

**Chemicals used for
treatment of water
intended for human
consumption —
Calcium carbonate,
high-calcium lime,
half-burnt dolomite,
magnesium oxide and
calcium magnesium
carbonate — Test
methods**

ICS 13.060.20; 71.100.80

National foreword

This British Standard is the UK implementation of EN 12485:2010. It supersedes BS EN 12485:2001 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment.

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

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Chemicals used for treatment of water intended for human consumption - Calcium carbonate, high-calcium lime, half-burnt dolomite, magnesium oxide and calcium magnesium carbonate - Test methods

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Carbonate de calcium, chaux et dolomie semi calcinée - Méthodes d'analyse

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Calciumcarbonat, Weißkalk, halbgebrannter Dolomit, Magnesiumoxid und Calciummagnesiumcarbonat - Analytische Verfahren

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Foreword

This document (EN 12485:2010) has been prepared by Technical Committee CEN/TC 164 "Water supply", the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by October 2010, and conflicting national standards shall be withdrawn at the latest by October 2010.

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

This document supersedes EN 12485:2001.

Annexes A and B are informative.

Significant technical differences between this edition and EN 12485:2001 are as follows:

- a) addition of a method for determination of sugar-soluble calcium oxide or calcium hydroxide (see 6.6);
- b) addition of a method for determination of solubility index (see 6.11).

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies the methods used for the chemical analyses and the determination of physical properties of calcium carbonate, high-calcium lime, half-burnt dolomite, magnesium oxide and calcium magnesium carbonate used to treat water for human consumption.

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.

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.

NOTE Schematic diagrams of the analyses are given in Annex A (Figures A.1 to A.6).

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.

EN 459-2, *Building lime — Part 2: Test methods*

EN 1017, *Chemicals used for treatment of water intended for human consumption — Half-burnt dolomite*

EN 1018, *Chemicals used for treatment of water intended for human consumption — Calcium carbonate*

EN 12518, *Chemicals used for treatment of water intended for human consumption — High-calcium lime*

prEN 16003, *Chemicals used for treatment of water intended for human consumption — Calcium magnesium carbonate*

prEN 16004, *Chemicals used for treatment of water intended for human consumption — Magnesium oxide*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

3 General requirements

3.1 Number of determinations

Two analyses shall be carried out to determine the various constituents (see Clause 5 to Clause 8, see also 3.6).

3.2 Methods for analysis

The methods to be used for the analysis of half-burnt dolomite, calcium carbonate, high calcium lime, magnesium oxide and calcium magnesium carbonate and the principle of each method are listed in Table 1.

The requirement values for free MgO and free Mg(OH)₂ in half-burnt dolomite shall be expressed as free MgO in accordance with EN 1017. The same requirement is related to free CaO. The requirement value for MgO in magnesium oxide shall be expressed as MgO in dry substance in accordance with prEN 16004. Therefore,

the analysis of half-burnt dolomite and magnesium oxide shall be performed on a sample which is bound-water free. Before starting the chemical analysis, the loss on ignition at 450 °C shall be determined as described in 6.2. The analysis itself shall be performed on the material obtained after the determination of the loss on ignition.

The requirement values for calcium carbonate, hydrated lime and calcium magnesium carbonate shall be expressed in dry substance in accordance with EN 1018, EN 12518 and prEN 16003. Therefore, the analysis of these products shall be performed on a sample which has been dried in accordance with the procedure described in 6.1.

For the determination of the water-soluble content of high-calcium lime, the method in 6.5 is considered as the reference method. The sugar method described in 6.6 can be used as an alternative method if it is demonstrated that the results obtained with this method are equivalent to those of the reference method.

Table 1 — Methods for analysis

Determination	Method	Principle	Standard
Screen oversize	4.1	Air-jet sieving	EN 12518
	4.2	Wet sieving	EN 12518
Free water	6.1	Gravimetry	EN 1018, EN 12518, prEN 16003
Loss on ignition at 450 °C	6.2	Gravimetry	EN 1017, EN 12518, prEN 16004
Carbon dioxide	6.3	Gravimetry	EN 1017, EN 12518, prEN 16004
Residue insoluble in hydrochloric acid	6.4	Acidimetry, Gravimetry	EN 1018, prEN 16004
Water-soluble calcium oxide or calcium hydroxide	6.5	Acidimetric titration	EN 12518
Sugar-soluble calcium oxide or calcium hydroxide	6.6	Acidimetric titration	EN 12518
Water-insoluble constituents	6.7	Gravimetry	EN 12518
Free calcium oxide	6.8	Extraction, acidimetric titration	EN 1017, prEN 16004
Calcium oxide and magnesium oxide	6.9	Complexometric titration	EN 1017, EN 1018, prEN 16003, prEN 16004
Sulfate	6.10	Gravimetry	EN 1017
Solubility index	6.11	Conductivity	EN 12518
Magnesium	7.1	AAS (flame)	EN 1017, EN 1018, prEN 16003, prEN 16004
	7.2	ICP-OES	
Silicium, Aluminium, Iron,	7.1	AAS (flame)	EN 1017, EN 12518, prEN 16003, prEN 16004
	7.2	ICP-OES	

Table 1 (continued)

Determination	Method	Principle	Standard
Manganese	7.2	ICP-OES	EN 12518
Sulfur	7.2	ICP-OES	EN 1017
Lead, Cadmium, Chromium, Nickel	8.1 or 8.2	AAS (flameless) or ICP-OES	EN 1017, EN 1018, EN 12518, prEN 16003, prEN 16004
Arsenic, Antimony, Selenium	8.3	AAS (hydride)	EN 1017, EN 1018, EN 12518, prEN 16003, prEN 16004
Mercury	8.4	AAS (cold-vapour technique)	EN 1017, EN 1018, EN 12518, prEN 16003, prEN 16004

3.3 Sample preparation

The general recommendations specified in ISO 3165 shall be observed when sampling. Sampling shall be performed in accordance with EN 459-2. For products less than 6 mm grain size, the size of the sample shall be 1 l.

Before performing the chemical analyses, the size of the sample shall be reduced by using a sample divider and/or by dividing it into four parts in order to obtain a suitable subsample. The coarse-grain material in this sample shall be reduced to a size of less than 0,2 mm before performing the chemical analysis.

When sampling milk of lime, the material from which the sample is to be taken shall be thoroughly mixed with an electrically driven stirrer of adequate power. The milk of lime shall be dried at $(105 \pm 5) ^\circ\text{C}$ (see 6.1) before being analysed chemically.

Since the subsamples under examination are altered by the absorption of moisture and carbon dioxide, their exposure to air shall be minimized. They shall therefore be transported and stored in air-tight containers and all the handling shall be carried out as quickly as possible.

3.4 Reagents

All reagents shall be of a recognized analytical grade appropriate for the method being used. The water used shall conform to grade 3 in accordance with EN ISO 3696:1995 unless otherwise specified in the method. The concentration of the analytes in the water and reagents shall be negligible compared with the lowest concentration to be determined.

The concentrated liquids used for the reagents in this standard have the following densities (ρ) (in grams per millilitre at 20 °C):

- hydrochloric acid 1,16 to 1,19;
- nitric acid 1,40 to 1,42;
- ammonium hydroxide solution 0,88 to 0,91;
- triethanolamine 1,12.

Dilutions are specified as the sum of the volumes. Thus, (1 + 2) dilute hydrochloric acid means 1 part by volume of concentrated hydrochloric acid mixed with 2 parts by volume of water.

The concentrations of reference and standard volumetric solutions are specified as amount-of-substance concentrations, c (mol/l), while those of stock and standard solutions are specified as concentrations by mass, c (g/l or mg/l).

Suitable element solutions for atomic absorption spectroscopy (AAS) and for optical emission spectroscopy by inductively coupled plasma (ICP-OES) are commercially available and can be used as stock solutions. They shall be prepared for the purposes of analysis in accordance with the manufacturer's instructions. The appropriate element standard solutions are prepared in accordance with the instructions given in this European Standard.

This European Standard makes no stipulations relating to the shelf life of stock, standard and reference solutions. In the case of stock solutions having an element concentration of 1 g/l, the manufacturer generally specifies a shelf life of one year. It is advisable to check the calibration solutions regularly.

3.5 Glassware

Glass containers and pipettes shall be cleaned with hot dilute nitric acid immediately before use and then rinse with water. If determining trace elements rinse with grade 2 water.

3.6 Expression of results

The analytical results for the major and minor constituents shall be reported as mass fraction in %, while those for trace elements shall be reported as mass fraction in milligrams per kilogram, as the mean of two determinations. In general, analytical values shall be reported to three significant figures.

EXAMPLE

(CaO) = 91,2 %;

(SiO₂) = 3,70 %;

(MnO₂) = 0,15 %;

(Cr) = 0,32 mg/kg;

(Hg) = 0,05 mg/kg.

If the results of a duplicate determination differ from one another by more than twice the repeatability standard deviation, the determination shall be repeated. The result shall then be deemed to be the mean of the two results with the lowest difference.

To assess whether the analytical results meet the requirements laid down in EN 12518 for high-calcium lime, in EN 1018 for calcium carbonate products and in EN 1017 for half-burnt dolomites, in prEN 16003 for calcium magnesium carbonate and in prEN 16004 for magnesium oxide, the results have to be converted to the form in which the requirements are stated in the above standards.

Subclauses of this standard are given in Table 2 and contain the relevant calculation methods.

Table 2 — Methods for calculation of the results

Requirements from standard	Parameter	Required value for	Calculation described in
EN 1017	CaO _{free} , CaO CO ₂ MgO	CaCO ₃ MgCO ₃ MgO _{free}	6.12.2.3
EN 1018	CaO MgO	CaCO ₃ MgCO ₃	6.12.2.1
EN 12518	CO ₂	CaCO ₃	6.12.2.4
prEN 16004	MgO, loss on ignition at (1 000 ± 50) °C and (450 ± 25) °C	(CO ₂ and H ₂ O)	6.12.2.5
prEN 16003	MgO	CaMg(CO ₃) ₂	6.12.2.2

3.7 Repeatability and reproducibility limits

The repeatability and reproducibility limits were determined in an interlaboratory test (see Annex B) which was carried out in accordance with ISO 5725-2 and in which 28 laboratories took part.

3.8 Test report

The report shall contain the following information:

- a) a reference to the method used;
- b) a complete identification of the sample;
- c) results obtained and the method of expression used (see 3.6)
- d) sample pretreatment, e.g. method of digestion (see Clause 5);
- e) any deviation from this standard and an indication of any circumstances which can have affected the results.

4 Determination of screen oversize of high-calcium lime

4.1 Air-jet sieving method

4.1.1 General

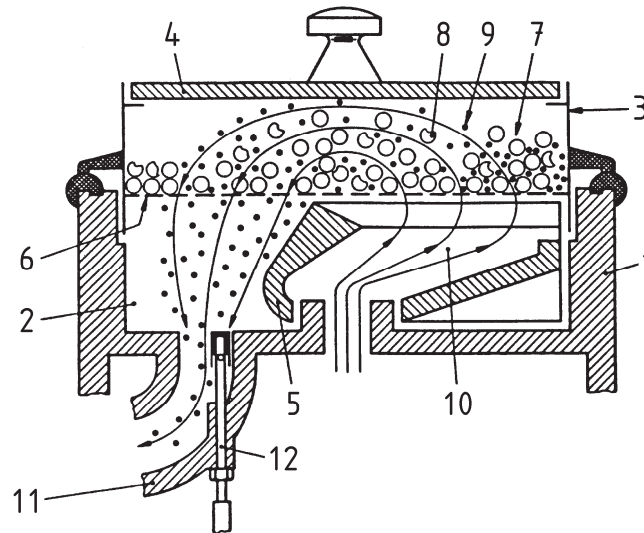
The method is used to determine the retention on sieving of high-calcium quicklime and hydrated lime as specified in EN 12518.

The particle size distribution of high-calcium quicklime and hydrated lime can be determined using airjet sieving apparatus.

For quicklime, the method is suitable for particles which substantially pass a 2,0 mm test sieve. For hydrated lime, the method can be used to determine the particle size distribution of the agglomerates of very fine particles produced by the manufacturing process. This method uses test sieves with aperture sizes of 0,60 mm and 0,09 mm.

4.1.2 Apparatus

4.1.2.1 Air-jet sieving apparatus, of the general form shown in Figure 1. The apparatus shall be set to give a pressure difference of 2 kPa to 2,5 kPa across the sieves.



Key

1 housing	7 test sample
2 dish	8 oversize material
3 sieve drum	9 undersize material
4 lid	10 air jet
5 slit-nozzle	11 air discharge
6 sieve	12 pressure gauge socket, with dust hood

Figure 1 — Air-jet sieving apparatus

4.1.2.2 Test sieves, 200 mm diameter, aperture sizes 0,60 mm and 0,09 mm.

NOTE The effective operation of some makes of air-jet apparatus can require non-standard sieve frames and additional gaskets. This is permissible, provided the sieving medium and general method of construction comply with the requirements of this standard.

4.1.2.3 Trays or other suitable containers of sufficient size to contain the test portion.

4.1.2.4 Balance, accurate to 0,1 mg.

4.1.2.5 Soft brush.

4.1.2.6 Ultrasonic cleaning bath for cleaning the mesh of the sieves.

4.1.2.7 Mallet, if there is a tendency for material to adhere to the lid of the apparatus. A rubber or plastics tipped mallet is preferred.

4.1.2.8 Drying oven (optional), thermostatically controlled to maintain a temperature of $(105 \pm 5) ^\circ\text{C}$.

4.1.3 Procedure

Weigh to the nearest 1 mg ($10 \pm 0,5$) g of quicklime (m) or ($25 \pm 0,5$) g of hydrated lime (m). Fit the test sieve with the aperture size 0,09 mm into the apparatus and transfer all of the test portion onto the sieve mesh. Take care not to lose any of the test portion.

Fit the lid and switch on the apparatus. Check that the vacuum created is above the minimum value stated in the manufacturer's instructions, and that the slit nozzle is rotating properly.

If material adheres to the lid of the apparatus, gently tap the centre of the lid with the mallet.

If the material agglomerates under the action of the air-jet, interrupt the sieving process, and break up the agglomerates with the soft brush.

After ($5 \pm 0,2$) min, switch off the apparatus and carefully remove the sieve. Transfer the material retained on the sieve into a tray or other suitable container. Carefully clean the mesh of the sieve over the tray using a soft brush.

Determine the mass of the residue, including the material brushed from the sieve mesh, and record the mass to the nearest 1 mg.

Refit the sieve into the apparatus and transfer all of the residue back to the sieve mesh. Repeat the weighing and sieving stages until the sieving end-point has been achieved, and record the end-point mass to the nearest 1 mg. The sieving end-point is defined as being when not more than 0,2 % of the mass of the original test portion passes through the sieve in 1 min.

Fit the 0,60 mm test sieve into the apparatus, and repeat the weighing and sieving stages until the mass of the residue confirms that the sieving end-point has been reached. Record the end-point mass to the nearest 1 mg.

4.1.4 Expression of results

The mass retained on each sieve expressed as $m (P_{0,60 \text{ or } 0,09})$ in mass fraction in %, is given by the following equation:

$$m (P_{0,60 \text{ or } 0,09}) = \frac{m_1 \times 100}{m} \quad (1)$$

where

m is the mass of the dry substance in the test portion, in grams;

m_1 is the mass of the residue retained on the test sieves, in grams.

4.2 Wet sieving method

4.2.1 General

The method is used for the determination of the retentions on sieving of milk of lime as specified in EN 12518.

4.2.2 Apparatus

4.2.2.1 Balance, accurate to 0,1 mg.

4.2.2.2 500 ml wide-mouthed bottle, or other suitable vessel which can be sealed with a stopper.

4.2.2.3 200 mm diameter 0,60 mm and 0,09 mm aperture size test sieves.

4.2.2.4 5 mm bore rubber or plastics tubing.

4.2.2.5 Ventilated drying oven (optional), thermostatically controlled to maintain a temperature of (105 ± 5) °C.

4.2.2.6 Two sintered glass filter crucibles, of porosity 2 (as specified in ISO 4793:1980) (maximum porosity diameter 40 µm to 100 µm) with filter flask and adapter funnel for crucibles.

4.2.2.7 Desiccator.

4.2.2.8 Wash bottle.

4.2.2.9 Filtration apparatus.

4.2.3 Procedure

Superimpose the 0,60 mm mesh test sieve on the 0,09 mm mesh test sieve and wet the sieves with water. Place a volume of milk of lime containing $(50 \pm 0,5)$ g of dry substance in a 500 ml wide-mouthed bottle. Replace the stopper and shake the bottle for about 30 s. Remove the stopper immediately and pour the contents of the bottle onto the sieves. Wash any residue remaining in the bottle or on the stopper with a jet of water from the 5 mm bore tubing and at a pressure equal to a head of 1,2 m (approximately 10 kPa) on to the sieves. Then use the jet to wash the residue on the 0,60 mm mesh test sieve for $(2 \pm 0,1)$ min. Do not rub the residue through the sieve and take care not to flood the lower sieve during the operation. At the end of this period, wash the residue to one side of the sieve.

Detach the 0,60 mm mesh test sieve and, using a wash bottle, transfer the residue from the sieve through a glass funnel into one of the tared, sintered glass filter crucibles connected to the filtration apparatus. When all the residue has been washed into the filter, and the water extracted, remove the filter containing the residue and dry it at (105 ± 5) °C for 1 h. Cool the dried filter in a desiccator and reweigh.

Wash the residue on the 0,09 mm mesh test sieve for $(5 \pm 0,2)$ min. Transfer the residue to a tared filter crucible, dry at (105 ± 5) °C until constant mass is reached, cool and reweigh as described above.

4.2.4 Expression of results

The mass retained on each sieve expressed as $m(P_{0,60 \text{ or } 0,09})$ in mass fraction in % is given by the following equation:

$$m(P_{0,60 \text{ or } 0,09}) = \frac{m_1 \times 100}{m} \quad (2)$$

where

m is the mass of the dry substance in the test portion, in grams;

m_1 is the mass of the residue retained on the test sieves, in grams.

5 Preparation of test solutions

5.1 Fusion with lithium tetraborate

5.1.1 General

Fusion with lithium tetraborate is used to dissolve:

- high-calcium lime as specified in EN 12518 in order to determine silicon, aluminium, iron and manganese;
- half-burnt dolomite as specified in EN 1017 in order to determine magnesium, silicon, aluminium and iron;
- calcium carbonate as specified in EN 1018 in order to determine calcium and magnesium;
- magnesium oxide as specified in prEN 16004 in order to determine magnesium, silicon, aluminium and iron;
- calcium magnesium carbonate as specified in prEN 16003 in order to determine calcium and magnesium.

5.1.2 Principle

After fusing the sparingly soluble oxide constituents of the lime sample with lithium tetraborate, the fusion cake is dissolved in hydrochloric acid and the solution made up to 250 ml in a volumetric flask. Magnesium, silicon, aluminium, iron and manganese are determined in aliquot parts of this solution by flame-AAS (7.1) or ICP-OES (7.2).

5.1.3 Reagents

5.1.3.1 Lithium tetraborate, $\text{Li}_2\text{B}_4\text{O}_7$.

5.1.3.2 Hydrochloric acid, $\rho = 1,16$ g/ml.

5.1.3.3 Hydrochloric acid, diluted, (1 + 5).

5.1.4 Apparatus

Ordinary laboratory apparatus and the following:

5.1.4.1 Platinum-gold crucible.

5.1.4.2 Hot plate.

5.1.5 Procedure

Weigh $(0,25 \pm 0,02)$ g to the nearest 0,1 mg of the sample into a platinum-gold crucible and add 1,5 g of lithium tetraborate (5.1.3.1). Roast at $(1\ 000 \pm 25)$ °C until the melt is clear. Remove from the heat, cover the crucible with a watch glass and stand the crucible in water for a few seconds, remove and allow it to stand until it has cooled completely.

Transfer the cold melt to a beaker using approximately 50 ml of hydrochloric acid (5.1.3.3) and dissolve while stirring and heating at 100 °C. Then transfer the solution to a 250 ml volumetric flask with water (3.4) and, after cooling to room temperature, add each 10 ml of the appropriate reagent solutions (7.1.2.6 and 7.1.2.7 for the AAS measurement) or 1 ml of scandium solution (7.2.2.2, internal standard solution for the ICP measurement) and make up to the mark with water (digestion solution (I) for AAS and (II) for ICP).

5.2 Extraction with hydrochloric acid

5.2.1 General

Extraction with hydrochloric acid is used to dissolve calcium carbonate as specified in EN 1018 or calcium magnesium carbonate as specified in prEN 16003 in order to determine calcium and magnesium.

5.2.2 Principle

The sample is boiled with hydrochloric acid and the solution filtered. The pH value is adjusted to 6 to 7 to precipitate the iron (III) and aluminium oxides. After refiltering, the filtrate is transferred to a suitable volumetric flask.

5.2.3 Reagents

5.2.3.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

5.2.3.2 Hydrogen peroxide solution, $c(\text{H}_2\text{O}_2) = 30\%$ (m/m).

5.2.3.3 Hydrogen peroxide solution, diluted, 1 + 9.

5.2.3.4 Ammonium hydroxide solution, $c(\text{NH}_3) = 25\%$ (m/m).

5.2.3.5 Ammonium hydroxide solution, diluted, 1 + 9.

5.2.3.6 Ammonium chloride, NH_4Cl .

5.2.4 Apparatus

Ordinary laboratory apparatus and the following:

5.2.4.1 Hot plate.

5.2.4.2 Magnetic stirrer and magnetic rod.

5.2.4.3 pH-meter with glass electrode.

5.2.5 Procedure

Weigh $(1 \pm 0,1)$ g of the sample to the nearest 1 mg, transfer it to a 250 ml beaker, moisten with 10 ml of water, then gradually add 30 ml of hydrochloric acid (5.2.3.1). Make the solution up to about 100 ml with water then boil it for 10 min. After boiling, filter the solution immediately through a fluted filter paper (particle retention size 2,5 μm) into a 400 ml beaker and wash the residue well with water.

Add about 4 g of ammonium chloride (5.2.3.6) and a few drops of hydrogen peroxide (5.2.3.3) to the solution, then dilute with about 150 ml of water and heat to boiling. During boiling, add ammonium hydroxide solution (5.2.3.4) to adjust the pH value to 6 to 7 and precipitate aluminium hydroxides and iron hydroxides and the silicic acid.

Continue boiling for 3 min and, after the precipitate has settled, filter the solution immediately through a fluted filter paper (particle retention size 2,5 μm) into a 500 ml volumetric flask. Wash the filter residue three times with ammonium hydroxide solution (5.2.3.5) and three times with water. After the solution has cooled to room temperature, make the solution up to the mark with water and shake the contents of the flask thoroughly (digestion solution III).

5.3 Microwave digestion with nitric acid

5.3.1 General

The purpose of this method of digestion is to release trace elements from the accompanying matrix and determine the content of the various elements. The method is applied to high-calcium limes as specified in EN 12518, to calcium carbonate as specified in EN 1018, to calcium magnesium carbonate as specified in prEN 16003, to magnesium oxide as specified in prEN 16004 and to half-burnt dolomite as specified in EN 1017.

5.3.2 Principle

The sample is weighed into a perfluoroalkoxyethylene (PFA) beaker and nitric acid is added. After the mixture has been placed in a microwave apparatus, digestion is carried out. Any undissolved component is removed by filtering and the supernatant is used to determine the elements concerned.

5.3.3 Reagents

5.3.3.1 Nitric acid, $\rho = 1,40$ g/ml.

5.3.4 Apparatus

Ordinary laboratory apparatus and the following:

5.3.4.1 Microwave digestion apparatus, equipped with PFA digestion vessels and a programmable pressure and temperature control unit. Performance ≥ 600 W.

5.3.4.2 50 ml polypropylene pressure vessel with screw lid.

5.3.4.3 Filtering apparatus.

5.3.5 Procedure

The mass of the test sample depends on the test method. For AAS, the recommended mass is $(0,5 \pm 0,05)$ g and for ICP-OES $(3 \pm 0,05)$ g, weighed to the nearest 0,1 mg. In the first case, moisten the sample with 4 ml of water and carefully add 3 ml of nitric acid (5.3.3.1), in the second case moisten with 5 ml of water and add 10 ml of nitric acid (5.3.3.1).

Seal the digestion vessel and place in the microwave apparatus. Before programming the apparatus, the heating conditions shall be determined, and a temperature and pressure versus time plot shall be prepared.

Subject the test sample to a pressure of 500 kPa to 700 kPa and to a temperature of 90 °C for 10 min during a heating-up phase. Then subject the test sample to a pressure of 1 000 kPa and a temperature between 120 °C and 150 °C for 15 min to 20 min. Allow the digestion vessel to cool to room temperature. Open the digestion vessel, introduce the solution into a 100 ml volumetric flask rinse and make up to the mark with water. Filter and transfer the solution (digestion solution IV) to a polypropylene vessel in order to avoid adsorption on the glass.

5.4 Pressurized digestion with nitric acid

5.4.1 General

The purpose of this method of digestion is to release trace elements from the accompanying matrix and determine the content of the various elements. The method is applied to high-calcium limes as specified in EN 12518, to calcium carbonate as specified in EN 1018, to calcium magnesium carbonate as specified in

prEN 16003, to magnesium oxide as specified in prEN 16004 and to half-burnt dolomite as specified in EN 1017.

5.4.2 Principle

The sample is weighed out into a polytetrafluorethylen (PTFE) beaker and nitric acid is added. After the mixture has been placed in a pressure shell, digestion is carried out at 130 °C. Any undissolved component is removed by filtering and the supernatant is used to determine the elements concerned.

5.4.3 Reagent

5.4.3.1 Nitric acid, ρ (HNO₃) = 1,40 g/ml.

5.4.4 Apparatus

Ordinary laboratory apparatus and the following:

5.4.4.1 Pressure digestion system, consisting of a PTFE digestion vessel, pressure shell and a heater.

5.4.4.2 50 ml polypropylene pressure vessel with screw lid.

5.4.4.3 Filtering apparatus.

5.4.5 Procedure

Weigh ($0,5 \pm 0,05$) g to the nearest of 0,1 mg of the sample into the digestion vessel, moisten the sample with 2 ml of water and add carefully 5 ml of nitric acid (5.4.3.1). Seal the pressure vessel, place it in a cold drying oven and heat to 130 °C. After about 15 min, remove the pressure vessel from the drying oven and cool it to room temperature. Open the pressurized digestion system, introduce the solution into a 100 ml volumetric flask, rinse and make up to the mark with water. Filter and transfer the solution (digestion solution V) to a polypropylene vessel in order to avoid adsorption on the glass.

6 Conventional methods of determining major and minor constituents

6.1 Determination of free water

6.1.1 General

The method is used to determine free water in high-calcium lime as specified in EN 12518, calcium carbonate as specified in EN 1018 and calcium magnesium carbonate as specified in prEN 16003. In the case of hydrated high-calcium lime, calcium carbonate or calcium magnesium carbonate, free water means the moisture attached to the product, in the case of milk of lime, it refers to the water content of the suspension. The method does not apply for high-calcium quicklime. The determination of the water content of milk of lime is required to calculate the water-soluble content of the suspended hydrated lime (see 6.5).

6.1.2 Principle

When heating a sample of hydrated high-calcium lime, calcium carbonate or calcium magnesium carbonate to (105 ± 5) °C, in the drying oven the free water escapes. The loss of mass at this temperature is referred to as free water in the case of hydrated high-calcium lime, calcium carbonate and calcium magnesium carbonate and as the content of water in the milk of lime.

6.1.3 Apparatus

Ordinary laboratory apparatus and the following:

6.1.3.1 Drying oven, thermostatically controlled to maintain a temperature of $(105 \pm 5) ^\circ\text{C}$.

6.1.3.2 Analytical balance accurate to 0,1 mg.

6.1.3.3 Desiccator containing drying agent.

6.1.3.4 Unglazed porcelain or platinum crucible.

6.1.3.5 Pipette.

6.1.4 Procedure

6.1.4.1 Hydrated high-calcium lime, calcium carbonate and calcium magnesium carbonate

Weigh $(5 \pm 0,1)$ g to a nearest 1 mg of the sample in the as-delivered state in a pre-weighed crucible. Dry the sample of high-calcium lime, calcium carbonate or calcium magnesium carbonate at $(105 \pm 5) ^\circ\text{C}$ in the drying oven until constant mass. Cover the crucible after removing it from the oven to prevent carbon dioxide and water vapour in the atmosphere from being absorbed. Cool in the desiccator and reweigh.

6.1.4.2 Milk of lime

Homogenise the suspension by shaking before taking the sample aliquot. Use a pipette to take approximately 20 g and weigh to the nearest of 0,1 mg in a glass vessel. Dry the sample to constant mass in the drying oven at $(105 \pm 5) ^\circ\text{C}$. Cover the crucible after removing it from the oven to prevent carbon dioxide and water vapour in the atmosphere from being absorbed. After cooling down to ambient temperature in the desiccator, determine the loss in mass.

6.1.5 Expression of results

The free water content of hydrated high-calcium lime, milk of lime, calcium carbonate or calcium magnesium carbonate expressed as (H_2O) in mass fraction in % is given by the following equation:

$$(\text{H}_2\text{O}) = \frac{(m - m_1)}{m} \times 100 \quad (3)$$

where

m is the mass of the test portion before heating, in grams;

m_1 is the mass of the test portion after heating, in grams.

6.2 Loss on ignition at 450 °C

6.2.1 General

The method is used to determine the loss on ignition in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017 and in magnesium oxide as specified in prEN 16004.

6.2.2 Principle

The loss on ignition at 450 °C is basically due the water of hydration.

6.2.3 Apparatus

Ordinary laboratory apparatus and the following:

6.2.3.1 Electric furnace capable of being maintained at (450 ± 25) °C, with a thermoelectric temperature indicator.

6.2.3.2 Analytical balance accurate to 0,1 mg.

6.2.3.3 Desiccator containing phosphorous pentoxide, P_2O_5 .

6.2.3.4 Unglazed porcelain or platinum crucible.

6.2.4 Procedure

6.2.4.1 High-calcium quicklime, high-calcium hydrated lime, magnesium oxide and half-burnt dolomite

Weigh $(5 \pm 0,1)$ g to the nearest of 1 mg of the sample (m_1) in the as-delivered state in a pre-weighed crucible. Heat the sample in the furnace at (450 ± 25) °C for 2 h and then cool it in a desiccator. Cover the crucible after removing it from the furnace to prevent carbon dioxide and water vapour in the atmosphere from being absorbed. Cool in the desiccator and weigh (m_2).

6.2.4.2 Milk of lime

The water content of the milk of lime shall be determined as specified in 6.1.4.2. After drying the sample this way, the determination shall be carried out as specified in 6.2.4.1.

6.2.5 Expression of results

The loss on ignition at 450 °C expressed as LoI in mass fraction in % is given by the following equation:

$$(\text{LoI}) = \frac{(m_1 - m_2)}{m_1} \times 100 \quad (4)$$

where

m_1 is the mass of the sample before ignition at (450 ± 25) °C, in grams;

m_2 is the mass of the sample after ignition at (450 ± 25) °C, in grams.

6.3 Determination of carbon dioxide

6.3.1 General

The method is used to determine carbon dioxide in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017 and in magnesium oxide as specified in prEN 16004.

6.3.2 Principle

The carbon dioxide content of the materials concerned is determined from the loss on ignition at 1 000 °C. The loss on ignition at 450 °C is basically due to free water and the water of hydration. The difference in mass between the loss on ignition at $(1\ 000 \pm 50)$ °C and the loss on ignition at (450 ± 25) °C is equal to the carbon dioxide content of the product.

6.3.3 Apparatus

Ordinary laboratory apparatus and the following:

6.3.3.1 Electric furnace capable of being maintained at $(1\ 000 \pm 50)$ °C, with a thermoelectric temperature indicator.

6.3.3.2 Analytical balance accurate to 0,1 mg.

6.3.3.3 Desiccator containing phosphorous pentoxide, P_2O_5 .

6.3.3.4 Unglazed porcelain or platinum crucible.

6.3.4 Procedure for high-calcium quicklime, high-calcium hydrated lime, milk of lime, magnesium oxide and half-burnt dolomite

After determining the mass (m_2) from the determination of the loss on ignition at (450 ± 25) °C (6.2.5), heat the sample at $(1\ 000 \pm 50)$ °C for 3 h. Cover the crucible after removing it from the furnace to prevent carbon dioxide and water vapour in the atmosphere from being absorbed. Cool in the desiccator and reweigh (m_3).

6.3.5 Expression of results

The carbon dioxide content expressed as CO_2 in mass fraction in % is given by the following equation:

$$c(CO_2) = \frac{(m_2 - m_3)}{m_1} \times 100 \quad (5)$$

where

m_1 is the mass of the sample before ignition at (450 ± 25) °C (6.2.5), in grams;

m_2 is the mass of the sample before ignition at $(1\ 000 \pm 50)$ °C, in grams;

m_3 is the mass of the sample after ignition at $(1\ 000 \pm 50)$ °C, in grams.

6.4 Determination of residue insoluble in hydrochloric acid

6.4.1 General

The method is used to determine the residue in calcium carbonate as specified in EN 1018 and in calcium magnesium carbonate as specified in prEN 16003 which is insoluble in hydrochloric acid.

6.4.2 Principle

After the sample has been dissolved in hydrochloric acid and filtered, the filtration residue is washed, dried and incinerated to constant mass to determine the insoluble component gravimetrically.

6.4.3 Reagents

6.4.3.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

6.4.3.2 Hydrochloric acid, diluted, 1 + 1.

6.4.3.3 Hydrochloric acid, diluted, 1 + 3.

6.4.4 Apparatus

Ordinary laboratory apparatus and the following:

6.4.4.1 Magnetic stirrer with hot plate.

6.4.4.2 Platinum crucible.

6.4.4.3 Electric furnace capable of being maintained at $(1\ 000 \pm 50)$ °C with a thermoelectric temperature indicator.

6.4.5 Procedure

Weigh $(1 \pm 0,1)$ g to the nearest of 1 mg of the sample into a 250 ml beaker. Suspend the sample in 5 ml to 10 ml of water and dissolve it by adding 25 ml of hydrochloric acid (6.4.3.2). After boiling this solution for 2 min, dilute it with 50 ml of water as soon as the dissolution is complete and immediately filter it through a filter (particle retention size 2,5 µm, ash < 0,01%) into a 250 ml beaker. Use a rubber-tipped glass rod to ensure that all the insoluble residue is transferred to the filter. Wash the filtration residue twice with 10 ml of hot dilute hydrochloric acid (6.4.3.3) and then several times with small portions of hot water.

Reduce the washed filter to ash in a roasted and pre-weighed platinum crucible. After incinerating to constant mass at $(1\ 000 \pm 50)$ °C, cool in a desiccator and weigh. An incineration time of 15 min will generally be sufficient to achieve constant mass.

6.4.6 Expression of results

The content of residue insoluble in hydrochloric acid expressed as $\text{HCl}_{\text{insol}}$ in mass fraction in % is given by the following equation:

$$(\text{HCl}_{\text{insol}}) = \frac{m_1 \times 100}{m} \quad (6)$$

where

m_1 is the incineration residue, in grams;

m is the mass of the sample, in grams.

6.5 Determination of content of water soluble calcium oxide or calcium hydroxide (reference method)

6.5.1 General

The method serves to determine the water-soluble lime content (calcium oxide and calcium hydroxide) in high-calcium lime products as specified in EN 12518. It is also used to determine the water-soluble calcium hydroxide in milk of lime.

This method designates those constituents which enter into the reaction under the conditions of this specified method. The interpretation of results obtained by the following method shall be determined in consideration of this limiting definition.

6.5.2 Principle

The amount of water-soluble lime which can be titrated with hydrochloric acid after digesting the lime sample in water is determined. To avoid agglomeration of calcium oxide on slaking which can lead to incomplete

suspension of a high-calcium lime sample such limes shall be heated. The indicator used and the low rate of titration ensure that the titration proceeds in the alkaline range.

6.5.3 Reagents

6.5.3.1 Hydrochloric acid, standard volumetric solution, $c(\text{HCl}) = 1 \text{ mol/l}$.

6.5.3.2 Phenolphthalein indicator solution: dissolve 0,5 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml with water.

6.5.3.3 Ethanol, $\rho = 0,79 \text{ g/ml}$.

6.5.3.4 Water grade 3 freshly boiled to remove CO_2 and cooled.

6.5.4 Apparatus

Ordinary laboratory apparatus and the following:

6.5.4.1 Analytical balance, accurate to 0,1 mg.

6.5.4.2 pH-meter with glass electrode.

6.5.4.3 Heatable magnetic stirrer with magnetic rod.

6.5.4.4 Pipette.

6.5.5 Procedure

6.5.5.1 High-calcium lime

Weigh $(1 \pm 0,05) \text{ g}$ of pulverized high-calcium lime (m_1) to the nearest of 0,1 mg and transfer it immediately to a conical flask containing about 200 ml of water (6.5.3.4).

Cover the conical flask containing the pulverized high-calcium lime sample with a watch glass and bring the contents to the boil while stirring on the heatable magnetic stirrer. After boiling for 4 min, spray the wall of the conical flask with approximately 50 ml of water (6.5.3.4). Allow the contents to cool to room temperature.

6.5.5.2 Hydrated high-calcium lime

Weigh $(1,3 \pm 0,05) \text{ g}$ of hydrated high-calcium lime (m_2) to a nearest of 0,1 mg and transfer it immediately to a conical flask containing about 200 ml of water (6.5.3.4). The sample of hydrated high-calcium lime shall be analysed immediately after preparation of the suspension at room temperature.

6.5.5.3 Milk of lime

Before starting measuring, the water content of the milk of lime shall be determined as specified in 6.1. Homogenise the suspension by shaking before taking the sample aliquot. Use a pipette to take a volume corresponding to a solid matter content of approximately 1,3 g, weigh to the nearest of 0,1 mg (m_3) and, while stirring, put into a conical flask containing enough water (6.5.3.4) to reach a volume of 200 ml after addition of the suspension.

6.5.5.4 Determination

Add a few drops of phenolphthalein indicator solution (6.5.3.2). Then slowly add hydrochloric acid (6.5.3.1) dropwise (at a rate of 12 ml/min) until the solution just becomes decoloured (pH value 9,5). Now stir for 60 s

without adding further hydrochloric acid and then titrate dropwise (at a rate of 4 ml/min) to final decolouration, ignoring any red colouration of the solution which returns after a few seconds.

Keep the titrated solution for the determination of water insoluble matter (6.7).

6.5.6 Expression of results

The water-soluble CaO or Ca(OH)₂ content of the products, expressed as water-soluble(CaO) or water-soluble (Ca(OH)₂) in mass fraction in %, is given by one of the following equations:

$$\text{for high-calcium lime: } (\text{CaO}) = \frac{28,04 \times V \times 100}{1000 \times m_1} = \frac{2,804 \times V}{m_1} \quad (7)$$

$$\text{for hydrated high-calcium lime: } (\text{Ca(OH)}_2) = \frac{37,05 \times V \times 100}{1000 \times m_2} = \frac{3,705 \times V}{m_2} \quad (8)$$

$$\text{for milk of lime: } (\text{Ca(OH)}_2) = \frac{37,05 \times V \times 100 \times 100}{1000 \times m_3 (100 - (\text{H}_2\text{O}))} = \frac{370,5 \times V}{m_3 \times (100 - (\text{H}_2\text{O}))} \quad (9)$$

where

V is the volume of hydrochloric acid (6.4.3.1) used, in millilitres;

m_1 is the mass of the sample of CaO product, in grams;

m_2 is the mass of the sample of Ca(OH)₂ product, in grams;

m_3 is the mass of the milk of lime sample, in grams;

(H₂O) is the content of water in the milk of lime (see 6.1.5).

6.6 Determination of sugar soluble calcium oxide or calcium hydroxide (alternative method)

6.6.1 General

The method serves to determine the available lime content (unbound calcium oxide or calcium hydroxide). It can also be used to determine the available calcium hydroxide in milk of lime.

This method designates those constituents which enter into the reaction under the conditions of this specified method. The interpretation of results obtained by the following method shall be determined in consideration of this limiting definition.

6.6.2 Principle

The sample is slaked and dispersed with water. To avoid agglomeration of calcium oxide on slaking which can lead to incomplete suspension of a high-calcium lime sample such limes shall be heated. The lime is solubilized by reaction with sugar to form calcium sucrate which is then determined by titration against hydrochloric acid using phenolphthalein as the indicator.

6.6.3 Reagents

6.6.3.1 Hydrochloric acid, standard volumetric solution, $c(\text{HCl}) = 1 \text{ mol/l}$.

6.6.3.2 Sodium hydroxide solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

6.6.3.3 Phenolphthalein indicator solution: dissolve 0,5 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml with water.

6.6.3.4 Ethanol, $\rho = 0,79$ g/ml.

6.6.3.5 Water grade 3 freshly boiled to remove CO_2 and cooled.

6.6.3.6 Sucrose Solution:

Prepare a 400 g/l solution using pure cane sugar and CO_2 -free water in a large beaker and stir until dissolved. Add several drops of phenolphthalein indicator solution. Add NaOH solution (0,1 mol/l) dropwise with stirring until a faint pink colour persists. A stock solution of sugar may be made for convenience; however, it should not be stored for more than two days. As an alternative, the acidity of each lot of sugar can be determined, and a correction applied to the titration.

6.6.4 Apparatus

Ordinary laboratory apparatus and the following:

6.6.4.1 Analytical balance, accurate to 0,1 mg.

6.6.4.2 Heatable magnetic stirrer with magnetic rod.

6.6.4.3 Cold-water bath.

6.6.4.4 Buchner funnel.

6.6.4.5 Burette, 50 ml.

6.6.4.6 Erlenmeyer flask, 500 ml

6.6.4.7 Hot plate.

6.6.5 Procedure

6.6.5.1 For quicklime

Weigh ($1 \pm 0,05$) g of pulverized high-calcium lime (m_1) to the nearest of 0,1 mg and transfer it immediately to a 500 ml Erlenmeyer flask containing about 50 ml of CO_2 -free water. Place the flask on a hot plate and immediately add 50 ml of boiling water to the flask.

Cover the flask with a watch glass and bring the contents to the boil while stirring on the heatable magnetic stirrer. After boiling for 5 min, spray the wall of the flask with approximately 50 ml of water. Remove from the hot plate, stopper the flask loosely, and place in a cold-water bath to cool to room temperature.

6.6.5.2 For hydrated lime

Weigh ($1,3 \pm 0,05$) g of hydrated lime (m_2) to a nearest of 0,1 mg and transfer it immediately to a 500 ml Erlenmeyer flask containing about 150 ml of water.

6.6.6 Sugar extraction

Add 50 ml of the neutralized sugar solution (or, alternatively, 20 g of pure sugar and 50 ml of water). Stopper the flask, swirl, and let stand for (10 ± 2) min to react. Swirl at 4-min intervals during reaction.

6.6.7 Determination

Remove stopper, add 4 to 5 drops of phenolphthalein indicator solution and wash down the stopper and sides of the flask with water.

Then slowly add hydrochloric acid dropwise (at a rate of 12 ml/min) from a 50 ml burette until the solution just becomes colourless. Now stir for 60 s without adding further hydrochloric acid and then titrate dropwise (at a rate of 4 ml/min) to decolouration, ignoring any red colouration of the solution which might return after some seconds.

6.6.8 Expression of results

The available lime, expressed as CaO-available or Ca(OH)₂-available content of the products, c (CaO) or c (Ca(OH)₂) in mass fraction in % is given by one of the following equations:

$$\text{for quicklime: available lime (CaO)} = \frac{28,04 \times V \times 100}{1000 \times m_1} = \frac{2,804 \times V}{m_1} \quad (10)$$

$$\text{for hydrated lime: available lime (Ca(OH)}_2) = \frac{37,05 \times V \times 100}{1000 \times m_2} = \frac{3,705 \times V}{m_2} \quad (11)$$

where

V is the volume of hydrochloric acid used, in millilitres;

m_1 is the mass of the sample of CaO product, in grams;

m_2 is the mass of the sample of Ca(OH)₂ product, in grams.

6.7 Water-insoluble matter

6.7.1 General

The method of determining the water-insoluble matter is applied to high-calcium lime products as specified in EN 12518.

6.7.2 Principle

The water-insoluble matter in the solutions titrated as described in 6.5.5 are determined gravimetrically by filtering the solutions and drying the residues.

6.7.3 Apparatus

Ordinary laboratory apparatus and the following:

6.7.3.1 Drying oven, thermostatically controlled to maintain a temperature of (105 ± 5) °C.

6.7.3.2 Filtration apparatus.

6.7.4 Procedure

Immediately after completing the titration described in 6.5.5, filter the solution through a pre-washed, dried and weighed filter paper, particle retention size 2,5 µm, and wash the filtration residue four times with 10 ml portions of water. Dry the filter and residue to constant mass in a drying oven at (105 ± 5) °C and weigh.

6.7.5 Expression of results

6.7.5.1 Pulverized and granular high-calcium lime, hydrated high-calcium lime

The water-insoluble matter in the sample expressed as $(\text{H}_2\text{O}_{\text{insol}})$ in mass fraction in % is given by the following equation:

$$(\text{H}_2\text{O}_{\text{insol}}) = \frac{m_1 \times 100}{m} \quad (12)$$

where

m_1 is the mass after drying, in grams;

m is the mass of the sample of CaO or Ca(OH)₂ product from 6.5.5, in grams.

6.7.5.2 Milk of lime

The water-insoluble matter in the sample, $c(\text{H}_2\text{O}_{\text{insol}})$ expressed as $(\text{H}_2\text{O}_{\text{insol}})$ in mass fraction in % is given by the following equation:

$$(\text{H}_2\text{O}_{\text{insol}}) = \frac{m_2 \times 100 \times 100}{m_3 \times (100 - c(\text{H}_2\text{O}))} \quad (13)$$

where

m_2 is the mass after drying, in grams;

m_3 is the mass of the sample of Ca(OH)₂ product from 6.5.5, in grams;

$c(\text{H}_2\text{O})$ is the content of water in the milk of lime (see 6.1.5).

6.8 Determination of free CaO

6.8.1 General

The method is used to determine free, unbound calcium oxide in half-burnt dolomite as specified in EN 1017 and in magnesium oxide as specified in prEN 16004.

6.8.2 Principle

The sample is suspended in a sucrose solution and titrated after filtration with hydrochloric acid using phenolphthalein as indicator.

6.8.3 Reagents

6.8.3.1 Commercial refined sucrose.

6.8.3.2 Hydrochloric acid standard volumetric solution, $c(\text{HCl}) = 0,1 \text{ mol/l}$.

6.8.3.3 Phenolphthalein indicator solution: dissolve 0,5 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml with water.

6.8.3.4 Ethanol, $\rho = 0,79 \text{ g/ml}$.

6.8.4 Apparatus

Ordinary laboratory apparatus and the following:

6.8.4.1 Filtering apparatus.

6.8.5 Procedure

Weigh $(1 \pm 0,05)$ g of the sample to the nearest 0,1 mg and suspend uniformly in 50 ml of water in a 300 ml conical flask by swirling the contents. Add 5 g of sucrose (6.8.3.1), seal the flask and stir the suspension for 12 min to 15 min. Filter through a Buchner funnel using a double layer of fine filter paper (particle retention 2,5 μm), wash the filter with six 25 ml portions of cold water and titrate the filtrate with hydrochloric acid (6.8.3.2) using phenolphthalein (6.8.3.3) as indicator.

6.8.6 Expression of results

The content of free CaO expressed as $(\text{CaO}_{\text{free}})$ in mass fraction in % is given by the following equation:

$$(\text{CaO}_{\text{free}}) = \frac{2,804 \times V \times 100}{1000 \times m} = \frac{0,2804 \times V}{m} \quad (14)$$

where

V is the volume of hydrochloric acid used in the titration, in millilitres;

m is the mass of the sample, in grams.

6.9 Determination of calcium oxide and magnesium oxide

6.9.1 General

The method is suitable for:

- determining calcium oxide and magnesium oxide in calcium carbonate as specified in EN 1018 when the content of MgO is greater than 1 %;
- determining calcium oxide and magnesium oxide in half-burnt dolomite as specified in EN 1017.

6.9.2 Principle

Calcium oxide is first determined in an aliquot of the test solution by complexation titration with EDTA solution at a pH value of 13, the colour change of a calcium-specific indicator being used to indicate the end point. During the titration, the EDTA first reacts with the free calcium ions and then with the calcium ions bonded to the indicator, causing the colour of the latter to change sharply from wine red to blue.

In the same way, the total calcium oxide and magnesium oxide ($\Sigma \text{CaO} + \text{MgO}$) is determined at a pH value of 10 by titration with EDTA using Eriochrome Black T as indicator. During the titration, the EDTA first reacts with the free calcium and magnesium ions and then with those bonded to the indicator, causing the colour of the latter to change from red to blue. The difference in the amount-of-substance concentrations, $c(\text{CaO} + \text{MgO})$ and $c(\text{CaO})$, gives the magnesium content, $c(\text{MgO})$.

6.9.3 Reagents

6.9.3.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

6.9.3.2 Hydrochloric acid, diluted, 1 + 1.

- 6.9.3.3 Triethanolamine**, c [$\text{N}(\text{C}_2\text{H}_5\text{OH})_3$] = 99 % (m/m).
- 6.9.3.4 Triethanolamine solution**, diluted, 1 + 1.
- 6.9.3.5 Sodium hydroxide solution**, c (NaOH) = 4 mol/l.
- 6.9.3.6 Ammonium hydroxide solution**, c (NH_4OH) = 25 % (m/m).
- 6.9.3.7 Ammonium chloride**, NH_4Cl .
- 6.9.3.8 Ethylenediaminetetraacetic acid disodium salt (EDTA)**, ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2 \text{H}_2\text{O}$), dried to constant mass at 80 °C before weighing.
- 6.9.3.9 Calcium carbonate**, c (CaCO_3) = 99,9 % (dried at 150 °C).
- 6.9.3.10 Buffer solution**, make 70 g of ammonium chloride (6.9.3.7) and 570 ml of ammonium hydroxide solution (6.9.3.6) up to the mark with water in a 1 l volumetric flask.
- 6.9.3.11 EDTA solution**, c (EDTA) = 0,04 mol/l.

a) Preparation:

dissolve 14,89 g of EDTA (6.9.3.8) in water and making up to 1 l in a volumetric flask.

b) Standardization

Pipette 50 ml of the calcium ion reference solution (6.9.3.12) into a 400 ml beaker and dilute with 100 ml of water. Adjust the pH value of the solution to 13 with sodium hydroxide solution (6.9.3.5) using a pH meter. Add 0,1 g of calconcarboxylic indicator (6.9.3.13) and titrate with the EDTA solution being standardized until the colour changes to blue.

The concentration of the EDTA solution is given by the following equation:

$$c = \frac{50 \times m}{100,09 \times 0,04 \times V} = \frac{12,489 \times m}{V} \quad (15)$$

where

m is the initial mass of calcium carbonate taken to prepare the calcium ion reference solution, in grams;

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

6.9.3.12 Calcium ion reference solution, c (Ca^{2+}) = 0,01 mol/l: transfer ($1 \pm 0,002$) g of calcium carbonate (6.9.3.9) and about 100 ml of water to a 400 ml beaker, cover the beaker with a watch glass and carefully add about 10 ml of hydrochloric acid (6.9.3.2). After the calcium carbonate has dissolved completely, remove the carbon dioxide by boiling, then allow the solution to cool and make it up to 1 l in a volumetric flask.

6.9.3.13 Calconcarboxylic acid indicator: triturate 0,2 g of calconcarboxylic acid intensively with 20 g of anhydrous sodium sulfate in a mortar.

6.9.3.14 Eriochrome Black T indicator: triturate 1 g of Eriochrome Black T intensively with 100 g of sodium chloride in a mortar.

6.9.4 Apparatus

Ordinary laboratory apparatus and the following:

6.9.4.1 Magnetic stirrer with magnetic rod.

6.9.4.2 pH meter with glass electrode.

6.9.5 Procedure

6.9.5.1 Determination of CaO

To determine the calcium oxide content, transfer 25 ml (V_1) from the volumetric flask containing the solution to be analysed (I, II or III) to a 400 ml beaker, dilute the solution with about 150 ml of water and add 5 ml of triethanolamine solution (6.9.3.4).

Adjust the pH value of this solution to 13 with sodium hydroxide solution (6.9.3.5) using a pH meter and ensure that the pH value does not drop below 13 during the titration. Add 0,1 g of calconcarboxylic acid indicator (6.9.3.13) and titrate with the EDTA solution while stirring constantly with a magnetic stirrer until the colour changes from wine red to blue. During titration the pH-value shall not fall below 13.

6.9.5.2 Determination of total CaO and MgO content

Transfer about 150 ml of water and 25 ml (V_2) of solution from the volumetric flask containing the solution to be analysed (I, II or III) to a 400 ml beaker. Add 5 ml of triethanolamine solution (6.9.3.4) and adjust the pH value of the solution to 10,5 with buffer solution (6.9.3.10) using a pH-meter. Then add about 90 % of the volume of EDTA solution used during the calcium oxide titration (as described in 6.9.5.1) and, after adding 0,1 g of Eriochrome Black T indicator (6.9.3.14), titrate the solution until the colour changes from wine red to blue.

6.9.6 Expression of results

The calcium oxide content of the sample expressed as CaO in mass fraction in % is given by the following equation:

$$c(\text{CaO}) = \frac{V \times 0,04 \times 56,08 \times c \times V_3 \times 100}{V_1 \times 1000 \times m} \quad (16)$$

where

V is the volume of the digestion solution I, II (5.1.5) or III (5.2.5), in millilitres;

V_1 is the volume of the aliquot of the digestion solution taken for titration as described in 6.9.5.1, in millilitres;

V_3 is the volume of EDTA solution used for the CaO determination as described in 6.9.5.1, in millilitres;

c is the concentration of the EDTA solution, as determined in 6.9.3.11;

m is the mass, in grams, of the test portion as in 5.1.5 or 5.2.5.

The magnesium oxide content of the sample expressed as MgO in mass fraction in % is given by the following equation:

$$c(\text{MgO}) = \frac{V \times 0,04 \times 40,311 \times c \times (V_4 - V_3) \times 100}{V_2 \times 1000 \times m} \quad (17)$$

where

V is the volume of the digestion solution I, II (5.1.5) or III (5.2.5), in millilitres;

V_2 is the volume of the aliquot of the digestion solution taken for titration as described in 6.9.5.2, in millilitres;

V_3 is the volume of EDTA solution used for the CaO determination as described in 6.9.5.1 in millilitres;

V_4 is the volume of EDTA solution used for the determination of the total CaO and MgO as described in 6.9.5.2, in millilitres;

c is the concentration of the EDTA solution, as determined in 6.9.3.11;

m is the mass, in grams, of the test portion as in 5.1.5 or 5.2.5.

6.10 Determination of sulfate

6.10.1 General

The method is used to determine the content of sulfate in half-burnt dolomite as specified in EN 1017.

6.10.2 Principle

The sulfate compounds in the sample are dissolved in hydrochloric acid and the pH value is adjusted to 1 to 1,5 to prevent precipitation of the oxides of iron and aluminium. The sulfate content is determined gravimetrically by boiling the solution and precipitating the sparingly soluble barium sulfate with a barium chloride solution.

6.10.3 Reagents

6.10.3.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

6.10.3.2 Hydrochloric acid, diluted, 1 + 1.

6.10.3.3 Hydrochloric acid, diluted, 1 + 50.

6.10.3.4 Nitric acid, $\rho = 1,40$ g/ml.

6.10.3.5 Ammonium hydroxide solution, $c(\text{NH}_3) = 25\%$ (m/m).

6.10.3.6 Ammonium hydroxide solution, diluted, 1 + 16.

6.10.3.7 Barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

6.10.3.8 Barium chloride solution: dissolve 120 g of barium chloride in water and make up to 1 l with water in a volumetric flask.

6.10.3.9 Silver nitrate, AgNO_3 .

6.10.3.10 Silver nitrate solution: dissolve 5 g of silver nitrate in water, add 10 ml of nitric acid (6.10.3.4) and making up to 1 l with water in a volumetric flask.

6.10.4 Apparatus

Ordinary laboratory apparatus and the following:

6.10.4.1 Hot plate or sand bath.

6.10.4.2 Muffle furnace.

6.10.5 Procedure

Weigh out $(1 \pm 0,1)$ g to the nearest 1 mg of the sample into a 250 ml beaker, add 90 ml of cold water and then add 10 ml of hydrochloric acid (6.10.3.1) while stirring vigorously. Carefully heat the solution in a fume cupboard on a hot plate or in a sand bath to just below boiling point and leave at this temperature for 15 min. Filter through a filter paper, particle retention size 2,5 μm , into a 400 ml beaker and wash the residue several times with small portions of hot diluted hydrochloric acid (6.10.3.3).

Dilute the filtrate to about 250 ml with water and, if necessary, adjust the pH value to 1 with hydrochloric acid (6.10.3.2) or ammonium hydroxide solution (6.10.3.6). Boil the solution for 5 min and then add 10 ml of hot barium chloride solution (6.10.3.8) dropwise to the still boiling solution while stirring continuously. Allow the solution to boil for a further 15 min to enable the precipitate to form satisfactorily. Leave the precipitation vessel on a hot plate at 60 °C overnight, ensuring that the solution will not evaporate down.

Filter the precipitate through a filter paper, particle retention size 2,5 μm (ash content < 0,01 %), and wash the residue until chloride-free with boiling water, using silver nitrate solution (6.10.3.10) to test the filtrate. After washing the precipitate, rinse the stem of the funnel with a few drops of water. Wash the filter paper and contents with a few millilitres of water, collect the latter in a test tube and add a few drops of silver nitrate solution. If no cloudiness or precipitate appears in the solution, chloride is absent. If this is not the case, repeat the washing process until the silver nitrate test is negative.

Transfer the filter paper and residue to a preweighed platinum crucible and incinerate to constant mass at (925 ± 25) °C in a muffle furnace. An incineration time of 15 min will generally be sufficient to achieve constant mass.

6.10.6 Expression of results

The sulfate content expressed as SO_4^{2-} in mass fraction in % is given by the following equation:

$$\left(\text{SO}_4^{2-}\right) = \frac{0,4116 \times m_1 \times 100}{m} = \frac{41,16 \times m_1}{m} \quad (18)$$

where

m_1 is the final mass, in grams, of BaSO_4 ;

m is the mass, in grams, of the test portion.

6.11 Determination of solubility index by conductivity

6.11.1 General

The method is used for the determination of the reactivity (rate of dissolution) of milk of lime and of hydrated lime by means of conductivity measurements. The method can be used to measure the quality of different milk of lime suspensions. These suspensions are used, for example, for lime softening of drinking water to reduce total hardness. The processes of deacidification and lime softening depend on the rate of dissolution and chemical reactivity of the lime products used. This test method involves the use of readily available laboratory techniques and can be easily reproduced.

Figure 2 shows the conductivities of different concentrations of technical hydrated limes measured at 20 °C versus time. Conductivity increases immediately and then changes asymptotically until it reaches its final value. Beginning at a concentration of 300 mg/l calcium hydroxide, far below the solubility of approximately 1600 mg/l, the linear relationship between concentration and conductivity changes to a lower order.

Best results can be obtained if a 1 % suspension of calcium hydroxide is used for the measurement. The sample volume depends on the dimension of the measurement cell, the final concentrations of the test solutions should be equal.

6.11.2 Principle

The test is based on the evaluation of a conductivity-time graph which is plotted by measuring the time taken for the product to dissolve under controlled conditions. The increase of conductivity in water is caused by the calcium and hydroxyl ions produced when calcium hydroxide dissociates following Equation (19):



6.11.3 Reagents

6.11.3.1 Potassium chloride solution, c (KCl) = 0,01 mol/l.

6.11.3.2 Potassium chloride solution, c (KCl) = 3 % (m/m).

6.11.3.3 Nitrogen gas, N₂.

6.11.4 Apparatus

Ordinary laboratory apparatus and the following:

6.11.4.1 Conductivity meter, which has a RS-232 Interface and an external pt-100 Temperature sensor.

6.11.4.2 Computer system for the measurement of data and for the calculation of conductivity-time charts.

6.11.4.3 The measurement cell consists of a glass vessel with a thermal insulation and a mixer fitted with a tight lid with four glass-seal openings including an inert gas inlet, a gas outlet, a probe inlet and a further opening for the positioning of the sensors.

6.11.4.4 Thermostat.

6.11.4.5 Pipette.

6.11.5 Procedure

6.11.5.1 Preparation of the equipment

In order to measure conductivity vs. time, the design of the measurement cell and the cell constant of the conductivity sensor are of great importance. Therefore prior to each test series, the cell constant of the electrode needs to be determined by using the potassium chloride solution (6.11.3.1).

Only dissolution times which are greater than the mixing time of the cell can be accurately measured. The mixing time required to reach a homogeneous mixture depends on the type of mixer, the mixing speed, the vessel dimension and the position of measuring sensors. It is therefore necessary to define the measurement apparatus very precisely.

6.11.5.2 Measurement of homogenization time

Pipette 100 ml of water into the measurement cell and adjust the temperature to 25 °C using the thermostat. In order to prevent absorption of carbon dioxide, bubble nitrogen gas into the vessel during the measurement. Finally, start the stirrer and pipette 1,5 ml of potassium chloride solution (6.11.3.2) into the water.

For different vessel dimensions a homogenization time of less than 2,5 s following injection of a 3 % potassium chloride solution can be achieved.

6.11.5.3 Determination of dissolution speed

Before commencing the measurement, determine the content of dry matter of the milk of lime according to the procedure described in 6.1.4.2.

Initially, take an aliquot of the milk of lime to get a suspension containing 1,000 g in 100 ml of the suspension. Homogenise the milk of lime by shaking before taking the sample aliquot. Use a pipette to take the aliquot volume, put it into a volumetric flask and make up with water to 100 ml.

When testing solid hydrated lime a suspension is also prepared with a mass concentration of 1,000 g/100 ml. Leave the suspension undisturbed for at least 30 min before testing (complete wetting of the surface). Shake the suspension well before taking the aliquot for measurement.

Take 1,5 ml from the sample and transfer it very quickly to the reaction vessel containing 100 ml of water at 25 °C.

6.11.6 Evaluation

6.11.6.1 The starting time (t=0) and the definition of the endpoint of conductivity

Measure the conductivity at least every 0,1 s. The starting time (t = 0) is set to the first point with a conductivity change of more than 20 µS/(cm • 0,1 s).

Conductivity endpoint, α_{\max} , is reached when the conductivity changes by less than 10 µS/cm in 1 min. α_{\max} is then calculated as the mean of all measurements from endpoint to endpoint +1 min. An example is shown in Figure 2.

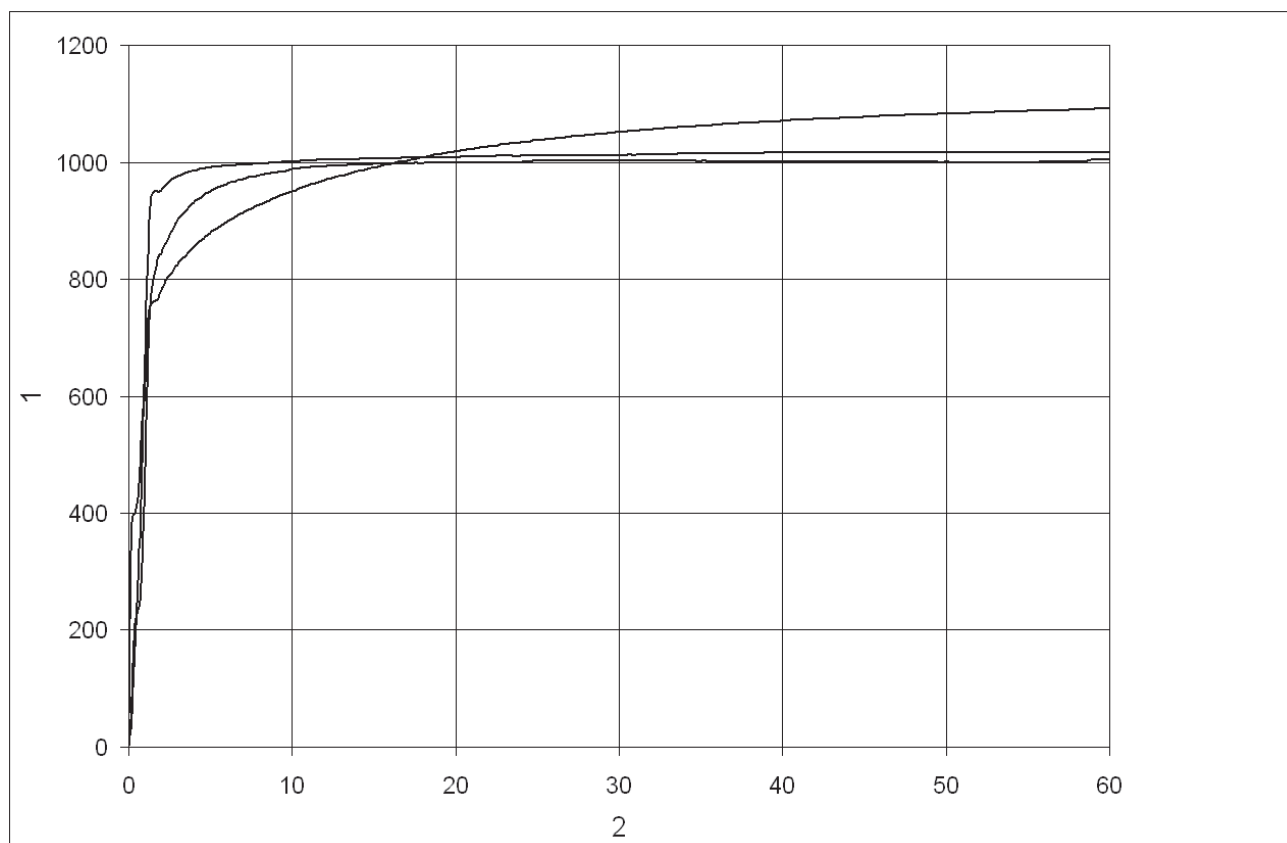
6.11.6.2 Evaluation of conductivity vs. time graphs and calculation of results

Calculate the conductivity α (x %) for x (%) = 63 %, 80 %, 90 % and 95 % of the endpoint conductivity (α_{\max}) using the following Equation (20):

$$\alpha(x\%) = \frac{x \times \alpha_{\max}}{100} \quad (20)$$

The corresponding dissolution times t(x%) (Figure 2) in s, obtained from the the conductivity vs. time graph, are given as the result.

NOTE When using other equipment than that described in 6.11.4 it should be ensured that the homogenization time mentioned in 6.11.5.2 is reached. For the determination of the homogenization time the volume of the suspension should be such that the end conductivity reaches (900 ± 50) µS/cm.



Key

- 1 conductivity in $\mu\text{m}/\text{cm}$
- 2 time in s

Figure 2 — Conductivity vs. time graphs for 3 samples of milk lime

6.12 Calculation of the composition of a commercial product

6.12.1 General

In order to assess whether the analytical results meet the requirements set in EN 12518 for high-calcium lime, in EN 1018 for calcium carbonate, in EN 1017 for half-burnt dolomite, in prEN 16004 for magnesium oxide and in prEN 16003 for calcium magnesium carbonate, the results have to be converted to the form in which the requirements are stated in the above standards.

6.12.2 Calculations

6.12.2.1 Values for calcium carbonate

The requirement values for calcium carbonate shall be expressed in dry substance in accordance with EN 1018. The content of calcium carbonate, (CaCO_3) in %, and the sum of the contents of calcium carbonate and magnesium carbonate, $(\text{CaCO}_3) + (\text{MgCO}_3)$ in %, are given by the following equations:

$$(\text{CaCO}_3) = 1,7848 \times c(\text{CaO}) \tag{21}$$

$$(\text{CaCO}_3 + \text{MgCO}_3) = 1,7848 \times (\text{CaO}) + 2,092 \times (\text{MgO}) \tag{22}$$

where

(CaO) is the content of CaO in % as in 6.9.6;

(MgO) is the content of MgO in % as in 6.9.6.

6.12.2.2 Values for calcium magnesium carbonate

The requirement values for calcium magnesium carbonate shall be expressed in dry substance in accordance with prEN 16003. The content of calcium magnesium carbonate, $(\text{CaMg}(\text{CO}_3)_2)$ in % and the content of magnesium carbonate, (MgCO_3) in %, are given by the following equations:

$$(\text{CaMg}(\text{CO}_3)_2) = 4,5753 \times (\text{MgO}) \quad (23)$$

$$(\text{MgCO}_3) = 2,092 \times (\text{MgO}) \quad (24)$$

where

(MgO) is the content of MgO in % as in 6.9.6 or in 7.2.8.2.

6.12.2.3 Values for half-burnt dolomite

The requirement values for free MgO and free $\text{Mg}(\text{OH})_2$ shall be expressed as free MgO in accordance with EN 1017. According to 3.2, the chemical analysis of CaO, MgO, CO_2 and CaO_{free} shall be performed on the bound-water free substance. According to EN 1017, both the content of calcium carbonate, (CaCO_3) in %, and the content of free magnesium oxide and magnesium hydroxide, $(\text{MgO}_{\text{free}})$ in %, shall be calculated. The content of calcium carbonate is given by subtracting $(\text{CaO}_{\text{free}})$ (6.8.6) from (CaO) (6.9.6) and the content of magnesium carbonate by subtracting the proportion of CO_2 accounted for by (CaCO_3) in % from (CO_2) in % (6.3.5). Finally, the content of free magnesium oxide and magnesium hydroxide is given by subtracting the proportion of MgO accounted for by MgCO_3 in % from (MgO) in % (6.9.6 or 7.2.8.2).

The constituents is given by the following equations:

$$(\text{CaCO}_3) = [(\text{CaO}_{\text{total}}) - (\text{CaO}_{\text{free}})] \times 1,7848 \quad (25)$$

$$(\text{MgCO}_3) = [(\text{CO}_2) - (\text{CaCO}_3) \times 0,4397] \times 1,9158 \quad (26)$$

$$(\text{MgO}_{\text{free}}) = (\text{MgO}_{\text{total}}) - (\text{MgCO}_3) \times 0,478 \quad (27)$$

where

$(\text{CaO}_{\text{total}})$ is the content of CaO as in 6.9.6 in %;

$(\text{MgO}_{\text{total}})$ is the content of MgO as in 6.9.6 or in 7.2.8.2 in %;

$(\text{CaO}_{\text{free}})$ is the content of free CaO as in 6.8.6 in %;

(CO_2) is the content of CO_2 as in 6.3.5 in %.

6.12.2.4 Values for high-calcium lime

The requirement values for hydrated high-calcium lime and for milk of lime shall be expressed in dry substance in accordance with EN 12518. The content of calcium carbonate in high-calcium lime products shall be calculated.

The content of calcium carbonate, (CaCO₃), is given by the following equation:

$$(\text{CaCO}_3) = 2,2742 \times (\text{CO}_2) \quad (28)$$

where

(CO₂) is the content of CO₂ as in 6.3.5 in %.

6.12.2.5 Values for magnesium oxide

The content of magnesium oxide shall be expressed as (MgO) in % in dry substance in accordance with prEN 16004. According to 3.2, the chemical analysis of MgO shall be performed on the bound-water free substance. The loss on ignition shall be expressed as the sum of (CO₂ and H₂O) in %, using the value for the loss on ignition at (1 000 ± 50) °C from 6.3.5 and the value for the loss on ignition at (450 ± 25) °C from 6.2.5.

7 Determination of constituents by modern techniques

7.1 Determination of minor constituents by AAS flame technique

7.1.1 General

The method is suitable for determining:

- less than 1 % by mass of magnesium oxide in calcium carbonate;
- silicon, aluminium, iron and manganese in high-calcium limes; and
- silicon, aluminium and iron in half-burnt dolomite and in magnesium oxide;

as specified in EN 1017, EN 1018, EN 12518 and prEN 16004.

To carry out the determination, the test solution is injected either into the ethyne (C₂H₂)/air flame or the ethyne/dinitrogen monoxide (N₂O) flame of an atomic absorption spectrometer, a check being made to ensure that the absorption signal is proportional to the concentration of the element in the test solution over a certain range.

Accompanying minor components in the sample material can suppress the absorption signal when an ethyne/air flame is used for the determination. Most interferences in the measured signal can be eliminated by adding a spectrochemical buffer to the sample and reference solutions. The element to be determined can be prevented from forming a thermally stable compound which is consequently difficult to dissociate by adding lanthanum oxide as a scavenger since lanthanum reacts preferentially with interfering anions from the matrix. Interference due to ionization can be expected if an ethyne/dinitrogen monoxide flame is used for the determination since a larger proportion of the atoms of the element to be determined are ionized at the higher temperatures. Alkali metal salts can be used as an ionization buffer if this occurs.

Transport interferences which affect nebulization of the sample and its transport into the flame shall be corrected by matching the matrix of the test solution and that of the comparison solutions used for the calibration.

A releasing agent, an ionization suppressant and a calcium matrix solution are added one after the other to the digestion solutions I (5.1) and the appropriate reference solutions, and the mixtures are diluted to the required test solution volume with water.

Table 3 lists the type of flame, the measurement wavelengths and the concentration ranges in which direct determination of the individual constituents of the digestion solution is possible. If the specified concentration

range is exceeded, the digestion solution shall be diluted, but the additions of releasing agent and ionisation suppressant shall be increased to maintain the required concentrations.

Table 3 — Types of flame, wavelength and concentration range

Element	Flame gas mixture	Measurement wavelength nm	Concentration range mg/l
Mg	Air/C ₂ H ₂	202,6	<i>c</i> (Mg) 2 to 20
Si	N ₂ O/C ₂ H ₂	251,6	<i>c</i> (Si) 5 to 50
Al	N ₂ O/C ₂ H ₂	309,3	<i>c</i> (Al) 2 to 5
Fe	Air/C ₂ H ₂	248,3	<i>c</i> (Fe) 1 to 5
Mn	Air/C ₂ H ₂	279,5	<i>c</i> (Mn) 0,2 to 2

7.1.2 Reagents

7.1.2.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

7.1.2.2 Calcium carbonate, c (CaCO₃) = 99,9 % (m/m) (dried at 150 °C).

7.1.2.3 Lanthanum oxide, La₂O₃.

7.1.2.4 Caesium chloride, CsCl.

7.1.2.5 Matrix solution, calcium – lithium tetraborate c (Ca²⁺) \approx 2,5 g/l, c (Li₂B₄O₇) \approx 30 g/l, prepared from calcium carbonate and lithium tetraborate, melt about 6,25 g of calcium carbonate (7.1.2.2) in portions with about 30 g of lithium tetraborate (5.1.3.1) at (1 000 \pm 50) °C. Cool and add carefully 170 ml of hydrochloric acid (7.1.2.1) to the cold melt in an appropriate beaker. Cover the beaker and dissolve while stirring and heating. Cool the solution and make it up with water to 1 l in a volumetric flask.

7.1.2.6 Releasing agent solution, prepared by dissolving 23,5 g of lanthanum oxide (7.1.2.3) in 200 ml of hydrochloric acid (7.1.2.1) and making up to 1 l with water.

7.1.2.7 Ionization suppressant solution, prepared by dissolving 25 g of caesium chloride (7.1.2.4) in a small amount of hydrochloric acid (7.1.2.1) and making up to 1 l with water.

7.1.2.8 Element stock solution [c (Mg, Si, Al, Fe, Mn) = 1 g/l].

7.1.2.9 Standard element solutions:

— **standard element solution I** [c (Mg, Si) = 100 mg/l, c (Mn) = 10 mg/l, prepared by making 10 ml of Mg and Si stock solution (7.1.2.8) and 1 ml of Mn stock solution (7.1.2.8) up to the mark with water in a 100 ml volumetric flask;

— **standard element solution II** [c (Al, Fe) = 100 mg/l], prepared by making 10 ml of Al and Fe stock solution (7.1.2.8) up to the mark with water in a 100 ml volumetric flask.

7.1.2.10 Element reference solutions, prepared by pipetting 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of the standard element solution I and 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of the standard element solution II into a series of five 100 ml volumetric flasks, adding 20 ml of the matrix solution (7.1.2.5) and each 10 ml of the two buffer solutions (7.1.2.6 and 7.1.2.7) to each of the flasks, making up to the mark with water and shaking well. The concentrations of each element in the reference solutions are specified in Table 4.

Table 4 — Concentrations of reference solutions

Elements	Concentrations, c (EI) mg/l				
	Mg	1	2	5	10
Si	1	2	5	10	20
Al	1	2	3	4	5
Fe	1	2	3	4	5
Mn	0,1	0,2	0,5	1	2

7.1.2.11 Blank solution for calibration, prepared in the same way as the reference solutions, but omitting the solutions of the elements.

7.1.2.12 Test blank solution, prepared in the same way and with the same reagents in parallel with the test solutions, but not containing sample substances.

7.1.3 Apparatus

Ordinary laboratory apparatus and the following:

7.1.3.1 Atomic absorption spectrometer equipped:

- for operation with an ethyne/air flame and an ethyne/dinitrogen monoxide flame;
- a background compensator; and
- a hollow cathode lamp or electrodeless discharge lamp as radiation source for determining the element concerned.

7.1.3.2 Air, ethyne and dinitrogen monoxide gas supply.

7.1.4 Interferences

In the case of flame AAS, the only significant spectral interference is background absorption caused by the scattering of radiation by particles. It can be eliminated by using a suitable background correction.

In the determination of magnesium, aluminium, iron and manganese, a lanthanum salt is added to the test and calibration solutions to correct chemical interferences from thermally stable compound formation. Any interferences due to ionization in the ethyne/dinitrogen monoxide flame are eliminated by adding caesium salts to the test and calibration solutions.

Transport interferences can be due to various physical properties of the test and reference solution, errors in measurement being caused by differences in density, viscosity, surface tension and temperature. These parameters affect the size distribution of the droplets in the aerosol during nebulization, thereby delaying the evaporation of particles. Such interferences shall be corrected by matching the matrix of the test solution to that of the reference solutions used for calibration.

7.1.5 Procedure

7.1.5.1 Spectrometer settings

Before starting the determination, set the operating parameters of the spectrometer as stated in the operating manual issued by the manufacturer. Pay particular attention to optimizing the nebulizer, the flame conditions and the lamp adjustment. Operate the spectrometer with the background correction adjusted to the optimum wavelength for each element (see Table 3).

7.1.5.2 Calibration

Optimize the nebulizer, the burner and the flame conditions using a reference solution and zero the equipment by injecting water into the flame. Then carry out the calibration by injecting the blank solution (7.1.2.11) and the five reference solutions (7.1.2.10) in ascending order of concentration into the flame. Record the measured values and check the zero after every reference solution.

7.1.5.3 Determination

Measure the blank solution (7.1.2.12) and the test solutions in two measurement series, ensuring that measurement is carried out in the linear part of the calibration graph (7.1.6.1). If the analytical value obtained for the test solution is beyond the range of validity of the reference curve, dilute the digestion solution accordingly. After each series of test solutions, and in any case after not more than 10 to 20 measurements, use the blank solution and a reference solution to check whether the absorbance values measured still agree with the calibration graph. If this is not the case, recalibrate and repeat the readings made since the previous successful calibration check.

7.1.6 Calculation and expression of results

7.1.6.1 Calibration graph

Determine the calibration function by a regression calculation based on the measured data for the reference solutions, averaging the absorption values for the respective concentrations. Alternatively, carry out a graphical evaluation using a calibration graph, use graph paper to plot the absorbances corrected for the blank value along the vertical axis against the concentration values of the respective element reference solutions in milligrammes per millilitre plotted along the horizontal axis. Computer data handling systems can also be used.

7.1.6.2 Expression of results

The content of the element to be determined in the sample expressed as the element oxide (El_xO_y) in mass fraction in % is given by the following general equation:

$$(\text{El}_x\text{O}_y) = \frac{(c(\text{El}) - c(\text{El})_b) \times V_1 \times V_3 \times F \times 100}{1000 \times 1000 \times V_2 \times m} \quad (29)$$

where

- $c(\text{El})$ is the concentration of the element to be determined in the test solution, in milligrams per litre;
- $c(\text{El})_b$ is the concentration of the element to be determined in the test blank solution, in milligrams per litre;
- V_1 is the volume of the digestion solution I (5.1), in millilitres;
- V_2 is the volume of digestion solution taken to prepare the test solution, in millilitres;
- V_3 is the volume of the test solution, in millilitres;
- F is a factor for converting to El_xO_y ;
- m is the mass, in grams, of the test portion (5.1).

The calculation for the individual constituents is as follows:

$$(\text{MgO}) = \frac{c(\text{Mg}) \times V_3 \times 0,0415}{V_2 \times m} \quad (30)$$

$$(\text{SiO}_2) = \frac{c(\text{Si}) \times V_3 \times 0,053475}{V_2 \times m} \quad (31)$$

$$(\text{Al}_2\text{O}_3) = \frac{c(\text{Al}) \times V_3 \times 0,04724}{V_2 \times m} \quad (32)$$

$$(\text{Fe}_2\text{O}_3) = \frac{c(\text{Fe}) \times V_3 \times 0,03575}{V_2 \times m} \quad (33)$$

$$(\text{MnO}_2) = \frac{c(\text{Mn}) \times V_3 \times 0,03957}{V_2 \times m} \quad (34)$$

7.2 Determination of major and minor constituents by ICP-OES

7.2.1 General

The method is suitable for determining:

- magnesium in calcium carbonate, in calcium magnesium carbonate, in magnesium oxide and in half-burnt dolomite;
- silicon, aluminium, iron and manganese in high-calcium limes;
- silicon, aluminium, iron and sulfur in half-burnt dolomite; and
- silicon, aluminium and iron and in magnesium oxide

as specified in EN 1017, EN 1018, EN 12518, prEN 16004 and prEN 16003.

An inductively coupled plasma (ICP) is the excitation source most widely used in optic emission spectrometry. To generate the plasma, a gas (argon) is ionized by passing it through a quartz tube in which a field is produced by an induction coil mounted around the tube and connected to a high-frequency generator. A nebulizer is used to nebulize the test solution in an argon carrier-gas stream which transports the aerosol axially into the plasma. A very high degree of excitation is achieved at the temperatures of 6 000 K to 8 000 K prevailing in the plasma so that the excited atoms are made to emit their characteristic emission spectrum. The light emitted is projected through the entrance slit onto the disperser of a monochromator or polychromator in order to separate the analytical line from adjacent spectral lines of other elements.

A monochromator driven by a stepping motor is employed for sequential multi-element determination, the grating traversing the corresponding element wavelengths in sequence. For simultaneous multi-element determination, entrance slit, concave grating and exit slits are mounted in fixed positions on the Rowland circle, spectral dispersion of the polychromatic radiation and focusing being achieved at the same time. The intensity of the element lines is amplified to produce an electric current using photomultipliers and converted to concentration units.

In contrast to AAS, there is a linear relationship in OES between the intensity of the emission line and the element concentration over several powers of ten.

Table 5 summarizes the elements to be determined, the emission lines frequently used and the limits of determination.

Table 5 — Measurement wavelength, lower limit of determination

Element	Element line nm	Compound	Lower limit of determination, in %
Al	308,215	Al ₂ O ₃	0,02
	396,152		0,02
Fe	259,940	Fe ₂ O ₃	0,02
Mg	279,079	MgO	0,5
	279,553		0,01
Mn	257,610	MnO ₂	0,005
S	182,040	SO ₄ ²⁻	0,05
Si	251,611	SiO ₂	0,05
	212,412		0,1
	288,158		0,1

7.2.2 Reagents

7.2.2.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

7.2.2.2 Scandium solution (internal standard) c (Sc) = 1 g/l.

7.2.2.3 Element stock solutions c (Mg, Al, Fe, Si, Mn, SO₄) = 1 g/l.

7.2.2.4 Standard multi-element solution

Standard multi-element solution c (Mg, Si, Al, Fe) = 50 mg/l; c (SO₄) = 150 mg/l, c (Mn) = 10 mg/l, prepared by making up 50 ml of each of the Mg, Al, Fe, Si stock solutions (7.2.2.3), 150 ml of the SO₄ stock solution (7.2.2.3) and 10 ml of the Mn stock solution (7.2.2.3) together with 10 ml of hydrochloric acid (7.2.2.1) to 1 l with water in a 1 l volumetric flask.

7.2.2.5 Element reference solutions, prepared by pipetting 1 ml, 2 ml, 10 ml, 20 ml and 40 ml of the standard solution (7.2.2.4) into a series of five 100 ml volumetric flasks and adding 20 ml of matrix solution (7.1.2.5) into each volumetric flask. To carry out determinations using an internal standard, pipette 0,4 ml of the scandium solution (7.2.2.2) into each volumetric flask. Make up to the mark with water and shake well. The concentrations of each element in the reference solutions are specified in Table 6.

Table 6 — Concentrations of reference solutions

Element	Concentrations c (EI) in mg/l				
	0,5	1	5	10	20
Mg	0,5	1	5	10	20
Si	0,5	1	5	10	20
Al	0,5	1	5	10	20
Fe	0,5	1	5	10	20
SO ₄ ²⁻	1,5	3	15	30	60
Mn	0,1	0,2	1	2	4

7.2.2.6 Blank solution for calibration, prepared in the same way as the reference solutions but omitting the solutions of the elements.

7.2.2.7 Test blank solution, prepared in the same way and with the same reagents in parallel with the test solutions, but not containing sample substances.

7.2.3 Apparatus

Ordinary laboratory apparatus and the following:

7.2.3.1 Atomic emission spectrometer equipped with:

- inductively coupled plasma;
- suitable pneumatic nebulizer system;
- background compensation system; and
- computer system for instrument control and data processing.

7.2.3.2 Argon gas supply.

7.2.4 Spectral interferences

7.2.4.1 Line coincidences

This interference occurs when spectral lines overlap. Figure 3 shows spectral interference with the sulfur line at 180,734 nm due to 500 mg/l of calcium. A line coincidence will often only be noticed when the ratio of the concentrations of interfering element and analyte is high.

7.2.4.2 Band coincidences

Polyatomic species (OH^- , N_2^+ , NO^+) formed in the plasma from the accompanying matrix can emit bands which coincide with the analyte lines.

7.2.4.3 Background effects

The spectral background is due to recombination continua and is strongly dependent on the matrix. Thus, Figure 4 shows the effect of 500 mg/l of calcium on the aluminium line at 396,152 nm.

7.2.4.4 Line reversal

An increase in the concentration of an element in the cooler outer zones of a plasma results in the radiation from the element in the hot zones being absorbed and a reduction in the intensities.

7.2.4.5 Spurious radiation

This is radiation which is not element-specific and is due to scattering from other lines.

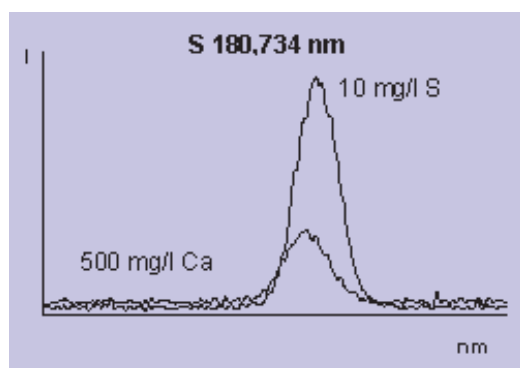


Figure 3 — Spectral interference with the sulfur line at 180,734 nm due to calcium

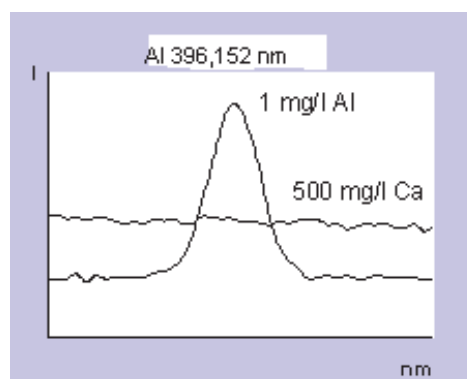


Figure 4 — Spectral background imposed on the aluminium line at 396,152 nm by calcium as a matrix element

7.2.5 Non spectral interferences

7.2.5.1 Interference due to physical properties of solutions

Differences between reference and test solutions due to viscosity, surface tension or density can affect the nebulization characteristics and the aerosol transport.

7.2.5.2 Interference due to sediments

Crystallization can occur in the nebulizer system as a result of high salt concentrations in the solutions.

7.2.5.3 Interference due to entrainment

Residues in the test solution feed system can result in measurement errors (memory effect).

7.2.6 Methods of eliminating or reducing interferences

7.2.6.1 Spectral interferences

Line interference can be overcome by switching to a line which is not subject to interference. For this reason, sulfur determination shall be carried out using the less sensitive line at 182,040 nm. A mathematical correction can be made for the effect of the interfering element in the regression program.

The spectral background shall be measured using a rotatable quartz refractor plate in the beam path. If the sample matrix is expected to give a constant spectral background, it will be sufficient to measure the background imposed on the analyte line using a matrix-matched blank solution.

7.2.6.2 Non spectral interferences

Interferences due to differences in the physical properties of test and reference solutions can be compensated for by matrix matching. Since different digestion reagents are used to analyse lime products and the calcium concentrations in the individual products vary, it is advisable to use an internal standard when carrying out determinations.

7.2.7 Procedure

7.2.7.1 Spectrometer settings

Before starting the determination, set the operating parameters of the spectrometer as stated in the operating manual issued by the manufacturer. Pay particular attention to optimizing the nebulizer and the plasma conditions, to reprofiling the optics and to checking the stability of the spectrometer. Specify the positions at which the background is to be measured in drawing up the analysis program.

7.2.7.2 Calibration

Plot a calibration graph for every element to be determined at the start of the analysis. To carry out the baseline calibration, inject the blank solution (7.2.2.6) and the five reference solutions (7.2.2.5) in order of ascending concentration into the plasma. Flush the system with the blank solution after injecting each reference solution. The calibration function will be automatically determined by the computer unit.

7.2.7.3 Determination using an internal standard

It is recommended that this method be used if differences between test and reference solutions in terms of viscosity, surface tension and density cannot be eliminated. The internal standard used will preferably be an element which is not present in the analytical solution, such as lanthanum (408,670 nm), scandium (361,380 nm) or yttrium (371,030 nm). In this document, the internal standard recommended is scandium. To carry out determinations using an internal standard, add 0,4 ml and 1 ml of scandium solution (7.2.2.2) to the reference solutions and test solutions, respectively, before making up to the final volume.

7.2.7.4 Determination

At the beginning of every measurement series, check the baseline calibration by means of a two-point recalibration using the blank solution and the reference solution with the highest concentration. If permitted instrument errors in the factors concerned are exceeded, discontinue the determination in order to determine the cause and repeat the calibration using freshly prepared calibration solutions.

Verify the quality of the recalibration by checking that the analytical results for a control sample do not differ by more than 5 % from the true concentration of the solution. If greater errors are encountered, repeat the recalibration. It is advisable to use a certified standard solution or a solution prepared from certified lime material as control sample.

Carry out the determination of the test solutions in duplicate, flushing the test solution feed system between individual determinations to eliminate any memory effects. After each series of test solutions, and in any case after not more than 10 to 20 determinations, carry out a fresh recalibration with the two standards and check it with the control sample.

7.2.8 Calculation and expression of results

7.2.8.1 Calibration graph

Determine the calibration function by a computerized regression calculation based on the measured data for the reference solutions. Alternatively, plot the measured intensities, or if an internal standard is used, the intensity ratios (ratio of the measured intensity of the element to the measured intensity of the internal standard) against the respective concentrations, correcting the intensity values for the blank value or the background intensities.

7.2.8.2 Expression of results

The content of the element to be determined in the sample expressed as the element oxide (EI_xO_y), in mass fraction in % is given by the following general equation:

$$(El_xO_y) = \frac{(c(El) - c(El)_b) \times V_2 \times F \times 100}{1000 \times 1000 \times m} \quad (35)$$

where

$c(El)$ is the concentration, in milligrams per litre, of the element to be determined in the test solution;

$c(El)_b$ is the concentration, in milligrams per litre, of the element to be determined in the test blank solution;

V_2 is the volume, in millilitres, of the digestion solution II (5.1);

F is a factor for converting to El_xO_y ;

m is the mass, in grams, of the test portion (5.1).

The calculations for the individual constituents are as follows:

$$c(MgO) = \frac{c(Mg) \times 0,0415}{m} \quad (36)$$

$$c(SiO_2) = \frac{c(Si) \times 0,053475}{m} \quad (37)$$

$$c(Al_2O_3) = \frac{c(Al) \times 0,04724}{m} \quad (38)$$

$$c(Fe_2O_3) = \frac{c(Fe) \times 0,03575}{m} \quad (39)$$

$$c(MnO_2) = \frac{c(Mn) \times 0,03957}{m} \quad (40)$$

$$c(SO_4^{2-}) = \frac{c(SO_4^{2-}) \times 0,025}{m} \quad (41)$$

8 Determination of trace elements

8.1 Determination of lead, cadmium, chromium and nickel by AAS graphite tube technique

8.1.1 General

The method is suitable for determining lead, cadmium, chromium and nickel in calcium carbonate as specified in EN 1018, in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017, in calcium magnesium carbonate as specified in prEN 16003 and in magnesium oxide as specified in prEN 16004.

The elements to be examined are converted to the atomic state by thermal dissociation in an electrically heated graphite tube of an atomic absorption spectrometer. As the temperature is raised in steps, the stages of drying, thermal decomposition of the matrix and thermal cleavage into free atoms are passed through in that order. The measurement signal obtained shall be a sharp peak whose area is proportional to the concentration of the element in the test solution over a certain range.

The injection of the test solution IV (5.3) or V (5.4) into the graphite tube is controlled by the apparatus and measurement is carried out at a wavelength specific to the element (Table 7). The concentrations of the element to be examined shall be covered by the ranges specified in Table 7, but if the concentration range specified is exceeded, the digestion solution shall be diluted accordingly.

Table 7 — Measurement wavelength, concentration range

Element	Measurement wavelength nm	Concentration range $\mu\text{g/l}$
Pb	283,3	c (Pb) 10 to 100
Cd	228,8	c (Cd) 1 to 5
Cr	357,9	c (Cr) 5 to 50
Ni	232,0	c (Ni) 5 to 50

8.1.2 Reagents

8.1.2.1 Nitric acid, $\rho = 1,40$ g/ml.

8.1.2.2 Calcium carbonate, c (CaCO_3) = 99,9 % (*m/m*) (dried at 150 °C).

8.1.2.3 Calcium matrix solution, c (Ca^{2+}) ≈ 4 g/l, prepared by making a slurry of about 10 g of calcium carbonate (8.1.2.2) and about 100 ml of water in a 500 ml beaker and by carefully adding 80 ml of nitric acid (8.1.2.1) while stirring. After the calcium carbonate has dissolved completely, remove the carbon dioxide by boiling, then allow the solution to cool and make it up with water to 1 l in a volumetric flask.

8.1.2.4 Element stock solution [c (Pb, Cd, Cr, Ni) = 1 g/l].

8.1.2.5 Standard element solution I c (Pb, Cd, Cr, Ni) = 10 mg/l, prepared by making 10 ml of stock solution (8.1.2.4) up to the mark with 1 ml of nitric acid (8.1.2.1) and water in a 1 l volumetric flask.

8.1.2.6 Standard element solutions II:

- standard lead solution II c (Pb) = 1 mg/l, prepared by making 10 ml of the standard element solution I (8.1.2.5) up to the mark with 1 ml of nitric acid (8.1.2.1) and water in a 100 ml volumetric flask;
- standard chromium and nickel solution II c (Cr, Ni) = 0,5 mg/l, prepared by making 5 ml of the standard element solution I (8.1.2.5) up to the mark with 1 ml of nitric acid (8.1.2.1) and water in a 100 ml volumetric flask;
- standard cadmium solution II c (Cd) = 0,1 mg/l, prepared by making 10 ml of standard cadmium solution I (8.1.2.5) up to the mark with 1 ml of nitric acid (8.1.2.1) and water in a 1 l volumetric flask.

8.1.2.7 Element reference solutions, prepared by pipetting the volumes from Table 8 into a series of 100 ml volumetric flasks, adding 50 ml of the matrix solution (8.1.2.3) to each of the flasks, making up to the mark with water and shaking well.

Table 8 - Volumes and concentration of reference solutions

Elements	Volumes from standard element solutions II ml					Concentrations, c (EI) µg/l				
	Pb	1	2	5	8	10	10	20	50	80
Cr	1	2	4	6	10	5	10	20	30	50
Ni	1	2	4	6	10	5	10	20	30	50
Cd	1	2	5	8	10	1	2	5	8	10

8.1.2.8 Blank solution for calibration, prepared by making 50 ml of the matrix solution (8.1.2.3) up to the mark with water in a 100 ml volumetric flask.

8.1.2.9 Test blank solution, prepared in the same way and with the test reagents in parallel with the test solutions, but without using sample substance.

8.1.3 Apparatus

Ordinary laboratory apparatus and the following:

8.1.3.1 Atomic absorption spectrometer equipped with:

- graphite tube furnace and controller;
- hollow cathode lamp or electrodeless discharge lamp as radiation source for determining the element concerned, the current supply to the lamp being set in accordance with the manufacturer's instructions;
- background compensator; and
- auto-sampler, capable of being adjusted to pipetting volumes from 5 µl to 20 µl.

8.1.4 Interferences

Any interferences due to background absorption resulting from high salt concentrations can be suppressed with the background correction system, but it shall be borne in mind that the application of continuum sources is limited and relatively high background signals can be compensated for by Zeeman or Smith-Heifje background correction.

The limit of detection for the individual elements can be improved by suitable matrix modifiers (accompanied by carefully developed temperature programs), by applying the platform technique or by using tubes coated with pyrolytic graphite. Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) is used for matrix modification in the case of chromium, and diammonium hydrogenphosphate ($(\text{NH}_4)_2\text{HPO}_4$) and magnesium nitrate in the case of lead and cadmium. Any interferences due to carbide formation can be eliminated by using suitably coated tube materials. In many cases, matrix effects can be compensated for by using the standard addition method of analysis (8.1.6).

Because of the high sensitivity of electrothermal atomic absorption, it is necessary to pay attention to the cleanliness of the glassware used and to avoid contamination of the test and standard solutions with foreign material and dust from the laboratory air.

8.1.5 Procedure

8.1.5.1 Spectrometer setting

Before starting the analysis, adjust the operating parameters of the spectrometer in accordance with the operating manual issued by the manufacturer and align the atomization unit in the beam path. Operate the spectrometer with the background correction switched on at the wavelength specified for each element (Table 7). Also optimize the auto-sampler and adjust it to the appropriate pipetting volume. Key the furnace cycle into the temperature control system. Ensure that the solutions are always in the same temperature range. Check the stability of the zero by analysing water between the reference solutions. At the end of the measurement series, run through the temperature program without a sample to check for memory effects and repeat this procedure to ensure that the base line is stable.

8.1.5.2 Calibration and analysis of test solution by the calibration curve method

First zero the spectrometer using water. To plot the calibration function, pipette certain volumes (5 μl to 20 μl) of the blank solution (8.1.2.8), of the reference solutions (8.1.2.7) and of the test solutions into the graphite tube for analysis using the auto-sampler. Arrange the reference solutions in an ascending order of concentration and the test solutions in groups having similar analyte contents so that the analysis starts at the lowest concentrations. Atomize the test solution and record the reading on the spectrometer. If the peak height or peak area of the test solution exceeds the value of the calibration solution with the maximum concentration, dilute the test solution.

Perform the analysis of the test solutions in duplicate and, if the reproducibility is within the standard deviation range (see Annex B), average the measurements. After each series of test solutions, and in any case after not more than 10 to 20 measurements, use the test blank solution and a reference solution to check whether the measured values still agree with the calibration graph.

8.1.5.3 Analysis of the test solution by the standard addition method

If the matrix formed by the sample in the test solution is expected to cause interferences, these shall be compensated for by the standard addition method. For this purpose, divide the test solution into four aliquots and add equal volumes of three reference solutions. The standard solutions added contain different concentrations of the element. Dilute the fourth aliquot of the test solution with an equivalent amount of water. When thoroughly mixed, all the test solutions have the same matrix composition, with the result that the effect of accompanying substances on the element to be determined is the same in all the solutions. Ensure that the test solutions with the standard additions are analysed in the linear working range.

Adopt the same procedure for the test blank solution.

8.1.6 Calculation and expression of results

8.1.6.1 Calibration graph

For the purpose of graphical evaluation using a calibration graph, use graph paper to plot the concentrations (after correcting for the blank value) of the element reference solutions (8.1.2.7), in micrograms per litre, on the horizontal axis and the associated peak heights or peak areas on the vertical axis. The graph obtained will normally be linear.

8.1.6.2 Calculation by the calibration graph method

Use the calibration line (8.1.6.1) to determine the concentration of the element, in micrograms per millilitre, in the test solution and in the test blank solution (8.1.2.9) from the absorbance values.

The content of the element, (EI), expressed in milligrams per kilogram of products is given by the following equation:

$$(El) = \frac{(A_{El} - A_{Elb}) \times V}{f_1 \times b \times m} \quad (42)$$

where

A_{El} is the peak height or peak area of the test solution;

A_{Elb} is the peak height or peak area of the test blank solution;

V is the volume, in millilitres, of the test solution IV (5.3) or V (5.4);

f_1 is a factor for converting, 1000 ml/l;

b is the slope of the calibration function ($\Delta A_{El}/\Delta A_{Elb}$), in litres per microgram (this is a measure of the sensitivity of the method);

m is the mass, in grams, of the test portion (5.3 or 5.4).

8.1.6.3 Calculation by the standard addition method

For the purpose of graphical evaluation use graph paper to plot the peak areas or peak heights on the vertical axis against the individual concentrations in the test solutions with standard additions on the horizontal axis. When a straight regression line is drawn through the points, it will intercept the horizontal axis on the negative side. The concentration of the element, in micrograms per litre, in the test solution is given by the distance of the intercept from the origin (Figure 5). Ensure that the test solutions with standard additions do not fall outside the linear working range of the calibration graph.

Adopt the same procedure for the test blank solution (Figure 6).

The content of the element, (El), expressed in milligrams per kilogram of products, from the concentrations in the test and blank solutions determined graphically is given by the following equation:

$$(El) = \frac{(c(El)_t - c(El)_b) \times V}{f_2 \times m} \quad (43)$$

where

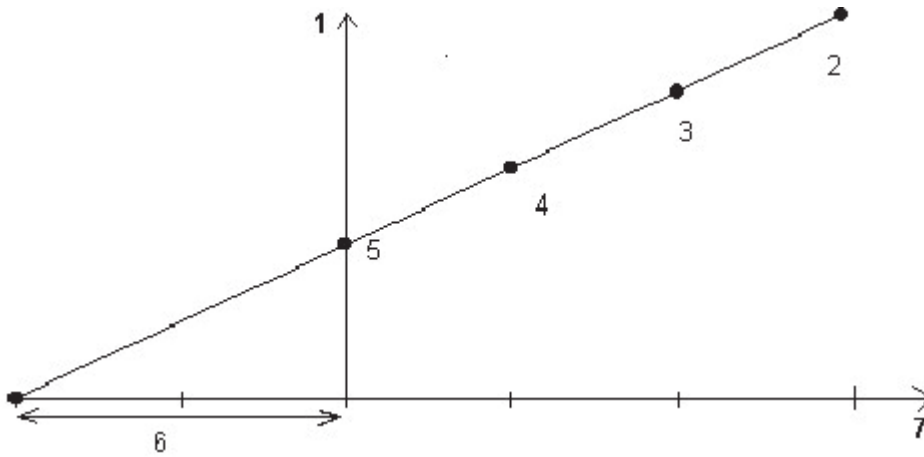
$c(El)_t$ is the concentration, in micrograms per litre, in the test solution;

$c(El)_b$ is the concentration, in micrograms per litre, in the test blank solution;

V is the volume, in millilitres, of the test solution IV (5.3) or V (5.4);

f_2 is a factor for converting, 1 l/l;

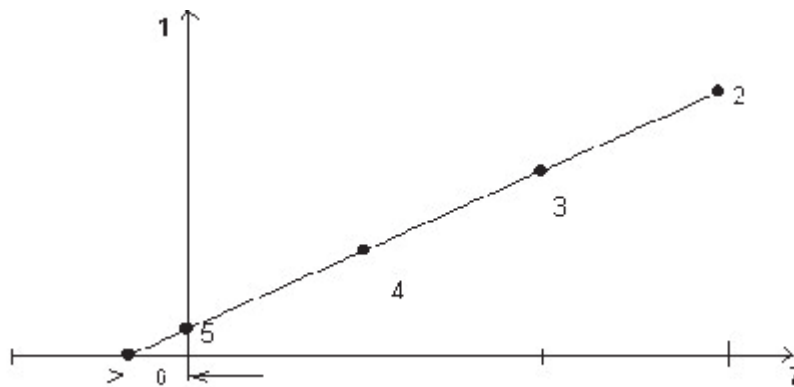
m is the mass, in grams, of the test portion (5.3 or 5.4).



Key

- 1 absorbance A
- 2 standard addition
- 3 standard addition
- 4 standard addition
- 5 test solution
- 6 concentration in the test solution
- 7 concentration in micrograms per litre

Figure 5 — Calculation of the metal contents in the test solution



Key

- 1 absorbance A
- 2 standard addition
- 3 standard addition
- 4 standard addition
- 5 blank solution
- 6 concentration in the test blank solution
- 7 concentration in micrograms per litre

Figure 6 — Calculation of the metal contents in the test blank solution

8.2 Determination of lead, cadmium, chromium and nickel by ICP-OES

8.2.1 General

The method is suitable for determining lead, cadmium, chromium and nickel in calcium carbonate as specified in EN 1018, in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017, in calcium magnesium carbonate as specified in prEN 16003 and in magnesium oxide as specified in prEN 16004.

The principle of operation of the spectrometer is described in 7.2.1.

If the digestion method described in 5.3 or 5.4 is used, the proportions by mass of the trace elements shall not be below the limits of determination specified in Table 9. Since greater test portion masses can be used for the ICP method than for the AAS method, amounts of sample material greater than 0,5 g can be digested, resulting in an improvement of the limits of determination for solids content.

Producing the sample aerosol by means of an ultrasonic nebulizer instead of a pneumatic one generally results in limits of detection which are lower by a power of 10. However, this is no longer the case if the matrix concentration is high and in such cases greater test portion masses are to be preferred. Table 9 summarizes the frequently used emission lines and limits of determination for the elements to be determined.

Table 9 — Measurement wavelength, limit of determination

Element	Measurement wavelength nm	Limit of determination mg/l	Limit for a test portion	
			0,5 g	3 g
			mg/kg	
Pb	220,253	0,1	20	3
Cd	214,438	0,01	2	0,5
	226,502	0,01	2	0,5
	228,802	0,01	2	0,5
Cr	267,716	0,05	10	2
	283,563	0,05	10	2
	284,325	0,05	10	2
Ni	231,604	0,1	20	3

8.2.2 Reagents

8.2.2.1 Nitric acid, $\rho = 1,40$ g/ml.

8.2.2.2 Scandium solution (internal standard) $c(\text{Sc}) = 1$ g/l.

8.2.2.3 Calcium matrix solution for ICP-OES, $c(\text{Ca}^{2+}) \approx 40$ g/l, prepared by making a slurry of about 100 g of calcium carbonate (7.1.2.2) and about 100 ml of water in a 500 ml beaker and by carefully adding 200 ml of nitric acid (8.2.2.1) while stirring. After the calcium carbonate has dissolved completely, remove the carbon dioxide by boiling, then allow the solution to cool and make it up with water to 1 l in a volumetric flask.

8.2.2.4 Element stock solution $c(\text{Pb, Cd, Cr, Ni}) = 1$ g/l.

8.2.2.5 Standard multi-element solution I $c(\text{Pb, Cd, Cr, Ni}) = 100$ mg/l, prepared by transferring 10 ml of each of the individual element stock solutions (8.2.2.4) to a 100 ml volumetric flask, adding 1 ml of nitric acid (8.2.2.1) and making up to 100 ml with water.

8.2.2.6 Standard multi-element solution II c (Pb, Cd, Cr, Ni) = 10 mg/l, prepared by transferring 10 ml of the standard multi-element solution I (8.2.2.5) to a 100 ml volumetric flask, adding 1 ml of nitric acid (8.2.2.1) and making up to the mark with water.

8.2.2.7 Multi-element reference solutions, prepared by pipetting 1 ml, 5 ml und 10 ml of standard multi-element solution II (8.2.2.6) into a series of three 100 ml volumetric flasks. Add an appropriate quantity of calcium matrix solution (8.2.2.3) to the solutions so that the calcium concentrations in the reference solutions are the same as in the test solutions. To carry out measurements with an internal standard, pipette 0,4 ml of the scandium solution (8.2.2.2) into the volumetric flasks. Make up to the mark with water and shake well. The contents of the elements to determine in the reference solutions are 0,1 mg/l, 0,5 mg/l and 1 mg/l.

8.2.2.8 Blank solution for calibration, prepared by making up 50 ml of the matrix solution (8.2.2.3) to the mark with water in a 100 ml volumetric flask.

8.2.2.9 Test blank solution, prepared in the same way and with the same reagents in parallel with the test solutions, but not containing sample substances.

8.2.3 Apparatus

Ordinary laboratory apparatus and the following:

8.2.3.1 Atomic emission spectrometer equipped with:

- inductively coupled plasma;
- suitable pneumatic nebulizer system;
- a background compensation system; and
- an instrument control and data processing computer system.

8.2.3.2 Argon gas supply.

8.2.4 Spectral interferences

8.2.4.1 Line coincidences

This interference occurs when spectral lines overlap. A line coincidence will often only be noticed when the ratio of the concentrations of interfering element and analyte is high. Thus, if the As concentration is 5 mg/l or more, the arsenic emission at 228,812 nm is spectrally superimposed on the cadmium line at 228,802 nm. High matrix element concentrations also cause spectral interferences.

8.2.4.2 Band coincidences

Polyatomic species (OH^- , N_2^+ , NO^+) formed in the plasma from the accompanying matrix can emit bands which coincide with the analyte lines.

8.2.4.3 Background effects

The spectral background is due to recombination continua and is strongly dependent on the matrix.

8.2.4.4 Line reversal

An increase in the concentration of an element in the cooler outer zones of a plasma results in the radiation from the element in the hot zones being absorbed and a reduction in the intensities.

8.2.4.5 Spurious radiation

This is radiation which is not element-specific and is due to scattering from other lines.

8.2.5 Non spectral interferences

8.2.5.1 Interference due to matrix effects

Acid mixtures containing salts behave differently during aerosol formation and test solution aspiration due to their different viscosities. Different matrix concentrations affect the plasma characteristics and excitation conditions, resulting in changes in signal intensities. For a solution containing 1 mg/l of the trace elements Cd, Cr, Ni and Pb, the signal is reduced to 40 % of the intensity for a pure solution with a calcium matrix of 3000 mg/l (equivalent to a test portion of 0,5 g).

8.2.5.2 Interference due to sediments

Crystallization can occur in the nebulizer system as a result of high salt concentrations in the solutions.

8.2.5.3 Interference due to entrainment

Residues in the test solution feed system can result in measurement errors (memory effect).

8.2.6 Methods of eliminating or reducing interferences

8.2.6.1 Spectral interferences

Line interference can be overcome by switching to a line which is not subject to interference.

The spectral background shall be measured using a rotatable quartz refractor plate in the beam path. If the sample matrix is expected to give a constant spectral background, it will be sufficient to measure the background imposed on the analyte line using a matrix-matched blank solution.

8.2.6.2 Non spectral interferences

Interferences due to differences in the physical properties of test and reference solutions can be compensated for by matrix matching. Since different digestion reagents are used to analyse lime products and the calcium concentrations in the individual products vary, it is advisable to use an internal standard when carrying out determinations.

8.2.7 Procedure

8.2.7.1 Spectrometer settings

Before starting the determination, set the operating parameters of the spectrometer as stated in the operating manual issued by the manufacturer. Pay particular attention to optimizing the nebulizer and the plasma conditions, to reprofiling the optics and to checking the stability of the spectrometer. Specify the positions at which the background is to be measured in drawing up the analysis program.

8.2.7.2 Calibration

Plot a calibration graph for every element to be determined at the start of the analysis. To carry out the baseline calibration, inject the blank solution (8.2.2.8) and the three reference solutions (8.2.2.7) in order of increasing concentration into the plasma. Flush the system with the blank solution after injecting each reference solution. The calibration function will be automatically determined by the computer unit.

8.2.7.3 Determination using an internal standard

It is recommended that this method be used if differences between test and reference solutions in terms of viscosity, surface tension and density cannot be eliminated. This is particularly the case if the test portion is increased to improve the limit of determination of the method, when the standard solutions used for recalibration will have to be matched to the more highly concentrated calcium matrix.

The internal standard used will preferably be an element which is not present in the analytical solution, such as lanthanum (408,670 nm), scandium (361,380 nm) or yttrium (371,030 nm). In this document, the internal standard recommended is scandium. To carry out determinations using an internal standard, add 0,4 ml of scandium solution (8.2.2.2) to the reference solutions and test solutions, respectively, before making up to the final volume.

8.2.7.4 Determination

At the beginning of every measurement series, check the baseline calibration by means of a two-point recalibration using the blank solution and the reference solution (8.2.2.7) with the highest concentration. If permitted instrument errors in the factors concerned are exceeded, discontinue the determination in order to determine the cause and repeat the calibration using freshly prepared calibration solutions.

Verify the quality of the recalibration by checking that the analytical results for a control sample do not differ by more than 5 % from the true concentration of the solution. If greater errors are encountered, repeat the recalibration. It is advisable to use a certified standard solution as control sample.

Carry out the determination of the test solutions in duplicate, flushing the test solution feed system between individual determinations to eliminate any memory effects. After each series of test solutions, and in any case after not more than 10 determinations, carry out a fresh recalibration with the two standards and check it with the control sample.

8.2.8 Calculation and expression of results

8.2.8.1 Calibration graph

Determine the calibration function by a computerized regression calculation based on the measured data for the reference solutions. Alternatively, plot the measured intensities, or if an internal standard is used, the intensity ratios (ratio of the measured intensity of the element to the measured intensity of the internal standard) against the respective concentrations, correcting the intensity values for the blank value or the background intensities.

8.2.8.2 Calculation by the calibration graph method

Determine the concentration of the element, in milligrams per litre, in the test solution and in the test blank solution (8.2.2.9) from the measured values using the calibration graph (8.2.6.2).

The content of the element, c (EI) expressed in milligrams per kilogram of dry product, is given by the following equation:

$$(EI) = \frac{(c(EI)_t - c(EI)_b) \times z}{m} \quad (44)$$

where

$c(EI)_t$ is the concentration, in milligrams per litre, of the element to be determined in the test solution;

$c(EI)_b$ is the concentration, in milligrams per litre, of the element to be determined in the test blank solution;

z is the intermediate value;

m is the mass, in grams, of the test portion (5.3 or 5.4).

The intermediate value z is given by the following equation:

$$z = \frac{V \times f_2}{f_1} \quad (45)$$

where

V is the volume, in millilitres, of the test solution IV (5.3) or V (5.4);

f_1 is a factor for converting, 1000 ml/l;

f_2 is a factor for converting, 1 000 g/kg.

8.3 Determination of arsenic, antimony and selenium by AAS hydride technique

8.3.1 General

The method is suitable for determining arsenic, antimony and selenium in calcium carbonate as specified in EN 1018, in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017, in calcium magnesium carbonate as specified in prEN 16003 and in magnesium oxide as specified in prEN 16004.

The method of analysis is based on the fact that arsenite, antimonite and selenite ions are reduced to the elemental hydrides AsH₃, SbH₃ and SeH₄ by sodium tetrahydroborate in acid solution. The gaseous hydride, together with the hydrogen gas also formed, is conveyed in a stream of argon gas to a heated quartz cuvette and thermally decomposed in the latter. The absorption of the atoms is measured in the beam path of an atomic absorption spectrometer at a wavelength specific to the element (Table 10). The measured signal shall contain a sharp peak whose height or area is proportional to concentration of the element in the test solution over a certain range.

The concentrations of the elements in the digestion solution IV (5.3) or V (5.4) obtained shall cover the ranges specified in Table 10. If the concentration range is exceeded, dilute the volume V_2 taken for analysis accordingly. When using flow injection, the sensitivity is also affected by the sample volume which is defined by the size of the sample loop.

Table 10 — Measurement wavelength, concentration range

Element	Measurement wavelength nm	Concentration range µg/l
As	193,7	$c(\text{As})$ 1 to 10
Sb	217,6	$c(\text{Sb})$ 1 to 10
Se	196,0	$c(\text{Se})$ 1 to 10

8.3.2 Reagents

8.3.2.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

8.3.2.2 Potassium iodide, KI.

8.3.2.3 L-ascorbic acid, C₆H₈O₈.

8.3.2.4 Sodium hydroxide, NaOH.

8.3.2.5 Sodium tetrahydroborate, NaBH₄.

8.3.2.6 Potassium iodide/ascorbic acid reducing solution, prepared by dissolving 10 g of potassium iodide (8.3.2.2) and 5 g of L-ascorbic acid (8.3.2.3) in 100 ml of water. Prepare this solution immediately before use.

8.3.2.7 Sodium tetrahydroborate solution, prepared by dissolving 1 g of sodium hydroxide (8.3.2.4) and 3 g of sodium tetrahydroborate (8.3.2.5) in 20 ml of water in each case, filtering the solutions through a fluted filter paper into a 100 ml volumetric flask and making up to the mark with water. For flow injection systems, a solution of 0,2 g sodium tetrahydroborate (8.3.2.5) and 0,05 g sodium hydroxide (8.3.2.4) in 100 ml water shall be used. The solutions shall be prepared fresh every day.

8.3.2.8 Element stock solution *c* (As, Sb, Se) = 1 g/l.

8.3.2.9 Standard element solution I *c* (As, Sb, Se) = 10 mg/l], prepared by transferring 10 ml of each stock solution (8.3.2.8) to a 1 l volumetric flask and making up to the mark with 10 ml of hydrochloric acid (8.3.2.1) and water.

8.3.2.10 Standard element solution II *c* (As, Sb, Se) = 0,1 mg/l, prepared by transferring 10 ml of each of the standard element solutions I (8.3.2.9) to a 1 l volumetric flask and making up to the mark with 10 ml of hydrochloric acid (8.3.2.1) and water.

8.3.2.11 Element reference solutions, prepared by pipetting 1 ml, 2 ml, 4 ml, 8 ml and 10 ml of each of the standard element solutions II (8.3.2.10) into 100 ml volumetric flask, adding 5 ml of hydrochloric acid (8.3.2.1), adding 5 ml of the reducing solution (8.3.2.6) to the flasks with As and Sb and making up to the mark with water.

The concentrations of the reference solutions will be 1 µg/l, 2 µg/l, 4 µg/l, 8 µg/l and 10 µg/l. The masses of the elements, As, Sb, Se introduced into the reaction vessel on dispensing a volume of 5 ml will be 5 ng, 10 ng, 20 ng, 40 ng and 50 ng.

8.3.2.12 Blank solution for calibration, prepared by making 5 ml of hydrochloric acid (8.3.2.1) up to the mark with water in a 100 ml volumetric flask.

8.3.2.13 Test blank solution, prepared in the same way and with the same reagents in parallel with the test solutions but without sample substance. For matrix adjustment, use the quantity of calcium carbonate (8.1.2.2) corresponding to the weighed-in test portion.

8.3.3 Apparatus

Ordinary laboratory apparatus and the following:

8.3.3.1 Atomic absorption spectrometer with hollow cathode lamp or electrodeless discharge lamp as radiation source for the determination of the element.

8.3.3.2 Hydride system consisting of a heatable quartz cuvette, a reaction unit and a control unit for controlling the heater, carrier gas stream and metering pump.

8.3.3.3 Argon gas supply.

8.3.4 Interferences

In the hydride technique, the element to be determined is volatilized as a gaseous hydride and separated from the matrix. Consequently, if the technique is carried out correctly, no interferences due to background absorption will occur. Nevertheless, a test shall be carried out with the background compensator in order to ensure that the measurements are specific to the element and are not distorted by non specific absorption.

Since only a few elements (Sb, As, Hg, Bi, Se, Te, Sn) can be determined by this technique, spectral interferences in the gas phase are virtually out of the question.

Interference in solution is mainly due to heavy metal ions, which are readily reduced by sodium tetrahydroborate. This competition for reduction between the analyte and the interfering ion results not only in a slower formation of the hydride, but also in its being coprecipitated or in forming insoluble compounds. This interference can, however, be eliminated by increasing the acid concentration or diluting the sample solution by using smaller aliquots.

In the hydride technique, the valency of the elements to be determined has a considerable effect on the measurement sensitivity. The difference in sensitivity is noticeable in terms of peak height for the oxidation levels + 3 and + 5 of arsenic and antimony, but the sensitivity is the same if the peak area is measured. The hexavalent state of selenium does not produce a measurable signal and a preliminary reduction shall therefore be incorporated in the selenium determination; it shall also be carried out for arsenic and antimony in order to standardize the conditions of measurement. In addition, pentavalent arsenic exhibits relatively severe chemical interferences under certain conditions. The preliminary reduction is carried out with a mixture of potassium iodide and ascorbic acid. It proceeds spontaneously in the case of antimony, while arsenic responds more slowly. To reduce selenium completely, the sample shall be heated with concentrated hydrochloric acid; this shall be done in a sealed vessel to avoid selenium losses.

8.3.5 Procedure

8.3.5.1 Spectrometer settings

Before starting the analysis adjust the operating parameters of the spectrometer in accordance with the operating manual issued by the manufacturer. Operate the spectrometer at the wavelength specified for each element (Table 10). Adjust the temperature of the quartz cuvette to suit each element.

8.3.5.2 Calibration and analysis of the test solution by the calibration curve method

Adjust the zero of the spectrometer by passing a stream of argon through an empty reaction vessel. Connect the reaction vessel containing the required test blank solution to the hydride system and pass argon until an absorption signal can no longer be detected.

Depending on the equipment type, transfer about 5 ml to 10 ml of each of the reference solutions (8.3.2.11) to the reaction vessel. To plot the calibration function, analyse the blank solution (8.3.2.12) and each of the five reference solutions in an ascending order of concentration at least three times.

For the determination of arsenic and antimony, take, for example, 7 ml from the digestion solution IV (5.3) or V (5.4) and add 4 ml of hydrochloric acid (8.3.2.1) and 3 ml of reducing solution (8.3.2.6) in that order to the reaction vessel. For the determination of selenium, add, for example, 7 ml of hydrochloric acid (8.3.2.1) to 7 ml of the digestion solution.

The antimony can be determined immediately, but the arsenic shall be allowed to stand for 15 min in a covered vessel. To determine selenium, it shall be boiled for 15 min in a sealed vessel at about 80 °C.

Analyse the test solutions in a duplicate determination and in two measurement series in order to check the repeatability. After each series of test solutions, and in any case after not more than 10 to 20 measurements, use the blank solution and test solutions reference solution to check whether the measured values still agree with the calibration graph.

8.3.5.3 Analysis of test solution by the standard addition method

Any interferences due to the matrix of the test solution can be compensated for by the standard addition method. Ensure that the test solutions with standard additions are analysed in the linear working range. For this purpose, add different known volumes of the reference solution (8.3.2.11) of the element to be determined three times to the reaction vessel after adding the test solution.

Proceed in the same way for the test blank solution.

Analyse the test and test blank solutions with standard additions in order of ascending concentrations.

8.3.6 Expression of results

Prepare a calibration curve by plotting the concentrations of the element reference solutions, in micrograms per litre, on the horizontal axis against the associated absorbance values on the vertical axis. The graph obtained will normally be linear.

The content of the element to be determined $c(\text{El})$, (El = As, Sb, Se) expressed in milligrams per kilogram of products, from the calibration function is given by the following equation:

$$(\text{El}) = \frac{(c(\text{El})_t - c(\text{El})_b) \times V \times V_1}{f \times V_2 \times m} \quad (46)$$

where

- $c(\text{El})_t$ is concentration, in micrograms per litre, of the element to be determined in the test solution;
- $c(\text{El})_b$ is the concentration, in micrograms per litre, of the element to be determined in the test blank solution;
- V is the volume, in millilitres, of the digestion solution IV (5.3) or V (5.4);
- V_1 is the volume, in millilitres, of test solution taken for analysis;
- V_2 is the volume, in millilitres, of the digestion solution taken to prepare the test solution;
- f is a factor for converting, 1000 ml/l;
- m is the mass, in grams, of the test portion (5.3 or 5.4).

8.4 Determination of mercury by cold-vapour technique

8.4.1 General

The method is suitable for determining mercury in calcium carbonate as specified in EN 1018, in high-calcium lime as specified in EN 12518, in half-burnt dolomite as specified in EN 1017, in calcium magnesium carbonate as specified in prEN 16003 and in magnesium oxide as specified in prEN 16004.

Mercury can be determined:

- after reduction with tin(II) chloride, with or without enrichment; or
- after reduction with sodium tetrahydroborate, with or without enrichment.

The choice between these two reduction methods will depend on established laboratory practice.

The method is applicable for concentrations of mercury in the digestion solution IV (5.3) or V (5.4) of 0,5 µg/l to 10 µg/l.

The method of analysis is based on the fact that tin(II) chloride or sodium tetrahydroborate reduces mono- or divalent mercury in acid solution to the element. The latter is stripped from the solution in an inert gas stream and can quantitatively be converted to the amalgam on a gold/platinum gauze for the purpose of enrichment. The mercury is released again by rapidly heating the absorber and conveyed to a heated quartz cuvette in a

carrier gas stream and the absorption of the mercury atoms is measured in the beam path of an atomic absorption spectrometer at 253,6 nm. The measurement signal obtained shall be a sharp peak whose height or area is proportional to the mercury concentration in the test solution over a certain range.

8.4.2 Reagents

8.4.2.1 Hydrochloric acid, $\rho = 1,16$ g/ml.

8.4.2.2 Sodium hydroxide, NaOH.

8.4.2.3 Sodium tetrahydroborate, NaBH₄.

8.4.2.4 Tin(II) chloride-hydrate, SnCl₂·2 H₂O.

8.4.2.5 Sodium tetrahydroborate solution, prepared by dissolving 1 g of sodium hydroxide (8.4.2.2) and 3 g of sodium tetrahydroborate (8.4.2.3) in 20 ml of water in each case, filtering the solutions through a fluted filter paper into a 100 ml volumetric flask and making up to the mark with water. For flow injection systems a solution of 0,2 g sodium tetrahydroborate (8.4.2.3) and 0,05 g sodium hydroxide (8.4.2.2) shall be put into 100 ml water. The solutions shall be prepared fresh every day.

8.4.2.6 Tin(II) chloride solution, prepared by dissolving 5 g of tin(II) chloride-hydrate (8.4.2.4) in 30 ml of hydrochloric acid (8.4.2.1) and making up to 100 ml with water.

8.4.2.7 Mercury stock solution c (Hg) = 1 g/l.

8.4.2.8 Standard mercury solution I c (Hg) = 10 mg/l, prepared by adding 1 ml of hydrochloric acid (8.4.2.1) to 10 ml of stock solution (8.4.2.7) in a 1 l volumetric flask and making up to the mark with water.

8.4.2.9 Standard mercury solution II c (Hg) = 0,1 mg/l, prepared by adding 1 ml of hydrochloric acid (8.4.2.1) to 10 ml of standard mercury solution I (8.4.2.8) in a 1 l volumetric flask and making up to the mark with water.

8.4.2.10 Mercury reference solutions, prepared by transferring 0,5 ml, 2 ml, 4 ml, 8 ml and 10 ml of standard mercury solution II (8.4.2.9), respectively, to a series of 100 ml volumetric flasks, each containing 5 ml of hydrochloric acid (8.4.2.1) and making up to the mark with water. The reference solutions contain 0,5 µg/l, 2 µg/l, 4 µg/l, 8 µg/l and 10 µg/l mercury. The amounts of mercury, Hg introduced into the reaction vessel when 5 ml are injected are 2,5 ng, 10 ng, 20 ng, 40 ng and 50 ng.

8.4.2.11 Blank solution for calibration, prepared by making 5 ml of hydrochloric acid (8.4.2.1) up to the mark with water in a 100 ml volumetric flask.

8.4.2.12 Test blank solution, prepared in the same way and with the same reagents in parallel with the test solutions, but without sample substance. For matrix adjustment, the quantity of calcium carbonate (8.1.2.2) corresponding to the weighed-in test portion shall be used.

8.4.3 Apparatus

Ordinary laboratory apparatus and the following:

8.4.3.1 Atomic absorption spectrometer with recording indicator and background compensator.

8.4.3.2 Hollow cathode lamp as radiation source for the mercury determination.

8.4.3.3 Hydride system for the SnCl₂ or the NaBH₄ reduction method, consisting of a heatable quartz cuvette, a reaction unit and a control unit containing the control systems for the heater, carrier gas stream and metering pump.

8.4.3.4 Attachment for the amalgaming technique (optional).

8.4.3.5 Argon gas supply.

8.4.4 Interferences

The main interferences are due to heavy metal ions which are readily reduced by sodium tetrahydroborate, but such interferences are much lower if tin(II) chloride is used. As a result of enrichment by amalgamation, the dilution of the test solutions can often be increased, thereby reducing or eliminating interferences.

If tin(II) chloride is used, the equipment is so heavily contaminated with tin that considerable interferences are encountered in subsequent work with sodium tetrahydroborate. Separate equipment shall therefore be used for the two methods of reduction.

The danger of exchange reactions (adsorption and desorption) with the vessels used is particularly high in the case of mercury and this shall also be borne in mind when selecting flexible hose material. Vessels made of fluorinated ethylene propylene (FEP) are best suited for storage of the solutions. When using potassium permanganate as stabilising agent brownstone can form on the walls of the plastics sample vessels. Repeated use of the vessels can then lead to less precise results.

8.4.5 Procedure

8.4.5.1 Spectrometer settings

Before starting the analysis, set the operating parameters in accordance with the operating manual issued by the manufacturer. Operate the spectrometer at a wavelength of 253,6 nm with the background compensation switched on. Bring the quartz cuvette to the required temperature.

8.4.5.2 Analysis of test solution by calibration curve method

Connect the reducing agent stock bottle containing the chosen reducing agent (8.4.2.5 or 8.4.2.6) to the reaction unit. Connect the reaction vessel containing the required test blank solution to the hydride system and pass through a stream of argon (8.4.3.5) to adjust the equipment zero. Start up the control unit for the mercury program and record the absorption signal using a computer or chart recorder.

To plot the calibration function, analyse the blank solution (8.4.2.11) and the five reference solutions (8.4.2.10) in ascending order of concentration at least three times.

Analyse the test solutions in duplicate and, to check the reproducibility, in two measurement series. After each series of test solutions, and in any case after not more than 10 to 20 measurements, use the blank solution and a reference solution to check whether the measured values still agree with the calibration graph.

8.4.5.3 Analysis of test solution by standard addition method

Compensate for any interferences expected to arise from the matrix of the sample in the test solution by using the addition method, ensuring that the measurements of test solutions with standard additions fall within the linear working range. For this purpose, dispense the test solution (*V*) into three reaction vessels and add different, known amounts of mercury (8.4.2.10).

Proceed in the same way with the test blank solution.

Analyse the test and test blank solutions twice in ascending order of concentration.

8.4.6 Expression of results

Prepare the calibration graph by plotting the concentrations of mercury, in micrograms per litre, on the horizontal axis against the associated absorbance values on the vertical axis. The graph obtained will normally be linear.

The mercury content, c (Hg), expressed in milligrams per kilogram of products from the calibration function is given by the following equation:

$$c(\text{Hg}) = \frac{(c_1 - c_2) \times V}{f \times m} \quad (47)$$

where

c_1 is concentration, in micrograms per litre, of mercury in the test solution;

c_2 is concentration, in micrograms per litre, of mercury in the test blank solution;

V is the volume, in millilitres, of digestion solution IV (5.3) or V (5.4);

f is a factor for converting, 1000 ml/l;

m is the mass, in grams, of the test portion (5.3 or 5.4).

Annex A (informative)

Analytical scheme

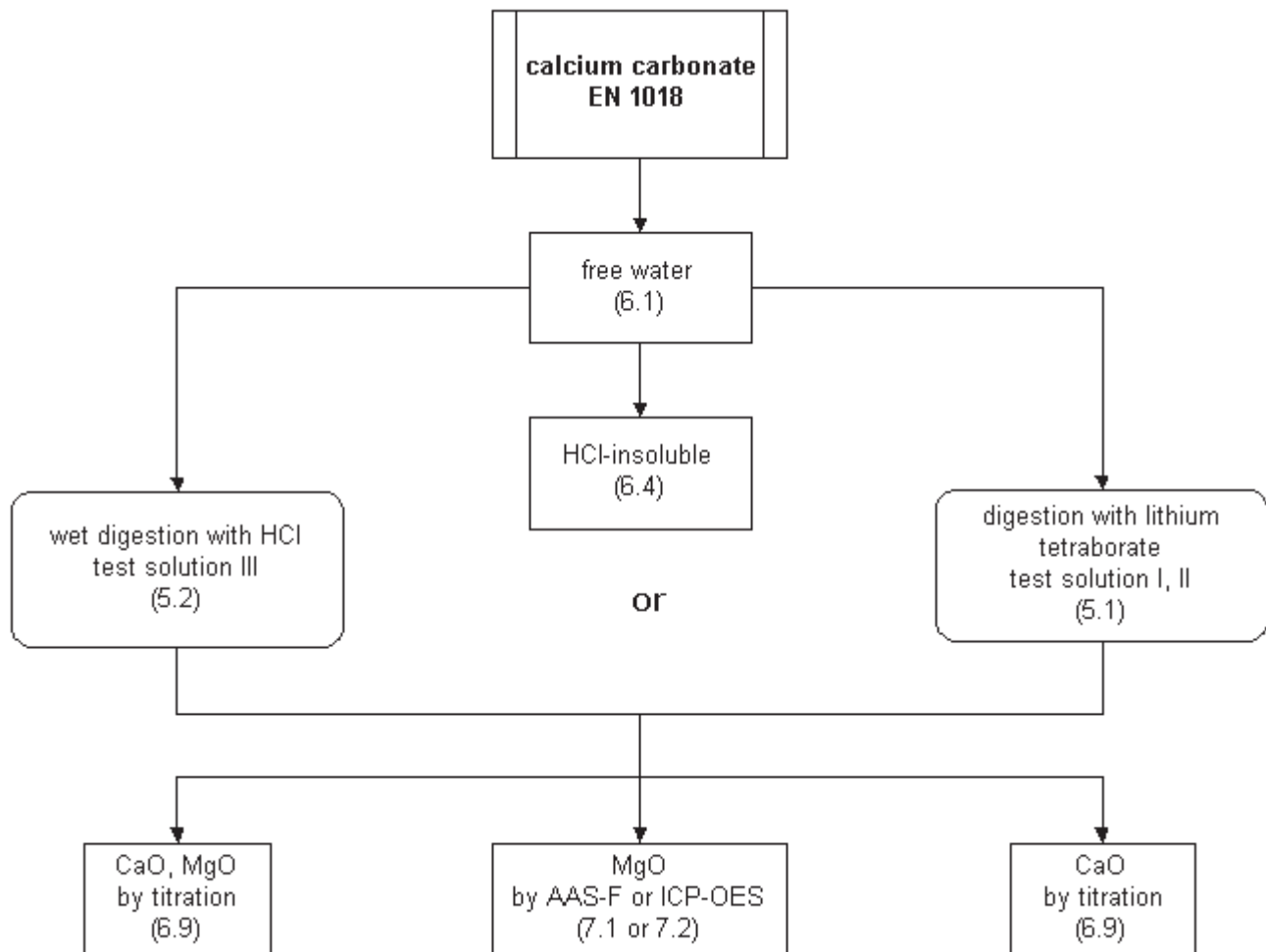


Figure A.1 — Analytical scheme for calcium carbonate

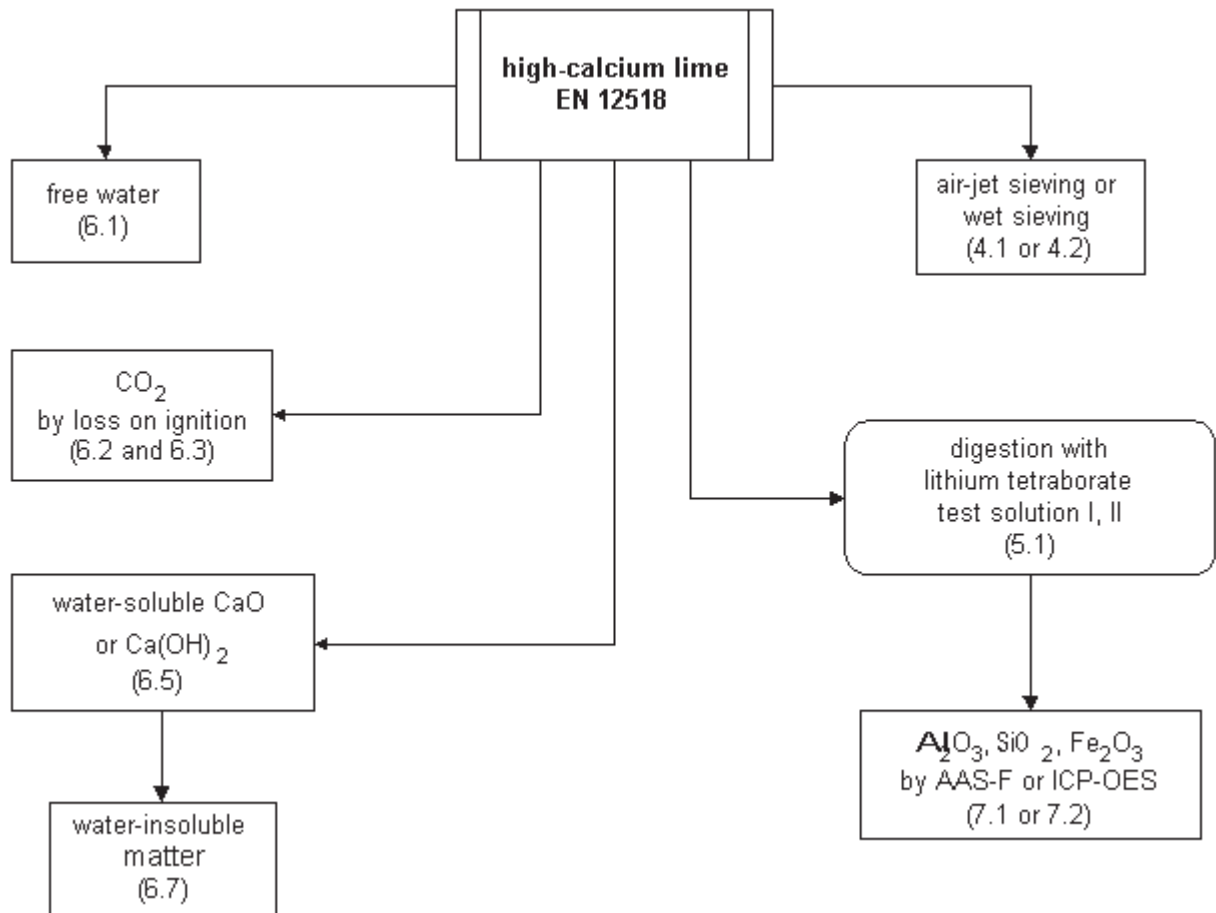


Figure A.2 — Analytical scheme for high-calcium lime

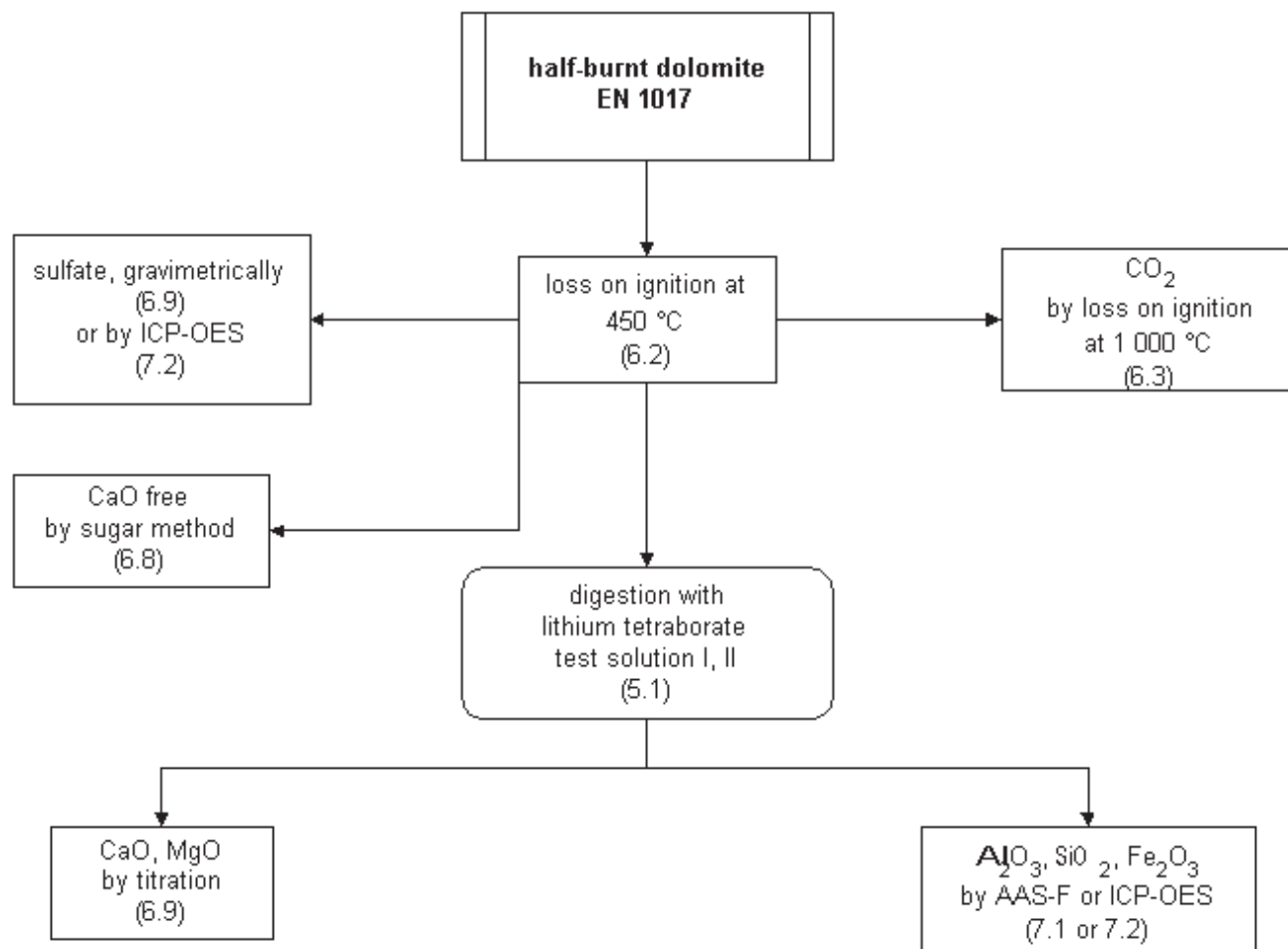


Figure A.3 — Analytical scheme for half-burnt dolomite

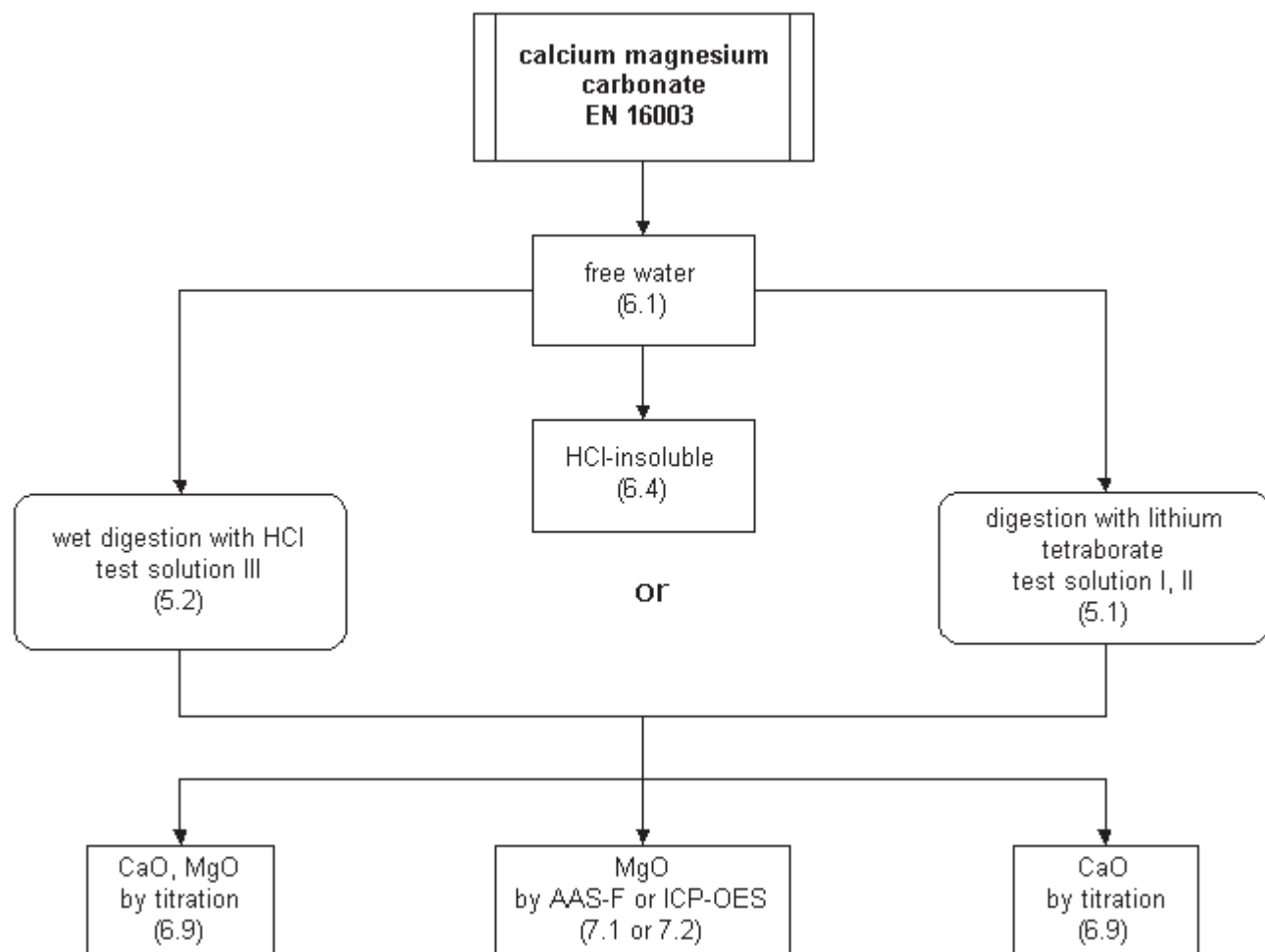


Figure A.4 — Analytical scheme for calcium magnesium carbonate

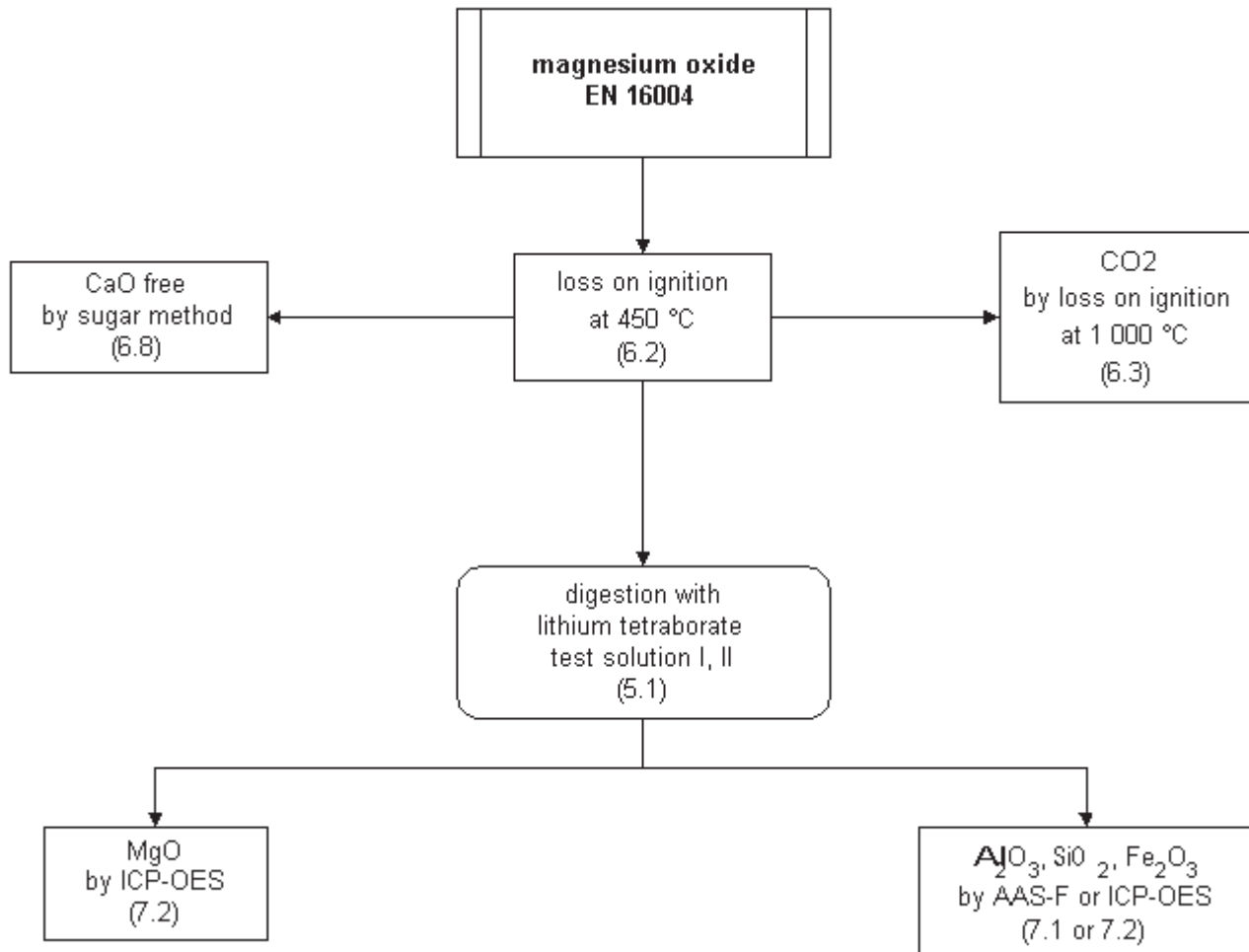


Figure A.5 — Analytical scheme for magnesium oxide

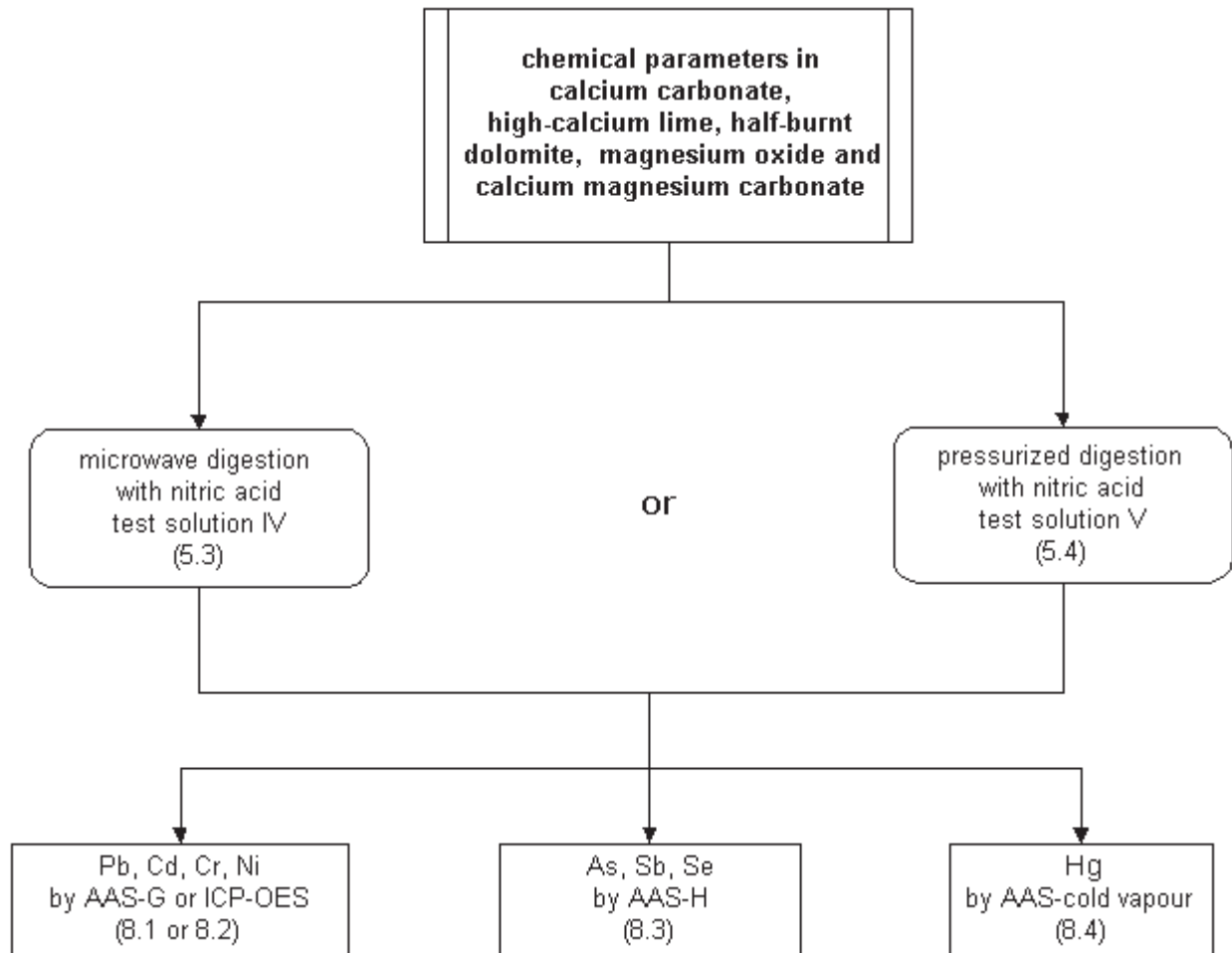


Figure A.6 — Analytical scheme for determining trace elements in calcium carbonate, high-calcium lime, half-burnt dolomite, magnesium oxide and calcium magnesium carbonate

Annex B (informative)

Table B.1: Precision data for the test methods

Parameter	L	N	$\bar{\bar{x}}$	$\bar{x}_{\min} - \bar{x}_{\max}$	s_r	V_r	f_r	s_R	V_R	f_R	r	R
retentions on sieving by air-jet sieving on sieve 0,09 mm [% (m/m)]												
quicklime	12	33	1,9	1,2 - 2,4	0,1	0,4	22	0,33	1,8	32	0,3	0,9
hydrat. lime	12	33	1,6	0,8 - 2,0	0,1	0,6	24	0,37	2,3	35	0,3	1,0
retentions on sieving by wet sieving on sieve 0,09 mm [% (m/m)]												
hydrat. lime	10	27	1,4	0,8 - 2,2	0,1	0,4	22	0,5	3,5	26	0,3	1,4
non-porous calcium carbonate [% (m/m)]												
HCl _{insol}	11	38	0,326	0,235 - 0,405	0,0284	8,71	28	0,0674	20,7	37	0,08	0,189
CaO	9	34	54,97	54,26 - 55,76	0,2206	0,40	25	0,5811	1,06	33	0,617	1,63
MgO	8	32	0,366	0,313 - 0,42	0,009	2,37	24	0,0355	9,72	31	0,025	0,1
half-burnt dolomite [% (m/m)]												
CO ₂	8	32	35,87	35,67 - 36,01	0,0242	0,067	24	0,1402	0,391	31	0,068	0,39
CaO _{free}	8	32	0,923	0,655 - 1,248	0,03	3,26	24	0,1874	20,31	31	0,08	0,525
CaO	9	34	40,48	39,19 - 41,58	0,1318	0,326	25	0,7987	1,973	33	0,37	2,24
MgO	8	30	22,93	22,18 - 24,24	0,1576	0,687	22	0,7243	3,16	29	0,44	2,03
SO ₄ ²⁻	4	16	0,04	0,023 - 0,07	0,0063	15,49	12	0,0216	53,06	15	0,02	0,06
water-soluble content in high-calcium lime [% (m/m)]												
CaO	17	66	95,52	93,89 - 97,25	0,147	0,154	49	0,7737	0,81	65	0,412	2,17
Ca(OH) ₂	17	64	96,21	95,15 - 97,19	0,1997	0,208	47	0,6721	0,699	63	0,56	1,88
water-insoluble constituents in high-calcium lime [% (m/m)]												
CaO	13	49	3,0	1,77 - 4,57	0,37	12	36	0,84	28	48	1,03	2,3
Ca(OH) ₂	10	36	2,3	1,49 - 3,1	0,2	8,9	26	0,54	24	35	0,6	1,5
minor constituents in high-calcium lime [% (m/m)]												
MgO	12	48	1,42	1,32 - 1,55	0,02	1,4	36	0,07	5,0	47	0,06	0,2
SiO ₂	11	44	2,21	1,97 - 2,42	0,04	2,0	33	0,15	6,7	43	0,11	0,4
Al ₂ O ₃	12	48	0,62	0,55 - 0,75	0,01	2,1	36	0,07	10,6	47	0,03	0,2
Fe ₂ O ₃	13	52	0,31	0,27 - 0,34	0,015	4,9	39	0,025	8,3	51	0,04	0,07
MnO ₂	12	48	0,05	0,02 - 0,11	0,003	5,7	36	0,02	43,3	47	0,01	0,06
trace elements in high-calcium lime (mg/kg)												
Pb	10	37	36,75	29,55 - 41,35	1,49	4,1	27	4,13	11,3	36	4,2	11,6
Cd	8	32	0,17	0,1 - 0,29	0,01	7,7	24	0,055	32,0	31	0,03	0,15
Cr	10	37	5,7	4,0 - 6,9	0,34	6,0	27	0,9	15,7	36	0,95	2,5
Ni	10	37	4,1	2,7 - 5,5	0,3	7,4	27	0,96	23,5	36	0,84	2,7
As	7	25	2,2	1,3 - 3,5	0,43	19,6	18	1,03	46,5	24	1,2	2,9
Sb	4	13	0,32	0,02 - 0,4	0,06	18	9	0,1	30	12		
Se	5	17	0,24	0,06 - 0,4	0,05	22	12	0,17	73	16		
Hg	8	26	0,04	0,02 - 0,08	0,003	7,8	18	0,02	53	25		
L	number of laboratories evaluated					s_R	standard deviation of reproducibility					
N	number of single analytical values without outliers					V_R	coefficient of variation of reproducibility					
$\bar{\bar{x}}$	total mean value					f_R	degrees of freedom of reproducibility					
$\bar{x}_{\min} - \bar{x}_{\max}$	range of mean values					r	repeatability					
s_r	standard deviation of repeatability					R	reproducibility					
V_r	coefficient of variation of repeatability											
f_r	degrees of freedom of repeatability											

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