5.3.18.1), adjust the pH to $(7,0 \pm 0,5)$ by adding dilute hydrochloric acid (1 + 2) (5.2.4), 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.

5.2.69.3 Standardization

Pipette 50 ml of the standard calcium ion solution (5.2.65) into a beaker appropriate for the measuring apparatus (5.3.12). Then dilute with water to a volume suitable for the correct operation of the apparatus.

Using the pH meter (5.3.18.1), adjust the pH of this solution to $(10,5 \pm 0,2)$ with concentrated ammonium hydroxide (5.2.26).

Add, without weighing, about 0,1 g of murexide indicator (5.2.70) or of calcein indicator (5.2.71). Place the beaker in the apparatus for measuring absorbance (5.3.12) set at 620 nm when using murexide indicator 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, take note of 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 the formula:

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

where

m_6 is the mass of calcium carbonate taken to prepare the standard calcium ion solution (5.2.65), in grams;

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

5.2.70 Murexide indicator

Prepare by grinding $(1,0 \pm 0,1)$ g of murexide (ammonium purpurate, $C_8H_4N_5O_6 \cdot NH_4$) with (100 ± 1) g of sodium chloride (NaCl).

5.2.71 Calcein indicator

Prepare by grinding $(1,0 \pm 0,1)$ g of calcein (bis [(bis (carboxymethyl)-amino-methyl)] -2', 7'-fluorescein, Fluoresceindi-(methylimino diacetic acid) sodium salt) with (100 ± 1) g of potassium nitrate (KNO_3).

5.2.72 Calcon indicator

Prepare by grinding $(1,0 \pm 0,1)$ g of Calcon (sodium 2-hydroxy-4-(2-hydroxy-1-naphthylazo) naphthalene-1-sulfonate, Eriochrome Blue-Black R) with (100 ± 1) g of anhydrous sodium sulfate (Na_2SO_4).

5.2.73 Sulfosalicylic acid indicator (5-sulfosalicylic acid dihydrate)

5.2.74 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 ethanol (C_2H_5OH , density = $0,79 \text{ g/cm}^3$).

5.2.75 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]-thymolsulphophthalein, $C_{37}H_{41}N_2O_{13}SNa_3$) with (100 ± 1) g of potassium nitrate (KNO_3).

5.2.76 Mixed calcein and methylthymol blue indicator

Prepare by grinding $(0,20 \pm 0,02)$ g of calcein (see 5.2.71) and $(0,10 \pm 0,01)$ g of methylthymol blue (see 5.2.75) with (100 ± 1) g of potassium nitrate (KNO_3).

5.2.77 Patton and Reeder's reagent

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

5.2.78 Mixed indicator

Prepare by mixing $(0,10 \pm 0,01)$ g *o*-cresolphthalein 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 (5.2.38).

5.2.79 Ammonium thiocyanate (NH_4SCN)

5.2.80 Ammonium thiocyanate solution, approximately 0,05 mol/l

Prepare by dissolving $(3,8 \pm 0,1)$ g of ammonium thiocyanate (5.2.79) in water and making up to 1 000 ml.

5.2.81 Saturated water solution of ammonium iron(III) sulfate dodecahydrate, ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$)

5.2.82 Indicator solution

Prepare by adding 10 ml of dilute nitric acid (1 + 2) (5.2.14) to 100 ml of a cold saturated water solution of ammonium iron (III) sulfate (5.2.81).

5.2.83 Copper (II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

5.2.84 Saturated water solution of copper (II) sulfate (5.2.83)

5.2.85 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 (5.2.84) so 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.

5.2.86 Absorbent for water

Anhydrous magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) with a particle size between 0,6 mm and 1,2 mm.

5.2.87 Absorbent for carbon dioxide

Synthetic silicates with a particle size between 0,6 mm to 1,2 mm impregnated with sodium hydroxide (NaOH) (5.2.30).

NOTE This absorbent can be obtained ready for use.

5.2.88 Mercuric (II) chloride (HgCl_2)

5.2.89 Alkali stock solution

Weigh $(0,566 0 \pm 0,000 5)$ g of sodium chloride (5.2.38) and $(0,475 0 \pm 0,000 5)$ g of potassium chloride (5.2.39) 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).

5.2.90 Acid stock solution, ($\text{HCl}/\text{H}_3\text{PO}_4$)

To approximately 500 ml of water, placed in a 1 000 ml volumetric flask, add 50 ml of concentrated hydrochloric acid (5.2.2) and 50 ml of concentrated phosphoric acid (5.2.20). Allow to cool then make up to the mark with water and mix thoroughly.

5.2.91 Calcium stock solution

Weigh $(11,25 \pm 0,01)$ g of calcium carbonate (5.2.54) into a 600 ml beaker. Add 100 ml of water and dissolve the calcium carbonate by cautiously adding 25 ml of concentrated hydrochloric acid (5.2.2). 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.

5.2.92 Alkali stock solution (alternative method)

Dissolve $(0,2542 \pm 0,0005)$ g of sodium chloride (5.2.38) and $(0,1907 \pm 0,0005)$ g of potassium chloride (5.2.39) in water in a 1 000 ml volumetric flask and make up to the mark.

NOTE These solutions can be obtained made up ready for use.

5.2.93 Caesium chloride (CsCl)

5.2.94 Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)

5.2.95 Buffer solution

Dissolve 50 g of caesium chloride (5.2.93) and 250 g of aluminium nitrate (5.2.94) in water and make up to 1 000 ml.

NOTE These solutions can be obtained made up ready for use.

5.2.96 Reagent for determination of total carbonate content

Dissolve 1,50 g of cuprous chloride and 2,50 g of copper chloride in 350 ml of dilute hydrochloric acid (1 + 9) (5.2.6)

5.2.97 Tetrafluoroboric acid, (HBF_4 , $\geq 38 \text{ M.-%}$)

5.2.98 Tartraic acid ($\text{C}_4\text{H}_6\text{O}_6$) solution 1 %

Dissolve 1,00 g tartaric acid in 99 g demineralized water. To prevent the formation of mould in the solution, a few mg of mercury (II) iodide advisable be added.

5.2.99 Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) solution 10 %

Dissolve 10,0 g oxalic acid in 90,0 g demineralized water.

5.2.100 Ascorbic acid, ($\text{C}_6\text{H}_8\text{O}_6$) solution 2,8 %

Dissolve 2,8 g ascorbic acid in 97,2 g demineralized water. To prevent the formation of mould in the solution, a few mg of mercury (II) iodide advisable be added.

5.2.101 Acetone, ($\text{C}_3\text{H}_6\text{O}$)

5.3 Apparatus

5.3.1 Balance(s), with maximum permissible error of $\pm 0,0005 \text{ g}$

5.3.2 Crucibles

5.3.2.1 Porcelain and/or platinum crucibles, 20 ml to 25 ml capacity

The methods specify where platinum crucibles are to be used. Unless platinum is specified, porcelain crucibles may be used.

5.3.2.2 Lids, suitable lids to be fitted to crucibles (5.3.2.1) where required

5.3.3 Fireproof ceramic support(s)

For preventing overheating of the crucible, it shall be in thermal equilibrium with the furnace at the moment the crucible is introduced.

5.3.4 Porcelain evaporating dish, of approximately 200 ml

5.3.5 Electric furnaces(s), naturally ventilated and capable of being set at the following temperatures: $(500 \pm 10)^\circ\text{C}$, $(950 \pm 25)^\circ\text{C}$ and $(1\,175 \pm 25)^\circ\text{C}$

5.3.6 Laboratory oven(s), capable of being set at the following temperatures: $(110 \pm 5)^\circ\text{C}$, $(120 \pm 5)^\circ\text{C}$, $(150 \pm 5)^\circ\text{C}$, $(200 \pm 10)^\circ\text{C}$, and $(250 \pm 10)^\circ\text{C}$

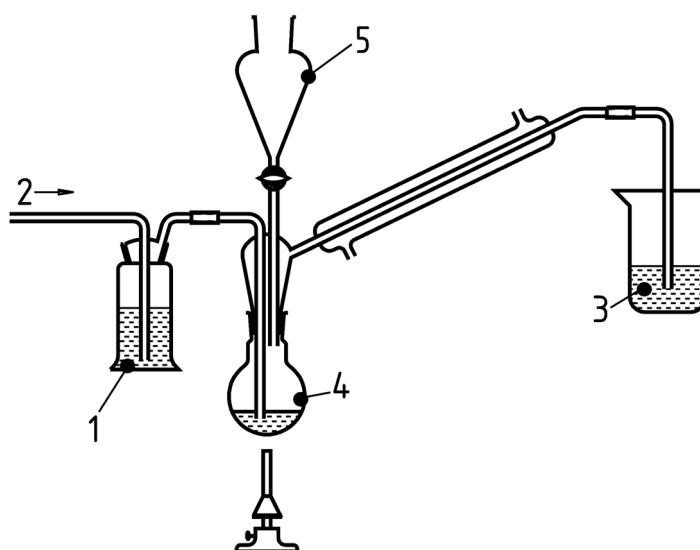
5.3.7 Desiccator(s), containing anhydrous magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) or silica gel. Where self-indicating silica gel is used, a non-toxic indicator is recommended.

5.3.8 Bulb condenser

5.3.9 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.).



Key

- 1 lead acetate solution (5.2.49)
- 2 air, nitrogen or argon
- 3 ammoniacal solution of zinc sulfate (5.2.48)
- 4 reaction flask
- 5 dropping funnel

Figure 1 — Typical apparatus for the determination of sulphide

5.3.10 Photometer(s), for measuring the absorbance of a solution in the vicinity of 525 nm, 815 nm and 810 nm

5.3.11 Cells, for the photometer

5.3.12 Apparatus for measuring the absorbance, at 520 nm and 620 nm of a solution contained in a titration beaker, while stirring

5.3.13 Magnetic stirrer and stirrer bar, e.g. magnetic stirrer bar, with inert, e.g. PTFE, covered bar

5.3.14 Evaporating apparatus, controlled at $(105 \pm 5) ^\circ\text{C}$, e.g. water bath or hot plate

5.3.15 Sand bath or hot plate, controlled at approximately $400 ^\circ\text{C}$

5.3.16 Ashless filter papers

Ashless filter papers with a mean pore diameter of around $2 \mu\text{m}$ are termed fine, those with a mean pore diameter of around $7 \mu\text{m}$ are termed medium and those with a mean pore diameter of around $20 \mu\text{m}$ are termed coarse.

5.3.17 Volumetric glassware, shall be of analytical accuracy, i.e. class A as defined in EN ISO 385 and EN ISO 835

5.3.18 pH measuring equipment

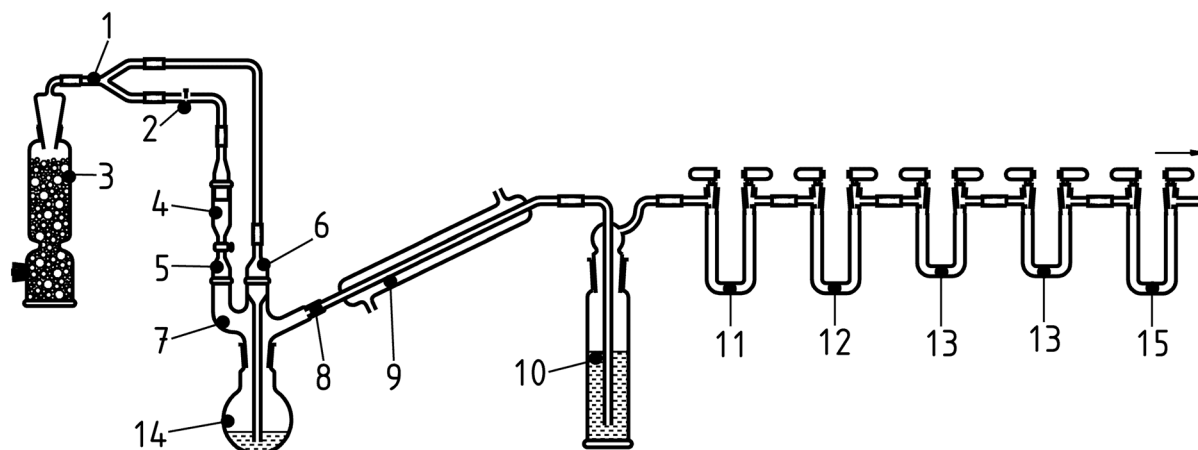
5.3.18.1 pH meter, with maximum permissible error of $\pm 0,05$

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

5.3.19 Apparatus for the determination of the total carbonate content (reference method)

Figure 2 shows a typical apparatus which can be fitted with either a cylindrical pressure container, a small electrical compressor or a suitable suction pump which will ensure an even flow of gas or air. The gas (air or nitrogen) entering the apparatus has previously had its carbon dioxide removed by first being passed through an absorbent tube or tower containing the carbon dioxide absorbent (5.2.87). The apparatus consists of a 100 ml distillation flask (14) fitted with a three-neck adaptor. Neck (5) is connected to a dropping funnel (4), neck (6) to a connecting tube and neck (8) to a water-cooled condenser. The funnel onto (5) and the connecting tube onto (6) are joined together by means of a Y-piece (1), so that the carbon dioxide-free air can flow either through the connecting tube or the funnel by means of a Mohr clip (2).

After the condenser (9), the gas is passed through concentrated sulfuric acid (5.2.16) (10), then through absorption tubes containing the absorbent for hydrogen sulfide (5.2.85) (11) and adsorbent for water (5.2.86) (12) and subsequently through two absorption tubes (13) which can be weighed and which are three-quarters filled with the absorbent for carbon dioxide (5.2.87) and a quarter with the absorbent for water (5.2.86). The absorbent for carbon dioxide (5.2.87) is placed upstream of the absorbent for water (5.2.86) with respect to the gas flow. Absorption tubes (13) are followed by an additional absorption tube (15), which also contains the absorbent for carbon dioxide and water, which is fitted in order to protect second absorption tube (13) against penetration by carbon dioxide and water from the air.

**Key**

- | | |
|---|--|
| 1 Y-piece | 9 condenser |
| 2 mohr clip | 10 wash bottle with concentrated sulfuric acid (5.2.16) |
| 3 absorption tower containing carbon dioxide absorbent (5.2.87) | 11 absorption tube with absorbent for hydrogen sulfide (5.2.85) |
| 4 dropping funnel | 12 absorption tube with absorbent for water (5.2.86) |
| 5 dropping funnel connector | 13 absorption tubes with absorbents for carbon dioxide (5.2.87) and water (5.2.86) |
| 6 connecting tube connector | 14 100 ml distillation flask |
| 7 three-armed still head | 15 absorption tubes with absorbents for carbon dioxide (5.2.87) and water (5.2.86) |
| 8 condenser connector | |

Figure 2 — Typical apparatus for the determination of total carbonate content (reference method)

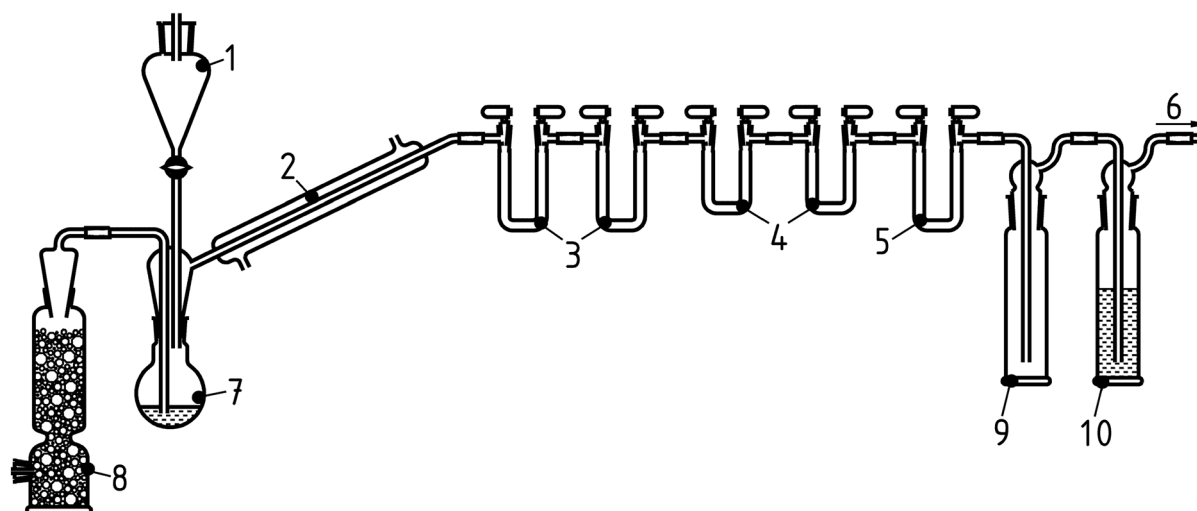
The absorption tubes (13) which are to be weighed may have, for example, the following approximate sizes:

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

5.3.20 Apparatus for the determination of the total carbonate content (alternative method)

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

Paraffin may be used instead of sulfuric acid in the final wash bottle (Figure 3) as this bottle only serves as a bubble counter.



Key

1	dropping funnel for diluted sulfuric acid (1 + 4)(5.2.18)	6	to the vacuum pump
2	condenser	7	100 ml distillation flask
3	absorption tubes containing absorbent for water (5.2.86)	8	absorption tower containing absorbent for carbon dioxide (5.2.87)
4	absorption tubes containing absorbent for carbon dioxide (5.2.87) and water (5.2.86)	9	washing bottle (empty)
5	absorption tubes with absorbents for carbon dioxide (5.2.87) and water (5.2.86)	10	washing bottle containing concentrated sulfuric acid (5.2.16) or paraffin

Figure 3 — Typical apparatus for the determination of total carbonate content (alternative method)

5.3.21 Apparatus for the determination of the total carbonate content Dietrich-Frühling apparatus (alternative method)

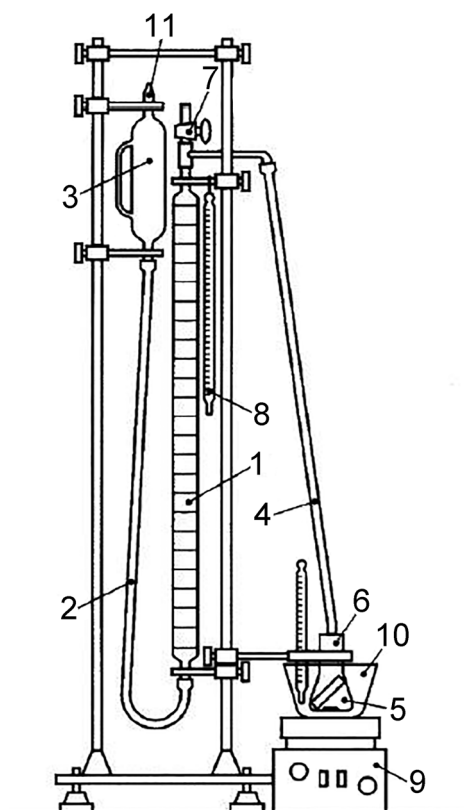
A typical apparatus is shown in Figure 4. Comprised of a fixed burette 1 with class A graduation, containing dilute hydrochloric acid (1 + 9) (5.2.6) connected at the bottom via flexible acid-resistant tubing 2 to a reservoir 3 held in a vertically sliding clamp. The top of the graduated burette is connected via flexible acid-resistant tubing 4 to a flask 5 with a bored stopper 6 forming an airtight seal (use preferably a flask with ground rim and a silicone rubber stopper).

At this same end, the burette 1 is also connected to the external atmosphere by way of a vacuum tap 7.

When assembling a new apparatus, when changing the manometric liquid or when the manometric liquid has remained in contact with the external atmosphere for more than 3h with the apparatus inactive, it will be necessary to recondition the apparatus.

In this case, using any carbonate, perform a series of 3-4 CO₂ releases at 70 to 100 % of the capacity of the graduated burette, with a pause of at least 2 min between each release.

On completion of the series of CO₂ releases, both for the conditioning and for the measurements, close the three points of possible contact with the external atmosphere at 6, 7 and 11, balance approximately the levels in 1 and 3 and maintain the apparatus in this condition while not in use.

**Key**

- 1 fixed burette
- 2 flexible tubing
- 3 reservoir
- 4 flexible pipe
- 5 flask
- 6 stopper with bore
- 7 vacuum tap
- 8 thermometer
- 9 magnetic stirrer
- 10 water bath
- 11 stopper for apparatus when not in use

Figure 4 — Typical Dietrich-Frühling apparatus for the determination of total carbonate (alternative method)

5.3.22 Flame photometer, with sufficient stability and capable of measuring the intensity of light emitted from the flame at a wavelength with maximum permissible error of ± 1 nm. In order to avoid any interference of the determination by alkaline earths, the flame photometer shall be operated with a relatively low temperature by using a propane-air or butane-air flame.

Note Some flame photometers are designed for use with acetylene-air as fuel gas.