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Aluminium fluoride for industrial use – Determination of silica content – Spectrophotometric method using the reduced silicomolybdic complex

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FOREWORD

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It was approved in December 1971 by the Member Bodies of the following countries :

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- France
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Aluminium fluoride for industrial use — Determination of silica content — Spectrophotometric method using the reduced silicomolybdic complex

1 SCOPE

This International Standard specifies a spectrophotometric method, using the reduced silicomolybdic complex, for determining the silica content of aluminium fluoride for industrial use.

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 %.

3 REFERENCE

ISO 2925, *Aluminium fluoride for industrial use — Preparation and storage of test samples.*[1]

4 PRINCIPLE

Alkaline fusion of a test portion by means of a mixture of sodium carbonate and boric acid. Solution of the fused mass in excess nitric acid so that the pH of the final solution is between 0,3 and 0,5 after being diluted to 250 ml.

Formation, in a suitable aliquot portion, of the (yellow) oxidized silicomolybdic complex under clearly defined conditions of acidity, concentration of reagents, temperature and time.

Selective reduction of the complex in a high acidity sulphuric acid medium and in the presence of tartaric acid.

Spectrophotometric measurement of the reduced complex at a wavelength of about 815 nm.

5 REAGENTS

Redistilled water shall be used in the test.

5.1 Sodium carbonate, anhydrous.

5.2 Boric acid (H_3BO_3).

5.3 Nitric acid, approximately 8 N solution.

Dilute 540 ml of nitric acid solution, ρ 1,40 g/ml, 68 % (*m/m*) approximately, with water to 1 000 ml and mix.

5.4 Sodium molybdate, 195 g/l (0,8 M approximately) solution.

Dissolve, in a PTFE[2] beaker, 19,5 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in hot water and, after cooling, dilute to 100 ml and mix.

Transfer the solution to a plastics[3] bottle and, if necessary, filter before use.

5.5 Tartaric acid, 100 g/l solution.

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

5.6 Sulphuric acid, approximately 16 N 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, dilute to 1 000 ml and mix.

5.7 Reducing solution

Either of the following solutions may be used :

5.7.1 *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 plastics bottle, in a cool place.

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[1] At present at the stage of draft.

[2] Polytetrafluorethylene (PTFE).

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

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

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

Use a freshly prepared solution.

5.8 **Silica** standard solution, with a silica (SiO_2) content of 0,500 g/l.

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

- either 0,500 g 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 0,500 g of finely ground pure quartz, previously heated at 1 000 °C for 1 h and cooled in a desiccator.

Add to the crucible 5 g of the sodium carbonate (5.1). Mix thoroughly, using a platinum spatula, and fuse carefully until a clear, transparent melt is obtained.

Allow to cool, add hot water directly 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, dilute to the mark and mix.

Transfer immediately to a plastics¹⁾ bottle.

1 ml of this standard solution contains 0,500 mg of SiO_2.

5.9 **Silica** standard solution, with a silica (SiO_2) content of 0,020 g/l.

Take 40,0 ml of the silica standard solution (5.8), place in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

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

This solution shall be prepared just before use.

5.10 **Silica** standard solution, with a silica (SiO_2) content of 0,005 g/l.

Take 50,0 ml of the silica standard solution (5.9), place in a 200 ml one-mark volumetric flask, dilute to the mark and mix.

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

This solution shall be prepared just before use.

6 APPARATUS

Ordinary laboratory apparatus and

6.1 **Platinum dish,** with a flat bottom, diameter approximately 70 mm, height approximately 35 mm, fitted with a platinum lid.

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

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

6.4 **pH meter,** provided with a glass electrode.

6.5 **Spectrophotometer.**

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

7 PROCEDURE

7.1 Test portion

Weigh, to the nearest 1 mg, exactly 1 g of the dried test sample.²⁾

7.2 Preparation of the calibration curve

7.2.1 *Preparation of the base solution*

Into the platinum dish (6.1) weigh

- 24 g of the sodium carbonate (5.1)
- 8 g of the boric acid (5.2)

and mix carefully using a platinum spatula. Cover the dish with its lid and place it in the electric furnace (6.2), controlled at 550 ± 25 °C, until the reaction has ceased, taking care to isolate the dish from the floor of the furnace, using a support that does not involve the risk of introducing impurities (platinum support for preference).

Then transfer the dish to the electric furnace (6.3), controlled at 750 ± 25 °C, isolating it, as before, from the floor of the furnace. Do not allow the dish to stay in this furnace for more than 5 min. Remove the dish from the furnace and allow to cool in air. Add boiling water to the dish and heat gently to complete dissolution.

After cooling slightly, transfer the contents of the dish to a PTFE beaker of suitable capacity containing 40 ml of the nitric acid solution (5.3). Carefully wash the dish and lid with 36 ml of the nitric acid solution (5.3), then successively with hot water, collecting the washings in the PTFE beaker; heat gently for a few minutes at a temperature near to the boiling point.

Cool somewhat and transfer to a 200 ml one-mark volumetric flask. After cooling, dilute to the mark and mix.

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1) For example PTFE, polypropylene or polyethylene may be used.

2) See ISO 2925.

7.2.2 *Preliminary test for the control and adjustment of pH*

Transfer 20,0 ml of the base solution (7.2.1) to a beaker of suitable capacity.

Add to the beaker 15 ml of water, 15 ml of the silica standard solution (5.10), 5 ml of the sodium molybdate solution (5.4), mix and check the pH value with the pH meter (6.4). 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 (5.3) 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 approximately 65 ml and check that the pH value is between 0,85 and 0,90.

Note the volume of nitric acid solution (5.3) used to correct the pH and discard the solution.

7.2.3 *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 (7.2.1) and then add the quantity of the nitric acid solution (5.3) used to correct the pH in the preliminary test (7.2.2).

Then add to the flasks the volumes of the silica standard solution (5.10) shown in the following table :

Volume of silica standard solution (5.10)	Corresponding mass of SiO_2
ml	µg
0*	0
5,0	25
10,0	50
15,0	75
20,0	100
25,0	125

* Compensation solution.

Then dilute the solutions to approximately 60 ml.

7.2.4 *Colour development*

To each flask add 5 ml of the sodium molybdate solution (5.4), mix and allow to stand for between 15 and 25 min at 20 to 25 °C. Then add, without interruption, 5 ml of the tartaric acid solution (5.5), 11 ml of the sulphuric acid solution (5.6) and finally 2 ml of the reducing solution (5.7.1 or 5.7.2).

Dilute to the mark and mix.

7.2.5 *Spectrophotometric measurements*

After 10 min, but not longer than 40 min, carry out the spectrophotometric measurements using the spectrophotometer (6.5) at a wavelength of about 815 nm, after having adjusted the instrument to zero absorbance against the compensation solution.

NOTE — Carefully calibrate the cells used.

7.2.6 *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 solution, as abscissae and the corresponding values of absorbance as ordinates.

7.3 Determination

7.3.1 *Preparation of the test solution*

7.3.1.1 Fusion of the test portion

Into the platinum dish (6.1) weigh 12 g of the sodium carbonate (5.1) and 4 g of the boric acid (5.2). Mix carefully Add the test portion (7.1) and mix the whole quantity carefully using a platinum spatula.

Cover the dish with its lid and place it in the electric furnace (6.2), controlled at 550 ± 25 °C, taking the precaution of isolating it from the floor of the furnace, using a support that does not involve the risk of introducing impurities (platinum support for preference).

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

Then transfer the dish to the electric furnace (6.3), controlled at 750 ± 25 °C, isolating it from the floor of the furnace in the same manner as before.

Leave the dish in this furnace for 30 min, making sure that the temperature of 750 ± 25 °C is maintained for at least 20 min.

7.3.1.2 Dissolving the fused mass

Remove the dish from the furnace and allow to cool in air. Add boiling water to the dish, heating moderately until dissolution occurs.

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 solution (5.3).

Dissolve the residue (mainly iron(III) oxide) still adhering to the walls of the dish with 18 ml of the nitric acid solution (5.3) and carefully wash the dish and lid in hot water, transferring the whole mixture to the plastics beaker.

Heat for a few minutes at a temperature approaching boiling point until complete dissolution occurs. Allow to cool slightly.

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

Cool, dilute to the mark and mix. Transfer the solution immediately to a plastics[1] container.

7.3.2 *Colour reaction*

7.3.2.1 Taking of aliquots

Take two 50,0 ml aliquot parts from the test solution (7.3.1.2) and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask.

7.3.2.2 Preliminary test for the control and adjustment of pH

Add 5 ml of the sodium molybdate solution (5.4) to the aliquot of the sample solution in the beaker and mix.

Check the pH value using the pH meter (6.4), adjust to a value of between 0,85 and 0,90 as indicated in 7.2.2 and discard this solution.

7.3.2.3 Colour development

To the aliquot of the test solution in the 100 ml one-mark volumetric flask, add the quantity of the nitric acid solution (5.3) used to correct the pH in the preliminary test (7.3.2.2) and mix.

Then proceed with the colour development as indicated in 7.2.4.

7.3.2.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement according to the procedure described in 7.2.5, taking care to adjust the instrument to zero absorbance against water.

7.3.3 *Blank test*

7.3.3.1 Preparation of the solution

Prepare the blank test solution according to the procedure described in 7.2.1, using only half of the quantities of reagents indicated, and dilute to a final volume of 250 ml.

7.3.3.2 Colour development

Develop the colour as described in 7.3.2.3.

7.3.3.3 Spectrophotometric measurement

Carry out the spectrophotometric measurement as described in 7.3.2.4.

8 EXPRESSION OF RESULTS

By reference to the calibration curve (see 7.2.6), determine the quantities of silica corresponding to the values of the spectrophotometric measurements on the aliquot part of the test solution, and on the blank test solution.

The silica content (SiO_2) is given, as a percentage by mass, by the formula :

$$(m_0 - m_1) \times \frac{500}{1\ 000} = \frac{m_0 - m_1}{2}$$

where

m_0 is the mass, in milligrams, of silica (SiO_2) found in the aliquot part of the test solution (containing 0,200 g of dried sample);

m_1 is the mass, in milligrams, of silica (SiO_2) found in the corresponding aliquot part of the blank test solution.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or that document to which reference is made, or regarded as optional.

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[1] For example PTFE, polypropylene and polyethylene may be used.