INTERNATIONAL STANDARD ISO 3429

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Sodium fluoride primarily used for the production of aluminium – Determination of iron content – 1,10-phenanthroline photometric method

Fluorure de sodium principalement utilisé pour la production de l'aluminium – Dosage du fer – Méthode photométrique à la phénanthroline-1,10

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FOREWORD

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International Standard ISO 3429 was drawn up by Technical Committee ISO/TC 47, *Chemistry,* and was circulated to the Member Bodies in March 1974.

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 iron content – 1,10-phenanthroline photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method, using 1,10-phenanthroline, for the determination of the iron content of sodium fluoride primarily used for the production of aluminium.

The method is applicable to the determination of iron contents, expressed as Fe_2O_3, greater than 0,020 % (*m/m*).

2 REFERENCE

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

3 PRINCIPLE

Dissolution of a test portion by alkaline fusion. Preliminary reduction of iron(III) by means of hydroxylammonium chloride. Formation of the iron(II)-1,10-phenanthroline complex, in a buffered medium (pH value between 3,5 and 4,2).

Photometric measurement of the coloured complex at a wavelength of about 510 nm.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

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, ρ approximately 1,40 g/ml, about 68 % (*m/m*) solution, with water, dilute to 1 000 ml and mix.

4.4 Hydrochloric acid, approximately 6 N solution.

Dilute 515 ml of hydrochloric acid, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution, with water, dilute to 1 000 ml and mix.

4.5 Hydroxylammonium chloride, 10 g/l solution.

Dissolve 1 g of hydroxylammonium chloride ($NH_2OH.HCl$) in water, dilute to 100 ml and mix.

4.6 1,10-phenanthroline hydrochloride, 2,5 g/l solution.

Dissolve 2,5 g of 1,10-phenanthroline hydrochloride monohydrate ($C_{12}H_8N_2.HCl.H_2O$) in water, dilute to 1 000 ml and mix.

NOTE – 1,10-phenanthroline hydrochloride monohydrate can be replaced by 1,10-phenanthroline monohydrate. If this product is used, it should be dissolved in 10 ml of ethanol, 95 % (*V/V*), before adding water.

4.7 Buffer solution, pH 4,9.

Dissolve 272 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$) in approximately 500 ml of water. Add 240 ml of glacial acetic acid, ρ approximately 1,05 g/ml, about 17,4 N, dilute to 1 000 ml and mix.

4.8 Sodium acetate trihydrate, 500 g/l solution.

Dissolve 50 g of sodium acetate trihydrate in water, dilute to 100 ml and mix.

4.9 Acetic acid, dilute solution.

Dilute 500 ml of glacial acetic acid, ρ approximately 1,05 g/ml, about 17,4 N, with water, dilute to 1 000 ml and mix.

4.10 Iron, standard solution, corresponding to 0,200 g of Fe_2O_3 per litre.

This solution can be prepared by either of the two following methods :

4.10.1 Weigh, to the nearest 0,001 g, 0,982 g of ammonium iron(II) sulphate hexahydrate, $[(NH_4)_2Fe(SO_4)_2.6H_2O)]$, place in a beaker of suitable capacity (100 ml, for example) and dissolve in water. Add 20 ml of sulphuric acid solution, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.10.2 Weigh, to the nearest 0,001 g, 0,200 g of iron(III) oxide (Fe_2O_3) previously heated at 600 °C and cooled in a desiccator. Transfer to a beaker of suitable capacity (100 ml, for example), add 10 ml of hydrochloric acid solution, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution, and heat gently to dissolve. Allow to cool, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,200 mg of Fe_2O_3.

4.11 Iron, standard solution, corresponding to 0,010 g of Fe_2O_3 per litre.

Transfer 50,0 ml of the standard solution (4.10) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,010 mg of Fe_2O_3.

Prepare this solution just before use.

4.12 Indicator paper, covering the pH range 3,5 to 4,2 at intervals of 0,2 unit.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum dish, flat-bottomed, approximately 80 mm in diameter and approximately 35 mm deep, 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, or

5.6 Photoelectric absorptiometer, fitted with filters giving a maximum transmission between 500 and 520 nm.

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 Blank test

Weigh into the platinum dish (5.1), 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2). Mix thoroughly, using a platinum spatula. Cover the dish with its lid and place in the electric furnace (5.2) controlled at 550 ± 25 °C taking care to isolate the dish from the floor of the furnace by means of a support to avoid the risk of contamination. Leave the dish in the furnace until the reaction subsides.

Then transfer the dish to the electric furnace (5.3) controlled at 750 ± 25 °C, again isolating it 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 air. Add boiling water to the dish and heat gently until dissolution is complete.

After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity containing 20 ml of the nitric acid solution (4.3). Carefully wash the dish and lid with 18 ml of the nitric acid solution (4.3) and then with hot water, collecting the washings in the beaker, and simmer gently for a few minutes until complete dissolution is obtained.

Allow to cool slightly and transfer quantitatively to a one-mark volumetric flask of the same capacity as that used for the preparation of the sample solution (6.4.1). After cooling, dilute to the mark and mix. Continue as specified in 6.4.2, taking an aliquot portion equal to that taken for the determination.

6.3 Preparation of calibration graph

6.3.1 *Preparation of the standard colorimetric solutions* for photometric measurements carried out in cells of 1 cm optical path length.

Into each of a series of eight 100 ml one-mark volumetric flasks transfer respectively the volumes of the standard iron solution (4.11) shown in the following table.

Standard iron solution (4.11)	Corresponding mass of Fe_2O_3
ml	mg
0*	0
1,0	0,010
2,5	0,025
5,0	0,050
10,0	0,100
15,0	0,150
20,0	0,200
25,0	0,250

* Compensation solution.

Add to each flask an amount of water sufficient to dilute to approximately 50 ml, then add 5 ml of the hydroxylammonium chloride solution (4.5), 5 ml of the 1,10-phenanthroline solution (4.6) and 25 ml of the buffer solution (4.7). Dilute to the mark and mix.

6.3.2 *Photometric measurement*

After 10 min, carry out the photometric measurement with the spectrophotometer (5.5) at a wavelength of about 510 nm or with the photoelectric absorptiometer (5.6) with suitable filters, after having adjusted the instrument to zero absorbance against the compensation solution.

6.3.3 *Plotting of the calibration graph*

Plot a graph having, for example, the Fe_2O_3 content in milligrams per 100 ml of standard colorimetric solution as abscissae and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

Weigh into the platinum dish (5.1) 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2). Mix thoroughly using a platinum spatula. Add to the mixture the test portion (6.1) and mix thoroughly. 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 by means of a support to avoid the risk of contamination. Keep at 550 ± 25 °C until the reaction subsides (about 30 min).

Then transfer the dish to the electric furnace (5.3) controlled at 750 ± 25 °C, again taking care to isolate it from the floor of the furnace. Keep the dish in the furnace for 30 min, making sure that the temperature of 750 ± 25 °C is maintained for at least 20 min.

Remove the dish from the furnace and allow to cool in the air. Add boiling water to the dish and heat gently until dissolution is complete.

After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity, containing 20 ml of the nitric acid solution (4.3).

Dissolve the residue (which consists essentially of iron(III) oxide) adhering to the walls of the dish with 18 ml of the nitric acid solution (4.3) and carefully wash the dish and its lid with hot water, collecting the washings in the beaker.

Simmer the solution for a few minutes to ensure complete dissolution. Allow to cool slightly and transfer quantitatively to a one-mark volumetric flask of either 250 or 500 ml capacity, according to the iron content to be determined. After cooling, dilute to the mark and mix.

6.4.2 *Colour reaction*

6.4.2.1 Taking of aliquot portions

Take two aliquot portions of the test solution (6.4.1) each containing between 0,050 and 0,250 mg of Fe_2O_3 and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask.

6.4.2.2 Preliminary test to adjust pH

Dilute the aliquot in the beaker to approximately 50 ml with water. Then add 5 ml of the hydroxylammonium chloride solution (4.5), 5 ml of the 1,10-phenanthroline solution (4.6) and 25 ml of the buffer solution (4.7). Check the pH value of the solution using either the indicator paper (4.12) or the pH meter (5.4). This value should be between 3,5 and 4,2; if not, adjust the pH value by slowly adding the required volume of the sodium acetate solution (4.8) or acetic acid solution (4.9), as appropriate; stir after each addition.

Note the volume of reagent used to adjust the pH and discard the solution.

6.4.2.3 Colour development

To the aliquot portion placed in the 100 ml one-mark volumetric flask, add the same quantities of all the reagents used in the preliminary test (6.4.2.2).

Dilute to the mark and mix.

6.4.2.4 Photometric measurements

After 10 min carry out the photometric measurements of the test solution and blank solution following the procedure specified in 6.3.2, after having adjusted the instrument to zero absorbance against water.

7 EXPRESSION OF RESULTS

By reference to the calibration graph (6.3.3), read the Fe_2O_3 content corresponding to the value of the photometric measurements.

The iron content, expressed as a percentage by mass of iron(III) oxide (Fe_2O_3), is given by the formula

$$(m_1 - m_2) \times \frac{D}{1\,000} \times \frac{100}{m_0} = (m_1 - m_2) \times \frac{D}{10 \times m_0}$$

where

D is the ratio of volume of test solution to volume of aliquot portion taken for the colour reaction;

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

m_1 is the mass, in milligrams, of iron(III) oxide (Fe_2O_3) determined in the aliquot portion of the test solution;

m_2 is the mass, in milligrams, of iron(III) oxide (Fe_2O_3) determined in the corresponding aliquot portion of the blank test solution.

8 NOTES ON PROCEDURE

Generally, the aliquot portion of the blank solution after treatment for photometric measurement shows a slight coloration. In this case, it will be advisable to use it as the compensation solution.

In this case, the formula for calculation becomes

$$m_1 \times \frac{D}{10 \times m_0}$$

where the symbols have the same meaning as those given in clause 7.

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 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.