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International Standard ISO 6677

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Hexafluorosilicic acid for industrial use — Determination of available fluorine content — Potentiometric method after distillation

Acide hexafluorosilicique à usage industriel — Dosage du fluor utilisable — Méthode potentiométrique après distillation

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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:

Austria
Belgium
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Egypt, Arab Rep. of
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No member body expressed disapproval of the document.

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Hexafluorosilicic acid for industrial use — Determination of available fluorine content — Potentiometric method after distillation

WARNING — Hexafluorosilicic acid is a highly corrosive and toxic liquid which may attack glass. Its action on the skin and eyes is strongly corrosive, producing severe and painful burns which may not be immediately evident. In the event of contact or suspected contact, wash the affected part(s) copiously with water and seek immediate medical attention. Wear rubber gloves and safety goggles when handling it.

The manufacturers' literature should be consulted for further information.

1 Scope and field of application

This International Standard specifies a potentiometric titration method, using an ion-selective electrode, after distillation, for the determination of the available fluorine content of hexafluorosilicic acid for industrial use.

The method is applicable to products having total available fluorine contents, expressed as hexafluorosilicic acid (H_2SiF_6), in the range 15 to 35 % (m/m).

2 References

ISO 2362, *Aluminium fluoride for industrial use — Determination of fluorine content — Modified Willard-Winter method.*

ISO 6227, *Chemical products for industrial use — General method for determination of chloride ions — Potentiometric method.*

3 Principle

Separation of fluorine from a test portion by distillation in the presence of perchloric acid using a temperature-controlled distillation apparatus. Potentiometric titration of the distillate with lanthanum nitrate solution using a fluoride ion-selective electrode.

4 Reagents

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

4.1 Silver sulphate (Ag_2SO_4), or

4.2 Silver phosphate (Ag_3PO_4).

4.3 Silica powder, finely ground.

4.4 Sodium fluoride.

Heat about 2 g of sodium fluoride in a platinum dish for 1 h in the electric furnace (5.9), controlled at approximately 600 °C, and allow to cool in a desiccator.

NOTE — If an analytical grade of sodium fluoride is not available, the sodium fluoride may be recrystallized following the procedure described in the note to sub-clause 4.6.2.1 of ISO 2362.

4.5 Ethanol or propan-2-ol.

4.6 Perchloric acid, ϱ approximately 1,54 g/ml, about 60 % (m/m) solution.

4.7 Perchloric acid, approximately 10 % (m/m) solution.

Dilute 16,5 ml of the perchloric acid solution (4.6) to 100 ml.

4.8 Sodium hydroxide, approximately 40 g/l solution.

Store the solution in a plastics bottle.

4.9 Lanthanum nitrate, standard volumetric solution, $c[La(NO_3)_3.6H_2O] \approx 0{,}01$ mol/l.

4.9.1 Preparation of the solution

Use carbon-dioxide free water for the preparation of this solution.

Dissolve 4,33 g of lanthanum nitrate hexahydrate $[La(NO_3)_3.6H_2O]$ in water. Add 10 ml of approximately 6,3 g/l nitric acid solution, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.9.2 Standardization of the solution

See 6.5.

4.10 Buffer solution, of pH 6,5.

Dissolve 79 g of pyridine in about 800 ml of water and neutralize with the perchloric acid solution (4.7) to pH 6,5 ± 0,2. Dilute to 1 000 ml with water.

WARNING — Carry out these operations in a well-ventilated fume cupboard.

4.11 Phenolphthalein, 5 g/l solution in 95 % (*V*/*V*) ethanol.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Distillation apparatus (see figure 1), incorporating a steam generator, two electric heating jackets and a contact thermometer with relay capable of controlling the temperature in the distillation flask at 135 ± 2 °C.

The power required for the heating jacket is

a) for the distillation flask: approximately 150 W;

b) for the steam generator: minimum of 500 W.

It is essential that the steam generator heating jacket is equipped with a regulator in order to adjust the power input to give the desired steam rate.

NOTE — Alternatively, the apparatus specified in ISO 2362 for the determination of the fluorine content of aluminium fluoride may be used.

5.2 Magnetic stirrer.

5.3 pH meter, fitted with glass and saturated calomel electrodes.

5.4 Burette, of capacity 25 ml, graduated at 0,02 ml intervals.

5.5 Fluoride ion-selective electrode.

5.6 Reference electrode, saturated calomel or other suitable type.

NOTE — If available, a combined electrode assembly may be used instead of the electrodes (5.5 and 5.6).

5.7 Potentiometer, sensitivity 0,5 mV, covering the range −500 to +500 mV.

For fixed end-point measurements, the equipment, using a specific set of electrodes, should reproduce the end-point to ± 0,5 mV.

Automatic apparatus for registering titration graphs or for titrations to a pre-determined end-point potential are available commercially and may be used as alternatives.

5.8 Electric oven, capable of being controlled at 105 ± 2 °C.

5.9 Electric furnace, capable of being controlled at approximately 600 °C.

5.10 Screw-capped polyethylene sample bottles, of capacities 250 and 500 ml.

5.11 Polyethylene weighing bottles, of capacity approximately 25 ml.

6 Procedure

6.1 Test portion

According to the expected available fluorine content, weigh, to the nearest 0,000 2 g, a mass of test sample as indicated in the following table.

Expected available fluorine content expressed as H_2SiF_6	Mass of test portion
% (*m*/*m*)	g
15 to 20	1
20 to 30	0,75
30 to 35	0,5

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 [except the lanthanum nitrate solution (4.9)] as used in the determination, but omitting the test portion.

6.3 Distillation

Assemble the distillation apparatus (5.1). Remove the contact thermometer and add 0,5 g of the silica powder (4.3) and 0,2 g of the silver sulphate (4.1) or 0,2 g of the silver phosphate (4.2) to the distillation flask. Transfer the test portion (6.1) quantitatively into the distillation flask, add 35 ml of the perchloric acid solution (4.6) and immediately close the apparatus with the contact thermometer.

Place a 500 ml one-mark volumetric flask, containing 25 ml of the sodium hydroxide solution (4.8) and 40 ml of water, under the delivery tube, which should dip into the liquid.

Turn the stopcock between the steam generator and the distillation apparatus to position 1, set the contact thermometer to 135 °C and switch on the electric heating to the distillation flask and the steam generator. Heat the contents of the distillation flask to 135 °C for approximately 15 min, turn the stopcock to position 2 and pass steam into the distillation flask at a rate corresponding to about 10 ml of water per minute. Collect about 400 ml of distillate and then stop the distillation.

Rinse the delivery tube, inside and outside, with water, collecting the washings in the 500 ml one-mark volumetric flask. Neutralize the distillate with the perchloric acid solution (4.7), using a few drops of the phenolphthalein solution (4.11) as indicator. Dilute to the mark and mix.

6.4 Potentiometric titration

Place a 50,0 ml aliquot portion from the 500 ml one-mark volumetric flask in a 250 ml beaker. Add 10 ml of the buffer solution (4.10) and 60 ml of the ethanol or propan-2-ol (4.5). Introduce the magnetized follower of the magnetic stirrer (5.2) into the beaker, place the beaker on the stirrer, immerse the fluoride ion-selective electrode (5.5) and the reference electrode (5.6) (or the combined electrode assembly) in the solution and connect the potentiometer (5.7). Start the magnetic stirrer and titrate with the standard volumetric lanthanum nitrate solution (4.9) adding about 0,5 ml at a time. After each addition, allow the potentiometric readings to reach a steady value and record this value and the corresponding volume of titrant. Toward the end-point, the value of the potentiometric readings increases sharply. At this stage, reduce the volume of the titrant for each addition from 0,5 to 0,1 ml.

Plot a graph having, for example, the volumes of the lanthanum nitrate solution added as abscissae and the corresponding potentiometric readings as ordinates. The end-point corresponds to the volume added at the point of inflection of the graph. Alternatively, the graph may be obtained from an automatic titrator fitted with a pen recorder.

An example of a typical graph is given in figure 2.

NOTE — The end-point may also be determined mathematically by the method described in ISO 6227.

6.5 Standardization

Follow the procedure specified in 6.3 and 6.4 using approximately 0,200 g, weighed to the nearest 0,000 1 g, of the recrystallized sodium fluoride (4.4) instead of the test portion (6.1). Calculate the mass of sodium fluoride equivalent to 1 ml of the standard volumetric lanthanum nitrate solution (4.9), taking account of the blank test (6.2).

7 Expression of results

The available fluorine content, expressed as hexafluorosilicic acid (H_2SiF_6) as a percentage by mass, is given by the formula

$$\frac{0{,}571\,9 \times m_1 (V_1 - V_0) \times 1\,000}{m_0}$$

where

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

m_1 is the mass, in grams, of sodium fluoride corresponding to 1 ml of the standard volumetric lanthanum nitrate solution (4.9);

V_0 is the volume, in millilitres, of the standard volumetric lanthanum nitrate solution (4.9) used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric lanthanum nitrate solution (4.9) used for the determination;

0,571 9 is the conversion factor from sodium fluoride to hexafluorosilicic acid.

8 Test report

The test report shall include the following particulars:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

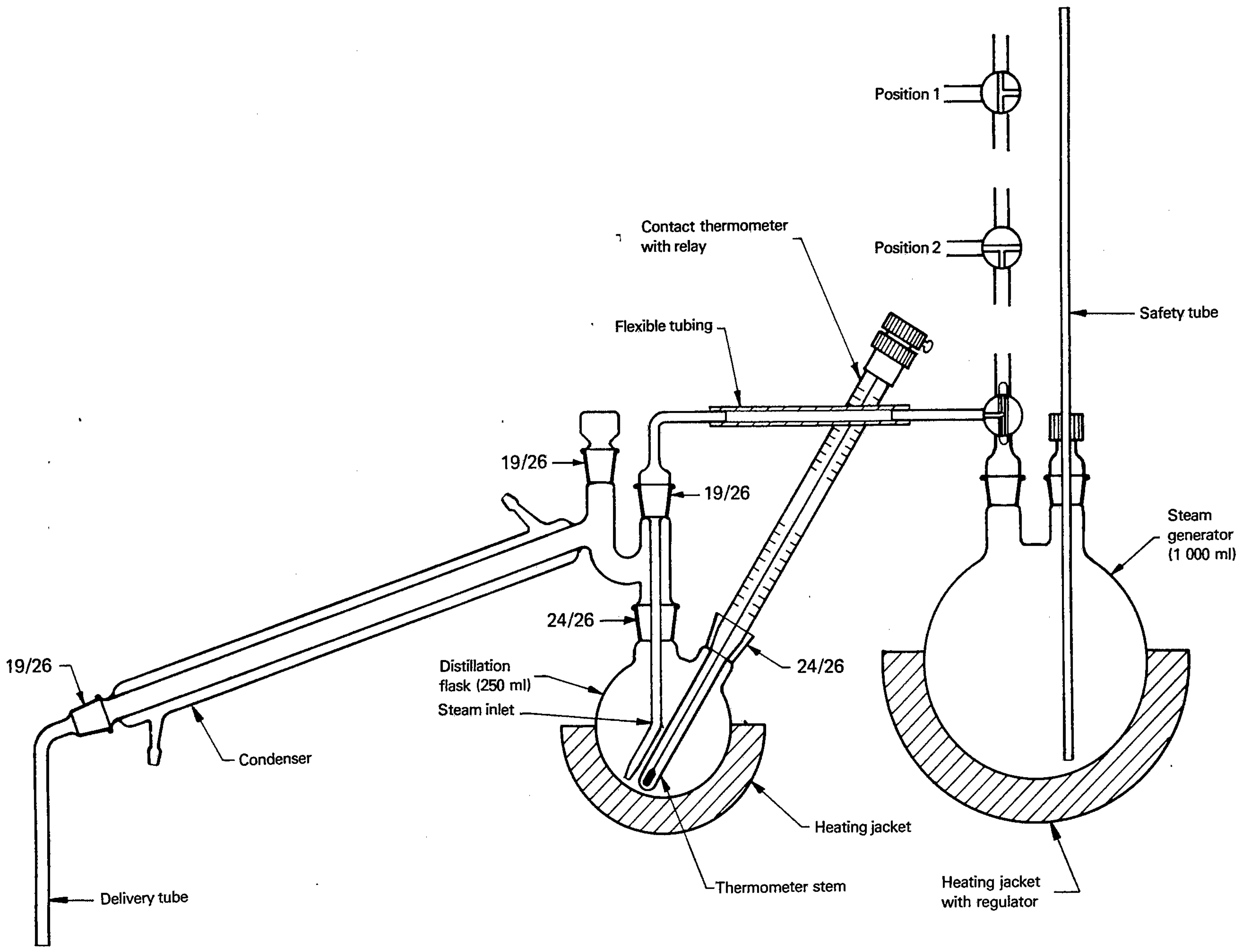

Figure 1 — Distillation apparatus

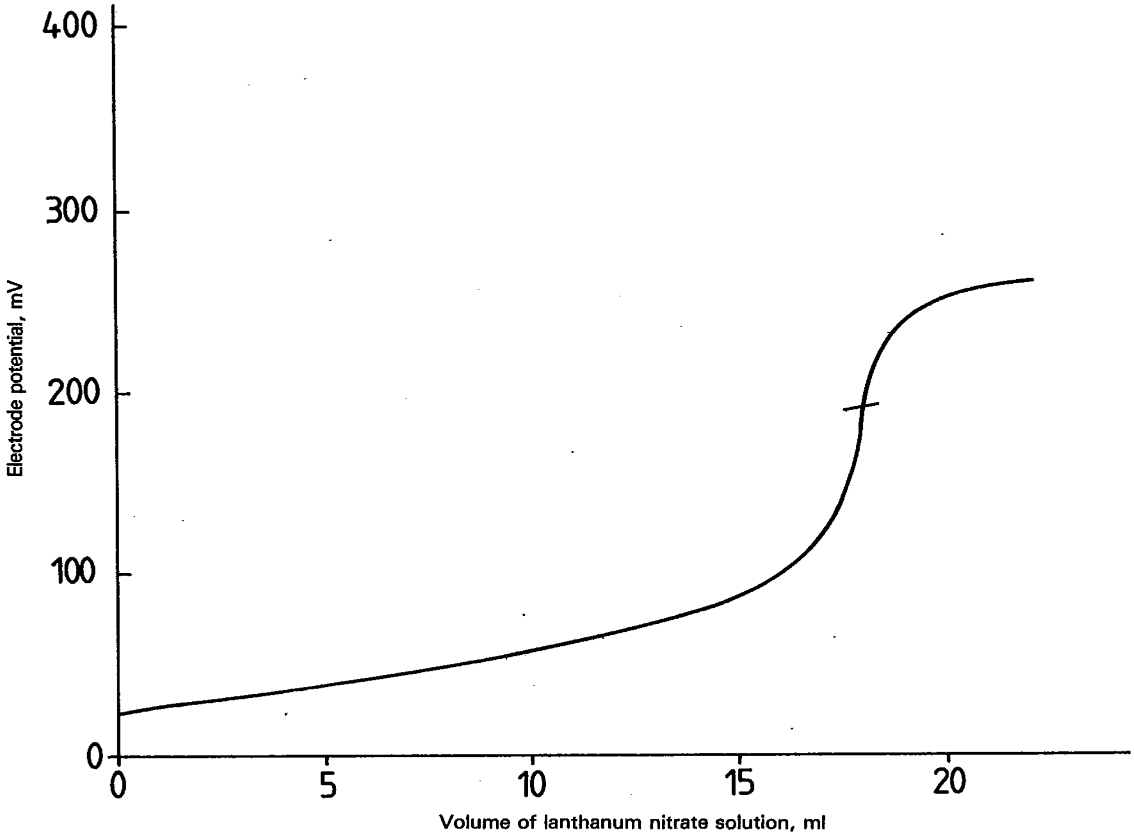

Figure 2 — Example of typical titration graph