INTERNATIONAL STANDARD

ISO 10136-3

First edition
1993-07-01

Glass and glassware — Analysis of extract solutions —

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

Verre et verrerie — Analyse des solutions d'attaque —

Partie 3: Dosage de l'oxyde de calcium et de l'oxyde de magnésium par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 10136-3:1993(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 10136-3 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

Classifications of glass or glassware, in National or International Standards and in the various pharmacopoeia, have relied for many years on a titration of extract solutions with a diluted mineral acid. Such solutions may contain not only the alkali metal oxides (sodium and potassium), but also the alkaline earth oxides (calcium and magnesium), which are also titrated by acid. Thus, the determination is actually of the total alkalinity of the extract solution, although this is sometimes calculated as the equivalent mass of sodium oxide. In recent years, with the advent of more modern techniques, such as flame atomic absorption spectrometry, there has been a move towards a more complete analysis of extract solutions and a measurement of the concentrations of the separate elements present.

Technical Committee 2, Chemical Durability and Analysis, of the International Commission on Glass (ICG), investigated colorimetric methods for determining calcium and magnesium (see [5] in annex A) but concluded that none was particularly suitable for the determination of the very low concentrations normally found in extract solutions. In round-robin studies involving ten laboratories, a procedure using flame atomic absorption spectrometry was devised and recommended for analysing extract solutions.

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

Glass and glassware — Analysis of extract solutions —

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

1 Scope

This part of ISO 10136 specifies the analytical procedure, using flame atomic absoprtion spectrometry, for measuring the concentrations of calcium and magnesium, expressed as their oxides (CaO and MgO), 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.*

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 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.

3.8 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.

3.9 optimum working range: The range of concentrations of an analyte in solution over which the relationship between absorption (or emission) and concentration is linear.

3.10 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

Atomizing of the extract solution to be analysed in the flame of an air/acetylene or dinitrogen monoxide/acetylene burner through which is passed the characteristics light emitted by a calcium or magnesium hollow cathode lamp. Measurement of the portion of the 422,7 nm line absorbed by calcium atoms and of the 285,2 nm line absorbed by magnesium atoms using a flame atomic absorption spectrometer, and comparison with the absorption produced by reference solutions of known calcium and magnesium concentrations atomized under the same conditions.

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 stock or standard solutions.

5.1 Calcium carbonate ($CaCO_3$), dried at 110 °C (at least) and stored in a desiccator.

5.2 Calcium oxide, stock solution.

Weigh, to the nearest 0,1 mg, 1,785 8 g of calcium carbonate (5.1) and transfer to a 150 ml dish. Cover with a watch glass and carefully add 100 ml of hydrochloric acid (5.5) to dissolve. Heat almost to boiling until all the gas has been evolved, rinse the underside of the watch glass into the solution, cool and transfer the solution to a 1 000 ml one-mark volumetric flask (6.4). Make up to the mark with water and mix.

Transfer to a 1 000 ml stoppered bottle (6.3) for storage.

1 ml of this stock solution contains 1 mg of CaO.

5.3 Calcium oxide, standard solution.

Using a one-mark pipette (6.6), transfer 25 ml of the calcium oxide stock solution (5.2) to a 250 ml one-mark volumetric flask (6.4), make up to the mark with water and mix.

Transfer to a 250 ml stoppered bottle (6.3) for storage.

This solution shall be freshly prepared immediately before use.

1 ml of this standard solution contains 100 µg of CaO.

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

5.5 Hydrochloric acid, diluted 1 + 12.

5.6 Magnesium oxide (MgO), ignited at 1 050 °C for 1 h and allowed to cool in a desiccator.

5.7 Magnesium oxide, stock solution.

Weigh, to the nearest 0,1 mg, 0,100 0 g of magnesium oxide (5.6) and transfer it to a 250 ml beaker (6.2). Add 70 ml of hydrochloric acid (5.5) and heat, if necessary, to dissolve. Cool the solution, then transfer it to a 1 000 ml one-mark volumetric flask (6.4), make up to the mark with water and mix.

Transfer to a 1 000 ml stoppered bottle (6.3) for storage. Discard after 1 month.

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

5.8 Magnesium oxide, standard solution.

Using a one-mark pipette (6.6), transfer 25 ml of the magnesium oxide stock solution (5.7) to a 250 ml one-mark volumetric flask (6.4), make up to the mark with water and mix.

Transfer to a 250 ml stoppered bottle (6.3) for storage.

This solution shall be freshly prepared immediately before use.

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

5.9 Lanthanum oxide (La_2O_3).

5.10 Spectrochemical buffer solution

Transfer 11,7 g of lanthanium oxide (5.9) to a 250 ml beaker (6.2), add 100 ml of hydrochloric acid (5.4) and dissolve while heating gently. Cool, transfer to a 1 000 ml one-mark volumetric flask (6.4), 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 Flame atomic absorption spectrometer, equipped with line sources for calcium (422,7 nm) and magnesium (285,2 nm) and with gas supplies and burners for air/acetylene or dinitrogen monoxide/acetylene gas mixtures.

6.2 Beakers, of a suitable capacity e.g. about 250 ml, and complying with the requirements in ISO 3819.

6.3 Bottles, stoppered, of a suitable capacity e.g. about 250 ml and 1 000 ml.

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

6.5 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.

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

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

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

6.9 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 Instrumentation

Adjust the flame atomic absorption spectrometer to the optimum operating condition, as specified in the operating manual, using the parameters shown in table 1.

Table 1 — Parameters for the measurements of (Ca) and (Mg)

Element	Usual optimum working range (µg/ml)	Gas mixture	Detection line nm
Ca	1 to 5	air/acetylene or N_2O /acetylene	422,7
Mg	0,1 to 0,5		285,2

8.2 Preparation of reference solutions

8.2.1 For calcium

Using a graduated pipette (6.5), transfer 0 ml, 1,00 ml, 2,00 ml, 3,00 ml, 4,00 ml and 5,00 ml volumes of the calcium oxide standard solution (5.3) to separate 50 ml one-mark volumetric flasks (6.4). Add, with a graduated pipette (6.5) or a burette (6.7), 5 ml of the spectrochemical buffer solution (5.10) to each one-mark volumetric flask. Then make up each solution to the mark and mix.

These solutions shall be prepared immediately before use.

1 ml of the reference solution contains 0 µg, 2 µg, 4 µg, 6 µg, 8 µg and 10 µg of CaMgO respectively.

8.2.2 For magnesium

Using a graduated pipette (6.5), transfer 0 ml, 1,00 ml, 2,00 ml, 3,00 ml, 4,00 ml and 5,00 ml volumes of the magnesium oxide standard solution (5.8) to separate 50 ml one-mark volumetric flasks (6.4). Add, with a graduated pipette (6.5) or a burette (6.7), 5 ml of the spectrochemical buffer solution (5.10) to each one-mark volumetric flask. Then make up each solution to the mark and mix.

These solutions shall be prepared immediately before use.

1 ml of the reference solution contains 0 µg, 0,2 µg, 0,4 µg, 0,6 µg, 0,8 µg and 1,0 µg of MgO respectively.

8.3 Preparation of the calibration graphs

8.3.1 For measurement of calcium oxide (CaO)

Spray the reference solution (8.2.1) containing 10 µg/ml of CaO into the flame of the burner and adjust the instrument to optimum sensitivity. Using precisely the same instrumental conditions spray the series of reference solutions (in order of increasing concentration) and note the readings. Repeat the adjustment and spraying sequence at least three times and note the readings. Calculate the mean values of the readings and plot the graph of readings against CaO concentrations.

8.3.2 For measurement of magnesium oxide (MgO)

Spray the reference solution (8.2.2) containing 1,0 µg/ml of MgO into the flame of the burner and adjust the instrument to optimum sensitivity. Using precisely the same instrumental conditions, spray the series of reference solutions (in order of increasing concentration) and note the readings. Repeat the adjustment and spraying sequence at least three times and note the readings. Calculate the mean values of the readings and plot the graph of readings against MgO concentrations.

8.4 Preparation of the sample measuring solution and the blank test solution

8.4.1 Sample measuring solution

Using a one-mark pipette (6.6), transfer a 25 ml aliquot of the extract solution into a beaker (6.2) and add 5 ml of the spectrochemical buffer solution (5.10). Heat till boiling, cool and filter the solution using an appropriate filter (6.9) into a 50 ml one-mark volumetric flask (6.4). Wash the filter carefully with small portions of warm water, to make up to the mark.

NOTE 1 If the measured concentrations of CaO or MgO are too low or too high, concentrate by evaporating or diluting respectively. Ensure that the volume of spectrochemical buffer added is equal to 10 % of the volume of the volumetric flask.

8.4.2 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.

8.5 Determination of CaO and MgO

8.5.1 Determination of CaO

Spray the reference solution (8.2.1) containing 10 µg/ml of CaO into the flame of the burner and adjust the spectrometer to optimum sensitivity. Using precisely the same instrumental conditions, spray the sample measuring solution (8.4.1) and the blank test solution (8.4.2) and note the readings. Repeat the adjustment and measurement of the sample measuring solution and blank test solution at least three times and calculate the mean values of the readings.

8.5.2 Determination of MgO

Spray the reference solution (8.2.2) containing 1,0 µg/ml of MgO into the flame of the burner and adjust the spectrometer to optimum sensitivity. Using precisely the same instrumental conditions, spray the sample measuring solution (8.4.1) and the blank test solution (8.4.2) and note the readings. Repeat the adjustment and measurement of the sample measuring solution and blank test solution at least three times and calculate the mean values of the readings.

9 Expression of results

Determine the masses of calcium oxide (CaO) and magnesium oxide (MgO) in the sample measuring solution (8.4.1) and the blank test solution (8.4.2) from the calibration graphs (8.3.1 and 8.3.2, respectively). Subtract and calculate the concentrations of calcium oxide and magnesium oxide in the extract solution and express as micrograms of CaO and MgO 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. using air/acetylene or dinitrogen monoxide/acetylen mixtures;

e) the results obtained, expressed as micrograms of CaO per millilitre and/or micrograms of MgO per millilitre of extract solution;

f) any unusual features noted during the determination.