

First edition
2008-01-15

Corrected version
2008-05-01

**Determination of boron(III) oxide in
refractory products —**

Part 1:

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

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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*

ISO 21078-1:2008

<https://standards.iteh.ai/catalog/standards/sist/c800764a-5aea-49ea-936a-b4f0d0f00683/iso-21078-1-2008>



Reference number
ISO 21078-1:2008(E)

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Published in Switzerland

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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 (rthocyanine 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 riffing 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 $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for a minimum of 10 h. Then crush to pass through a 6,7 mm sieve, reduce to about 100 g by riffing 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 $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ 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, C₂₁H₁₆Br₂O₅S, 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 B₂O₃/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, C₆H₁₄O₆.

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).

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

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 CaCO₃ 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):

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

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 B₂O₃/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, C₇H₁₂NNaO₈S₂.

7.2.9 L(+)-ascorbic acid, C₆H₈O₆.

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, CH₃COONH₄.

7.2.12 Acetic acid (ISO 6353-2 R 1), minimum mass fraction 99,7 % as CH₃COOH.

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 NH₃.

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7.2.15 Ammonium hydroxide solution (1+6), NH₄OH.

7.2.16 Disodium ethylenediaminetetraacetate (EDTA-Na₂), C₁₀H₁₄N₂Na₂O₈·2H₂O.

7.2.17 Citric acid monohydrate, C₆H₈O₇·H₂O.

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, C₂₄H₂₆O₆.

7.2.20 Ethanol (ISO 6353-2 R 11), minimum mass fraction 99,8 %, as C₂H₅OH.

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.

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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):

$$V_S = (1,45 - 0,058 \times V_A) \times \frac{1000}{241,7} \quad (3)$$

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.