BS 4993-3: 1974

Incorporating Amendment No. 1

Methods of test for

Aluminium fluoride for industrial use —

Part 3: Determination of silica content

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Co-operating organizations

The Chemicals Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

British Steel Industry
Chemical Industries Association*
Department of Health and Social Security
Department of Trade and Industry
Fertilizer Manufacturers' Association Limited
Ministry of Agriculture, Fisheries and Food
National Sulphuric Acid Association
Royal Institute of Public Health and Hygiene
Soap and Detergent Industry Association

This British Standard, having been approved by the Chemicals Industry Standards Committee, was published under the authority of the Executive Board on 28 February 1974

The following BSI references relate to the work on this standard:
Committee reference CIC/24
Drafts for comment/approval 71/53613 and 73/50651

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Contents

Foreword

This British Standard has been prepared under the authority of the Chemicals Industry Standards Committee in order to provide methods for the analysis of aluminium fluoride.

For some years the United Kingdom has participated in the work of preparing methods of test applicable to aluminium fluoride for industrial use, organized by Sub-Committee 7 “Alumina and related compounds” of Technical Committee 47 “Chemistry” of the International Organization for Standardization (ISO). As international agreement is reached on the methods, it is proposed to publish them as parts of this British Standard.

This part is based on the International Standard ISO 2369, “*Aluminium fluoride for industrial use — Determination of silica content — Spectrophotometric method using the reduced silicomolybdic complex*”, modified to take into account the comments made by the United Kingdom during its development.

This standard prescribes methods of test only, and should not be used or quoted as a Specification defining limits of purity. Reference to the standard should be in a form of words indicating that the methods of test used conform to BS 4993.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 4, 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.

1 Scope

This Part of BS 4993 specifies a spectrophotometric method for the determination of the silica content of aluminium fluoride for industrial use.

NOTE The titles of the British Standards referred to in this standard are listed on the inside back cover.

2 Field of application

The method can be applied to the determination of the silica content of aluminium fluoride for industrial use, provided that the P_2O_5 content does not exceed 0.02 %. A method for the determination of silica when P_2O_5 contents greater than 0.02 % are present is in course of preparation.

3 Principle

A test portion is fused under alkaline conditions with a mixture of sodium carbonate and boric acid. The fused mass is dissolved in excess nitric acid so that the pH of the final solution is between 0.3 and 0.5.

The (yellow) oxidized molybdophosphoric complex is formed, from a suitable aliquot portion, under clearly defined conditions of acidity, concentration of reagents, temperature and time.

The complex is selectively reduced in a high acidity sulphuric acid medium and in the presence of tartaric acid. The reduced complex is measured spectrophotometrically at a wavelength of 815 nm.

4 Reagents

The reagents used shall be of recognized analytical reagent quality. Redistilled water shall be used throughout.

4.1 *Sodium carbonate*, anhydrous.

4.2 *Boric acid*, (H_3BO_3).

4.3 *Nitric acid*, approximately 8N solution.

Dilute 540 ml of nitric acid solution, ρ 1.40 g/ml, 68 % (m/m) approximately, with water to 1 000 ml.

4.4 *Sodium molybdate*, 195 g/l (0.8M approximately) solution.

Dissolve, in a plastics beaker (PTFE[1], for example), 19.5 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in hot water and, after cooling, dilute to 100 ml.

Transfer the solution to a plastics[2] bottle and, if necessary, filter before use.

4.5 *Tartaric acid*, 100 g/l solution.

Dissolve 10 g of tartaric acid in water and dilute to 100 ml.

4.6 *Sulphuric acid*, approximately 16N solution.

Carefully add 450 ml of sulphuric acid, ρ 1.84 g/ml, approximately 96 % (m/m) solution, to about 500 ml of water.

Cool and dilute to 1 000 ml.

4.7 *Reducing solution.* Either of the following solutions may be used.

4.7.1 *1-Amino-2-naphthol-4-sulphonic acid*, 1.5 g/l solution.

a) Dissolve 7 g of anhydrous sodium sulphite in 50 ml of water. Add 1.5 g of 1-amino-2-naphthol-4-sulphonic acid.

b) Dissolve 90 g of sodium metabisulphite ($Na_2S_2O_5$) in 900 ml of water.

Mix the two solutions a) and b) and dilute to 1 000 ml.

Filter if necessary.

Store in an amber-coloured bottle, in a cool place.

4.7.2 *Ascorbic acid*, 20 g/l solution.

Dissolve 2 g of ascorbic acid in water and dilute to 100 ml.

Use a freshly prepared solution.

4.8 *Standard silica solution*, corresponding to a content of 0.500 g of silica (SiO_2) per litre.

Into a platinum crucible, weigh to the nearest 1 mg, either

500 mg of SiO_2 obtained from pure silicic acid (H_2SiO_3), heated to constant mass at 1 000 °C and cooled in a desiccator, or

500 mg of finely ground pure quartz, previously heated at 1 000 °C for 1 h and cooled in a desiccator.

Add 5 g of the sodium carbonate (**4.1**) to the crucible. Mix thoroughly, preferably with a platinum spatula, and fuse carefully until a clear transparent melt is obtained. Cool.

Add hot water to the crucible, heat gently to complete the dissolution and transfer the solution quantitatively into a PTFE beaker. Cool, dilute to about 500 ml and transfer quantitatively to a 1 000 ml one-mark volumetric flask (BS 1792), dilute to the mark and mix.

Transfer immediately to a plastics[3] bottle.

1 ml of this standard solution contains 0.500 mg of SiO_2.

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[1] Polytetrafluorethylene.

[2] For example PTFE, polypropylene or polyethylene may be used.

[3] For example PTFE, polypropylene or polyethylene may be used.

4.9 *Standard silica solution*, corresponding to a content of 0.020 g of silica (SiO_2) per litre.

Place 40.0 ml of the standard silica solution (**4.8**) in a 1 000 ml one-mark volumetric flask (BS 1792), dilute to the mark and mix.

1 ml of this standard solution contains 20 µg of SiO_2.

Prepare this solution just before use.

4.10 *Standard silica solution*, corresponding to a content of 0.005 g of silica (SiO_2) per litre.

Place 50.0 ml of the standard silica solution (**4.9**) in a 200 ml one-mark volumetric flask (BS 1792), dilute to the mark and mix.

1 ml of this standard solution contains 5 µg of SiO_2.

Prepare this solution just before use.

5 Apparatus

Ordinary laboratory apparatus and the following are required.

5.1 *Platinum dish*, flat-bottomed, diameter approximately 70 mm, height approximately 35 mm, fitted with a platinum lid.

5.2 *Electric furnace*, capable of being controlled at 550 ± 25 °C.

5.3 *Electric furnace*, capable of being controlled at 750 ± 25 °C.

5.4 *pH meter*, provided with a glass electrode. Essential requirements are given in BS 2586, and in BS 3145 or BS 3422.

5.5 *Spectrophotometer*

NOTE Glassware should be carefully washed with chromic-sulphuric acid mixture, thoroughly rinsed with water and finally with redistilled water. Do not dry. Avoid the use of glass vessels for alkaline solutions.

6 Procedure

6.1 Test portion

Weigh, to the nearest 0.001 g, exactly 1 g of the dried test sample.[4)]

6.2 Preparation of the calibration curve

6.2.1 *Preparation of the base solution.* Weigh 24 g of the sodium carbonate (**4.1**) and 8 g of the boric acid (**4.2**) into the platinum dish (**5.1**). Mix thoroughly, preferably with a platinum spatula. Cover the dish with its lid and place it in the electric furnace (**5.2**), controlled at 550 ± 25 °C, taking care to isolate the dish from the floor of the furnace, using a support which avoids the risk of contamination (platinum support for preference). Maintain at 550 ± 25 °C until the reaction subsides.

Transfer the dish to the electric furnace (**5.3**), controlled at 750 ± 25 °C, isolating it, as before, from the furnace floor, and allow to remain for a maximum of 5 min. Remove the dish from the furnace and allow to cool in the atmosphere. Add boiling water to the dish and heat gently until the contents are completely dissolved.

After cooling slightly, transfer the contents of the dish to a plastics beaker (PTFE for example) of suitable capacity, containing 40 ml of the nitric acid (**4.3**). Carefully wash the dish and lid with 36 ml of the nitric acid, and then with hot water, collecting the washings in the beaker. Heat gently for a few minutes at a temperature near to the boiling point.

Allow to cool slightly and transfer to a 200 ml one-mark volumetric flask (BS 1792). After cooling dilute to the mark and mix.

6.2.2 *Preliminary test for the control and adjustment of pH.* Transfer 20.0 ml of the base solution (**6.2.1**) to a beaker of suitable capacity.

Add to the beaker 15 ml of water, 15 ml of the standard silica solution (**4.10**), 5 ml of the sodium molybdate solution (**4.4**), mix and check the pH value with the pH meter (**5.4**). This value should be between 0.85 and 0.90 but, if not, adjust the pH by slowly adding, drop by drop, the nitric acid solution (**4.3**) by means of a graduated pipette or burette, mixing after each drop. Dilute, if necessary, so that the final volume of the solution, after the introduction of the nitric acid solution, is 65 ml and check again the pH value (between 0.85 and 0.90).

Note the volume of the nitric acid (**4.3**) used to correct the pH and discard the solution.

6.2.3 *Preparation of the standard matching solutions for spectrophotometric measurements using a 1 cm cell.* Into each of a series of six 100 ml one-mark volumetric flasks, place 20 ml of the base solution (**6.2.1**) and then add the quantity of the nitric acid (**4.3**) used to correct the pH in the preliminary test (**6.2.2**).

[4)] Methods for the preparation and storage of test samples of aluminium fluoride are in course of preparation and will be published as a part of this standard.

Add to each flask the volumes of the standard silica solution (**4.10**) shown in the following table.

Volume of standard silica solution (4.10)	Corresponding mass of SiO_2
ml	µg
0[a]	0
5.0	25
10.0	50
15.0	75
20.0	100
25.0	125

[a] Compensation solution

Dilute the solutions to approximately 60 ml.

6.2.4 *Colour development.* To each flask add 5 ml of the sodium molybdate solution (**4.4**), mix and allow to stand for between 15 min and 25 min at 20 °C to 25 °C. Then add 5 ml of the tartaric acid solution (**4.5**), 11 ml of the sulphuric acid (**4.6**) and finally 2 ml of the reducing solution (**4.7.1** or **4.7.2**).

Dilute to the mark and mix.

6.2.5 *Spectrophotometric measurements.* After 10 min, but not longer than 40 min, carry out the spectrophotometric measurements by means of the spectrophotometer (**5.5**) at a wavelength of about 815 nm, after having adjusted the instrument to zero absorbance against the compensation solution.

6.2.6 *Preparation of the calibration chart.* Prepare a calibration chart having, for example, the silica contents, in milligrams of SiO_2 per 100 ml of standard matching solutions, as abscissae and the corresponding values of absorbance as ordinates.

6.3 Determination

6.3.1 *Preparation of the test solution*

6.3.1.1 *Fusion of the test portion.* Weigh 12 g of the sodium carbonate (**4.1**) and 4 g of the boric acid (**4.2**) into the platinum dish (**5.1**). Mix carefully. Add the test portion (**6.1**) and mix the whole quantity thoroughly, preferably with a platinum spatula.

Cover the dish with its lid and place it in the electric furnace (**5.2**), controlled at 550 ± 25 °C, taking care to isolate the dish from the furnace floor, using a support which avoids the risk of contamination (platinum support for preference).

Maintain at 550 ± 25 °C until the reaction subsides (the time required being approximately 30 min).

Transfer the dish to the electric furnace (**5.3**), controlled at 750 ± 25 °C, isolating it, as before, from the furnace floor. The dish should stay in this furnace for 30 min and the operator shall ensure that the temperature of 750 ± 25 °C is maintained for at least 20 min.

6.3.1.2 *Dissolving the fused mass.* Remove the dish from the furnace and allow to cool in the atmosphere. Add boiling water to the dish, heating moderately until the contents are completely dissolved.

After cooling slightly, transfer the contents of the dish to a plastics beaker (PTFE, for example), of a suitable capacity, containing 20 ml of the nitric acid (**4.3**).

Dissolve the residue [mainly iron (III) oxide] still adhering to the walls of the dish in 18 ml of the nitric acid (**4.3**) and carefully wash the dish and lid with hot water, transferring the whole mixture to the plastics beaker.

Heat for a few minutes at a temperature near to the boiling point until completely dissolved. Allow to cool slightly.

When the solution is tepid, transfer it to a 250 ml one-mark volumetric flask (BS 1792).

Cool, dilute to the mark and mix. Transfer the solution immediately to a plastics[5] container.

6.3.2 Colour reaction

6.3.2.1 *Taking of aliquot portions.* Take two 50.0 ml aliquot portions of the test solution (**6.3.1**) and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask (BS 1792).

6.3.2.2 *Preliminary test for the control and adjustment of pH.* Add 5 ml of the sodium molybdate solution (**4.4**) to the aliquot portion of the test solution in the beaker, and mix.

Check the pH value using the pH meter (**5.4**), adjust to a value of between 0.85 and 0.90 as indicated in **6.2.2**, noting the volume of the nitric acid (**4.3**) used, and discard this solution.

6.3.2.3 *Colour development.* To the aliquot portion of the test solution in the 100 ml one-mark volumetric flask, add the quantity of the nitric acid (**4.3**) used to correct the pH in the preliminary test (**6.3.2.2**) and mix.

Then proceed with the colour development as indicated in **6.2.4**.

6.3.2.4 *Spectrophotometric measurement.* Carry out the spectrophotometric measurement by the procedure described in **6.2.5**, after having adjusted the instrument to zero absorbance against water.

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[5] For example PTFE, polypropylene or polyethylene may be used.

6.3.3 *Blank test*

6.3.3.1 *Preparation of the solution.* Prepare the blank test solution according to the procedure described in **6.2.1**, but dilute to a final volume of 250 ml.

6.3.3.2 *Colour development.* Develop the colour as described in **6.3.2.3**.

6.3.3.3 *Spectrophotometric measurement.* Carry out the spectrophotometric measurement as described in **6.3.2.4**.

7 Calculation

By reference to the calibration chart (see **6.2.6**), determine the quantities of silica corresponding to the values of the spectrophotometric measurements on the aliquot portions of the test solution and the blank test solution.

Silica content, expressed as a percentage by mass of SiO_2, is given by the formula:

$$(m_1 - m_0) \times \frac{500}{1000} = 0.5\ (m_1 - m_0)$$

where

m_1 is the mass of silica (SiO_2) found in the aliquot portion of the test solution (containing 0.200 g of dried sample) (mg);

m_0 is the mass of silica (SiO_2) found in the corresponding aliquot portion of the blank test solution (mg).

The industrial organization marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

Aluminium Federation
British Ceramic Research Association
Society for Analytical Chemistry
Society of Chemical Industry

Publications referred to

This standard makes reference to the following British Standards:

BS 1792, *One-mark volumetric flasks.*

BS 2586, *Glass electrodes for the measurement of pH.*

BS 3145, *Laboratory potentiometric pH meters.*

BS 3422, *Laboratory deflection pH meters.*

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