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Sodium fluoride for industrial use — Determination of fluorine content — Modified Willard-Winter method

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FOREWORD

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International Standard ISO 2833 was drawn up by Technical Committee ISO/TC 47, *Chemistry*, and circulated to the Member Bodies in June 1972.

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

Australia	Italy	Sweden
Austria	Morocco	Switzerland
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Czechoslovakia	New Zealand	Turkey
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India	South Africa, Rep. of	

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

No Member Body expressed disapproval of the document.

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Sodium fluoride for industrial use — Determination of fluorine content — Modified Willard-Winter method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a modified Willard-Winter method for the determination of fluorine content of sodium fluoride for industrial use.

2 REFERENCE

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

3 PRINCIPLE

Separation of the fluorine from a test portion by distillation with sulphuric acid or perchloric acid. Titration with thorium nitrate solution using sodium alizarin-sulphonate and methylene blue as indicators.

Alternatively the thorium nitrate titration may be carried out using sodium alizarinsulphonate alone as indicator, the end-point being determined spectrophotometrically under carefully defined conditions when the absorbance at 525 nm reaches the arbitrary value of 0,60.

4 REAGENTS

Distilled water, or water of equivalent purity, shall be used in the test.

4.1 Hydrochloric acid, approximately 0,06 N solution.

Dilute 5 ml of hydrochloric acid, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution, with water to 1 000 ml.

4.2 Sodium hydroxide, 20 g/l solution.

4.3 Sulphuric acid, approximately 24 N solution.

Carefully add, in small quantities, 200 ml of sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution, to approximately 100 ml of water and, after cooling, dilute to 300 ml.

or

4.3.1 Perchloric acid, ρ approximately 1,60 g/ml, about 64,5 % (*m/m*) solution.

4.4 Buffer solution, pH 2,7

Dissolve 9,45 g of monochloracetic acid in 50 ml of N sodium hydroxide solution and dilute to 100 ml.

4.5 Thorium nitrate, approximately 0,067 N standard volumetric solution.

1 ml of this solution is equivalent to approximately 1,3 mg of fluorine (F).

4.5.1 *Preparation of the solution*

Dissolve 9,45 g of thorium nitrate tetrahydrate $[Th(NO_3)_4.4H_2O]$ or the corresponding mass of other hydrates in water and dilute to 1 000 ml.

4.5.2 *Standardization of the solution*

4.5.2.1 PREPARATION OF THE STANDARD REFERENCE SOLUTION

Weigh, to the nearest 0,000 1 g, about 0,2 g of extra pure anhydrous sodium fluoride, previously heated at 600 °C in a platinum dish and cooled in a desiccator. Transfer, using 20 to 30 ml of water, into the distillation flask (5.2.1) containing several glass balls (2 to 3 mm diameter).

1) In preparation.

Stopper the distillation flask and add, through the dropping funnel (5.2.5), either 50 ml of the sulphuric acid solution (4.3) or 30 ml of the perchloric acid solution (4.3.1), whichever has been selected.

Carry out the distillation as described in 6.3.1.

Collect the distillate in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

NOTE — If extra pure sodium fluoride is not available, recrystallize the product. Dissolve about 5 g of pure sodium fluoride in 125 ml of water and, after dissolution, filter under vacuum through a small Buchner funnel. Then evaporate the solution, in a platinum dish, down to approximately 60 ml.

Cool to about 50 °C and separate the sodium fluoride crystals by centrifuging. Wash the crystals three times, always by centrifuging, with small quantities of cold water.

Transfer the product to a platinum dish and dry in an electric oven, with natural draught, at 110 ± 2 °C.

Remove the dish from the oven, cool in a desiccator, grind the product in an agate mortar, and then pass it through a sieve with a mesh size of 355 μm (see ISO 565). Put the sieved sodium fluoride in a platinum dish, heat for 2 h at 600 °C, and allow to cool in a desiccator.

4.5.2.2 TITRATION

Transfer a 50,0 ml aliquot portion of the standard reference solution (4.5.2.1) to the beaker (5.5) and titrate as described in 6.3.2.

Towards the end of the titration, add the last few drops of thorium nitrate solution (4.5.1) with extreme caution, stirring vigorously.

4.5.2.3 BLANK TEST

Carry out a blank test at the same time and following the same procedure (distillation as described in 6.3.1 and titration as described in 6.3.2) with the same quantities of the reagents as used in the procedure described in 4.5.2.1. Titrate using the conditions described in 4.5.2.2.

4.5.2.4 CALCULATION OF STRENGTH OF THE SOLUTION

The mass, in milligrams, of fluorine (F) corresponding to 1 ml of thorium nitrate solution is given by the formula

$$\frac{m_1 \times 0{,}452\,5}{V_1 - V_2}$$

where

m_1 is the mass, in milligrams, of NaF contained in the aliquot portion of the standard reference solution (4.5.2.1) taken for the titration;

V_1 is the volume, in millilitres, of the thorium nitrate solution (4.5.1) used for the titration of the aliquot portion of the standard reference solution (4.5.2.1) taken for the titration;

V_2 is the volume, in millilitres, of the thorium nitrate solution (4.5.1) used for the titration of a corresponding aliquot portion of the blank test solution (4.5.2.3);

0,452 5 is the conversion factor from sodium fluoride to fluorine (F).

4.6 Sodium alizarinsulphonate, 0,5 g/l solution.

Dissolve 0,05 g of sodium alizarinsulphonate in water and dilute to 100 ml.

4.7 Methylene blue, 0,5 g/l solution.

Dissolve 0,05 g of methylene blue in water and dilute to 100 ml.

NOTE — For the visual titration (see 6.3.2.1), instead of using the two indicators 4.6 and 4.7, either the sodium alizarinsulphonate solution (4.6) alone can be used or it can be replaced by a solution of methylthymol blue or any other indicator giving equivalent results in the specified pH range.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Steam generator, for example a flask of approximately 3 000 ml capacity, fitted with a stopper into which three glass tubes a), b), c) of internal diameter about 6 mm, are inserted :

a) Double bend delivery tube, with parallel limbs, for introducing steam into the distillation flask (5.2.1). One limb shall dip into the distillation flask.

b) Tube for regulating the steam flow, fixed at its outer end with a rubber tube, fitted with a Mohr clip.

c) Safety tube, approximately 1 m in length.

5.2 Borosilicate glass apparatus, with ground glass joints, for the steam distillation, consisting of :

5.2.1 *Distillation flask, Claisen,* 250 ml capacity, with the following preferred dimensions :

— diameter of central neck : 36 mm;

— length of side neck (including the Vigreux column (5.2.2)) : 275 mm;

— distance between side neck and central neck : 65 mm;

— diameter of side neck : 20 mm.

5.2.2 *Distillation column, Vigreux,* preferably having the following dimensions :

— length of column between the first and last series of points : 120 mm;

— eleven groups of three points, spaced at 120° on the circumference, at 12 mm separation.

5.2.3 *Thermometer sheath.*

5.2.4 *Thermometer,* covering the range 0 to 200 °C, with an effective length of about 250 mm.

5.2.5 *Walter dropping funnel,* about 100 ml capacity, for insertion in the Vigreux column.

5.2.6 *Graham condenser,* effective length about 400 mm.

For a typical form of apparatus see the figure.

5.3 **Electric heater,** for heating the distillation flask (5.2.1), capable of being regulated so as to allow progressive heating of the solution up to 150 ± 1 °C.

5.4 **pH meter,** fitted with a glass electrode.

5.5 **Borosilicate glass beaker,** tall form, capacity 250 ml.

5.6 **Burette,** 10 ml capacity with 0,02 ml divisions.

5.7 **Stirrer, magnetic.**

5.8 **Spectrophotometer,** fitted with titration device.

5.9 **Titration cell,** 5 cm optical path, 5 cm wide and 7,5 cm high.

NOTE — All glassware shall be carefully washed with a hot chromic-sulphuric acid mixture, rinsed thoroughly with water and finally with distilled water.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,000 1 g, approximately 0,20 g of the dried test sample, prepared according to ISO . . . .

6.2 Blank test

Carry out a blank test at the same time as the determination and following the same procedure, with the same quantities of all the reagents used for the determination.

6.3 Determination

6.3.1 *Distillation*

Transfer the test portion (6.1), using 20 to 30 ml of water, into the distillation flask (5.2.1) containing several glass balls (2 to 3 mm diameter). Place a 500 ml one-mark volumetric flask under the condenser (5.2.6) to collect the distillate.

Connect the distillation flask (5.2.1) to the condenser (5.2.6) and start the water circulation.

Then stopper the distillation flask and add, through the dropping funnel (5.2.5), according to the distillation method chosen, either 50 ml of the sulphuric acid solution (4.3) or 30 ml of the perchloric acid solution (4.3.1).

Fill the steam generating flask (5.1) two-thirds full of water and add several small pieces of pumice stone. Heat the flask, leaving the steam regulating tube b) open, until the water boils.

Using the electric heater (5.3), heat the distillation flask (5.2.1) until the solution reaches 150 °C (for sulphuric acid) or 135 °C (for perchloric acid).

When the temperature in the distillation flask (5.2.1) has reached either 150 °C or 135 °C, pass the steam (at a rate of 250 to 300 g/h) through tube a), regulating the flow by means of the Mohr clip fitted to the tube b) so as to maintain the solution in the distillation flask (5.2.1), depending upon the distillation method chosen, at either 150 ± 1 °C or 135 ± 1 °C (the temperature to be accurately controlled) and to collect approximately 400 ml of distillate over a period of about 90 min.

Disconnect the distillation flask (5.2.1) from the steam generator (5.1), allowing the steam to escape to atmosphere, and remove the electric heater (5.3). Rinse the condenser with a jet of water from a wash bottle.

Dilute the distillate to the mark and mix.

6.3.2 *Titration*

6.3.2.1 VISUAL TITRATION

Transfer 50,0 ml of the solution obtained in 6.3.1 to the beaker (5.5). Add to the beaker approximately 50 ml of water and 0,50 ml of the sodium alizarinsulphonate solution (4.6) and then, in small portions, the sodium hydroxide solution (4.2) until a pink coloration appears (pH of colour change 6,6 to 6,8).

Checking by means of the pH meter (5.4), add the hydrochloric acid solution (4.1), drop by drop, until the pH value is between 4,9 and 5,2 (yellow coloration of the solution). Add 3,0 ml of the sodium alizarinsulphonate solution (4.6) and then, still checking with the pH meter (5.4), add the buffer solution (4.4), in small portions, until the pH is 3,4 ± 0,1 (about 1 ml of buffer solution is required).

Finally, add 0,50 ml of the methylene blue solution (4.7) (green coloration of the solution).

Immerse a small glass-encased iron bar in the solution, place the beaker on the stirrer (5.7) and stir vigorously.

Fill the burette (5.6) with the thorium nitrate solution (4.5) and titrate until a blue-violet colour develops.

Take care to work in the same lighting conditions as those used for the standardization of the thorium nitrate solution (4.5.2.2).

NOTE – Carry out the titration in daylight or fluorescent light only. The titration must not be carried out with the illumination provided by tungsten filament lamps.

6.3.2.2 SPECTROPHOTOMETRIC TITRATION

Transfer 50,0 ml of the solution obtained in 6.3.1, to the titration cell (5.9) and dilute to about 100 ml.

Add 3,0 ml of the sodium alizarinsulphonate solution (4.6) and then, in small portions, the sodium hydroxide solution (4.2) until a pink coloration appears (pH of colour change 6,6 to 6,8).

Checking by means of the pH meter (5.4), add the hydrochloric acid solution (4.1), drop by drop, until the pH value is between 4,9 and 5,2 (yellow coloration of the solution).

Still checking with the pH meter (5.4), add, in small portions, the buffer solution (4.4) until the pH is 3,4 ± 0,1 (approximately 1 ml of buffer solution is required).

Transfer the cell to the titration device of the spectrophotometer (5.8).

Place a small glass-encased iron bar in the solution. Place the tip of the burette (5.6), filled with thorium nitrate solution (4.5), into the solution and stir.

Cover the titration assembly, adjust the wavelength to 525 nm and select the appropriate sensitivity. Close the shutter and adjust to zero transmittance. Then open the shutter and adjust the slit width so as to give a reading of 100. By means of the burette (5.6), add the standard volumetric thorium nitrate solution (4.5) until an absorbance of 0,60 is reached (25 % transmittance). Read, to the nearest 0,01 ml, the volume of standardized solution used.

7 EXPRESSION OF RESULTS

7.1 Calculation

The fluorine (F) content is expressed, as a percentage by mass, by the formula

$$\frac{(V_3 - V_4) \times m_2}{m_0} \times 1\,000$$

where

V_3 is the volume, in millilitres, of the standard volumetric thorium nitrate solution (4.5) used for the titration of the aliquot portion of the solution obtained in 6.3.1;

V_4 is the volume, in millilitres, of the standard volumetric thorium nitrate solution (4.5) used for the titration of a corresponding aliquot portion of the blank test solution (6.2);

m_0 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of fluorine corresponding to 1 ml of the standardized thorium nitrate solution (4.5).

7.2 Precision

Collaborative tests in seven laboratories, in each of which the operator carried out five tests, gave the following information on precision :

Mean	44,55 % F
Standard deviation of reproducibility	0,13

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