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Sodium fluoride primarily used for the production of aluminium — Determination of silica content — Reduced molybdosilicate spectrophotometric method

Fluorure de sodium principalemenr utilisé pour la production de l'aluminium — Dosage de la silice — Méthode spectrophotométrique au molybdosilicate réduit

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FOREWORD

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Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the Member Bodies of the following countries :

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No Member Body expressed disapproval of the document.

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Sodium fluoride primarily used for the production of aluminium — Determination of silica content — Reduced molybdosilicate spectrophotometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a spectrophotometric method, using the reduced molybdosilicate, for determining the silica content of sodium fluoride primarily used for the production of aluminium.

The method is applicable to products of which the P_2O_5 content does not exceed 0,02 % (*m/m*).

2 REFERENCE

ISO 3428, *Sodium fluoride for industrial use — Preparation and storage of test samples.*

3 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 oxidized molybdosilicate (yellow) under well-defined conditions of acidity, concentration of reagents, temperature and time.

Selective reduction of the complex in a high acidity sulphuric medium and in the presence of tartaric acid to eliminate interference from phosphorus. Disturbing influence of fluorine is eliminated by the presence of boric acid.

Spectrophotometric measurement of the coloured complex at a wavelength of maximum absorption (about 815 nm).

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only redistilled water.

4.1 Sodium carbonate, anhydrous.

4.2 Boric acid (H_3BO_3).

4.3 Nitric acid, approximately 8 N solution.

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

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

Dissolve, in a beaker made of material free from silica, 19,5 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in hot water and, after cooling, dilute to 100 ml and mix. Transfer the solution to a bottle made of material free from silica and, if necessary, filter before use.

4.5 Tartaric acid, 100 g/l solution.

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

Store the solution in a bottle made of material free from silica.

4.6 Sulphuric acid, approximately 16 N solution.

Carefully add 450 ml of sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution, to about 500 ml of water. Cool, dilute to 1 000 ml and mix.

4.7 Reducing solution

Either of the following solutions may be used :

4.7.1 4-amino- 3-hydroxynaphthalene- 1-sulphonic acid, 1,5 g/l solution.

a) Dissolve 7 g of anhydrous sodium sulphite (Na_2SO_3) in 50 ml of water. Add 1,5 g of 4-amino- 3-hydroxynaphthalene- 1-sulphonic acid ($C_{10}H_9NO_4S$);

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

Mix the two solutions a) and b), dilute to 1 000 ml and mix. Filter if necessary and store in an amber-coloured bottle made of material free from silica, in a cool place.

4.7.2 Ascorbic acid, 20 g/l solution.

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

Store the solution in a bottle made of material free from silica and protect it from light.

Prepare this solution at the time of use.

4.8 Silica standard solution, corresponding to 0,500 g of SiO_2 per litre.

Into a platinum crucible, weigh, to the nearest 0,001 g :

- either 0,500 g of SiO_2 obtained from pure silicic acid (H_2SiO_3), heated to constant mass at 1 000 °C (i.e. until two consecutive weighings do not differ by more than 1 mg) 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 (4.1). Mix thoroughly using a platinum spatula, and fuse carefully until a clear, transparent melt is obtained.

Allow to cool, add hot water to the crucible, heat gently to complete the dissolution and transfer the solution quantitatively into a beaker made of material free from silica. 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 bottle made of material free from silica.

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

4.9 Silica, standard solution, corresponding to 0,020 g of SiO_2 per litre.

Take 40,0 ml of the standard silica solution (4.8), place in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,020 mg of SiO_2.

Prepare this solution at the time of use.

4.10 Silica, standard solution, corresponding to 0,005 g of SiO_2 per litre.

Take 50,0 ml of the standard silica solution (4.9), place in a 200 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,005 mg of SiO_2.

Prepare this solution at the time of use.

5 APPARATUS

Glassware shall be carefully washed, taking the necessary precautions, with chromic-sulphuric acid, thoroughly rinsed with water and finally with redistilled water. Do not dry either in an oven or by means of compressed air. For alkaline solutions, use only vessels made of material free from silica.

Ordinary laboratory apparatus and

5.1 Platinum dish, with a flat bottom, 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, fitted with a glass measuring electrode and a calomel reference electrode, sensitivity 0,05 pH unit.

5.5 Spectrophotometer.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,001 g, 1 g of the dried test sample (see ISO 3428, sub-clause 2.3).

6.2 Preparation of calibration graph

6.2.1 *Preparation of the base solution*

Into the platinum dish (5.1), weigh

- 24 g of the sodium carbonate (4.1)
- 8 g of the boric acid (4.2)

and mix carefully, using a platinum spatula. Cover the dish with its lid and place it in the electric furnace (5.2) 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 (5.3) 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 slowly the contents of the dish to a beaker made of material free from silica, of suitable capacity, containing 40 ml of the nitric acid solution (4.3). Carefully wash the dish and lid with 36 ml of the nitric acid solution, then successively with hot water, collecting the washings in the same beaker; heat gently for a few minutes at a temperature near to the boiling point.

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

Transfer the solution immediately to a bottle made of material free from silica.

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 approximately 65 ml and check that the pH value is between 0,85 and 0,90.

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

6.2.3 *Preparation of the standard colorimetric solutions,* for spectrophotometric measurements carried out with cells of 1 cm optical path length.

Into each of a series of six 100 ml beakers made of material free from silica, place 20 ml of the base solution (6.2.1) and then add the quantity of the nitric acid solution (4.3) used to correct the pH in the preliminary test (6.2.2).

Then add the volumes of the standard silica solution (4.10) shown in the following table :

Standard silica solution (4.10)	Corresponding mass of SiO_2
ml	mg
0*	0
5,0	0,025
10,0	0,050
15,0	0,075
20,0	0,100
25,0	0,125

* Compensation solution.

Then dilute the solution in each beaker to approximately 60 ml.

6.2.4 *Colour development*

To each beaker add 5 ml of the sodium molybdate solution (4.4), mix and allow to stand for between 15 and 25 min at 20 to 25 °C. Then add 5 ml of the tartaric acid solution (4.5), 11 ml of the sulphuric acid solution (4.6) and finally 2 ml of the reducing solution (4.7.1 or 4.7.2) and mix. Transfer the solution quantitatively to a series of 100 ml one-mark volumetric flasks made of material free from silica, 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 using the spectrophotometer (5.5) at a wavelength of maximum absorption (about 815 nm), after having adjusted the instrument to zero absorbance against the compensation solution.

NOTE — Carefully calibrate the cells used for the measurements.

6.2.6 *Plotting of the calibration graph*

Plot a graph having, for example, the masses, expressed in milligrams of silica (SiO_2) per 100 ml of standard colorimetric solution, 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

Into the platinum dish (5.1), weigh 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2). Mix carefully. Add the test portion (6.1) and mix the whole quantity carefully, using a platinum spatula.

Cover the dish with its lid and place it in the electric furnace (5.2) 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 (5.3) 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.

6.3.1.2 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 slowly the contents of the dish to a beaker made of material free from silica, of a suitable capacity, containing 20 ml of the nitric acid solution (4.3).

Dissolve the residue (mainly, iron(III) oxide) still adhering to the walls of the dish with 18 ml of the nitric acid solution (4.3) and carefully wash the dish and lid in hot water, transferring the whole mixture to the same 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 quantitatively to a 250 ml one-mark volumetric flask cool, dilute to the mark and mix. Transfer the solution immediately to a bottle made of material free from silica.

6.3.2 *Colour reaction*

6.3.2.1 TAKING OF ALIQUOT PARTS

Take two 50,0 ml aliquot parts from the test solution (6.3.1.2) and place in two beakers of suitable capacity, made of material free from silica.

6.3.2.2 PRELIMINARY TEST FOR THE CONTROL AND ADJUSTMENT OF pH

Add 5 ml of the sodium molybdate solution (4.4) to one of the aliquot parts of the test solution and mix.

Check the pH value using the pH meter (5.4), adjust to a value of between 0,85 and 0,90 as specified in 6.2.2 and discard this solution.

6.3.2.3 COLOUR DEVELOPMENT

To the other aliquot part of the test solution, add the quantity of the nitric acid solution (4.3) used to correct the pH in the preliminary test (6.3.2.2) and mix. Dilute, if necessary, to about 60 ml and mix.

Then proceed as specified in 6.2.4.

6.3.2.4 SPECTROPHOTOMETRIC MEASUREMENT

Carry out the spectrophotometric measurement according to the procedure specified in 6.2.5, after having adjusted the instrument to zero absorbance against water.

6.3.3 *Blank test*

6.3.3.1 PREPARATION OF THE SOLUTION

Prepare the blank test solution according to the procedure specified in 6.2.1, using only half of the quantities of reagents indicated, and dilute to a final volume of 250 ml.

6.3.3.2 COLOUR REACTION

Proceed as specified in 6.3.2.

7 EXPRESSION OF RESULTS

By reference to the calibration graph (6.2.6), determine the mass of silica corresponding to the value of the spectrophotometric measurement on the aliquot part of the test solution, and on the blank test solution.

The silica content, expressed as a percentage by mass of SiO_2, is given by the formula

$$\frac{m_1 - m_2}{1\,000} \times \frac{250}{50} \times \frac{100}{m_0} = \frac{m_1 - m_2}{2\,m_0}$$

where

m_0 is the mass, in grams, of the test portion (6.1);

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

m_2 is the mass, in milligrams, of silica (SiO_2) found in the corresponding aliquot part of the blank test solution.

8 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 in the International Standard to which reference is made, or regarded as optional.

ANNEX

ISO PUBLICATIONS RELATING TO SODIUM FLUORIDE FOR INDUSTRIAL USE AND SODIUM FLUORIDE PRIMARILY USED FOR THE PRODUCTION OF ALUMINIUM

SODIUM FLUORIDE FOR INDUSTRIAL USE

ISO 2831 – Determination of water-insoluble matter.

ISO 2832 – Determination of moisture content.

ISO 2833 – Determination of fluorine content – Modified Willard-Winter method.

ISO 3428 – Preparation and storage of test samples.

SODIUM FLUORIDE PRIMARILY USED FOR THE PRODUCTION OF ALUMINIUM

ISO 3429 – Determination of iron content – 1,10-Phenanthroline photometric method.

ISO 3430 – Determination of silica content – Reduced molybdosilicate spectrophotometric method.

ISO 3431 – Determination of soluble sulphates content – Turbidimetric method.

ISO 3566 – Determination of chlorides content – Turbidimetric method.

ISO 4278 – Determination of carbonates content – Gravimetric method.