BRITISH STANDARD

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ISO 10136-5:
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Analysis of extract solutions of glass —

Part 5: Method for determination of iron(III) oxide by molecular absorption spectrometry and flame atomic absorption spectrometry

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Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Laboratory Apparatus Standards Policy Committee (LBC/-) to Technical Committee LBC/36, upon which the following bodies were represented:

Association for Science Education
BLWA Ltd. (The Association of the Laboratory Supply Industry)
British Glass Manufacturers' Confederation
CLEAPSS School Science Service
Department of Trade and Industry (Laboratory of the Government Chemist)
Institute of Medical Laboratory Sciences

The following body was also represented in the drafting of the standard, through a subcommittee:

Society of Glass Technology

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Contents

National foreword

This Part of BS 7709 has been prepared under the direction of the Laboratory Apparatus Standards Policy Committee and is identical with ISO 10136-5:1993 *Glass and glassware — Analysis of extract solutions — Part 5: Determination of iron(III) oxide by molecular absorption spectrometry and flame atomic absorption spectrometry*, published by the International Organization for Standardization (ISO). ISO 10136-5 has been prepared by Subcommittee 5 of Technical Committee ISO/TC 48, with the active participation and approval of the UK.

BS 7709 is published in six Parts as follows:

- — *Part 1: Method for determination of silicon dioxide by molecular absorption spectrometry*;
- — *Part 2: Method for determination of sodium oxide and potassium oxide by flame spectrometric methods*;
- — *Part 3: Method for determination of calcium oxide and magnesium oxide by flame atomic absorption spectrometry*;
- — *Part 4: Method for determination of aluminium oxide by molecular absorption spectrometry*;
- — *Part 5: Method for determination of iron(III) oxide by molecular absorption spectrometry and flame atomic absorption spectrometry*;
- — *Part 6: Method for determination of boron(III) oxide by molecular absorption spectrometry*.

BS 2649 *Methods for analysis of glass* — Part 1:1988 *Glasses of the soda-lime-magnesia-silica type* and Part 3:1988 *Glasses of the potassium oxide-lead oxide-silica type* describe methods of determination primarily of the gravimetric type. The methods given in BS 7709 should be considered complementary to those of BS 2649.

Cross-references

International Standard	Corresponding British Standard
	BS 700 *Graduated pipettes*
ISO 835-1:1981	Part 1:1982 *Specification for general requirements* (Identical)
ISO 835-2:1981	Part 2:1982 *Specification for pipettes for which no waiting time is specified* (Identical)
ISO 1042:1983	BS 1792:1982 *Specification for one-mark volumetric flasks* (Identical)
ISO 1773:1976	BS 2734:1984 *Specification for boiling flasks (narrow-necked), conical, flat bottom and round bottom* (Identical)
ISO 3585:1991	BS 2598 *Glass plant, pipeline and fittings* Part 1:1991 *Specification for properties of borosilicate glass 3.3* (Identical)
ISO 3696:1987	BS 3978:1987 *Specification for water for laboratory use* (Identical)
ISO 3819:1985	BS 6523:1984 *Specification for glass beakers for laboratory use* (Technically equivalent)

The Technical Committee has reviewed the provisions of ISO 385-2, ISO 648, ISO 835-3 and ISO 6955, to which normative reference is made in the text, and has decided that they are acceptable for use in conjunction with this standard.

This British Standard describes a method of test only and should not be used or quoted as a specification defining limits of performance. Reference to this British Standard should indicate that the method of test used is in accordance with BS 7709-5:1993.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 6, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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Introduction

All silicate glasses contain some iron, although in very low concentrations, and in certain usages some of this iron can be released into the contents of a glass container. There may be serious consequences, for instance when solutions are sterilized by autoclaving after they have been poured into a container, or when solutions are stored (even at ambient temperatures) for long periods of time. Iron may be released into the extract solutions produced during hydrolytic resistance tests and, because the concentration will be very low, a very sensitive test method is required for its determination.

Technical Committee 2, Chemical Durability and Analysis, of the International Commission on Glass (ICG), investigated the problem (see [6] in Annex A) and considered flame-emission, flame atomic absorption and two molecular absorption spectrometric methods, using *ortho*-phenanthroline and bathophenanthroline. As a result of these deliberations, it was considered that the bathophenanthroline method probably offered the greatest sensitivity and freedom from interferences. Nine laboratories participated in the round-robin study to develop recommended procedures using both molecular absorption and flame atomic absorption spectrometry.

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.

1 Scope

This part of ISO 10136 specifies an analytical procedure, using molecular absorption spectrometry and flame atomic absorption spectrometry, for measuring the concentrations of iron, expressed as iron(III) oxide (Fe_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), neutral glass, or soda-lime-silica glass as defined in ISO 4802[3][4], food and drink packaging ware, table-ware 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 1773:1976, *Laboratory glassware — Boiling flasks (narrow-necked).*

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
flame atomic absorption spectrometry (FAAS)

a technique for determining the concentration of chemical elements based on the measurement of the absorption of characteristic electromagnetic radiation in a vapour phase in a flame

3.9
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

3.10
spectrochemical buffer solution

a solution of a substance or substances added to the sample measuring solution and to the reference solutions in order to reduce interferences during flame spectrometric measurements

3.11
optimum working range

the range of concentrations of an analyte in solution over which the relationship between absorption (or emission) and concentration is linear

4 Principle

4.1 Determination of iron by molecular absorption spectrometry

Reduction of the iron in the extract solution to be analysed to the iron(II) state by adding ascorbic acid. Addition of bathophenanthroline and buffering of the solution to pH 4 to 6. Then, extraction of the coloured iron complex into chloroform. Measurement of the optical density by means of a molecular absorption spectrometer at 533 nm using 40 mm optical cells. Determination of the concentration of iron from the calibration graph.

4.2 Determination of iron by flame atomic absorption spectrometry

Evaporation of a portion of the extract solution to be analysed with hydrofluoric and perchloric acids and dissolution of the residue in hydrochloric acid solution. Spraying the solution into an air/acetylene flame and measuring the absorption using a flame atomic absorption spectrometer at 248,3 nm. Determination of the concentration of iron from the calibration graph.

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 or atomic absorption spectrometry may be used for the preparation of stock or standard solutions.

5.1 *Ammonium hydroxide*, $c(NH_3)$ or $c(NH_4OH) \approx 5$ mol/l.

5.2 *Ammonium iron(II) sulfate*, $[(NH_4)_2Fe(SO_4)_2.6H_2O]$.

5.3 *Ascorbic acid* ($C_6H_8O_6$) 100 g/l solution, freshly prepared.

5.4 *Bathophenanthroline* (4,7-diphenyl-1,10-phenanthroline), solution, $c(C_{24}H_{16}N_2) = 0{,}001$ mol/l.

5.5 *Chloroform* ($CHCl_3$).

5.6 *Ethanol* (C_2H_5OH).

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

5.8 *Hydrochloric acid*, diluted 1 + 24.

5.9 *Perchloric acid* ($HClO_4$), 600 g/l solution.

5.10 *Sodium acetate trihydrate* ($CH_3COONa.3H_2O$).

5.11 *Iron*, stock solution.

Dissolve 0,491 1 g of ammonium iron(II) sulfate (**5.2**) in water and add 10 ml of hydrochloric acid (**5.7**). Transfer the solution to a 1 000 ml one-mark volumetric flask (**6.6**), make up to the mark and mix.

1 ml of this stock solution contains 100 µg of Fe_2O_3.

5.12 *Iron*, standard solution, for MAS.

Using a one-mark pipette (**6.9**), transfer 10 ml of the iron stock solution (**5.11**) to a 1 000 ml one-mark volumetric flask (**6.6**), make up to the mark with water and mix.

The solution shall be prepared immediately before use.

1 ml of this standard solution contains 1,0 µg of Fe_2O_3.

5.13 *Iron*, standard solution, for FAAS.

Using a one-mark pipette (**6.9**), transfer 100 ml of the iron stock solution (**5.11**) to a 1 000 ml one-mark volumetric flask (**6.6**), make up to the mark with water and mix.

1 ml of this standard solution contains 10 µg of Fe_2O_3.

5.14 *Butan-1-Ol* $[CH_3(CH_2)_3OH]$.

5.15 *Lanthanum oxide* (La_2O_3).

5.16 *Spectrochemical buffer solution*

Transfer 11,7 g of lanthanum oxide (**5.15**) to a 250 ml beaker (**6.4**), add 100 ml of hydrochloric acid (**5.7**) and dissolve while heating gently. Cool, transfer to a 1 000 ml one-mark volumetric flask (**6.6**), make up to the mark with water 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 533 nm.

6.2 *Optical cells*, 40 mm path length.

6.3 *Flame atomic absorption spectrometer*, equipped with a line source for iron (248,3 nm) and with a gas supply and burner for an air/acetylene gas mixture.

6.4 *Beakers*, of a suitable capacity e.g. 100 ml and 250 ml, and complying with the requirements in ISO 3819.

6.5 *Conical flasks*, of a suitable capacity e.g. 100 ml, and complying with the requirements in ISO 1773.

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

6.7 *Separating funnels*, of a suitable capacity e.g. 150 ml.

6.8 *Graduated pipettes*, of a suitable capacity, and complying with the requirements for class A graduated pipettes in ISO 835-1, ISO 835-2 or ISO 835-3.

6.9 *One-mark pipettes*, of a suitable capacity e.g. 10 ml, 50 ml and 100 ml, and complying with the requirements for class A one-mark pipettes in ISO 648.

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

6.11 *Balance*, with a discrimination of 0,1 mg.

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

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.

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 of the sample measuring solution and the blank test solution

8.1.1 *Sample measuring solution*

Using a one-mark pipette (**6.9**), transfer a 25 ml aliquot of the extract solution to a beaker (**6.4**) and acidify, under control of a pH-meter (**6.12**), with hydrochloric acid (**5.8**) to a pH-value of about 2,5 to 3. Then heat till boiling. Using an appropriate filter (**6.13**), filter the solution and wash with small volumes of water into another beaker (**6.4**). Evaporate, by boiling, to about 20 ml and cool. Transfer the solution 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.

8.2 Determination of iron by molecular absorption spectrometry

8.2.1 *Measurement of the sample measuring solution and the blank test solution*

Transfer an accurately measured volume of the sample measuring solution, prepared according to **8.1.1** and containing not more than 20 µg of Fe_2O_3, to a 100 ml conical flask (**6.5**). Dilute, if necessary, to about 25 ml and add 2,5 ml of perchloric acid (**5.9**). Add 5 ml of ascorbic acid solution (**5.3**), 10 ml of bathophenanthroline solution (**5.4**) and 0,5 g of sodium acetate trihydrate (**5.10**) and mix thoroughly. Using a pH-meter (**6.12**), adjust the pH-value to between 4 and 6 by adding ammonium hydroxide (**5.1**). Cover the conical flask (**6.5**) and allow to stand for 20 min.

Transfer the solution to a 150 ml separating funnel (**6.7**), add 5 ml of chloroform (**5.5**) and shake the mixture vigorously for 30 s. Allow the layers to separate, then run the lower layer of chloroform through a plug of dry, glass wool held in a small filter funnel, into a dry 25 ml one-mark volumetric flask (**6.6**). Add a further 5 ml of chloroform to the solution in the separating funnel and repeat the extraction, collecting the chloroform layer in the same 25 ml one-mark volumetric flask. Make up to the mark with ethanol (**5.6**) and mix.

Measure the optical density of the sample measuring solution at 533 nm (see **6.1**) using 40 mm optical cells (**6.2**), and also the blank test solution with the zero member (see **3.6**) as reference.

8.2.2 *Preparation of the calibration graph*

Using a burette (**6.10**) or a one-mark pipette (**6.9**), transfer 0 ml, 2,50 ml, 5,00 ml, 8,00 ml, 15,00 ml and 20,00 ml volumes of the iron standard solution for MAS (**5.12**) to separate 100 ml conical flasks (**6.5**). Dilute each to about 25 ml, then proceed as described in **8.2.1**.

Plot the optical densities against mass of iron to produce the calibration graph. These solutions contain 0 µg, 2,5 µg, 5,0 µg, 8,0 µg, 15,0 µg and 20,0 µg of iron(III) oxide (Fe_2O_3), respectively.

8.3 Determination of iron by flame atomic absorption spectrometry (FAAS)

8.3.1 *Measurement of the sample measuring solution and the blank test solution*

Transfer an accurately measured volume of the sample measuring solution, prepared according to **8.1.1** and containing not more than 25 µg of Fe_2O_3, to a 50 ml one-mark volumetric flask (**6.6**). Add 12,5 ml of the spectrochemical buffer solution (**5.16**) and 2,5 ml of butan-1-ol (**5.14**), make up to the mark and mix.

Adjust the flame atomic absorption spectrometer (**6.3**) to the optimum working conditions, according to the operating manual, for measurements at 248,3 nm using an air/acetylene gas mixture.

Spray the blank test solution into the flame of the spectrometer until a steady reading is obtained and noted. Spray the sample measuring solution in the same way and repeat the sequence four more times. Calculate the mean values of the readings and subtract the blank value from the sample value.

8.3.2 *Preparation of the calibration graph*

Using a burette (**6.10**) or a one-mark pipette (**6.9**), transfer 0 ml, 1,00 ml, 2,00 ml, 5,00 ml and 10,00 ml volumes of the iron standard solution for FAAS (**5.13**) to separate 100 ml one-mark volumetric flasks (**6.6**). Add 25,00 ml of the spectrochemical buffer solution (**5.16**) and 5 ml of butan-1-ol (**5.14**) to each one-mark volumetric flask, make up to the marks and mix. These solutions contain 0 µg, 0,1 µg, 0,2 µg, 0,5 µg and 1,0 µg of iron(III) oxide (Fe_2O_3) per millilitre, respectively.

Adjust the flame atomic absorption spectrometer (**6.3**) exactly as in **8.3.1**, then spray the series of calibration solutions, in order of increasing iron concentration, until steady readings are obtained. Repeat the spraying sequence four more times, calculate the mean values of the readings and plot the graph of reading against iron concentration.

9 Expression of results

Subtract the blank value from the value of the sample measuring solution and determine the concentration of iron(III) oxide (Fe_2O_3) from the calibration graph. Calculate its concentration first in the sample measuring solution, then in the extract solution, and express as micrograms of Fe_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) a reference to the method of measurement used, i.e. MAS or FAAS;

e) the results obtained, expressed as micrograms of Fe_2O_3 per millilitre of extract solution;

f) 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: determination of iron in extract solutions. (A report by Sub-Committee A2 of the International Commission on Glass). *Glasstechn. Ber.*, (1978), Vol. **51**, No. 4, pp. 79–82.

List of references

See national foreword.

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