BRITISH STANDARD

BS 6463-102: 2001

Quicklime, hydrated lime and natural calcium carbonate —

Part 102: Methods for chemical analysis

ICS 91.100.10

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee B/516, Cement and lime, to Subcommittee B/516/11, Lime, upon which the following bodies were represented:

Autoclaved Aerated Concrete Products Association

British Lime Association

Building Limes Forum

Department of the Environment, Transport and the Regions — Building Research Establishment

English Heritage

Mortar Industry Association

Quarry Products Association

Co-opted members

The following bodies from the Technical Committee were also involved in the preparation of this standard:

British Cement Association

British Precast Concrete Federation Ltd.

Cement Admixtures Association

Cementitious Slag Makers Association

County Surveyors Society

Department of the Environment, Transport and the Regions — Highways Agency

Environment Agency

Society of Chemical Industry

UK Quality Ash Association

This British Standard, having been prepared under the direction of the Sector Policy and Strategy Committee for Building and Civil Engineering, was published under the authority of the Sector Policy and Strategy Committee on 6 November 2001

First published as BS 6463-2, February 1984
Second edition as BS 6463-102, 6 November 2001

The following BSI references relate to work on this British Standard:
Committee reference B/516/11
Draft for comment 99/105742 DC

ISBN 0 580 33315 9

Amendments issued since publication

Amd. No.	Date	Comments

Contents

Foreword

This part of BS 6463 has been prepared by Subcommittee B/516/11, Lime, under the direction of Technical Committee B/516, Cement and lime. It supersedes BS 6463-2:1984 which is withdrawn.

BS 6463-2:1984 brought together standard methods of chemical analysis for quicklime, hydrated lime and natural calcium carbonate including those for use in connection with water treatment, agriculture, steel making and chemical processing.

In that edition, atomic absorption methods were permitted. Since 1984 the use of atomic spectrometry has been widely used in this field of activity. These methods require special attention to calibration using reference materials.

This edition describes alternative analytical methods for several elements. Where available and appropriate, atomic spectrometry using atomic absorption (AAS) is recommended, although classical methods are still used by many laboratories for the determination of certain analytes and parameters. Repeatability and reproducibility for the test methods are not yet available. However, when the necessary testing has been done, this standard will be updated accordingly.

Other atomic absorption spectrometric (AAS) methods are available in BS EN 12485, and include determinations of antimony, arsenic, mercury and selenium.

These methods are to be preferred over the classical methods and it is recommended that they are adopted in specifications as the reference methods.

NOTE There are other atomic spectrometric methods that can give the sensitivity, precision and accuracy required by this part of BS 6463, the results of which can be calibrated against the methods described in this part of BS 6463. However, if a standard specifies a reference to BS 6463-102, only methods actually given in this part of BS 6463 can be used in order to claim compliance with that standard.

A number of classical chemical methods that were given in BS 6463-2:1984 have now been incorporated into other standards, and are no longer included in this part of BS 6463. These methods, and the standards in which they are now given, are for:

— available lime (BS EN 459-2);
— silicon (BS EN 196-2);
— iron (BS EN 196-2);
— calcium (BS EN 12485);
— magnesium (BS EN 12485);
— water soluble calcium oxide and calcium hydroxide (BS EN 12485);
— water insoluble constituents (BS EN 12485).

This revision of BS 6463 is published in three parts, as follows:

— Part 101: *Methods for preparing samples for testing*;
— Part 102: *Methods for chemical analysis*;
— Part 103: *Methods for physical testing*.

Part 101 gives methods for sampling powdered, granular and lump quicklime and natural calcium carbonate, and of powdered hydrated lime, milk of lime and lime putty.

Part 103 gives the physical tests for quicklime, hydrated lime, lime putty and natural calcium carbonate, of which the tests for quicklime, hydrated lime and lime putty were previously included in BS 6463-3 and BS 6463-4.

A British Standard does not purport to include all necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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

Summary of pages

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1 Scope

This part of BS 6463 describes methods for the chemical analysis of quicklime, hydrated lime and natural calcium carbonate. It describes both classical methods and methods which use atomic absorption spectrometry (AAS).

It gives classical chemical methods for:

— fluorine, matter insoluble in acetic acid, matter insoluble in hydrochloric acid;

— loss on ignition, neutralizing value;

— free water in hydrated lime and also in lime putty;

— total sulfur;

— carbon dioxide in carbonate.

It gives flame atomic absorption spectrometric (AAS) methods for aluminium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, silicon, silver and zinc.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of this British Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. For undated references, the latest edition of the publication referred to applies.

BS 1752:1983, *Specification for laboratory sintered or fritted filters including porosity grading.*

BS 5898:1980, *Specification for principles of design and construction of volumetric glassware for laboratory use.*

BS 6463-101:1996, *Quicklime, hydrated lime and natural calcium carbonate — Part 101: Methods for preparing samples for testing.*

BS EN 12485, *Chemicals used for treatment of water intended for human consumption — Calcium carbonate, high-calcium lime and half-burnt dolomite — Test methods.*

BS EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods.*

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

3 General requirements for testing

3.1 Number of tests

For each of the determinations in clauses **4** and **5**, carry out two tests.

3.2 Reagents

Water shall conform to grade 2 of BS EN ISO 3696.

All reagents shall be of an analytical grade suitable for the method being used. For instrumental analysis, the instructions of the equipment manufacturer shall be observed. The content of the elements to be determined in the water or reagents used shall be negligible compared with the lowest concentration to be determined.

If commercially available AAS solutions are used as stock solutions, they shall be prepared for the purposes of analysis in accordance with the manufacturer's instructions.

The concentrated liquid reagents used in this standard shall have the densities shown in Table 1.

Table 1 — Densities of concentrated liquid reagents

Reagent	Density (ρ) at 20 °C g/ml
Acetic acid	1.05 to 1.06
Hydrochloric acid	1.16 to 1.19
Industrial methylated spirit	0.79
Nitric acid	1.40 to 1.42
Orthophosphoric acid	1.70 to 1.75
Sulfuric acid	1.84

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

3.3 Volumetric glassware

Volumetric glassware shall be of class B as specified in BS 5898.

3.4 Preparation of the sample

Prepare the laboratory sample as described in BS 6463-101. Carry out all operations as quickly as possible to ensure that the sample is exposed to ambient air only for the minimum time that is necessary. Store the sample in an air-tight container of such a volume that the sample fills the container as completely as possible.

3.5 Expression of results

Express the results as the mean of two determinations.

Express results of value not less than 1.00 % to three significant figures. Express results of value less than 1.00 % to two significant figures. If the value of the result is less than 0.10 % express it to two significant figures where feasible.

4 Determination of major and minor constituents by classical methods

4.1 Determination of hydrochloric acid extractable fluoride

4.1.1 *Principle*

The sample is stirred with concentrated hydrochloric acid and the extracted fluorine is determined using a specific fluoride ion electrode which develops a potential proportional to the logarithm of the fluoride ion concentration in solution.

The method is applicable to quicklimes and hydrated limes, with fluorine contents in the range 20 mg/kg to 500 mg/kg. It is also applicable to natural calcium carbonates which are used for the neutralization of moderately acidic solutions (pH > 1).

NOTE The extractable fluoride content of a natural calcium carbonate should not be used to predict the levels of extractable fluoride in quicklimes and hydrated limes. This is due partly to the effects of the calcination and hydration reactions and partly to the volatility of fluorides at elevated temperatures.

4.1.2 *Reagents*

4.1.2.1 *Sodium fluoride*, NaF, dried at (105 ± 5) °C for 1 h.

4.1.2.2 *Fluoride*, standard stock solution, with a concentration of fluoride ions of 500 µg/ml. Dissolve (1.105 ± 0.005) g of sodium fluoride (**4.1.2.1**) in water, make up to 1 000 ml in a volumetric flask and mix thoroughly. Store in a suitable container and under suitable conditions for up to 14 days if necessary (see note).

NOTE All fluoride solutions may be kept for limited periods providing they are placed in a cool dark cupboard in stoppered containers made of a material which has been shown not to interfere with the determination of fluorine. Laboratory grade polyethylene or polypropylene is usually suitable.

4.1.2.3 *Fluoride*, dilute solution, with a concentration of fluoride ions of 50 µg/ml. Pipette 50 ml of the standard stock fluoride solution (**4.1.2.2**) into a 500 ml volumetric flask. Make up to the mark with water and mix.

NOTE This solution can be kept for up to 14 days if stored as described (see note to **4.1.2.2**).

4.1.2.4 *Fluoride*, dilute solution, with a concentration of fluoride ions of 5 µg/ml. Pipette 50 ml of fluoride solution (**4.1.2.3**) into a 500 ml volumetric flask. Make up to the mark with water and mix.

NOTE This solution can be kept for up to 14 days if stored as described (see note to **4.1.2.2**).

4.1.2.5 *Reference standard calcium carbonate*, with less than 1 mg/kg of hydrochloric acid extractable fluorine.

4.1.2.6 *Trisodium citrate dihydrate*.

4.1.2.7 *Trisodium citrate solution*. Dissolve (147.0 ± 0.1) g of trisodium citrate dihydrate (**4.1.2.6**) in water and dilute to 1 l.

4.1.2.8 *Hydrochloric acid*, 1 + 19.

4.1.2.9 *Fluoride standard solution*, 10 µg in 80 ml. Pipette 2 ml of fluoride solution (**4.1.2.4**) into a polyethylene beaker. Add (0.20 ± 0.01) g of calcium carbonate (**4.1.2.5**), 18 ml of distilled water, 40 ml of trisodium citrate solution (**4.1.2.7**) and 20 ml of hydrochloric acid 1 + 19 (**4.1.2.8**). Add a magnetic follower and stir.

NOTE This solution can be kept for up to 48 h, if stored as described (see note to **4.1.2.2**).

4.1.2.10 *Fluoride standard solution*, 100 µg in 80 ml. Pipette 20 ml of fluoride solution (**4.1.2.4**) into a polyethylene beaker. Add (0.20 ± 0.01) g of calcium carbonate (**4.1.2.5**), 40 ml of trisodium citrate solution (**4.1.2.7**) and 20 ml of hydrochloric acid 1 + 19 (**4.1.2.8**). Add a magnetic follower and stir.

NOTE This solution can be kept for up to 48 h, if stored as described (see note to **4.1.2.2**).

4.1.3 *Apparatus*

4.1.3.1 *Plastics beaker*.

4.1.3.2 *Magnetic follower*.

4.1.3.3 *Millivoltmeter*, with an expandable scale and a specific ion electrode for fluorine, containing a lanthanum fluoride crystal across which a potential develops proportional to the fluoride ion concentration in solution. This potential is measured against a calomel reference electrode.

4.1.4 *Preparation of sample solution*

Accurately weigh (0.200 ± 0.005) g of sample into a plastics beaker (**4.1.3.1**). Add 25 ml of hydrochloric acid 1 + 19 (**4.1.2.8**) and a magnetic follower (**4.1.3.2**). Stir for 15 min and add 15 ml of distilled water and 40 ml of trisodium citrate solution (**4.1.2.7**).

4.1.5 *Procedure*

Operate the millivoltmeter (**4.1.3.3**), the specific fluoride ion electrode and the calomel reference electrode as described in the manufacturer's instructions. Allow sample solutions, reagents and apparatus to equilibrate at room temperature (±1 °C) before reading.

NOTE 1 When taking readings, it is advisable to transfer solutions into small beakers (made of a material which has been shown not to interfere with the determination of fluorine) and to agitate gently, without vortex, using a magnetic stirrer.

NOTE 2 The determination of fluorine in the sample should be completed within 0.5 h of preparing the sample solution (**4.1.4**).

NOTE 3 When a series of measurements has been completed, rinse the electrodes and store them as recommended by the manufacturer.

If the meter has slope and gain controls, calibrate the instrument and electrode, using the fluoride solutions as follows.

a) Rinse the electrodes in distilled water and dip them into the first fluoride standard solution (**4.1.2.9**). When a steady reading is obtained, adjust the meter calibration controls (i.e. the slope or gain control), to expand or contract the scale, until the display reads a convenient number (x) of the chosen units.

b) Rinse the electrodes in distilled water and dip them into the second fluoride standard solution (**4.1.2.10**). When a steady reading is obtained, adjust the meter calibration controls until the display reads $10x$ units.

c) Repeat step (a). If the reading is slightly different from x units, correct it using the calibration controls and repeat step (b).

Determine the concentration of fluorine in the sample as follows.

1) Rinse the electrodes in distilled water and dip them in the sample solution (**4.1.4**). The meter display will show the concentration of fluorine in the sample as y units.

2) Calculate the concentration of fluorine, c, in milligrams per kilogram from the equation:

$$c = 50(y/x) \qquad (1)$$

where

x is the millivoltmeter reading for the first fluoride standard solution;

y is the millivoltmeter reading for the sample solution.

If the meter has a concentration mode and an auto-ranging function, follow the manufacturer's calibration instructions, using the fluoride standard solutions specified in **4.1.2.9** and **4.1.2.10**.

Determine the concentration of fluorine in the sample by rinsing the electrodes in distilled water and dipping them in the sample solution (**4.1.4**). The display will give a direct reading of the concentration of fluorine in the sample.

4.2 Determination of matter insoluble in acetic acid

4.2.1 *Principle*

The sample is treated with acetic acid. The mixture is then boiled and the insoluble residue extracted by filtration and weighed.

4.2.2 *Reagents*

4.2.2.1 *Acetic acid*, 1 + 9.

4.2.3 *Apparatus*

4.2.3.1 *Sintered glass crucible*, of grade P 16 as specified in BS 1752:1983, pre-dried at 105 °C and tared.

4.2.4 *Procedure*

Take one of the following masses of dry sample and weigh it to the nearest 0.01 g:

— approximately 1.68 g quicklime;

— approximately 2.22 g hydrated lime; or

— approximately 3.00 g calcium carbonate.

Moisten the sample with 2 ml of water and add 50 ml of acetic acid 1 + 9 (**4.2.2.1**). When effervescence has subsided, boil for 2 min and then cool. Filter through the tared sintered glass crucible (**4.2.3.1**) and wash the beaker and crucible with 10 ml of acetic acid 1 + 9. Wash the residue in the crucible with four successive quantities of 5 ml of hot water. Dry in an oven at (105 ± 5) °C to constant mass, m_2.

4.2.5 *Calculation of results*

Calculate the content of insoluble matter, I, in percent from the equation:

$$I = \frac{m_2 - m_1}{m} \times 100 \qquad (2)$$

where

m is the mass of sample, in grams (g);

m_1 is the initial mass of the crucible, in grams (g);

m_2 is the mass of the crucible and residue, in grams (g).

4.3 Determination of matter insoluble in hydrochloric acid

4.3.1 *Principle*

The sample is treated with hydrochloric acid. The mixture is then boiled and the insoluble residue extracted by filtration and weighed.

4.3.2 *Reagents*

4.3.2.1 *Hydrochloric acid*, 1 + 4.

4.3.3 *Apparatus*

4.3.3.1 *Filter paper*, fine ashless, with a particle retention of 2.5 µm.

4.3.3.2 *Crucible*, platinum or silica, pre-ignited and tared.

4.3.3.3 *Furnace*, which can be controlled at (1 000 ± 50) °C.

4.3.3.4 *Desiccator*, containing phosphorous pentoxide as a desiccant.

4.3.4 *Procedure*

Take approximately 2 g of sample, weigh it to an accuracy of 0.001 g, and place it in a 500 ml flask. Add 50 ml of hydrochloric acid 1 + 4 (**4.3.2.1**). When effervescence has subsided, boil for 2 min and cool. Filter through the filter paper (**4.3.3.1**) and wash the beaker and filter paper with 10 ml of hydrochloric acid 1 + 4 (**4.3.2.1**). Wash the residue with five successive quantities of approximately 5 ml of hot water.

Transfer the paper to a tared pre-ignited crucible (**4.3.3.2**) and char the paper without flaming. Place the crucible with the charred paper and residue into the furnace (**4.3.3.3**) at (1 000 ± 50) °C for 1 h. Cool in a desiccator (**4.3.3.4**), and weigh.

4.3.5 *Calculation of results*

Calculate the content of insoluble matter, I, in percent from the equation:

$$I = \frac{m_2 - m_1}{m} \times 100 \quad (3)$$

where

m is the mass of sample, in grams (g);

m_1 is the initial mass of the crucible, in grams (g);

m_2 is the mass of the crucible and residue, in grams (g).

4.4 Determination of loss on ignition

4.4.1 *Principle*

A sample is heated at 575 °C to drive off any moisture and organic matter and to decompose any calcium hydroxide. It is then heated at 1 000 °C to decompose calcium carbonate.

4.4.2 *Apparatus*

4.4.2.1 *Crucible*, platinum or silica, pre-ignited and weighed, with a lid.

4.4.2.2 *Furnace*, which can be controlled at (575 ± 25) °C and at (1 000 ± 50) °C.

4.4.2.3 *Desiccator*, containing phosphorus pentoxide as a desiccant.

4.4.3 *Procedure*

Take approximately 1 g of sample, weigh it to an accuracy of 0.001 g, place it in a tared pre-ignited crucible (**4.4.2.1**) with a lid, transfer to a furnace (**4.4.2.2**) at (575 ± 25) °C, and continue the ignition for 1 h. Remove and cool in a desiccator (**4.4.2.3**) and weigh, to an accuracy of 0.001 g. Return the crucible to the furnace and repeat the procedure at half-hourly intervals until the crucible and contents reach constant mass, to determine the loss on ignition at 575 °C.

Return the lidded crucible to the furnace, increase the temperature to (1 000 ± 50) °C and repeat the heating and cooling procedure to determine the loss on ignition at 1 000 °C.

4.4.4 *Calculation of results*

Calculate the loss on ignition, L, in percent at 575 °C and 1 000 °C from the equations:

$$L_{575} = \frac{m - m_{575}}{m} \quad (4)$$

$$L_{575-1\,000} = \frac{m_{575} - m_{1\,000}}{m} \quad (5)$$

where

m is the initial mass of sample, in grams (g);

m_{575} is the mass of the sample after ignition at 575 °C, in grams (g);

$m_{1\,000}$ is the mass of the sample after ignition at 1 000 °C, in grams (g).

4.5 Determination of neutralizing value

4.5.1 *Principle*

The sample is boiled with a known volume of hydrochloric acid and the excess acid titrated against sodium hydroxide solution. The volume of acid neutralized by the sample is calculated in terms of calcium oxide.

4.5.2 *Reagents*

4.5.2.1 *Hydrochloric acid solution*, 1.0 M.

4.5.2.2 *Sodium hydroxide solution*, 0.5 M.

4.5.3 *Procedure*

Take approximately 0.5 g of sample, weigh it to an accuracy of 0.001 g, and transfer it to a 300 ml conical flask. Wet the sample with approximately 15 ml of water and add by pipette (50.0 ± 0.1) ml of hydrochloric acid solution, 1.0 M (**4.5.2.1**). Boil the contents of the flask gently for 2 min and then allow to cool.

Titrate the excess acid with sodium hydroxide solution, 0.5 M (**4.5.2.2**) using phenolphthalein as indicator.

4.5.4 *Calculation of results*

Calculate the neutralizing value, N, as a percentage of calcium oxide from the equation:

$$N = \frac{1.402\ (100 - V_1)}{m_3} \qquad (6)$$

where

V_1 is the volume of sodium hydroxide solution, in millimetres (ml);

m_3 is the mass of sample, in grams (g).

4.6 Determination of free water in hydrated lime and lime putty

4.6.1 *Principle*

Calcium carbide is mixed with the sample. The acetylene evolved is collected and the volume calculated in terms of water.

4.6.2 *Reagents*

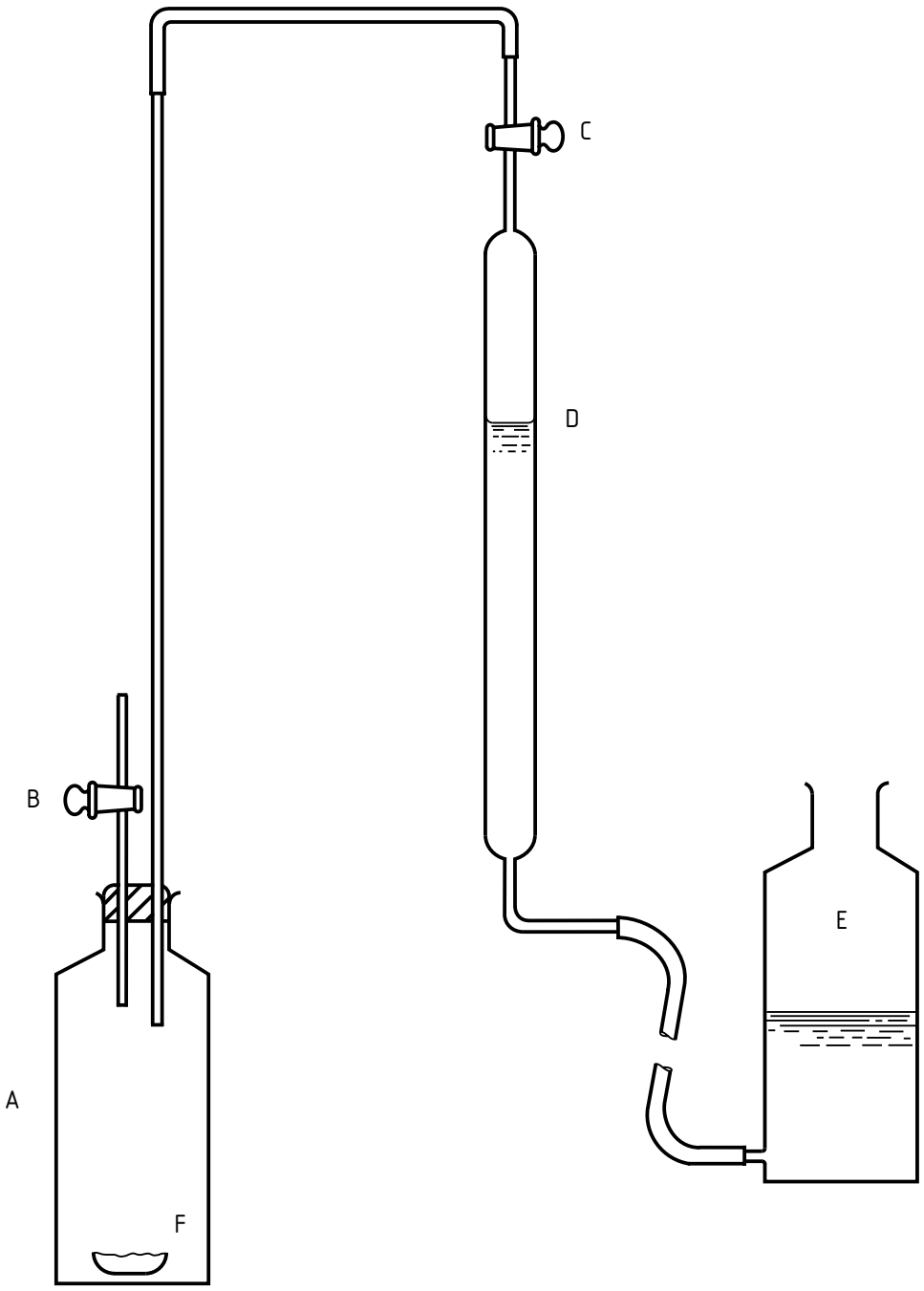
4.6.2.1 *Sodium chloride*, NaCl.

4.6.2.2 *Saturated sodium chloride solution*. Add 400 g of sodium chloride (**4.6.2.1**) to 1 000 ml of water in a beaker. Cover and stir for 30 min. Allow to stand for 1 h, and decant the supernatant liquor into a glass bottle, stopper and store for use.

4.6.2.3 *Calcium carbide*, CaC_2.

4.6.3 *Apparatus*

The apparatus is shown in Figure 1 and consists of a gas burette, D, graduated from 0 ml to 100 ml with a levelling bottle, E, containing saturated sodium chloride solution (**4.6.2.2**) as confining liquid. The top of the burette is connected via tap C to a reaction vessel, A, a 250 ml bottle fitted with a rubber bung containing a pressure release tap, B. F is a small container for calcium carbide which can be lowered into vessel A. Check the apparatus regularly for leaks and, ensure that, when tested with vessel A empty, the liquid level does not drop by more than 0.5 ml over a 20 min period.



A. Reaction vessel
B. Pressure release tap
C. Tap
D. Gas burette
E. Levelling bottle
F. Calcium carbide container

Figure 1 — Typical apparatus for determination of free water in hydrated lime and lime putty

4.6.4 *Procedure*

Take approximately 10 g of sample, weigh it to an accuracy of 0.1 g, and transfer it to vessel A. Put 2 g to 3 g of freshly ground calcium carbide (**4.6.2.3**) into container F and, by means of a wire hook, carefully lower container F into vessel A. With the burette filled with confining liquid, tap C closed and tap B open, fit the rubber bung firmly into vessel A and then close tap B.

Open tap C and shake vessel A to mix the contents thoroughly. Allow to stand for 20 min and shake the bottle occasionally during the period.

Using levelling bottle E, read off the volume of evolved gas.

4.6.5 *Calculation of results*

By means of a conversion table based on the equation:

$$2H_2O + CaC_2 \rightarrow Ca(OH)_2 + C_2H_2$$

determine the percentage of free water (or moisture), M, in the sample from the equation:

$$M = \frac{1.46 V_2}{m_4} \qquad (7)$$

where

m_4 is the mass of sample, in grams (g);

V_2 is the volume (at 20 °C and 101.32 kPa) of acetylene (saturated with water vapour) evolved, in millilitres (ml).

NOTE 1 Acetylene is evolved in proportion to the amount of free moisture present. In the specified apparatus, using 10 g of sample, free moisture contents up to 1.5 % may be measured.

NOTE 2 Corrections for pressure and temperature should be applied.

4.7 Determination of total sulfur

4.7.1 *Principle*

The total sulfur present is oxidized to sulfate and precipitated in the form of barium sulfate by the addition of barium chloride to a solution of the sample in hydrochloric acid. The suspension is filtered and the residual barium sulfate is washed and weighed. The concentration of total sulfur in the sample is calculated from the mass of barium sulfate produced.

4.7.2 *Reagents*

4.7.2.1 *Bromine*, ultra pure.

4.7.2.2 *Bromine water*. Dissolve (1.0 ± 0.1) ml of ultra pure bromine (**4.7.2.1**) in 24 ml of water. Store in the dark in a glass bottle. Renew this solution monthly.

4.7.2.3 *Barium chloride*, $BaCl_2.2H_2O$.

4.7.2.4 *Hydrochloric acid*, concentrated.

4.7.2.5 *Barium chloride solution*, 100 g/l. Dissolve 10.0 g of barium chloride (**4.7.2.3**) in 60 ml of water. Add 1 ml of hydrochloric acid (**4.7.2.4**) and dilute to 100 ml with water. Renew this solution daily.

4.7.3 ***Apparatus***

4.7.3.1 *Electrical hot plate or sand bath*, controlled at (105 ± 5) °C.

4.7.3.2 *Filter paper*, medium, with a particle retention of 8 µm.

4.7.3.3 *Filter paper*, fine ashless, with a particle retention of 2.5 µm.

4.7.3.4 *Crucible*, platinum or silica.

4.7.3.5 *Furnace*, controlled at (1 200 ± 50) °C.

4.7.4 ***Procedure***

Take approximately 5 g of sample, weigh it to an accuracy of 0.001 g and transfer it to a 400 ml conical flask. Cover with a watch glass and carefully add 5 ml of bromine water (**4.7.2.2**) and 25 ml of hydrochloric acid (**4.7.2.4**).

When the reaction has subsided, transfer the flask to the hot plate (**4.7.3.1**), evaporate to dryness and continue heating for 1 h at (105 ± 5) °C. Cool the flask and contents, add 20 ml of hydrochloric acid (**4.7.2.4**) and concentrate the solution to approximately 10 ml by further heating. Remove from the hotplate and wash off the watch glass with hot water (>60 °C) into the flask, adding hot water to give a final volume of approximately 80 ml. Bring to the boil, remove from the heat and allow the insoluble residue to settle for 3 min. Filter through a medium filter paper (**4.7.3.2**), collecting the filtrate in a 250 ml conical flask.

Transfer the residue from the conical flask to the filter paper and thoroughly wash with repeated portions of hot water to remove dissolved chlorides, draining between washes. Discard the filter paper and residue.

Add 2 ml of hydrochloric acid (**4.7.2.4**) to the filtrate and bring to the boil. Add 10 ml of barium chloride solution (**4.7.2.5**) and continue boiling for 20 min. Remove from the heat and stand the flask in a warm place overnight. Filter through the fine filter paper (**4.7.3.3**) and wash thoroughly with several portions of hot water, draining between washes. Transfer the filter paper and residue to a tared platinum or silica crucible (**4.7.3.4**). Place the crucible over a Bunsen burner or on a hotplate and char the paper without flaming. Place the crucible with charred paper and residue into the furnace (**4.7.3.5**) at (1 200 ± 50) °C for 20 min. Cool in a desiccator and weigh.

4.7.5 ***Calculation of results***

Calculate the amount of sulfur present, S_1, as a percentage from the equation:

$$S_1 = \frac{13.7 m_6}{m_5} \qquad (8)$$

where

m_5 is the mass of sample, in grams (g);

m_6 is the mass of the final residue, in grams (g).

4.8 Determination of carbon dioxide in carbonate

4.8.1 ***Principle***

Carbon dioxide is liberated from the sample by means of hydrochloric acid and absorbed in barium hydroxide solution. Phenolphthalein indicator is added to the resulting precipitate and the excess alkalinity removed by hydrochloric acid. This is followed by a further titration with hydrochloric acid using bromophenol blue as indicator and the carbon dioxide content calculated from the volume of acid used.

4.8.2 ***Reagents***

4.8.2.1 *Barium chloride*, $BaCl_2.2H_2O$.

4.8.2.2 *Sodium hydroxide solution*, approximately 1.0 M.

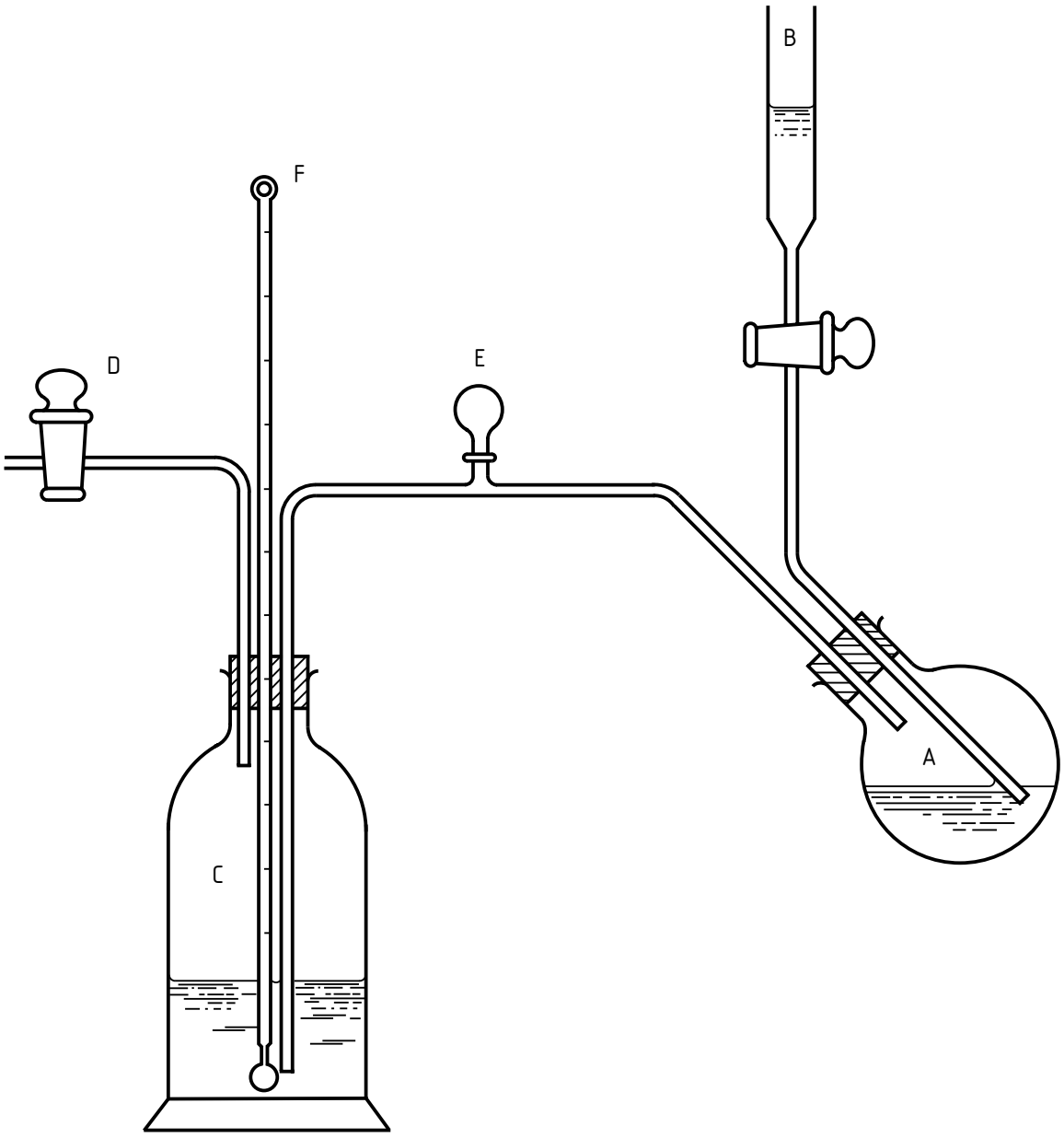
4.8.2.3 *Barium hydroxide solution*. Dissolve 125 g of barium chloride (**4.8.2.1**) in 1 l of water. Add 1 l of this solution to 1 l of sodium hydroxide solution (**4.8.2.2**) and mix in an aspirator fitted with a soda-lime guard tube. Allow any slight precipitate to settle before use.

4.8.2.4 *Hydrochloric acid solution*, 1.0 M.

4.8.3 ***Apparatus***

The apparatus required is shown in Figure 2 and consists of an 800 ml Kjeldahl flask (A), connected via a rubber stopper to funnel B, and to bottle C using glass tubing (with an internal diameter of approximately 5 mm) which is fitted with a rubber teat safety device (E). Bottle C is fitted with a thermometer (F) and is connected to a vacuum via tap D.

NOTE All components should be suitable for the vacuum to which they are subjected.



A. Flask
B. Funnel
C. Bottle
D. Tap
E. Safety device (rubber teat)
F. Thermometer

Figure 2 — Typical apparatus for determination of carbon dioxide

4.8.4 *Procedure*

Take one of the following masses of dry sample and weigh it to the nearest 0.1 g:

— 10 g quicklime;

— 10 g hydrated lime; or

— 1 g calcium carbonate.

Wash the sample into flask A, making sure that no particles adhere to the neck. Add water to give a total volume of approximately 100 ml.

Assemble the apparatus, adding 40 ml of barium hydroxide solution (**4.8.2.3**) to bottle C, place a small amount of water in funnel B and evacuate through tap D to below 4 kPa.

Close tap D and add 60 ml of hydrochloric acid (1 + 9) to funnel B. Carefully run the acid into flask A, taking care not to allow air into the apparatus, leaving 2 ml of the acid in the funnel. Close the tap of funnel B and add approximately 20 ml of water to act as a seal.

Heat flask A with a Bunsen burner while shaking bottle C continuously to assist the absorption of carbon dioxide. Continue heating until the temperature of bottle C reaches (70 ± 5) °C. Remove the burner and carefully open tap D. Remove bottle C, washing any precipitated barium carbonate from the delivery tube into the bottle.

Add a few drops of phenolphthalein and neutralize exactly with hydrochloric acid, 1.0 M (**4.8.2.4**). Adjust the volume of barium hydroxide solution (**4.8.2.3**) added to flask A if necessary to ensure that there is an excess of barium hydroxide throughout the determination equivalent to a titration of at least 5 ml of hydrochloric acid, 1.0 M (**4.8.2.4**).

Add bromophenol blue and titrate the precipitated barium carbonate with hydrochloric acid, 1.0 M (**4.8.2.4**). Towards the end of the titration, stopper the bottle and shake the contents thoroughly after the addition of each portion of acid and continue until the end point is reached. Note the volume required in the second titration using bromophenol blue, X.

Carry out blank determinations at frequent intervals.

4.8.5 *Calculation of result*

Calculate the amount of carbon dioxide as a percentage from the equation:

$$[CO_2] = \frac{2.2(X - Y)}{m} \qquad (9)$$

where

m is the mass of sample, in grams (g);

X is the volume of acid required in the second titration, in millilitres (ml);

Y is the volume of acid required in the blank titration, in millilitres (ml).

5 Determination of minor constituents by flame atomic absorption spectroscopy

NOTE A summary of the tests in this clause, with the relevant methods for the preparation of sample solutions, is shown in Figure 3.

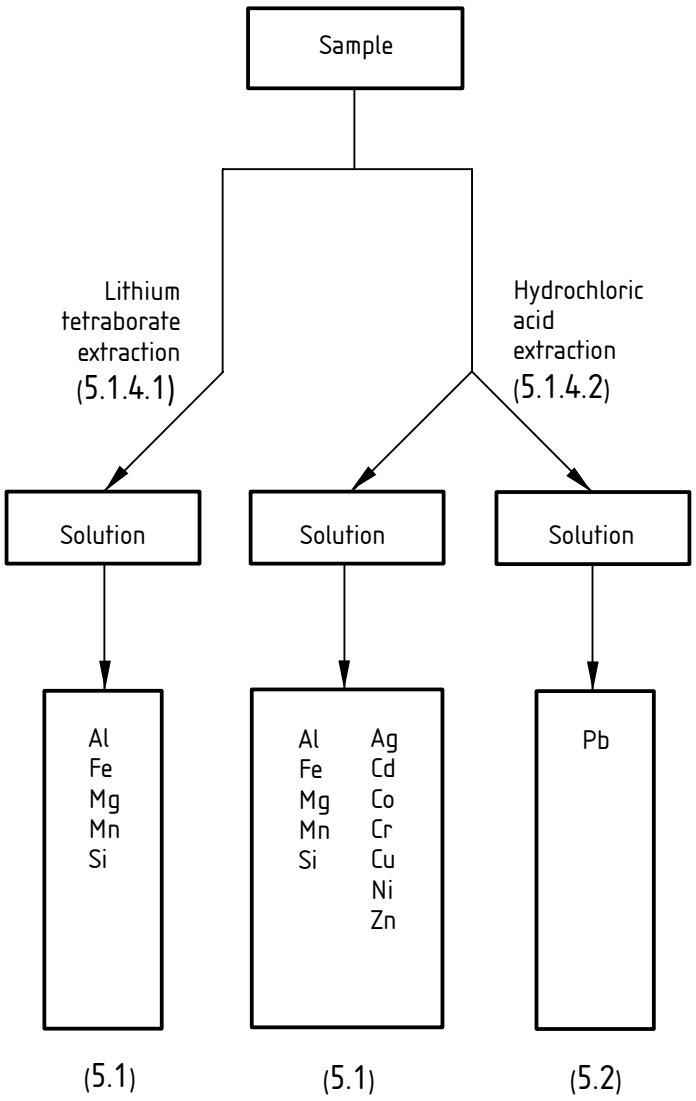


Figure 3 — Determinations using atomic absorption spectrometry

5.1 Determination of minor and trace elements in quicklime, hydrated lime and natural calcium carbonate

5.1.1 *Principle*

A sample solution, digested either by fusion (**5.1.4.1**) or by acid (**5.1.4.2**), is aspirated into a flame and atomized. Elemental concentrations are determined by graphically relating the absorption at specific wavelengths for an unknown sample to calibration curves made from standard extracts of known composition. Table 2 lists some of the elements that can be analysed by this test method, and the preferred wavelength and flame type.

Table 2 — Elements, preferred wavelengths and flame types

Element	Wavelength nm	Flame type
Minor elements		
Silicon	251.6	N_2O / C_2H_2
Aluminium	309.3	N_2O / C_2H_2
Iron	248.3	Air / C_2H_2
Manganese	279.5	Air / C_2H_2
Magnesium	202.5	Air / C_2H_2
Trace elements		
Silver	328.1	Air / C_2H_2
Copper	324.7	Air / C_2H_2
Zinc	213.9	Air / C_2H_2
Cadmium	228.8	Air / C_2H_2
Chromium	357.9	Air / C_2H_2
Nickel	232.0	Air / C_2H_2
Cobalt	240.7	Air / C_2H_2

5.1.2 *Reagents*

NOTE The high sensitivity of the tests requires reagents of high purity.

5.1.2.1 *Lithium metaborate* or *lithium tetraborate*.

5.1.2.2 *Nitric acid*, 1 + 4.

5.1.2.3 *Hydrochloric acid*, concentrated.

5.1.2.4 *Calcium carbonate*, minimum assay 99.0 %, lowest limits of impurities available. Typical analytical grades are not suitable. Limits of detection shall be calculated with reference to the levels of impurities.

5.1.2.5 *Standard element solutions*, l 000 mg/l (available commercially).

5.1.2.6 *Combined minor element solution*. Pipette the following amounts of l 000 mg/l standard element solutions (**5.1.2.5**) into a 500 ml volumetric flask, and make up to the mark with water:

— 60 ml magnesium;
— 100 ml silicon;
— 40 ml aluminium;
— 10 ml iron;
— 5 ml manganese.

5.1.2.7 *Combined trace element solution*. Pipette the following amounts of l 000 mg/l standard element solutions (**5.1.2.5**) into a 500 ml volumetric flask, and make up to the mark with water:

— 5 ml silver;
— 5 ml copper;
— 2 ml zinc;
— 10 ml cadmium;
— 25 ml chromium;
— 25 ml nickel;
— 25 ml cobalt.

5.1.3 ***Apparatus***

5.1.3.1 *Platinum crucibles*, 15 ml or 20 ml.

5.1.3.2 *Muffle furnace*, capable of maintaining 1 000 °C.

5.1.3.3 *Beakers*, 150 ml and 250 ml.

5.1.3.4 *Magnetic followers*.

5.1.3.5 *Volumetric flasks*, 100 ml, 250 ml and 500 ml.

5.1.3.6 *Cover glasses*.

5.1.3.7 *Hotplate*.

5.1.3.8 *Pipettes*, 2 ml, 5 ml, 10 ml, 20 ml, 25 ml and 50 ml.

5.1.3.9 *Atomic absorption spectrometer*, equipped with hollow-cathode lamps or electrodeless discharge lamps for each element of interest, and a simultaneous background correction system.

5.1.4 ***Preparation of sample solutions***

5.1.4.1 *Lithium tetraborate extraction*

NOTE 1 The following elements are determined by this method, using either lithium tetraborate or lithium metaborate as a flux:

— magnesium, when the mass fraction of MgO is less than 1 %;
— silicon;
— aluminium;
— iron;
— manganese.

NOTE 2 Hydrochloric acid extraction (**5.1.4.2**) may be used as a preparation method for the determination of "total recoverable" minor elements.

Take one of the following masses of dry sample and weigh it to the nearest 0.0001 g:

— approximately 0.76 g quicklime;
— approximately 1.00 g hydrated lime; or
— approximately 1.35 g calcium carbonate.

Place the weighed sample in a platinum crucible (**5.1.3.1**). Weigh 1.00 g of lithium metaborate (**5.1.2.1**) into the crucible. Mix the sample and lithium metaborate.

NOTE 3 Where samples of lower purity are analysed, it may be necessary to increase the mass of lithium metaborate used in order to obtain a clear melt.

Place the crucible in a muffle furnace (**5.1.3.2**) at 1 000 °C for 15 min or until a clear melt is obtained. Allow to cool.

Place the crucible in a 250 ml beaker, and place a magnetic follower (**5.1.3.4**) in the crucible. Add 20 ml of nitric acid 1 + 4 (**5.1.2.2**) to the beaker, and sufficient water to cover the crucible. Stir with the magnetic follower until the melt has dissolved.

NOTE 4 This process may be assisted by gently heating the beaker.

Transfer the solution from the beaker to a 250 ml volumetric flask and make up to the mark with water.

5.1.4.2 *Hydrochloric acid extraction*

5.1.4.2.1 *For determination of calcium and magnesium*

Boil a laboratory sample with concentrated hydrochloric acid and filter the resulting solution as described in BS EN 12485 to determine the contents of calcium and magnesium using the filtration methods described in that standard.

5.1.4.2.2 *For determination of minor and trace elements by flame atomic absorption spectroscopy*

NOTE The minor and trace element concentrations determined by this method are termed "total recoverable" (i.e. components not digested in hot acid are not recovered). The minor elements determined by this method are listed in note 1 to **5.1.4.1**. The trace elements determined by this method include silver, copper, zinc, cadmium, chromium, nickel and cobalt.

Take one of the following masses of dry sample and weigh it to the nearest 0.0001 g:

— approximately 3.75 g quicklime;
— approximately 5.00 g hydrated lime; or
— approximately 6.75 g calcium carbonate.

Transfer the sample to a 150 ml beaker and disperse in about 20 ml of water. Cautiously add 20 ml of concentrated hydrochloric acid (**5.1.2.3**).

Cover the beaker with a cover glass and bring to the boil on the hotplate (**5.1.3.7**). Boil for 5 min.

Quantitatively transfer the liquid and any undissolved residue into a 100 ml volumetric flask. Allow the contents of the flask to cool. Make the flask up to the mark with water.

5.1.5 ***Calibration standard extracts***

5.1.5.1 *General*

Prepare standard extracts in the same way as sample extracts, but using high purity calcium carbonate instead of the sample. Make fresh standard extracts for each batch of tests.

NOTE Where samples of lower purity are analysed, consideration should be given to reducing the calcium levels of the matrix-matched standard extracts.

5.1.5.2 *Minor elements*

Prepare three standard extracts following the procedures given in **5.1.4.2.1** using calcium carbonate (**5.1.2.4**) in place of the sample.

Transfer the three solutions from the beakers into 250 ml volumetric flasks. Allow the contents of the flasks to cool. Make the first flask up to the mark with water. This is the reagent blank. Add by pipette 25 ml of combined minor element solution (**5.1.2.6**) to the second flask and make up to the mark with water. This is standard solution 1. Add by pipette 50 ml of combined minor element solution (**5.1.2.6**) to the third flask and make up to the mark with water. This is standard solution 2. The element concentrations in the three standard extracts are given in Table 3.

Table 3 — Minor element concentrations in standard extracts

Element	Blank (minor elements)	Standard solution 1	Standard solution 2
Magnesium (Mg)	0	12	24
Silicon (Si)	0	20	40
Aluminium (Al)	0	8	16
Iron (Fe)	0	2	4
Manganese (Mn)	0	1	2

5.1.5.3 *Trace elements*

Prepare three standard extracts following the procedures given in **5.1.4.2.1** and **5.1.4.2.2** using calcium carbonate (**5.1.2.4**) in place of the sample.

Transfer the three solutions from the beakers into 100 ml volumetric flasks. Allow the contents of the flasks to cool. Make the first flask up to the mark with water. This is the reagent blank. Add by pipette 5 ml of combined trace element solution (**5.1.2.7**) to the second flask and make up to the mark with water. This is standard solution A. Add by pipette 10 ml of combined trace element solution (**5.1.2.7**) to the third flask and make up to the mark with water. This is standard solution B. The element concentrations in the three standard extracts are given in Table 4.

Table 4 — Trace element concentrations in standard extracts

Element	Blank (trace elements)	Standard solution A	Standard solution B
Silver (Ag)	0	0.5	1
Copper (Cu)	0	0.5	1
Zinc (Zn)	0	0.2	0.4
Cadmium (Cd)	0	1	2
Chromium (Cr)	0	2.5	5
Nickel (Ni)	0	2.5	5
Cobalt (Co)	0	2.5	5

5.1.6 ***Procedure***

NOTE The spectrometer should be prepared and operated in accordance with the manufacturer's instructions. Design differences between spectrometers make it impractical to specify the required steps in detail in this standard.

Calibrate the spectrometer (**5.1.3.9**) by aspirating the blank and standard extracts prepared in **5.1.5.2** or **5.1.5.3**.

Aspirate the sample extracts prepared in **5.1.4.1** or **5.1.4.2** using the same conditions as used during calibration.

Record the readings obtained while aspirating the sample extracts. If the readings exceed the highest reading obtained from the standard extracts (Standard 2 or Standard B), repeat the entire determination using a reduced mass of sample and equivalently reduced masses of calcium carbonate in new standard extracts.

5.1.7 ***Calculation and expression of results***

Plot graphs of the readings obtained for each element from the standard extracts against the known element concentrations. Use the calibration curves to determine the concentrations of the elements in the sample extracts.

Calculate the content of the element, E, as milligrams per kilogram of sample from the equation:

$$E = \frac{(A \times V)}{m} \qquad (10)$$

where

A is the concentration of the element in the sample extract, in milligrams per litre (mg/l);

V is the volume of the sample extract, in millilitres (ml);

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

NOTE On account of matrix-matching of the standard extracts, the practical quantitation limit for magnesium is estimated to be at least 25 mg/kg.

5.2 Determination of lead

5.2.1 *Principle*

A sample is digested in acid. The lead in the digest is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl ketone (MIBK). The extract is aspirated into a flame and atomized. Lead concentration is determined by graphically relating the absorption at a specific wavelength for an unknown sample to calibration curves prepared from standard extracts of known composition.

NOTE The preferred wavelength is 217.0 nm (air-acetylene flame).

5.2.2 *Reagents*

NOTE The high sensitivity of the test requires reagents of high purity.

5.2.2.1 *Hydrochloric acid*, 1 + 1.

5.2.2.2 *Ammonium pyrrolidine dithiocarbamate* (APDC).

5.2.2.3 *Ammonium pyrrolidine dithiocarbamate*, 1 % solution. Dissolve 1 g of APDC (**5.2.2.2**) in water in a 100 ml volumetric flask and make up to the mark with water.

5.2.2.4 *Methyl isobutyl ketone* (MIBK).

5.2.2.5 *Standard lead solution*, 1 000 mg/l.

5.2.2.6 *Lead working solution*. Pipette 1 ml of standard lead solution (**5.2.2.5**) into a 1 l volumetric flask and make up to the mark with water.

5.2.3 *Apparatus*

5.2.3.1 *Atomic absorption spectrometer*, equipped with a hollow-cathode lamp or an electrodeless discharge lamp for lead, and a simultaneous background correction system.

5.2.4 *Sample preparation*

Take approximately 5 g of sample and weigh it to the nearest 0.0001 g. Transfer the sample to a 150 ml beaker and cautiously add 20 ml of hydrochloric acid 1 + 1 (**5.2.2.1**).

Cover the beaker with a cover glass, bring to the boil on a hotplate and boil for 5 min.

Transfer the liquid and any undissolved residue into a 100 ml volumetric flask. Allow the contents of the flask to cool. Make the flask up to the mark with water.

Transfer the contents of the flask into a separating funnel. Pipette 5 ml of 1 % APDC solution (**5.2.2.3**) into the separating funnel and shake well. Then pipette 4 ml of MIBK (**5.2.2.4**) into the separating funnel and shake vigorously for at least 30 s. Allow the aqueous and non-aqueous layers to separate.

Run off the aqueous phase into a beaker, then collect the non-aqueous phase in a test tube and stopper it.

Return the aqueous phase to the separating funnel. Pipette 1 ml of MIBK (**5.2.2.4**) into the separating funnel and shake vigorously for at least 30 s. Allow the aqueous and non-aqueous layers to separate. Discard the aqueous phase. Combine the non-aqueous phase with the non-aqueous phase collected in the first extraction.

5.2.5 *Calibration standard extracts*

Place 100 ml of distilled water into each of four separating funnels. To the first funnel add 20 ml of lead working solution (**5.2.2.6**), to the second add 10 ml, to the third add 5 ml and to the fourth add none. Shake all funnels well.

Add 5 ml of 1 % APDC solution (**5.2.2.3**) to each funnel and shake well, then pipette 4 ml of MIBK (**5.2.2.4**) into each separating funnel and shake vigorously for at least 30 s. Allow the aqueous and non-aqueous layers to separate.

Continue, using the two-stage extraction procedure described in **5.2.4**, to produce four standard non-aqueous extracts with lead concentrations of 4 mg/l, 2 mg/l, 1 mg/l and 0 mg/l respectively.

5.2.6 *Procedure*

NOTE The spectrometer should be prepared and operated in accordance with the manufacturer's instructions. Design differences between spectrometers make it impractical to describe the required steps in detail in this standard. However, particular attention has to be given to setting up the flame conditions when aspirating MIBK. As a general guide, the flame should be run as lean as possible.

Calibrate the instrument by aspirating the standard non-aqueous extracts prepared in **5.2.5**.

Aspirate the sample extracts prepared in **5.2.4** using the same conditions as used during calibration.

Record the readings obtained while aspirating the sample extracts. If the readings exceed the highest reading obtained from the standard non-aqueous extracts, repeat the entire determination using a smaller sample.

5.2.7 *Calculation and expression of results*

Plot graphs of the readings obtained for each element from the standard non-aqueous extracts against the known lead concentrations. Use the calibration curve to determine the concentration of lead in the sample extracts.

Calculate the lead content, E, as milligrams per kilogram of sample from the equation:

$$E = \frac{(A \times 5)}{m} \qquad (11)$$

where

A is the concentration of the lead in the sample extract, in milligrams per litre (mg/l);

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

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