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CRYOLITE (NATURAL AND ARTIFICIAL)

DETERMINATION OF FLUORINE CONTENT

MODIFIED WILLARD-WINTER METHOD

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BRIEF HISTORY

The ISO Recommendation R 1693, *Cryolite (natural and artificial) – Determination of fluorine content – Modified Willard-Winter method*, was drawn up by Technical Committee ISO/TC 47, *Chemistry*, the Secretariat of which is held by the Ente Nazionale Italiano di Unificazione (UNI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1693, which was circulated to all the ISO Member Bodies for enquiry in March 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia	India	South Africa, Rep. of
Austria	Iran	Spain
Belgium	Israel	Switzerland
Brazil	Italy	Thailand
Canada	Netherlands	Turkey
Czechoslovakia	New Zealand	U.A.R.
France	Norway	United Kingdom
Germany	Peru	U.S.S.R.
Greece	Poland	Yugoslavia
Hungary	Romania	

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

ISO Recommendation | R 1693 | August 1970

CRYOLITE (NATURAL AND ARTIFICIAL)

DETERMINATION OF FLUORINE CONTENT

MODIFIED WILLARD-WINTER METHOD

1. SCOPE

This ISO Recommendation describes a method for the determination of fluorine in natural and artificial cryolite by titration with thorium nitrate solution.

2. FIELD OF APPLICATION

The method can be applied to the determination of fluorine in both natural and artificial cryolite.

NOTE. – The method is suitable for application to both the natural and synthetic materials whose ratio of NaF to AlF_3 is between 3 and 1.7.

3. PRINCIPLE

Fusion of a test portion with sodium carbonate.

Separation of fluorine in the form of hydrofluosilicic acid 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 is made using only sodium alizarinsulphonate, the end point being spectrophotometrically determined under carefully defined conditions when the optical density at 525 nm reaches the arbitrary value of 0.60.

4. REAGENTS

Distilled water or water of equal purity should be used in the test.

4.1 *Sodium carbonate, anhydrous.*

4.2 *Hydrochloric acid,* approximately 0.06 N solution.
Dilute 5 ml of hydrochloric acid, approximately ρ 1.19 (g/ml), 38 % (m/m), with water to 1000 ml.

4.3 *Sodium hydroxide,* 20 g/l solution.
Dissolve 20 g of sodium hydroxide in water and, after cooling, dilute to 1000 ml.

4.4 *Sulphuric acid*, approximately 24 N.

Carefully add in small quantities 200 ml of sulphuric acid, approximately ρ 1.84 (g/ml), 96 % (m/m) solution, to approximately 100 ml of water, cool and dilute to 300 ml.

or

4.4.1 *Perchloric acid*, approximately ρ 1.6 (g/ml), 64.5 % (m/m) solution.

4.5 *Buffer solution* (pH 2.7).

Dissolve 9.45 g of monochloroacetic acid in 50 ml of N sodium hydroxide solution and dilute to 100 ml.

4.6 *Thorium nitrate*, approximately 0.067 N solution.

1 ml of this solution is equivalent to approximately 1.3 mg of F.

4.6.1 *Preparation of the solution.* Dissolve 9.45 g of thorium nitrate tetrahydrate, $Th(NO_3)_4 .4H_2O$, in water and dilute to 1000 ml.

4.6.2 *Standardization of the solution*

4.6.2.1 PREPARATION OF THE STANDARD REFERENCE SOLUTION. Weigh, to the nearest 0.1 mg, about 0.2 g of extra pure anhydrous sodium fluoride (see section 8) 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) already containing several glass balls (2 to 3 mm diameter).

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

Carry out the distillation as described in clause 6.3.2.

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

4.6.2.2 TITRATION. Transfer a 50.0 ml aliquot of the standard reference solution (4.6.2.1) into a beaker (5.7) and titrate as described in clause 6.3.3 .

Towards the end of the titration add the last few drops of thorium nitrate (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 described in clause 6.3.2 and titration as described in clause 6.3.3) with the same quantity of all the reagents as used in the procedure described in clauses 4.6.2.1 and 4.6.2.2.

4.6.2.4 CALCULATION OF THE TITRE OF THE SOLUTION. The mass, in milligrammes, of fluorine (F) corresponding to 1 ml of thorium nitrate solution is given by the following formula :

$$\frac{m \times 0.4525}{V_1 - V_2}$$

where

m is the mass, in milligrammes, of NaF contained in the aliquot portion of the standard reference solution (4.6.2.1) taken for the titration;

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

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

0.4525 is the conversion factor from sodium fluoride to fluorine.

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.

5. APPARATUS

Ordinary laboratory apparatus and

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

5.2 *Electric furnace,* controlled at 800 ± 20 °C.

5.3 *Steam generating flask,* capacity about 3 litres, 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 for steam distillation,* with ground glass joints consisting of :

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

- diameter of central neck : 36 mm;
- length of side neck (including the Vigreux column) : 275 mm;
- 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;
- 11 groups of 3 points, set at 120 ° on the circumference, at 12 mm apart.

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,* about 100 ml capacity, for insertion in the Vigreux column.

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

For a typical form of apparatus, see Figure, page 11.

5.5 *Electric heater* for heating the distillation flask (5.4.1) regulated so as to permit progressive heating of the solution up to 150 ± 1 °C (when using sulphuric acid) or to 135 ± 1 °C (when using perchloric acid).

5.6 *pH-meter,* fitted with a glass electrode.

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

* Instead of using the two indicators 4.7 and 4.8 (see clause 6.3.3) the sodium alizarinsulphonate solution may be used alone, or replaced by methyl thymol blue or any other indicator that gives equivalent results in the specified pH range.

5.8 *Microburette*, 10 ml with 0.02 ml divisions.

5.9 *Stirrer*, magnetic.

5.10 *Spectrophotometer*, adapted for the titration.

5.11 *Titration cell*, with 50 mm optical path, 50 mm wide and 75 mm high.

All the glassware should be rinsed carefully with a hot chromic-sulphuric acid mixture, then rinsed freely with water and finally with distilled water.

6. PROCEDURE

6.1 Test portion.

Weigh, to the nearest 0.1 mg, about 0.2 g of the dried sample* into the platinum crucible (5.1).

6.2 Blank test.

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

6.3 Determination

6.3.1 *Preparation of the sample solution.* Introduce into the crucible (5.1) containing the test portion (6.1) 2 g of sodium carbonate (4.1) and mix carefully, preferably by means of a platinum wire. Place the covered crucible 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 (20 minutes approximately).

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 (2 to 3 mm diameter), 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, according to the method chosen, 50 ml of the sulphuric acid solution (4.4) or 30 ml of the perchloric acid solution (4.4.1).

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

Using the electric heater (5.5) heat the distillation flask (5.4.1) until the temperature of the solution reaches 150 °C (for sulphuric acid) or 135 °C (for perchloric acid).

When the temperature of the distillation flask (5.4.1) 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 solution in the distillation flask (5.4.1) 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 minutes.

Then disconnect the distillation flask (5.4.1) from the steam generator (5.3), 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.

* See ISO Recommendation R 1619, *Cryolite, (natural and artificial) – Preparation and storage of test samples*, clause 2.3.

6.3.3 *Titration*

6.3.3.1 VISUAL TITRATION. Transfer 50.0 ml of the solution (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, 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 (4.7) and then, still checking with the pH-meter (5.6), add the buffer solution (4.5) 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 microburette (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 (4.6.2).

6.3.3.2 SPECTROPHOTOMETRIC TITRATION. Transfer 50.0 ml of the solution (6.3.2) to the titration cell (5.11) and dilute to about 100 ml. Add 3 ml of the sodium alizarinsulphonate solution (4.7) and then, in small portions, 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 (5.6), 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).

Transfer the cell to the adapted spectrophotometer (5.10). Place a small glass-encased iron bar into the solution. Place the tip of the microburette (5.8) filled with the thorium nitrate solution (4.6) into the solution and stir.

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 microburette, titrate with the thorium nitrate solution (4.6) until the optical density is 0.60 (25 % transmittance). Read the volume of titrant to the nearest 0.01 ml.

7. EXPRESSION OF RESULTS

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

$$\frac{(V_3 - V_4) \times m_1}{m_0} \times 1000$$

where

V_3 is the volume, in millilitres, of thorium nitrate solution (4.6) used for the titration of the aliquot part of the sample solution (6.3.3);

V_4 is the volume, in millilitres, of thorium nitrate solution (4.6) used for the titration of a corresponding aliquot part of the solution of the blank test (6.2);

m_1 is the mass, in grammes, of fluorine corresponding to 1 ml of titrated thorium nitrate solution (4.6);

m_0 is the mass, in grammes, of the test portion.