INTERNATIONAL
STANDARD

ISO
10136-1

First edition
1993-07-01

Glass and glassware — Analysis of extract solutions —

Part 1:
Determination of silicon dioxide by molecular absorption spectrometry

Verre et verrerie — Analyse des solutions d'attaque —

Partie 1: Dosage du dioxyde de silicium par spectrométrie d'absorption moléculaire

Reference number
ISO 10136-1:1993(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 10136-1 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.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Introduction

The determination of silica (SiO_2) in durability extract solutions has not, hitherto, been included in classifications of glass or glassware according to chemical resistance. Indeed, in many applications the concentrations of silica found in such extract solutions, normally very low, are not significant and are of little interest. There are occasions where such releases could be important, for example from glassware used in the determination of small concentrations of silica in solutions or, in some cases, releases from medical and pharmaceutical ware. Then again, in examining the properties of new glass compositions it could be an advantage to know the full analysis of the durability extract solutions.

Technical Committee 2, Chemical Durability and Analysis, of the International Commission on Glass (ICG), investigated two procedures for determining silica (see [6] in annex A) by the molecular absorption spectrometric technique. Both were based on the formation of colour complexes in the presence of ammonium molybdate, one using the yellow colour of the complex formed, the other using the blue colour produced when a suitable reducing agent is added. In collaborative experimental work, twelve laboratories analysed silica in two synthetic solutions and in extract solutions produced by the test described in ISO 4802[3][4]. It was agreed that whilst determinations using the yellow complex were more consistent, they were also less sensitive and, since the concentrations of silica in extract solutions are normally very low, the blue complex method was preferred.

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.

This page intentionally left blank

INTERNATIONAL STANDARD **ISO 10136-1:1993(E)**

Glass and glassware — Analysis of extract solutions —

Part 1:
Determination of silicon dioxide by molecular absorption spectrometry

1 Scope

This part of ISO 10136 specifies an analytical procedure, using molecular absorption spectrometry, for measuring the concentrations of silicon, expressed as silicon dioxide or silica (SiO_2), 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), neutral glass, or soda-lime-silica glass as defined in ISO 4802[3][4], food and drink packaging ware, 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.*

ISO 7056:1981, *Plastics laboratory ware — Beakers.*

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 solution 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

Conditioning of the extract solution to be analysed and developing of the blue silicomolybdate complex using ammonium molybdate and a reducing solution. Measurement of the optical density of the colour complex, when measuring the sample measuring solution, by means of a molecular absorption spectrometer at 800 nm using 10 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 as 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 spectrometry may be used for the preparation of the stock or standard solutions.

5.1 4-Amino-3-hydroxynaphthalene-1-sulfonic acid or 1-amino-2-hydroxynaphthalene-4-sulfonic acid [$NH_2C_{10}H_5(OH)SO_3H$].

5.2 Ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$], 60 g/l aqueous solution.

5.3 Boric acid (H_3BO_3), 50 g/l solution.

5.4 2,4-Dinitrophenol [$2,4\text{-}(NO_2)_2C_6H_3OH$], 1 g/l indicator solution.

5.5 Hydrochloric acid (HCl), $\rho = 1{,}19$ g/ml.

5.5.1 Hydrochloric acid, diluted 1 + 5.

5.5.2 Hydrochloric acid, diluted 1 + 24.

5.6 Hydrofluoric acid (HF) solution, $\rho = 1{,}13$ g/ml.

5.7 Reducing solution

Dissolve 0,7 g of sodium sulfite (5.15) in 20 ml of water, add 0,15 g of 4-amino-3-hydroxynaphthalene-1-sulfonic acid or 1-amino-2-hydroxynaphthalene-4-sulfonic acid (5.1) and stir to dissolve. Dissolve 9 g of sodium metabisulfite (5.14) in 160 ml of water and transfer both solutions to the same 200 ml one-mark volumetric flask (6.7). Make up to the mark and mix.

This solution shall be discarded if the faintest blue coloration appears.

5.8 Silicon dioxide (also called silica) (SiO_2).

Use finely ground silica sand containing at least 99,9 % (*m/m*) SiO_2, dried at 110 °C at least.

5.9 Silica, stock solution.

Weigh, to the nearest 0,1 mg, about 1 g of silica (5.8) into a platinum dish (6.6). Add 4,5 g of sodium carbonate (5.11) and intimately mix using a dry rod (do not use a glass rod). Ease the mixture into the centre of the dish and flatten it to cover an area of diameter about 30 mm. Cover the mixture as evenly as possible with a further 0,5 g of sodium carbonate (5.11), then gently brush any particles adhering to the rod into the dish.

Cover the dish with a platinum lid (6.6) and place it in a muffle furnace at 300 °C to 400 °C. Gradually increase the temperature to 1 100 °C and maintain this for about 10 min or until fusion is complete. Remove the dish from the furnace and gently swirl the melt to incorporate any remaining particles. Allow to cool, wash any material adhering to the underside of the lid into the dish using hot water, then dissolve the fused mass in hot water. Cool, transfer the solution to a 1 000 ml one-mark volumetric flask (6.7), make up to the mark with water and mix.

Transfer the solution to the plastics bottle (6.3) for storage.

1 ml of this solution contains 1 mg of SiO_2.

5.10 Silica, standard solution.

Using a one-mark pipette (6.10), transfer 10,00 ml of the silica stock solution (5.9) to a 1 000 ml one-mark volumetric flask (6.7), 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 SiO_2.

5.11 Sodium carbonate (Na_2CO_3), anhydrous.

5.12 Sodium hydroxide, solution, $c(NaOH) \approx 2$ mol/l, stored in a plastics bottle (6.3).

5.13 Sodium hydroxide, solution, $c(NaOH) \approx 0{,}1$ mol/l, stored in a plastics bottle (6.3).

5.14 Sodium metabisulfite ($Na_2S_2O_5$).

5.15 Sodium sulfite (Na_2SO_3), anhydrous.

5.16 Tartaric acid [$(CHOH \cdot COOH)_2$] 200 g/l solution.

6 Apparatus

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 800 nm.

6.2 Optical cells, 10 mm path length.

6.3 Plastics bottles, stoppered, of a suitable capacity e.g. about 1 000 ml.

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

6.5 Plastics beakers, of a suitable capacity e.g. about 200 ml, and complying with the requirements in ISO 7056.

6.6 Platinum dishes with lids, of capacity about 75 ml, for example.

6.7 One-mark volumetric flasks, of a suitable capacity, and complying with the requirements for class A one-mark volumetric flasks in ISO 1042.

6.8 Graduated plastics pipette, of capacity 1 ml.

6.9 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.

6.10 One-mark pipette, of suitable capacity, and complying with the requirements for class A one-mark pipettes in ISO 648.

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

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

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

6.14 Magnetic stirrer, with a plastic coated rod.

6.15 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.

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 (6.10), transfer a 20 ml aliquot of the extract solution to a beaker (6.4) and acidify, under control of a pH-meter (6.13), with hydrochloric acid (5.5.2) to a pH-value of about 3. Then heat till boiling, cool and bring the pH back to a value of about 5 with sodium hydroxide solution (5.13). Using an appropriate filter (6.15), filter the solution into a 200 ml plastics beaker (6.5) and stir magnetically (see 6.14). Wash the filter carefully with small portions of warm water (maximum 10 ml) into the same beaker. It is important that stirring should be continued throughout all additions to the solution and until immediately prior to transferring the solution to the 100 ml one-mark volumetric flask (6.7).

Add one drop of 2,4-dinitrophenol (5.4) and neutralize with sodium hydroxide (5.12) or hydrochloric acid (5.5.1) until the solution just turns yellow. Add 0,5 ml of hydrofluoric acid (5.6) using the graduated plastics pipette (6.8) and allow to stand for 3 min. Add 40 ml of boric acid (5.3) and allow to stand for 3 min, then add 5 ml of ammonium molybdate (5.2). Allow to stand for 10 min, then add 5 ml of tartaric acid (5.16) and 5 ml of reducing solution (5.7). Mix thoroughly, remove the beaker from the magnetic stirrer and transfer the solution to a 100 ml one-mark volumetric flask (6.7). Make up to the mark with water, and allow to stand until colour development is complete (about 2 h is usually sufficient).

8.1.2 Blank test solution

Prepare the blank test solution using 20 ml of water and following the procedure exactly as for the sample measuring solution.

8.1.3 Measurement of optical density

Measure the optical density of the sample measuring solution at 800 nm (see 6.1) using 10 mm optical cells (6.2), and also of the blank test solution with the zero member (see 3.6) as reference.

8.2 Preparation of the calibration graph

Using a burette (6.11), transfer accurately measured volumes of the silica standard solution (5.10) to separate 200 ml plastics beakers (6.5) to cover the range 0 to 150 µg SiO_2. Dilute each to about 20 ml with water. Place on the magnetic stirrer (6.14), add one drop of 2,4-dinitrophenol (5.4), then add 5 ml of ammonium molybdate (5.2) and develop the blue colour of reduced siliconmolybdenic acid as described in 8.1.1.

Measure the optical densities of the solutions at 800 nm (see 6.1) using 10 mm optical cells (6.2) with the zero member as reference. Plot the optical densities against mass of silica to produce the calibration graph.

9 Expression of results

Determine the mass of silicon dioxide (SiO_2) 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 silicon dioxide in the extract solution and express as micrograms of SiO_2 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 SiO_2 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] The chemical durability of glass: the determination of silica in extract solutions. (A report by Sub Committee A2 of the International Commission on Glass.) *Glass technology,* 1975, vol. **16**, No. 4, pp. 80-83.