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Glass and glassware — Analysis of extract solutions —

Part 6:
Determination of boron(III) oxide by molecular absorption spectrometry

Verre et verrerie — Analyse des solutions d'attaque —

Partie 6: Dosage de l'oxyde de bore(III) par spectrométrie d'absorption moléculaire

Reference number
ISO 10136-6:1993(E)

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.

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.

International Standard ISO 10136-6 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*, Sub-Committee SC 5, *Quality of glassware*.

ISO 10136 consists of the following parts, under the general title *Glass and glassware — Analysis of extract solutions*:

— *Part 1: Determination of silicon dioxide by molecular absorption spectrometry*

— *Part 2: Determination of sodium oxide and potassium oxide by flame spectrometric methods*

— *Part 3: Determination of calcium oxide and magnesium oxide by flame atomic absorption spectrometry*

— *Part 4: Determination of aluminium oxide by molecular absorption spectrometry*

— *Part 5: Determination of iron(III) oxide by molecular absorption spectrometry and flame atomic absorption spectrometry*

— *Part 6: Determination of boron(III) oxide by molecular absorption spectrometry*

Annex A of this part of ISO 10136 is for information only.

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Introduction

The amounts of boron(III) oxide (B_2O_3) extracted from glass and glassware during hydrolytic resistance tests are normally very small, even from heat-resisting borosilicate glass 3.3 used for making laboratory ware. Therefore, neither macro-titration methods nor flame atomic absorption spectrometry are suitable for its determination, so recourse shall be made to colorimetric techniques using measurement by molecular absorption spectrometry. Boron(III) oxide forms coloured complexes with a number of organic reagents, but those most commonly used are curcumin, 1,1'-dianthrimide, carminic acid, quinalizarin, and for some years azomethine H.

Technical Committee 2, Chemical Durability and Analysis, of the International Commission on Glass (ICG), examined the determination of boron(III) oxide using all of these reagents (see [7] in annex A) and recommended the procedure using azomethine H, after consideration of all of the results and comments received. In a round-robin examination involving eleven laboratories, the participants were provided with a homogeneous extract solution obtained from ordinary borosilicate glass containers using an autoclave process according to ISO 4802. The results obtained were considered to be very satisfactory.

The results of investigations on turbidities, especially in grain test solutions, showed that acidification to dissolve possible hydroxides and/or carbonates is necessary prior to the analytical determination. This is achieved by using spectroscopic buffer solutions, which are normally strongly acidic, or by addition of acids.

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Glass and glassware — Analysis of extract solutions —

Part 6:
Determination of boron(III) oxide by molecular absorption spectrometry

1 Scope

This part of ISO 10136 specifies an analytical procedure, using molecular absorption spectrometry, for measuring the concentrations of boron, expressed as its oxide (B_2O_3), released into extract solutions during hydrolytic resistance test procedures.

This part of ISO 10136 applies to the analysis of extract solutions obtained from any kind of glass or glassware, including laboratory and pharmaceutical ware made, for example, from borosilicate glass (such as borosilicate glass 3.3 according to ISO 3585), or neutral glass as defined in ISO 4802[3][4], tableware and kitchenware. The extract solution may be obtained from glass articles, for example according to ISO 4802, or from glass as material, for example when tested according to ISO 719[1] or ISO 720[2]. In addition, it may be applied to the extract solutions produced by any method for measuring the hydrolytic resistance of glass or glassware.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10136. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10136 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-2:1984, *Laboratory glassware — Burettes — Part 2: Burettes for which no waiting time is specified.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements.*

ISO 835-2:1981, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified.*

ISO 835-3:1981, *Laboratory glassware — Graduated pipettes — Part 3: Pipettes for which a waiting time of 15 s is specified.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3585:1991, *Borosilicate glass 3.3 — Properties.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 3819:1985, *Laboratory glassware — Beakers.*

ISO 6955:1982, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary.*

3 Definitions

For the purposes of this part of ISO 10136, the following definitions apply.

3.1 extract solution: The aqueous solution obtained from the reaction of glass with water under specific conditions.

3.2 sample measuring solution: The solution actually used for measuring the concentration of the analyte. It may be the undiluted, diluted or modified extract solution.

3.3 analyte: The element or constituent to be determined.

3.4 stock solution: A solution of appropriate composition containing the analyte, expressed as its oxide, in a known but high concentration.

3.5 standard solution: A solution containing the analyte, expressed as its oxide, in a known concentration suitable for the preparation of reference or calibration solutions.

3.6 set of calibration solutions; set of reference solutions: A set of simple or synthetic reference solutions having different analyte concentrations. The zero member is, in principle, the solutions having zero concentration of the analyte. [ISO 6955]

3.7 molecular absorption spectrometry (MAS): A technique for determining the concentration of an analyte in solution by measuring the optical density of a colour complex of the analyte.

3.8 blank test solution: A solution prepared in the same way as the sample measuring solution but so that it does not contain the analyte to be determined.

4 Principle

Complexing of the boron in the extract solution to be analysed with azomethine H. Measurement of the optical density of the resulting colour complex by means of a molecular absorption spectrometer at 415 nm using 20 mm optical cells.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade, and grade 1 or grade 2 water specified in ISO 3696.

When acids and ammonium hydroxide are specified only by name or chemical formula, the concentrated reagent is intended. The concentrations of diluted acids or ammonium hydroxide are specified as a ratio, stating the number of volumes of the concentrated reagent to be added to a given number of volumes or water. For example, 1 + 3 means that 1 volume of the concentrated reagent shall be diluted with 3 volumes of water.

Commercially available standard solutions for colorimetry may be used for the preparation of stock or standard solutions.

5.1 Boric acid (H_3BO_3).

5.2 Boron(III) oxide, stock solution.

Dissolve 1,776 g of boric acid (5.1) in water contained in a 1 000 ml one-mark volumetric flask (6.5), make up to the mark and mix.

Transfer to a boron-free glass or plastics bottle (6.3) for storage.

1 ml of this stock solution contains 100 µg of B_2O_3.

5.3 Boron(III) oxide, standard solution.

Using a one-mark pipette (6.8), transfer 5 ml of the boron(III) oxide stock solution (5.2) to a 500 ml one-mark volumetric flask (6.5), make up to the mark with water and mix.

This solution shall be freshly prepared immediately before use.

1 ml of this standard solution contains 10 µg of B_2O_3.

5.4 Ascorbic acid ($C_6H_8O_6$).

5.5 Azomethine H ($C_{17}H_{12}NNaO_8S_2$), solution.

Dissolve 1 g of azomethine H and 3 g of ascorbic acid (5.4) in 100 ml of water. Filter the solution through a close filter paper and store in the dark. Discard after one week.

5.6 Acetic acid (CH_3COOH), glacial, ρ = 1,05 g/ml.

5.7 Ammonium acetate (CH_3COONH_4).

5.8 Ammonium hydroxide (NH_4OH), ρ = 0,88 g/ml.

5.9 Buffer solution

Dilute 80 ml of acetic acid (5.6) to 100 ml with water and add 50 g of ammonium acetate (5.7). After dissolving it, adjust the pH of the solution to 4,5 using the pH meter (6.11) and either acetic acid (5.6) or ammonium hydroxide (5.8).

Store in a plastics bottle (6.3).

5.10 Ethylene diaminetetraacetic acid disodium salt (EDTA) ($C_{10}H_{14}N_2Na_2O_8.2H_2O$).

5.11 Citric acid ($C_6H_8O_7.H_2O$).

5.12 Sodium hydroxide, solution, c(NaOH) ≈ 5 mol/l, stored in a plastics bottle (6.3).

5.13 Sodium hydroxide, solution, c(NaOH) ≈ 0,1 mol/l.

5.14 Hydrochloric acid (HCl), ρ = 1,19 g/ml.

5.15 Hydrochloric acid, diluted 1 + 24.

5.16 Screening solution

Dissolve 20 g of the EDTA (5.10) and 10 g of citric acid (5.11) in 450 ml of water by the progressive addition of sodium hydroxide solution (5.12) until the pH of the solution is 4.5 using the pH-meter (6.11). Transfer the solution to the 500 ml one-mark volumetric flask (6.5), make up to the mark and mix.

6 Apparatus

All laboratory glassware, except pipettes and burettes, shall be made of borosilicate glass, preferably of type 3.3 complying with the requirements in ISO 3585.

Ordinary laboratory apparatus, and

6.1 Molecular absorption spectrophotometer, capable of measuring optical density at 415 nm.

6.2 Optical cells, of suitable path length, e.g. 20 mm.

6.3 Bottles made of boron-free glass or plastics, stoppered, of a suitable capacity.

6.4 Beaker, of capacity 100 ml, and complying with the requirements in ISO 3819.

6.5 One-mark volumetric flasks, of a suitable capacity e.g. of 500 ml and 1 000 ml, and complying with the requirements for class A one-mark volumetric flasks in ISO 1042.

6.6 One-mark volumetric flasks, made of silica glass or from suitable plastics, of capacity 25 ml, and complying with the requirements for class A one-mark volumetric flasks in ISO 1042.

6.7 Graduated pipette, of capacity 5 ml, and complying with the requirements for class A graduated pipettes in ISO 835-1, ISO 835-2 or ISO 835-3.

6.8 One-mark pipette, of suitable capacity e.g. 5 ml or 50 ml, and complying with the requirements for class A one-mark pipettes in ISO 648.

6.9 Burettes, of a suitable capacity e.g. of 10 ml, and complying with the requirements for class A burettes in ISO 385-2.

6.10 Balance, with a discrimination of 0,1 mg.

6.11 pH-meter, with glass and calomel electrodes, or combined electrodes.

6.12 Magnetic stirrer, with a plastic coated rod.

6.13 Filter papers, of the ashless type washed twice with acid, and designated as follows:

"open" or "coarse" will have a porosity generally used for filtering aluminium hydroxide;

"medium" will have a porosity generally used for filtering calcium oxalate;

"close" or "fine" will have a porosity generally used for filtering barium sulfate.

6.14 Platinum dish.

7 Sampling and samples

The sample for analysis shall be the extract solution produced in any hydrolytic resistance test procedure.

8 Procedure

8.1 Preparation and measurement of the sample measuring solution and the blank test solution

8.1.1 Sample measuring solution

Using a one-mark pipette (6.8), transfer a 25 ml aliquot of the extract solution into a beaker (6.4) and acidify, under control of a pH-meter (6.11), with hydrochloric acid (5.15) to a pH-value of about 3. Then heat till boiling. Using an appropriate filter (6.13), filter the solution into another beaker (6.4). Wash the filter with small volumes of hot water. Evaporate the filtrate, by gently boiling, to about 20 ml in the platinum dish (6.14). Cool and then adjust the pH-value to about 5 with sodium hydroxide solution (5.13). Transfer to a 25 ml one-mark volumetric flask (6.6), and rinse the beaker with small portions of water to make up to the mark.

8.1.2 Blank test solution

Prepare the blank test solution using a volume of water equal to the volume of extract solution used to prepare the sample measuring solution.

Transfer an accurately measured volume of this extract solution containing not more than 50 µg B_2O_3 to

a 25 ml one-mark volumetric flask (6.6). Add 3 ml of the buffer solution (5.9), 3 ml of screening solution (5.16) and 5 ml of azomethine H solution (5.5), and mix after each addition. Then make up to the mark with water, mix again and allow to stand for 4 h in the dark.

8.1.3 Measurement of optical density

Measure the optical density of the sample measuring solution at 415 nm (see 6.1) using 20 mm cells (6.2), and also the blank test solution with the zero member (see 3.6) as reference.

8.2 Preparation of the calibration graph

Using a burette (6.9) or a one-mark pipette (6.8), transfer accurately measured volumes of the boron(III) oxide standard solution (5.3) to separate 25 ml one-mark volumetric flasks (6.6), to cover the range 0 to 50 µg B_2O_3. Dilute each to about 10 ml, add 3 ml of buffer solution (5.9) and proceed as described in 8.1.1.

Plot the optical densities against mass of B_2O_3 to produce the calibration graph.

9 Expression of results

Determine the mass of boron(III) oxide (B_2O_3) in the sample measuring solution (8.1.1) and in the blank test solution (8.1.2) from the calibration graph (8.2). Subtract, and calculate the concentration of boron(III) oxide in the extract solution and express as micrograms of B_2O_3 per millilitre of extract solution.

10 Test report

The test report shall include the following information:

a) a reference to this part of ISO 10136;

b) an identification of the extracted samples;

c) a reference to the hydrolytic resistance test method used (see annex A) to produce the extract solution;

d) the results obtained, expressed as micrograms of B_2O_3 per millilitre of extract solution;

e) any unusual features noted during the determination.

Annex A
(informative)

Bibliography

[1] ISO 719:1985, *Glass — Hydrolytic resistance of glass grains at 98 °C — Method of test and classification.*

[2] ISO 720:1985, *Glass — Hydrolytic resistance of glass grains at 121 °C — Method of test and classification.*

[3] ISO 4802-1:1988, *Glassware — Hydrolytic resistance of the interior surfaces of glass containers — Part 1: Determination by titration method and classification.*

[4] ISO 4802-2:1988, *Glassware — Hydrolytic resistance of the interior surfaces of glass containers — Part 2: Determination by flame spectrometry and classification.*

[5] ISO 6286:1982, *Molecular absorption spectrometry — Vocabulary — General — Apparatus.*

[6] DIN 52 296:1989, *Glass und Glaskeramik — Wasserbeständigkeit der Oberfläche von Glas- und Glaskeramik-Platten bei 98 °C — Prüfverfahren und Klasseneinteilung (Glass and glass ceramics — Hydrolytic resistance of the surface of glass and glass ceramic plates at 98 °C — Method of test and classification.).*

[7] The chemical durability of glass: the determination of boric oxide in durability extract solutions. (A report by Sub-Committee A2 of the International Commission on Glass). *Glass Technology,* (1973), Vol. **14**, No. 1, pp.14-19.