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Determination of boron(III) oxide in refractory products —

Part 2:
Acid extraction method for the determination of boron(III) oxide in binder components

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

Partie 2: Méthode d'extraction acide pour le dosage de l'oxyde de bore(III) dans les composants de liant

Reference number
ISO 21078-2:2006(E)

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Foreword

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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 21078-2 was prepared by Technical Committee ISO/TC 33, *Refractories*.

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

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

Determination of boron(III) oxide in refractory products —

Part 2:
Acid extraction method for the determination of boron(III) oxide in binder components

1 Scope

This part of ISO 21078 specifies procedures of chemical analysis for the determination of boron(III) oxide used as a binder component added to aluminosilicate refractories, using an acid extraction method.

It is applicable for refractories containing less than 1 % (mass fraction) of boron(III) oxide.

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, *Terminology for refractories*

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*

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

4 Preparation of the test sample

4.1 Refractory brick or its raw material

Sampling is carried out in accordance with the contract between the user and producer. A specified quantity taken from a lot of the sample is crushed to pass through a 6,7 mm sieve (see ISO 3310-1) and reduced to about 100 g by riffling or quartering. Then all the reduced sample is ground to pass through a 300 µm sieve (see ISO 3310-1).

4.2 Unshaped refractories

Prepare two approximately 100 g portions 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 in 4.3 to 4.5.

4.3 Dry unshaped refractories

Take one bag or 50 kg of the sample from a lot and reduce to about 100 g as above, and crush to pass through a 300 μm sieve.

4.4 Laboratory sample

The laboratory sample from 4.1 or 4.2 is reduced to approximately 25 g by quartering, and ground to pass through a 106 μm sieve. This is the test sample for analysis. It is transferred into a container [e.g. a flat weighing bottle (50 mm × 30 mm) or sample tube (50 mm × 25 mm)], and dried in a desiccator with silica gel desiccant for a minimum of 8 h.

4.5 Weighing of test portion

The specified quantity of the test portion for chemical analysis shall be weighed to the nearest 0,1 mg using an analytical balance and recorded.

Carry out the extraction process in duplicate.

5 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.

NOTE The reagents below are for the extraction process only. Reagents for the determination of B_2O_3 are listed in the appropriate clauses.

5.1 Dilute hydrochloric acid (1 + 1).

Add 1 volume of hydrochloric acid (concentrated, 35 % by mass) to 1 volume of water, then mix and allow to cool.

5.2 Dilute hydrochloric acid (1 + 50).

Add 1 volume of hydrochloric acid (concentrated, 35 % by mass) to 50 volumes of water.

6 Mass of test portion for extraction

Weigh out 5,0 g of the test sample.

7 Preparation of the test solution

Weigh and transfer the dry sample into a 200 ml plastics beaker. Using a measuring cylinder, add 20 ml of hydrochloric acid solution (1 + 1) (5.1) and 50 ml of warm water, and mix intimately. Allow to stand for approximately 30 min ± 2 min while stirring, to dissolve the soluble binder components.

Filter with a fine-textured filter paper and wash with warm dilute hydrochloric acid (1 + 50) (5.2). Transfer the filtrate and washings into a 250 ml volumetric flask, and dilute to the mark with water. Transfer into a plastics bottle. This solution is referred to as the “test solution” for the determination of boron(III) oxide.

8 Blank solution

Carry out the procedure given in Clause 7 without the sample. This solution is referred to as the “blank solution”.

9 Classification of determination methods

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

a) Sodium hydroxide titrimetry.

NOTE This method is applied to the sample containing more than 0,5 % (mass fraction) of boron(III) oxide.

b) Inductively coupled plasma atomic emission spectrometry (ICP/AES).

c) Curcumin absorption spectrophotometry (Rothocyanine method).

10 Determination of boron(III) oxide by sodium hydroxide titrimetry

10.1 Principle

A specified volume of test solution is taken and adjusted to pH approximately 5,0. The precipitate containing silicic acid is filtered off. The filtrate's pH is adjusted to 6,3 and D(–)-mannitol is added to the filtrate. Then, the H^+ ions liberated by the mannitol in the solution are titrated with the sodium hydroxide standard solution until the solution's pH becomes 6,3 again.

10.2 Reagents

10.2.1 Dilute hydrochloric acid.

Prepare dilute hydrochloric acid (1 + 50) as described in 5.2.

10.2.2 D(–)-Mannitol ($C_6H_{14}O_6$).

10.2.3 Bromocresol purple ($C_{21}H_{16}Br_2O_5S$) solution, 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 a low temperature for a maximum of 7 days.

10.2.4 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 with silica gel desiccant. Weigh 0,177 6 g of this dry boric acid and transfer into a 200 ml plastics beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

10.2.5 Sodium hydroxide standard volumetric solution.

Transfer 50 g of sodium hydroxide into a polyethylene bottle, add 50 ml of water, dissolve while cooling, and put a seal on it. Keep the sealed bottle for several days, 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 using a magnetic stirrer, put a pH electrode in 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 (10.2.2), set the electrode again, and titrate with the sodium hydroxide standard volumetric solution until the pH is 6,8.

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

$$F = \frac{0{,}01}{V} \tag{1}$$

where

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

0,01 is the concentration of the NaOH solution, in mol/l.

10.3 Procedure

Pipette precisely 50 ml of both test solutions (see 4.5 and Clause 7) into two 200 ml beakers and add 2 or 3 drops of bromocresol purple (10.2.3) solution as an indicator. Add the standard volumetric sodium hydroxide solution (10.2.5) until the colour of the solution becomes blue, and add drops of dilute hydrochloric acid (1 + 50) (5.2) until the colour becomes yellow.

Boil for 20 min with a watch glass as a cover, wash the watch glass with water and remove it, filter with a closed-pore filter paper, and wash several times with hot water.

NOTE If the yellow-green colour appears during the boiling period, keep the colour yellow by adding drops of dilute hydrochloric acid (1 + 50) (5.2).

Cool and dilute to 100 ml with water. Stir by using a magnetic stirrer, put a pH electrode in the solution, and add drops of the sodium hydroxide standard volumetric solution (10.2.5) until the pH is 6,3. Remove the electrode, add 10 g of D(–)-mannitol (10.2.2), set the electrode again, and titrate with the sodium hydroxide standard volumetric solution until the pH is 6,3.

10.4 Blank test

Repeat the process described in 10.3 using the blank solution (see Clause 8).

10.5 Calculation and expression of results

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

$$w_B = \frac{(V_1 - V_2) \times F}{m} \times \frac{250}{50} \times 100 \tag{2}$$

where

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

V_2 is the volume, in ml, of titration of sodium hydroxide standard volumetric solution for 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 Clause 6.

Express the result as the mean of three determinations, rounded off in accordance with ISO 31-0 (see Clause 14).

11 Determination of boron(III) oxide by inductived coupled plasma/atomic emission spectrometry

11.1 Principle

The sample solution is injected into the argon plasma of an inductively coupled plasma/atomic emission (ICP/AE) spectrometer and the B emission is determined at a wavelength of 249,678 nm, or at another suitable wavelength, against reference solutions.

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

11.2 Reagent

11.2.1 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 with silica gel desiccant. Weigh 0,177 6 g of this dry boric acid and transfer into a 200 ml plastics beaker. Dissolve in approximately 100 ml of water and dilute precisely to 1 000 ml in a volumetric flask.

11.3 Calibration

Transfer a range from 0 ml to 50,0 ml of the boron(III) oxide standard solution (10.2.4) [0 mg to 5 mg of boron(III) oxide] precisely into several 100 ml volumetric flasks. Add 25 ml of the blank solution obtained in Clause 8 to each flask and dilute to the mark with water.

Run these solutions on the ICP/AE spectrometer, ensuring that the correlation coefficient of the regression is $\geqslant$ 0,999.

After initial calibration, the instrument can be drift corrected on a zero and top calibration point, unless there has been a significant change in the instrument such as servicing, repair or change in sensitivity. In any event, a mid-point should be made using a different set of volumetric ware from the drift correction standards, preferably from a separate stock boron(III) oxide solution (11.2). This mid-point shall be run as an unknown to validate the calibration, and the difference between its actual and theoretical value must be less than twice the limits set for duplicates in Table 3. If not, the mid-point should be repeated and, if this fails to meet the criteria, the instrument shall be recalibrated.

An example of the preparation of calibration solutions is shown in Table 1. In accordance with the compositions of the samples, and the types and capabilities of instrument used, an appropriate solution series for calibration shall be prepared.

Table 1 — Example of preparation of calibration solutions

Calibration solution	Boron(III) oxide standard solution (10.2.4)	Blank solution	Mass of boron(III) oxide
No.	ml	ml	mg
1	0	25	0,0
2	5	25	0,5
3	10	25	1,0
4	20	25	2,0
5	30	25	3,0
6	40	25	4,0
7	50	25	5,0

To use this approach to calibration, it is essential that line interferences of any of these oxides on each other are checked for, and either found to be absent or, if present, appropriate corrections are applied.

If the volume of the test solution is changed, the volume of the added blank solution should be compatible with that of the test solution.

11.4 Procedure

Transfer a 25 ml aliquot portion of each test solution (see 4.5 and Clause 7) into two 100 ml volumetric flasks, and dilute to the mark with water.

Spray a portion of this solution into the Ar plasma flame of an ICP/AE spectrometer, and measure the emission intensity at the appropriate wavelength, for example, 208,96 nm.

11.5 Blank test

Repeat the process described in 11.4 using the blank solution (see Clause 8).

11.6 Plotting of calibration graph

Carry out the procedure described in 11.3 for all calibration solutions and plot the relation between the emission intensity and mass of boron(III) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

The measurement of calibration solutions should be carried out simultaneously as a pair of the measurements of the test and blank solutions. A new calibration line should be prepared from each measurement.

11.7 Calculation and expression of results

Calculate the mass fraction of boron(III) oxide in the sample, w_B, as a percentage, using the equation:

$$w_\mathrm{B} = \frac{m_1 - m_2}{m} \times \frac{250}{25} \times 100 \qquad (3)$$

where

m_1 is the mass, in grams, of boron(III) oxide in the aliquot portion of test solution, as read off the ICP calibration;

m_2 is the mass, in grams, of boron(III) oxide in the aliquot portion of blank solution, as read off the ICP calibration;

m is the mass, in grams, of the test portion in Clause 6.

Express the result as the mean of three determinations, rounded off in accordance with ISO 31-0 (see Clause 14).

12 Curcumine absorption spectrophotometry (Rothocyanine method)

12.1 Principle

A specified volume of test solution is dehydrated by adding sulfuric acid and heating; addition of curcumine to the solution generates rothocyanine. The residue is dissolved in water/ethanol and the absorbance is measured.

12.2 Reagents

12.2.1 Dilute sulfuric acid (1 + 1).

Cautiously add 1 volume of sulfuric acid (concentrated, 95 % by mass) to 1 volume of water, while stirring and cooling (e.g. allow the beaker to stand in flowing water).

12.2.2 Water-ethanol solvent.

Mix water and ethanol (99,5 % by mass) in a volume ratio of 1:3.

12.2.3 Curcumine acetic acid solution.

Weigh 0,15 g of curcumine into a 200 ml quartz beaker. Add 100 ml of acetic acid, and dissolve by heating. Use the solution within a week of preparation.

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

Dilute the boron(III) oxide standard solution precisely to a concentration of 1:200 with water.

12.3 Apparatus

12.3.1 Plastics Erlenmeyer flask, calibrated as follows.

Either

- wash a plastics flask thoroughly, invert it and allow it to stand to dry naturally, or
- wash a plastics flask with water, ethanol and diethylether, and dry it by blowing air into it.

Cut 20 graduations from a sheet of graph paper (1 mm squares) into a strip and attach it to the marked line of the plastics flask, so that the line coincides with the central line of the paper. Weigh the flask to the nearest 1 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, and obtain the correct marked line (i.e. the number of graduations counted from the bottom edge (B) of the graduation paper), S, using the following equation:

$$S = \frac{\left[\dfrac{1\,000\,000 - (m + m')}{V_\mathrm{f}}\right] - m_\mathrm{B}}{\left(\dfrac{m_\mathrm{A} - m_\mathrm{B}}{20}\right)} \qquad (4)$$

where

m_A is the mass of water up to the top edge (A) of the graduation paper, in mg [i.e. (mass obtained by second weighing) - (mass of Erlenmeyer flask)]; m_A is $m_B +$ [mass of water from (A) to (B)];

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

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

m' is the correction value (mg) due to deviation from 20 °C room temperature, atmospheric pressure 101,325 kPa (760 mmHg). It is $\pm$ 4,0 mg per $\pm$ 1 °C room temperature, $\pm$1,3 mg per $\pm$ 0,133 kPa (1 mmHg) atmospheric pressure;

V_f $=$ 1 000 ml (nominal capacity of plastics flask to be calibrated).

12.3.2 Platinum dish, thoroughly washed so that no boron residue remains.

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

12.4 Procedure

Transfer precisely an appropriate aliquotportion of each test solution (see Clause 7) into two 1 000 ml volumetric flasks and dilute to the mark with water. This solution is designated as the diluted test solution.

Transfer precisely an appropriate aliquot portion of diluted test solution (see Table 2) into a 90 ml platinum dish, add 1 ml of dilute sulfuric acid (1 + 1) (12.2.1), and evaporate on a hot plate by heating. When the sulfuric acid smoke appears, cool the bottom of the platinum dish by dipping into water for approximately 1 min. Without delay, wipe the water that is on the bottom of the platinum dish, add 1 ml of curcumine acetic acid solution (12.2.3), cover with a watch glass, and allow to stand for approximately 60 min. Add 20 ml of water-ethanol solvent (12.2.2), allow to stand for 30 min, stirring occasionally, and dissolve completely until the colour is uniform.

Put a portion of the coloured solution obtained in a cell, and measure the absorbance of the solution compared with water at a wavelength of 540 nm.

Table 2 — Aliquot portions taken from test solution and diluted test solution

Mass fraction of boron(III) oxide in the sample %	Aliquot portion of test solution ml	Aliquot portion of diluted test solution ml
less than 0,1	25	10
0,1 to 0,2	10	10
0,2 to 0,5	5	10
0,5 to 1,0	5	5

NOTE The aliquot portions taken from the test solution and diluted test solution are shown in Table 2, corresponding to the mass fraction of boron(III) oxide in the sample.

12.5 Blank test

Transfer an aliquot portion of blank solution obtained in Clause 8 and carry out the procedure described in 12.4, where the volumes of blank solution and diluted blank solution should be the same as those of the test solution and diluted test solution, respectively. The solution equivalent to the diluted test solution is referred to as “diluted blank solution”.

12.6 Plotting the calibration graph

Transfer 0 (as reference), 2, 4, 6, 8 and 10 ml aliquot portions of the diluted boron(III) oxide standard solution [0 µg to 5 µg as boron(III) oxide] into separate 90 ml platinum dishes. After the addition of 1 ml of dilute sulfuric acid (1 + 1) (12.2.1), carry out the procedure described in 12.4. 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.

12.7 Calculation of results

Calculate the mass fraction of boron(III) oxide in the sample, w_{B}, as a percentage, using Equation (5)

$$w_{\mathrm{B}} = \frac{m_1 - m_2}{m} \times \frac{250}{V_1} \times \frac{1\,000}{V_2} \times 100 \tag{5}$$

where

m_1 is the mass, in grams, of boron(III) oxide in the aliquot portion of diluted test solution;

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

m is the mass, in grams, of the test portion in Clause 6;

V_1 is the aliquot volume, in ml, of the test solution described in Clause 7;

V_2 is the aliquot volume, in ml, of diluted test solution.

Express the result as the mean of three determinations, rounded off in accordance with ISO 31-0 (see Clause 14).

13 Quality assurance and control

Weekly or on the day of the test, whichever is least frequent, carry out the determination of B_2O_3 in a certified reference material of similar content to those being analysed. Alternatively, a homogenised sample that has been well analysed by the laboratory may be used, providing it is in sufficient quantity not to run out. The difference between the measured and true results achieved must be within twice the limits set for duplicates in Table 3. If these are not met, the standard/sample must be re-analysed. If the results still fail to meet the criteria, an investigation must be carried out into the method and calibration until the source of error is identified and rectified.

Table 3 — Permissible difference in test values

	Mass fraction %			
	Less than 0,5	0,5 to 5	5 to 10	More than 10
Permissible absolute difference	0,02	0,05	0,1	0,2
NOTE If the mass fraction of a component is very small, the permissible difference shall be one-half of the test result.				

14 Expression of test results

14.1 General

Express the test results as percentage composition calculated on a dried basis, and rounded off in accordance with ISO 31-0, as follows:

a) if the integer part of the mass-fraction percentage has two digits, the value shall be rounded off to one decimal place;

b) if the integer part of the mass-fraction percentage has only one digit, the value shall be rounded off to two decimal places.

14.2 Examination and adoption of test results

If the absolute difference between the two determinations is less than the value given in Table 3, report the result as the arithmetic mean of the two determinations.

If the absolute difference between the two determinations is more than the value given in Table 3, carry out two further determinations. If the absolute difference between the second two determinations is equal to or less than the value given in Table 3, report the result as the arithmetic mean of the two determinations.

NOTE If one of the first pair of determinations lies within the appropriate limits of the second pair, the arithmetic mean of all three may be reported.

If the absolute difference between the determinations again exceeds the value in Table 3, report the result as the median of the four test results.

15 Test report

The test report shall include at least the following information:

a) all information necessary for identification of the sample tested;

b) a reference to this part of ISO 21078 (ISO 21078-2:2006);

c) the method(s) used and the determination(s) carried out, including all relevant details of the procedure;

d) the results of the test, including the results of the individual determinations and their means, calculated as specified in 10.5, 11.7 and/or 12.7, as appropriate;

e) any deviations from the procedure(s) specified;

f) any unusual features (anomalies) observed during the test;

g) the name of the testing establishment;

h) the date of the test.

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