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Determination of boron(III) oxide in refractory products —

Part 1:
Determination of total boron(III) oxide in oxidic materials for ceramics, glass and glazes

Dosage de l'oxyde de bore(III) dans les produits réfractaires —

Partie 1: Détermination de l'oxyde de bore(III) total dans les matériaux oxydants pour les céramiques, les verres et les émaux

Reference number
ISO 21078-1:2008(E)

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Foreword

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

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

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

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

ISO 21078-1 was prepared by Technical Committee ISO/TC 33, *Refractories*, in collaboration with Technical Committee CEN/TC 187, *Refractory products and materials.*

ISO 21078 consists of the following parts, under the general title *Determination of boron(III) oxide in refractory products*:

- *Part 1: Determination of total boron(III) oxide in oxidic materials for ceramics, glass and glazes*
- *Part 2: Acid extraction method for the determination of boron(III) oxide in binder components*

This corrected version of ISO 21078-1:2008 incorporates the following correction: in 7.2.10 (first line), “6 ml” has been replaced by “60 ml”.

Determination of boron(III) oxide in refractory products —

Part 1:
Determination of total boron(III) oxide in oxidic materials for ceramics, glass and glazes

1 Scope

This part of ISO 21078 specifies methods of determining boron(III) oxide in refractory products and raw materials, in mass fractions of 0,01 % or greater. It is applicable to the determination of total boron(III) oxide in oxidic materials for ceramics, glass and glazes.

The determination of boron(III) oxide is carried out using one of the following four methods:

a) alkaline titrimetry, which is applied to samples containing more than 0,5 % by mass of boron(III) oxide;

b) azomethine H absorption spectrophotometry, which is applied to samples containing from 0,01 % by mass to 2,5 % by mass of boron(III) oxide;

c) curcumin absorption spectrophotometry (rothocyanine method), which is applied to samples containing from 0,01 % by mass to 1,0 % by mass of boron(III) oxide;

d) inductively coupled plasma atomic emission spectrometry (ICP-AES), which is applied to samples containing from 0,01 % by mass to 15 % by mass of boron(III) oxide.

NOTE 1 The method can be extended to 30 % boron(III) oxide using modified oxidic fluxes.

NOTE 2 Interlaboratory test results for this part of ISO 21078 are given in Annex A.

2 Normative references

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

ISO 31-0, *Quantities and units — Part 0: General principles*

ISO 836, *Refractories — Vocabulary*

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

ISO 6353-3, *Reagents for chemical analysis — Part 3: Specifications — Second series*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 836 and the following apply.

3.1
dry unshaped refractories
dry particles and/or powder of unshaped refractories

3.2
wet unshaped refractories
wet particles and/or powder of unshaped refractories with liquid such as mortar and a mixture of refractory-aggregate and pitch or resin

4 Preparation of the test sample

4.1 Refractory brick or its raw material

Carry out sampling in accordance with the contract between the user and producer. Take a specified quantity from a lot of the sample and crush to pass through a 6,7 mm sieve (see ISO 3310-1). Reduce to about 100 g by riffling or coning and quartering, then grind all the reduced sample to pass through a 300 µm sieve (ISO 3310-1).

4.2 Unshaped refractories

Prepare two portions of approximately 100 g each of the sample for analysis (both dry and wet) and crush to pass through a 300 µm sieve (see ISO 3310-1) in accordance with the following procedure.

4.3 Dry unshaped refractories

Take one bag or 5 kg of the sample from a lot, reduce to about 100 g as described in 4.1 and crush to pass through a 300 µm sieve.

4.4 Wet unshaped refractories

Take a specified quantity from the sample and spread on a heat-resistant plate that does not react with the sample (for example, a polyethylene tetrafluoride plate) to form a charge of 10 mm thickness. Dry the sample in an air-bath or oven at 110°C ± 5°C for a minimum of 10 h. Then crush to pass through a 6,7 mm sieve, reduce to about 100 g by riffling or coning and quartering, and grind to pass through a 300 µm sieve (see ISO 3310-1).

4.5 Laboratory sample

Reduce the laboratory sample from 4.1 or 4.2 to approximately 25 g by coning and quartering, and grind to pass through a 106 µm sieve. This is the test sample for analysis. Transfer it into a container (e.g. a flat weighing bottle (50 mm × 30 mm) or sample tube (50 mm × 25 mm), dry in an oven at 110°C ± 5°C for a minimum of 2 h, cool and store it in a desiccator.

4.6 Weighing of test portion

Weigh the quantity of the test portion for the chemical analysis specified for the particular procedure, to the nearest 0,1 mg, using an analytical balance and record the actual mass.

5 Number of determinations

Carry out simultaneous duplicate determinations. Carry out a blank test on the reagents and make appropriate deductions from the results.

6 Determination of boron(III) oxide by alkaline titrimetry

6.1 Principle

The sample is fused with sodium hydroxide in a dish placed in a furnace at about 600 °C. After cooling, the melt is dissolved in water and the sample solution made up to about 100 ml with water. The interfering ions left in the sample solution are precipitated by adding calcium carbonate. After first adjusting the pH value to 6,5 with sodium hydroxide solution, mannitol is added and the H+ ions liberated as the result are titrated with sodium hydroxide to obtain a pH value of 6,8.

6.2 Reagents

Use only reagents of known analytical purity and water conforming to the requirements of grade 2 of ISO 3696 (e.g. double-distilled water).

The boron and borate ion concentrations in the water and the reagents shall be negligible compared with the lowest concentration to be determined. All solutions are aqueous, unless otherwise specified.

6.2.1 Sodium hydroxide (ISO 6353-2 R 34), assay, minimum mass fraction 98 %.

6.2.2 Hydrochloric acid (concentrated), (ISO 6353-2 R 13), mass fraction 35 %.

6.2.3 Hydrochloric acid (1+1), add 1 volume of hydrochloric acid (concentrated) to 1 volume of water.

6.2.4 Calcium carbonate (ISO 6353-3 R 53), assay, minimum mass fraction 99,5 %.

6.2.5 Bromocresol purple solution, $C_{21}H_{16}Br_2O_5S$, 1 g/l.

Dissolve 0,1 g of bromocresol purple in water and dilute to approximately 100 ml. Keep this solution in the dark at low temperature.

6.2.6 Boron(III) oxide standard solution, 0,1 mg B_2O_3/ml.

Transfer approximately 0,5 g of boric acid into a 100 ml beaker, spread it as a thin layer and dry for 24 h in a desiccator. Weigh 0,177 6 g of this dry boric acid and transfer into a 200 ml plastic beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

6.2.7 D(−)-mannitol, $C_6H_{14}O_6$.

6.2.8 Sodium hydroxide standard volumetric solution.

Transfer 50 g of sodium hydroxide into a polyethylene bottle, add 50 ml of water, and dissolve with cooling. Allow to stand for several days with a cover, pipette 4,0 ml of the supernatant fraction, and dilute to 2 000 ml in a volumetric flask. Transfer this solution into a polyethylene bottle using a 25 ml automatic filling burette with soda-lime tubes to absorb the carbon dioxide in the air.

Pipette precisely 100 ml of boron(III) oxide standard solution (0,1 mg/ml) into a 200 ml beaker and stir by using a magnetic stirrer, put a pH electrode into the solution and add drops of the sodium hydroxide standard volumetric solution until the pH is 6,5. Remove the electrode, add 10 g of D(−)-mannitol, set the electrode again, and titrate with the sodium hydroxide standard volumetric solution until the pH is 6,8.

Calculate the equivalent factor, F, the mass in g, of boron(III) oxide equivalent to 1 ml of sodium hydroxide standard volumetric solution, using Equation (1).

$$F = \frac{0{,}01}{V} \qquad (1)$$

where V is the volume, in ml, of titration of sodium hydroxide standard volumetric solution after addition of D(−)-mannitol.

6.3 Apparatus

Ordinary laboratory apparatus and the following.

6.3.1 Vitreous carbon dishes, of suitable nominal capacity.

6.3.2 Vitreous carbon lids, to fit 6.3.1.

6.3.3 Muffle furnace, capable of being controlled at temperatures up to at least 700 °C.

6.3.4 pH meter, with a glass electrode.

NOTE Automated titration equipment with a piston-operated burette and magnetic stirrer may be used to facilitate the analysis.

6.4 Mass of test portion

Weigh out 1,00 g of the test sample.

NOTE The mass of the test portion is a function of the boron mass fraction. It is usually 1,0 g.

6.5 Procedure

Weigh 1 g to 2 g of sodium hydroxide into a dish, cover the dish and fuse it in the furnace at approximately 600 °C for about 10 min. After cooling in the desiccator, add the weighed sample, cover it with 1 g to 2 g of sodium hydroxide, cover the dish and dissolve by digestion at approximately 600 °C for about 30 min until a clear melt is obtained, swirling repeatedly. After cooling, transfer the melt cake to a 250 ml beaker, dissolve any residue in the dish with water and transfer it to the beaker, repeating this procedure several times if necessary. Make up the solution to about 100 ml with water and heat until the melt cake has disintegrated.

Standardize the sample solution by titrating against hydrochloric acid (1+1), using bromocresol purple as indicator to precipitate interfering ions, ensuring that the indicator changes from violet to yellow. Then add an excess of a further 2 ml of hydrochloric acid (1+1), heat to boiling and allow to boil for 1 to 2 min. Remove the beaker from the hotplate and, after about 2 min, add a total of 1,5 g of calcium carbonate a little at a time, then boil again for a short time. Filter off the precipitate using a white-ribbon filter and wash it eight times with hot water. Transfer the residue to a 250 ml beaker, acidify with hydrochloric acid (1+1) and repeat the $CaCO_3$ precipitation as described above.

Make up the combined filtrate to about 250 ml with water and boil it for a short time. After cooling, adjust the pH value of the test solution to 6,5 with sodium hydroxide standard volumetric solution using the glass electrode of the pH meter. Now add 20 g of D(–)-mannitol to the solution and dissolve it while stirring. Then titrate with sodium hydroxide standard volumetric solution to a pH value of 6,8 and read off the volume of solution used to titrate from a pH value of 6,5 to a pH value of 6,8.

6.6 Blank test

Carry out the procedure given in 6.5 without the sample.

6.7 Calculation

Calculate the mass fraction of boron(III) oxide in the sample, w_{B1}, as a percentage, using Equation (2):

$$w_{B1} = \frac{(V_1 - V_2) \times F}{m} \times 100 \qquad (2)$$

where

V_1 is the volume, in ml, of sodium hydroxide standard volumetric solution used for titration of the test solution after addition of D(−)-mannitol;

V_2 is the volume, in ml, of sodium hydroxide standard volumetric solution used for titration of the blank solution after addition of D(−)-mannitol;

F is the equivalent factor, in g, of boron(III) oxide equivalent to 1 ml of sodium hydroxide standard volumetric solution;

m is the mass, in g, of the test portion in 6.4.

6.8 Interferences

If the D(−)-mannitol used for the determination is acidic, subtract the equivalent volume of sodium hydroxide solution from the volume used in the titration.

Germanium oxide will interfere with this alkaline titrimetry method. Germanium oxide is highly unlikely to be present in the materials in the scope of this part of ISO 21078. However, if this part of ISO 21078 is applied to glass samples and the presence of germanium oxide is suspected, one of the other three alternative procedures shall be used.

7 Determination of boron(III) oxide by azomethine H absorption spectrophotometry

7.1 Principle

The sample is fused with sodium hydroxide in a dish placed in a furnace at about 600 °C. After cooling, the melt is dissolved in water and the sample solution made up to about 100 ml with water. The pH value of the sample solution is adjusted to 5,2, azomethine H is added and the yellow complex is determined photometrically at a wavelength of 415 nm against reference solutions.

7.2 Reagents

Use only reagents of known analytical purity and water conforming to the requirements of grade 2 of ISO 3696 (e.g. double-distilled water).

The boron and borate ion concentrations in the water and the reagents shall be negligible compared with the lowest concentration to be determined. All solutions are aqueous unless otherwise specified.

7.2.1 Sodium hydroxide (ISO 6353-2 R 34), assay, minimum mass fraction 98 %.

7.2.2 Hydrochloric acid (concentrated) (ISO 6353-2 R 13), mass fraction 35 %.

7.2.3 Hydrochloric acid (1+1).

Add 1 volume of hydrochloric acid (concentrated) to 1 volume of water.

7.2.4 Boric acid, H_3BO_3.

7.2.5 Boron(III) oxide stock solution, 1 mg B_2O_3/ml.

Transfer approximately 2 g of boric acid into a 100 ml beaker, spread it as a thin layer and dry for 24 h in a desiccator. Weigh 1,776 g of this dry boric acid and transfer into a 200 ml plastic beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

7.2.6 Boron(III) oxide standard solution No. 1, 0,1 mg B_2O_3/ml.

Pipette 10 ml of the boron(III) oxide stock solution into a 100 ml volumetric flask and make up to the mark with water. Keep the solution, which is stable only for about 9 h, in a plastic bottle.

7.2.7 Boron(III) oxide standard solution No 2, 0,01 mg B_2O_3/ml.

Pipette 10 ml of boron(III) oxide standard solution No. 1 into a 100 ml plastic volumetric flask and make up to the mark with water. Make up a fresh solution before every determination.

7.2.8 Sodium salt of azomethine H, $C_7H_{12}NNaO_8S_2$.

7.2.9 L(+)-ascorbic acid, $C_6H_8O_6$.

7.2.10 Azomethine H solution.

Mix 1 g of azomethine H and 3 g of ascorbic acid in a 100 ml glass beaker with about 60 ml of water, transfer the mixture to a 100 ml volumetric flask and make up to the mark with water. During mixing, the solution becomes clear. Transfer the solution to a plastic bottle and store it in a refrigerator; it will be stable for one week.

7.2.11 Ammonium acetate, CH_3COONH_4.

7.2.12 Acetic acid (ISO 6353-2 R 1), minimum mass fraction 99,7 % as CH_3COOH.

7.2.13 Buffer solution.

Dissolve 200 g of ammonium acetate in a glass beaker with about 200 ml of water, add 50 ml of acetic acid, use water to rinse the solution into a 500 ml volumetric flask and make up to the mark with water. Store the solution in a plastic bottle.

7.2.14 Ammonium hydroxide solution (concentrated) (ISO 6353-2 R 3), minimum mass fraction 25 % as NH_3.

7.2.15 Ammonium hydroxide solution (1+6), NH_4OH.

7.2.16 Disodium ethylenediaminetetraacetate (EDTA-Na$_2$), $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$.

7.2.17 Citric acid monohydrate, $C_6H_8O_7 \cdot H_2O$.

7.2.18 Complexing solution.

Mix 37,2 g of disodium ethylenediaminetetraacetate and 5 g of citric acid monohydrate in a beaker with about 300 ml of water and add 2 mol/l ammonium hydroxide solution until the reagents have dissolved and the solution is clear. Then, using the glass electrode of the pH meter, adjust the pH value to 5 by adding further 2 mol/l ammonium hydroxide solution. Make up to 500 ml with water.

7.2.19 2,2′,2″,4,4′-pentamethoxytriphenylcarbinol, $C_{24}H_{26}O_6$.

7.2.20 Ethanol (ISO 6353-2 R 11), minimum mass fraction 99,8 %, as C_2H_5OH.

7.2.21 Indicator solution, prepared by dissolving 50 mg of 2,2′,2″,4,4′-pentamethoxytriphenylcarbinol in 50 ml of ethanol while heating gently. The indicator changes from violet to colourless at a pH value of 2 to 3.

7.2.22 Sodium chloride solution, 241,7 g/l.

7.3 Apparatus

Ordinary laboratory apparatus and the following.

7.3.1 Vitreous carbon dishes, of suitable nominal capacity.

7.3.2 Vitreous carbon lids, to fit 7.3.1.

7.3.3 Muffle furnace, capable of being controlled at temperatures up to at least 700 °C.

7.3.4 Photometer, with 1 cm cell.

7.4 Mass of test portion

Weigh out 0,50 g of the test sample.

NOTE The mass of the test portion is a function of the mass fraction of boron . It will usually be 0,5 g.

7.5 Procedure

Weigh 1 g to 2 g of sodium hydroxide into a dish, cover the dish and fuse in the furnace at approximately 600 °C for about 10 min. After cooling in the desiccator, add the weighed sample, cover it with 1 g to 2 g of sodium hydroxide, cover the dish and dissolve by digestion at approximately 600 °C for about 30 min until a clear melt is obtained, swirling repeatedly. Introduce 25 ml of hydrochloric acid (1+1) into a 100 ml plastic volumetric flask. After cooling the melt, dissolve the melt cake in a little hot water and transfer it to the volumetric flask, repeating this process several times if necessary. After cooling, make up to the mark with water.

This solution is designated as stock solution S1.

Prior to the analysis, remove any silicon(IV) oxide precipitate present in the sample solutions by centrifuging, filtering or allowing to settle.

Pipette an aliquot portion of the stock solution S1 into a 50 ml plastic volumetric flask. The volume of the aliquot portion to be taken depends on the expected mass fraction of boron(III) oxide and is shown in Table 1.

Table 1 — Preparation of test solution

Mass fraction of boron(III) oxide %	**Aliquot portion of stock solution S1** ml	**Volume of sodium chloride solution** (7.2.22) ml
2,5 to 0,5	2	5,5
0,6 to 0,11	5	4,8
0,12 to 0,01	25	0

An aliquot portion of stock solution S1 may also be chosen: less than 25 ml. In this case, calculate the volume of sodium chloride solution to be added, V_S, in ml, using Equation (3):

$$V_S = (1{,}45 - 0{,}058 \times V_A) \times \frac{1\,000}{241{,}7} \qquad (3)$$

where V_A is the volume of the aliquot portion, in ml.

Add the volume of sodium chloride solution specified in Table 1, two drops of indicator solution and 5 ml of complexing solution. Neutralize with ammonium hydroxide solution (1+6) until the indicator colour just disappears. Then add 5 ml of buffer solution and 5 ml of azomethine H solution, make the volumetric flask up to the mark with water and allow to stand in the dark for 4 h. The boron concentration in the test solution will then be about 0,2 mg/l to 1 mg/l. Measure the boron concentration photometrically using a 1 cm cell, at a wavelength of 415 nm against the calibration solution, with water in the reference cell.

7.6 Blank test

Carry out the procedure described in 7.5 but omit the fusion process without using the sample.

The solution obtained corresponds to stock solution S1 and is designated as blank solution B1. The volume of blank solution B1 is the same as that of stock solution S1.

7.7 Plotting the calibration graph

Transfer 0 (as reference), 5, 10, 15 and 20 ml aliquot portions of the boron(III) oxide standard solution No.2 [0 to 0,20 mg as boron(III) oxide] into a series of 50 ml plastic volumetric flasks, leaving one flask empty for the blank solution. Add 6 ml of sodium chloride solution, 5 ml of complexing solution, 5 ml of buffer solution and 5 ml of azomethine H solution, make up to the mark with water and allow to stand in the dark for 4 h.

Measure the respective absorbances by photometry at a wavelength of 415 nm using 1 cm cells, with water in the reference cell. Then plot the calibration graph.

7.8 Calculation

Calculate the mass fraction of boron(III) oxide in the sample, W_{B2}, as a percentage, using Equation (4):

$$W_{B2} = \frac{(m_1 - m_2)}{m} \times \frac{100}{V_A} \times 100 \qquad (4)$$

where

m_1 is the mass, in mg, of boron(III) oxide in the aliquot portion of stock solution S1;

m_2 is the mass, in mg, of boron(III) oxide in the aliquot portion of blank solution B1;

V_A is the aliquot portion of stock solution S1;

m is the mass, in mg, of the test portion in 7.4.

7.9 Interferences

The percentages of oxides shown in Table 1, for the mass fraction of boron(III) oxide of the sample and in the selection of aliquot portion size, shall not be exceeded.

8 Determination of boron(III) oxide by curcumin absorption spectrophotometry

8.1 Principle

The sample is fused with sodium carbonate and dissolved in hydrochloric acid. After dehydration by adding sulfuric acid and heating, an addition of curcumin to the solution generates rothocyanine. The residue is dissolved in water/ethanol and the absorbance is measured.

8.2 Reagents

Use only reagents of known analytical purity and water conforming to the requirements of grade 2 of ISO 3696 (e.g. double-distilled water).

The boron and borate ion concentrations in the water and the reagents shall be negligible compared with the lowest concentration to be determined. All solutions are aqueous, unless otherwise specified.

8.2.1 Sodium hydroxide (ISO 6353-2 R 34), assay, minimum mass fraction 98 %.

8.2.2 Hydrochloric acid (concentrated) (ISO 6353-2 R 13), assay, minimum mass fraction 35 %.

8.2.3 Hydrochloric acid (1+1).

Add 1 volume of hydrochloric acid (concentrated) to 1 volume of water.

8.2.4 Sulfuric acid (concentrated) (ISO 6353-2 R 37), assay, minimum mass fraction 95 %.

8.2.5 Sulfuric acid (1+1).

Cautiously add 1 volume of sulfuric acid (concentrated) to 1 volume of water, while stirring and cooling (e.g. stand the beaker in flowing water).

8.2.6 Sulfuric acid (1+5).

Cautiously add 1 volume of sulfuric acid (concentrated) to 5 volumes of water, while stirring and cooling (e.g. stand the beaker in flowing water).

8.2.7 Boron(III) oxide stock solution, 1 mg B_2O_3/ml.

Transfer approximately 2 g of boric acid into a 100 ml beaker, spread it as a thin layer and dry for 24 h in a desiccator. Weigh 1,776 g of this dry boric acid and transfer into a 200 ml plastic beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

8.2.8 Boron(III) oxide standard solution, 0,01 mg B_2O_3/ml.

Pipette 10 ml of the boron(III) oxide stock solution (8.2.7) into a 1 000 ml volumetric flask and make up to the mark with water. Make up a fresh solution before every determination.

8.2.9 Diluted boron(III) oxide standard solution, 0,5 µg B_2O_3/ml.

Pipette 5 ml of the boron(III) oxide stock solution (8.2.8) into a 100 ml volumetric flask and make up to the mark with water. Make up a fresh solution before every determination.

8.2.10 Ethanol (concentrated) (ISO 6353-2 R 11), minimum mass fraction 99,8 % as C_2H_5OH.

8.2.11 Water/ethanol solvent.

Mix water and ethanol in a volume ratio of 1:3.

8.2.12 Curcumin acetic acid solution.

Weigh 0,15 g of curcumin and put in a 200 ml quartz beaker. Add 100 ml of acetic acid, and dissolve by heating. Discard the solution one week after preparation.

8.3 Apparatus

Ordinary laboratory apparatus and the following.

8.3.1 Platinum alloy crucible, of suitable nominal capacity.

8.3.2 Platinum dish, of suitable nominal capacity, thoroughly washed so that no boron residue remains.

NOTE For example, this can be done by adding hydrofluoric acid and a small amount of sulfuric acid, heating it on a hotplate to evaporate the boron species, then washing thoroughly with water and drying.

8.3.3 Electric muffle furnace, capable of being controlled at temperatures up to at least 1 050 °C.

8.3.4 Bunsen burner.

8.3.5 Plastic volumetric flask, of capacity 500 ml, calibrated as follows. Either

a) wash a plastic flask thoroughly, invert it and allow it to stand to dry naturally, or

b) wash a plastic flask with water, ethanol and diethylether and dry it by blowing air into it.

Cut the 20 graduations from a sheet of section paper (1 mm squares) into a strip and attach it to the marked line of the plastic flask so that the line coincides with the central line of the paper. Weigh the flask to the nearest mg.

Add water at approximately room temperature up to the lower end (B) of the strip, and weigh the flask. Then add more water up to the upper end (A) of the strip, and weigh the flask. Separately, measure the water temperature, in °C, the room temperature, in °C, and the atmospheric pressure, in kPa, obtain the correct marked line, S, the number of graduations counted from the bottom edge (B) of graduated paper, using Equation (5):

$$S = \frac{\left[\dfrac{1\,000\,000 - (m + m')}{f}\right] - m_\mathrm{B}}{\dfrac{m_\mathrm{A} - m_\mathrm{B}}{20}} \tag{5}$$

where

m_A is the mass of water up to the top edge (A) of the graduated paper, in mg,
[i.e. (mass obtained by second weighting) – (mass of Erlenmeyer flask)];
$m_\mathrm{A} = m_\mathrm{B}$ + [mass of water from (A) to (B)];

m_B is the mass of water up to the bottom edge (B) of the graduated paper, in mg,
[i.e. (mass obtained by first weighting) – (mass of Erlenmeyer flask)];

m is the correction value, in mg, at 20 °C room temperature and 101,325 kPa (760 mmHg) atmospheric pressure;

m' is the correction value, in mg, due to deviation from a room temperature of 20 °C, and an atmospheric pressure of 101,325 kPa (760 mmHg). It is ± 4,0 mg per ± 1 °C of room temperature, and ± 1,3 mg per ± 0,133 kPa (1 mmHg) of atmospheric pressure;

f is a constant given by $\dfrac{100}{\text{normal capacity of plastic flask to be calibrated}}$.

Mark the new line on the strip.

NOTE When the correct line is shown on the flask, the strip can be removed.

8.3.6 Photometer, with 1 cm cell.

8.4 Mass of test portion

Weigh 0,20 g of the test sample.

8.5 Procedure

8.5.1 Preparation of stock solution S2

Weigh the dried sample in a platinum/gold dish (e.g. of capacity 150 ml), add 4,0 g of anhydrous sodium carbonate and heat over a burner or an electric furnace cautiously at first, and then gradually raise the temperature to the full heat of the burner or electric furnace. Finally, heat the dish and contents in an electric furnace at 1 000 °C for about 10 min.

Cover with a watch glass and remove the dish from the furnace and allow to cool. Then, add 50 ml of water and 20 ml of sulfuric acid (1+5) and heat on a steam bath until the melt is completely dissolved stirring occasionally. After cooling, remove the watch glass and wash it with a small amount of water. Transfer the obtained solution into a 500 ml plastic volumetric flask and dilute to the mark with water.

This solution is designated as stock solution S2.

NOTE If the solution is cloudy, filter with an ashless filter paper (close).

8.5.2 Coloration of curcumin complex

Transfer precisely an appropriate aliquot portion of stock solution S2 (see Table 2) into a platinum dish (e.g. 150 ml), add 1 ml of sulfuric acid (1+1), and evaporate on a hotplate by heating. When the sulfuric acid smoke appears, cool the bottom of the platinum dish by dipping into water for about 1 min. Without delay, wipe the water adhering to the bottom of the platinum dish, add 1 ml of curcumin acetic acid solution, cover with a watch glass, and allow to stand for about 60 min. Add 20 ml of water/ethanol solvent, allow to stand for 30 min while stirring occasionally, and dissolve completely until the colour is uniform.

Wash the platinum dish thoroughly so that no boron residue remains. For example, treat as follows: add hydrofluoric acid and a small amount of sulfuric acid, heat on a hotplate and evaporate the boron species. Then wash thoroughly with water and dry.

NOTE The aliquot portions taken from stock solution S2 is shown in Table 2, corresponding to the mass fraction of boron(III) oxide in the sample.

Table 2 — Aliquot portions taken from stock solution S2

Mass fraction of boron(III) oxide in the sample % by mass	**Aliquot portion of stock solution S2** ml
less than 0,2	10
0,2 to 0,5	5
0,5 to 1,0	2

8.5.3 Measurement of absorption

Put a portion of the coloured solution into a cell and measure the absorbance of the solution against water at a wavelength of 555 nm.

8.6 Blank test

Carry out the procedure described in 8.5 but omit the fusion process without using the sample.

The solution obtained corresponds to stock solution S2 and is designated as blank solution B2. The volume of blank test solution B2 is the same as that of stock solution S2.

8.7 Plotting the calibration graph

Transfer 0 (as reference), 2, 4, 6, 8 and 10 ml aliquot portions of the diluted standard solution of boron(III) oxide [0 µg to 5 µg as boron(III) oxide] into several platinum dishes (e.g. 150 ml). After the addition of 1 ml of sulfuric acid (1+1), carry out the procedure described in 8.5.2. Plot the relation between the absorbance and mass of boron(III) oxide, and prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

8.8 Calculation

Calculate the mass fraction of boron(III) oxide, w_{B3} as a percentage, using Equation (6), from the absorbance obtained in 8.5.3 and 8.6, and the calibration line prepared in 8.7.

$$w_{\mathrm{B3}} = \frac{m_1 - m_2}{m} \times \frac{500}{V} \times 100 \tag{6}$$

where

m_1 is the mass, in g, of boron(III) oxide in the aliquot portion of diluted stock solution S2;

m_2 is the mass, in g, of boron(III) oxide in the aliquot portion of diluted blank solution B2;

m is the mass, in g, of the test portion in 8.4;

V is the aliquot volume, in ml, of stock solution S2 in 8.5.2.

9 Determination of boron(III) oxide by inductively coupled plasma atomic emission spectrometry (ICP-AES)

9.1 Principle

The sample is fused with sodium carbonate and dissolved in hydrochloric acid. The sample solution is injected into the argon plasma of an ICP-AE spectrometer and the B emission is determined at a wavelength of 249,678 nm, or at another suitable wavelength, against reference solutions.

249,678 nm can suffer from a Fe overlap. If so, 208,959 nm should be used.

9.2 Reagents

Use only reagents of known analytical purity and water conforming to the requirements of grade 2 of ISO 3696 (e.g. double-distilled water).

The boron and borate ion concentrations in the water and the reagents shall be negligible compared with the lowest concentration to be determined. All solutions are aqueous, unless otherwise specified.

9.2.1 Sodium carbonate (ISO 6353-2 R34), assay, minimum mass fraction 98 %.

9.2.2 Hydrochloric acid (concentrated) (ISO 6353-2 R13), assay, minimum mass fraction 35 %.

9.2.3 Hydrochloric acid (1+1), add 1 volume of hydrochloric acid (concentrated) to 1 volume of water.

9.2.4 Boron(III) oxide stock solution, 1 mg B_2O_3/ml.

Transfer approximately 2 g of boric acid into a 100 ml beaker, spread it as a thin layer and dry for 24 h in a desiccator. Weigh 1,776 g of this dry boric acid and transfer into a 200 ml plastic beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

A traceable commercial standard solution may be used.

9.2.5 Yttrium internal standard stock solution, 0,5 mg Y/ml.

Dry about 2 g of yttrium oxide at 110 °C ± 5 °C for 60 min and cool in a desiccator. Weigh 1,270 g from this, transfer to a 250 ml beaker, gradually add 100 ml of hydrochloric acid (1+1) to dissolve. Dilute precisely to 2 000 ml in a volumetric flask with water.

A traceable commercial standard solution may be used.

9.2.6 Zero standard.

Into a polythene beaker, weigh 2,5 g of sodium carbonate and dissolve in water with the addition of 30 ml of hydrochloric acid (concentrated). Cool and transfer to a 500 ml volumetric flask. Add 10,0 ml of yttrium internal standard stock solution, dilute to 500 ml and mix.

9.2.7 Boron(III) oxide standard solution, 100 mg B_2O_3/l.

Prepare the fusion blank as described in 9.2.6. Add 50,0 ml of boron(III) oxide stock solution, 10,0 ml of yttrium internal standard stock solution, dilute to 500 ml in a volumetric flask and mix.

9.2.8 Additional low-range boron(III) oxide, 20 mg B_2O_3/l.

Prepare the fusion blank as described in 9.2.6. Add 10,0 ml of boron(III) oxide stock solution, and 10,0 ml of yttrium internal standard stock solution, dilute to 500 ml in a volumetric flask and mix.

9.2.9 Mid-range check standard, for each of the ranges specified above.

This check standard shall be made from a different source from standards 9.2.7 and 9.2.8.

9.3 Apparatus

9.3.1 Platinum alloy crucible, of suitable nominal capacity.

9.3.2 Electric muffle furnace, capable of being controlled at temperatures of at least 1 050 °C.

9.3.3 Gas Bunsen burner.

9.3.4 Inductively coupled plasma atomic emission spectrometer (ICP-AES), simultaneous with channels B and Y.

NOTE Suitable wavelengths for yttrium in internal standard mode are Y 371,0 nm or Y 224,3 nm.

9.4 Mass of test portion

Weigh 0,25 g of the test sample.

NOTE The sample mass is a function of the mass fraction of boron. It is usually 0,25 g.

9.5 Procedure

Weigh the sample into a platinum crucible.

Add 2,5 g ± 0,01 g of sodium carbonate and mix thoroughly. Cover the crucible with a lid and transfer to a low Bunsen flame. Carry out the fusion at as low a temperature and for as short a time as is necessary to obtain a satisfactory fusion.

NOTE For certain refractory materials, fusion in a furnace at 1 000 ± 25 °C for approximately 10 min might be required.