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Cryolite, natural and artificial — Determination of fluorine content — Modified Willard-Winter method

Cryolithe, naturelle et artificielle — Dosage du fluor — Méthode de Willard-Winter modifiée

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 47 has reviewed ISO Recommendation R 1693 and found it technically suitable for transformation. International Standard ISO 1693 therefore replaces ISO Recommendation R 1693-1970 to which it is technically identical.

ISO Recommendation R 1693 was approved by the Member Bodies of the following countries :

Australia
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Turkey
United Kingdom
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Yugoslavia

No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 1693 into an International Standard.

Printed in Switzerland

Cryolite, natural and artificial — 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 the fluorine content of natural and artificial cryolite and of natural and synthetic materials having a molar ratio (NaF/AlF_3) between 3 and 1,7 approximately.

2 REFERENCE

ISO 1619, *Cryolite, natural and artificial — Preparation and storage of test samples.*

3 PRINCIPLE

Fusion of a test portion with sodium carbonate.

Separation of fluorine by distillation with sulphuric acid or perchloric acid. Titration with thorium nitrate solution using sodium alizarinsulphonate-methylene blue as indicator.

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

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 Hydrochloric acid, approximately 0,06 N solution.

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

4.3 Sodium hydroxide, 20 g/l solution.

4.4 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, cool and dilute to 300 ml.

or

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

4.5 Buffer solution, of pH 2,7.

Dissolve 9,45 g of monochloroacetic acid in 50 ml of 1 N sodium hydroxide solution and dilute to 100 ml.

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

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

4.6.1 *Preparation of the solution*

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

4.6.2 *Standardization of the solution*

4.6.2.1 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 ignited at 600 °C in a platinum dish and cooled in a desiccator. Transfer, using 20 to 30 ml of water, into the distillation flask (5.4.1) containing several glass balls (diameter 2 to 3 mm).

Stopper the distillation flask and add through the dropping funnel (5.4.5) either 50 ml of the sulphuric acid solution (4.4) or 30 ml of the perchloric acid solution (4.4.1), depending on which has been selected.

Carry out the distillation as specified in 6.3.2.

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. For this, dissolve approximately 5 g of pure sodium fluoride in 125 ml of water and, after dissolution, filter under vacuum through a small Büchner funnel. Evaporate the solution in a platinum dish down to about 60 ml.

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

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

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

4.6.2.2 TITRATION

Transfer a 50,0 ml aliquot portion of the standard reference solution (4.6.2.1) into the beaker (5.7) and titrate as specified in 6.3.3.

Towards the end of the titration, add the last few drops of thorium nitrate solution (4.6) carefully with vigorous stirring.

4.6.2.3 BLANK TEST

At the same time, carry out a blank test following the same procedure (distillation as specified in 6.3.2 and titration as specified in 6.3.3), and using the same quantity of all the reagents as used in the procedure specified in 4.6.2.1.

Titrate in accordance with 4.6.2.2.

4.6.2.4 CALCULATION OF THE 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 sodium fluoride (NaF) contained in the aliquot portion of the standard reference solution (4.6.2.1) taken for the titration (4.6.2.2);

V_1 is the volume, in millilitres, of the thorium nitrate solution (4.6) used for the titration of the aliquot portion of the standard reference solution (4.6.2.1);

V_2 is the volume, in millilitres, of the thorium nitrate solution (4.6) used for the titration of a corresponding aliquot portion of the blank test solution (4.6.2.3);

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

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

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

4.8 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 (6.3.3.1), instead of the two indicators (4.7) and (4.8), the sodium alizarinsulphonate solution may be used alone, or may be replaced by methyl thymol blue or any other indicator that gives equivalent results in the specified pH range.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum crucible, flat-bottomed, of upper diameter approximately 30 mm, lower diameter approximately 15 mm and height approximately 30 mm, fitted with a platinum lid.

5.2 Electric furnace, capable of being controlled up to 880 ± 20 °C.

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

a) Vertical recovery bend tube, for introducing the steam into the distillation flask (5.4.1) (one limb dipping into the distillation flask).

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

c) Safety tube, about 1 m long.

5.4 Apparatus in borosilicate glass, with ground glass joints, for steam distillation, consisting of :

5.4.1 Flask, Claisen, of capacity 250 ml, with the following preferred dimensions :

- diameter of central neck : 36 mm;
- length of side neck (including the Vigreux column (5.4.2)) : 275 nm;
- distance between side neck and central neck : 65 mm;
- diameter of side neck : 20 mm.

5.4.2 Distilling column, Vigreux, with the following preferred dimensions :

- column length between the first and last of the series of points : 120 mm;
- eleven groups of three points, spaced at 120° on the circumference, at 12 mm separation.

5.4.3 Thermometer sheath.

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

5.4.5 Dropping funnel, Walter, of capacity about 100 ml, for insertion in the Vigreux column (5.4.2).

5.4.6 Condenser, Graham, with an effective length of about 400 mm.

For an example, see the diagram of a typical form of apparatus shown in the figure.

5.5 Electric heater, for heating the distillation flask (5.4.1), capable of being regulated so as to allow progressive heating of the solution up to 150 ± 1 °C (distillation in sulphuric medium) or up to 135 ± 1 °C (distillation in perchloric medium).

5.6 pH meter.

5.7 Beaker, of borosilicate glass, of capacity 250 ml, tall form.

5.8 Burette, of capacity 10 ml, graduated in 0,02 ml.

5.9 Stirrer, magnetic.

5.10 Spectrophotometer, fitted with titration device.

5.11 Titration cell, having an optical path length of 5 cm, of width 5 cm and height 7,5 cm.

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

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,000 1 g, about 0,2 g of the test sample, dried at 110 °C (see 3.3 of ISO 1619) into the platinum crucible (5.1).

6.2 Blank test

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

6.3 Determination

6.3.1 *Preparation of the test solution*

Introduce into the crucible (5.1) containing the test protion (6.1) 2 g of the sodium carbonate (4.1) and mix carefully, preferably by means of a platinum wire. Place the lid on the crucible and insert in the electric furnace (5.2) previously heated to about 200 °C, and increase the temperature progressively up to 800 ± 20 °C. Keep at this temperature until the elimination of the carbon dioxide and melting of the sample is complete. (Time necessary : approximately 20 min.)

Remove the crucible from the furnace and cool rapidly by plunging the base of the crucible into a bath of cold water.

Transfer the fused mass directly to the distillation flask (5.4.1), already containing several glass balls (diameter 2 to 3 mm), and wash the crucible and its lid carefully with 20 to 30 ml of hot water in order to dissolve that part of the melt still adhering to the crucible, collecting the washings in the distillation flask (5.4.1).

6.3.2 *Distillation*

Place under the condenser (5.4.6) a 500 ml one-mark volumetric flask for collecting the distillate.

Connect the distillation flask (5.4.1) to the condenser (5.4.6) and start the water circulation through the condenser.

Stopper the distillation flask and add through the dropping funnel (5.4.5) either 50 ml of the sulphuric acid solution (4.4) or 30 ml of the perchloric acid solution (4.4.1), depending on the method chosen.

Fill the steam-generator (5.3) two-thirds full of water and add several small pieces of pumice stone. Heat the flask, leaving the regulating tube (b) open until the water boils.

Using the electric heater (5.5), heat the distillation flask until the temperature of the solution reaches 150 °C (in sulphuric medium) or 135 °C (in perchloric medium).

When the temperature of the distillation flask reaches 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 tube (b), so as to maintain the temperature of the solution in the distillation flask at the appropriate value of either 150 ± 1 °C or 135 ± 1 °C (controlled precisely), and collect about 400 ml of the distillate over a period of about 90 min.

Then disconnect the distillation flask from the steam-generator, allowing the steam to escape into the air, and remove the heater (5.5). Wash the condenser with a jet of water.

Dilute the distillate to the mark and mix.

6.3.3 *Titration*

6.3.3.1 VISUAL TITRATION

Transfer 50,0 ml of the solution obtained in 6.3.2 to the beaker (5.7). Add to the beaker about 50 ml of water and 0,50 ml of the sodium alizarinsulphonate solution (4.7) and then, in small portions, the sodium hydroxide solution (4.3) until a pink coloration appears (pH of the colour change 6,6 to 6,8).

Checking by means of the pH meter (5.6), add, drop by drop, the hydrochloric acid solution (4.2) until the pH value is between 4,9 and 5,2 (yellow coloration of the solution). Add 3,0 ml of sodium alizarinsulphonate solution and then, still checking with the pH meter, add the buffer solution (4.6) in small portions until the pH is 3,4 ± 0,1 (about 1 ml of the buffer solution is needed). Add 0,50 ml of the methylene blue solution (4.8) (green coloration of the solution).

Place a small glass-encased iron bar in the solution and stir vigorously using the stirrer (5.9).

Fill the burette (5.8) with the thorium nitrate solution (4.6) and titrate just to the development of a blue-violet colour.

Ensure that the same lighting conditions are used as for the standardization of the thorium nitrate solution (see 4.6.2.2).

NOTE — Carry out the titration either in daylight or under fluorescent lighting. Avoid using the light produced by a tungsten filament lamp.

6.3.3.2 SPECTROPHOTOMETRIC TITRATION

Transfer 50,0 ml of the solution obtained in 6.3.2 to the titration cell (5.11) and dilute to about 100 ml.

Add 3,0 ml of the sodium alizarinsulphonate solution (4.7) and then, in small portions, the sodium hydroxide solution (4.3) until a pink coloration appears (pH of the colour change 6,6 to 6,8).

Checking by means of the pH meter (5.6), add the hydrochloric acid solution (4.2) 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, add in small portions the buffer solution (4.5) until the pH is 3,4 ± 0,1 (about 1 ml of the buffer solution is needed).

Place the cell in the titration device of the spectrophotometer (5.10).

Place a small glass-encased iron bar into the solution. Place the tip of the burette (5.8), filled with the thorium nitrate solution (4.6), into the solution and begin to stir using the stirrer (5.9).

Cover the titration assembly, adjust the wavelength to 525 nm and choose an appropriate sensitivity. Close the shutter and adjust to zero transmittance. Open the shutter and adjust the slit width to give a transmittance of 100. Using the burette, titrate with the thorium nitrate solution until the absorbance is 0,60 (25 % transmittance). Read, to the nearest 0,01 ml, the volume of standard volumetric solution used.

7 EXPRESSION OF RESULTS

The fluorine (F) content, expressed as a percentage by mass, is given 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 (4.6) used for the titration of the aliquot portion of the test solution (6.3.3);

V_4 is the volume, in millilitres, of the standard volumetric thorium nitrate solution (4.6) 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 (6.1);

m_2 is the mass, in grams, of flourine corresponding to 1 ml of the standard volumetric thorium nitrate solution (4.6).

8 TEST REPORT

The test report shall include the following particulars :

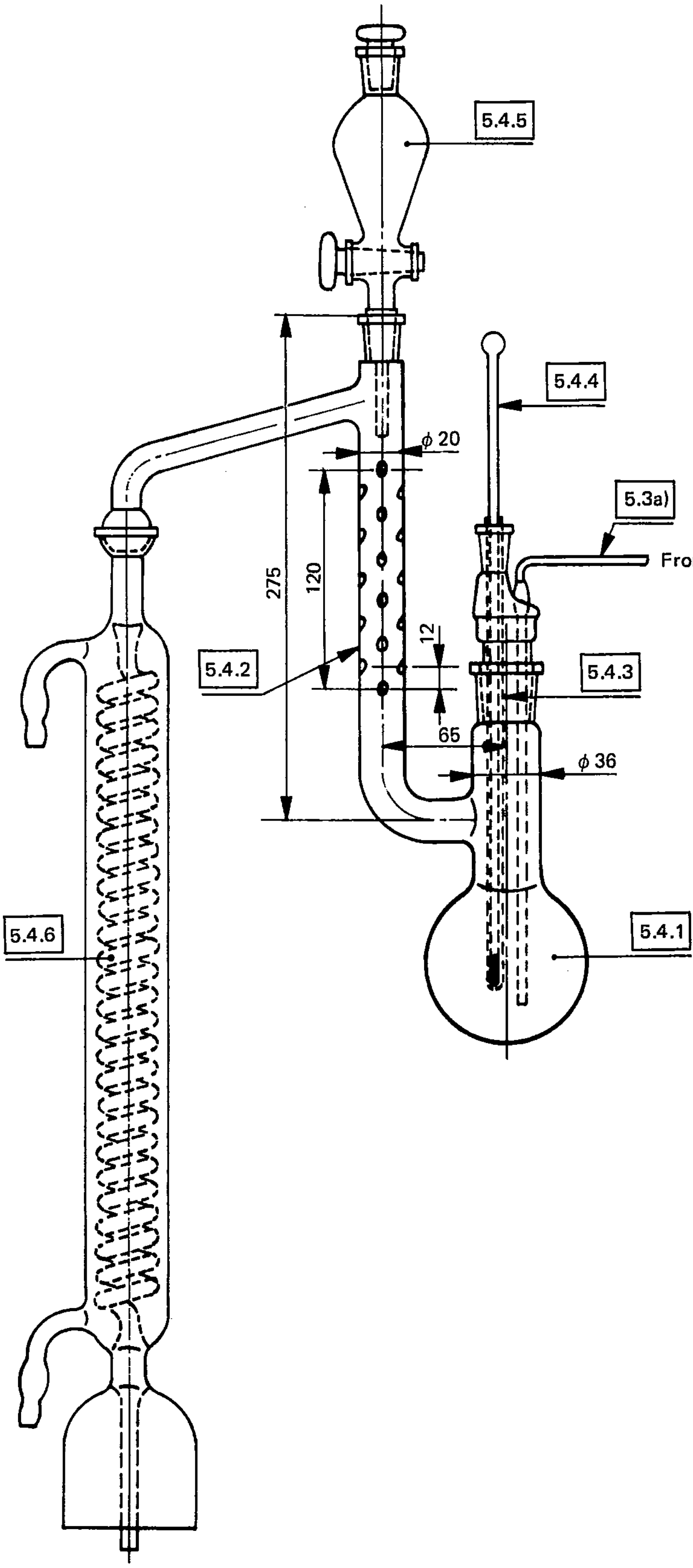
a) the reference of the method used;

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.

Dimensions in millimetres



From the steam-generator (5.3)

FIGURE – **Typical form of apparatus for steam distillation**

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ANNEX

ISO PUBLICATIONS RELATING TO CYROLITE, NATURAL AND ARTIFICIAL

ISO 1619 – Preparation and storage of test samples.

ISO 1620 – Determination of silica content – Reduced molybdosilicate spectrophotometric method.

ISO 1693 – Determination of fluorine content – Modified Willard-Winter method.

ISO 1694 – Determination of iron content – 1,10-Phenanthroline photometric method.

ISO 2366 – Determination of sodium content – Flame emission and atomic absorption spectrophotometric methods.

ISO 2367 – Determination of aluminium content – 8-Hydroxyquinoline gravimetric method.

ISO 2830 – Determination of aluminium content – Atomic absorption method.

ISO 3391 – Determination of calcium content – Flame atomic absorption method.

ISO 3392 – Determination of water content – Electrometric method.

ISO 3393 – Determination of moisture content – Gravimetric method.

ISO 4277 – Evaluation of free fluorides content – Conventional titrimetric method.

ISO 4280 – Determination of sulphates content – Barium sulphate gravimetric method.

ISO . . ., – Sampling.