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1974

Methods of test for

Aluminium fluoride for industrial use —

Part 1: Determination of fluorine content

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Co-operating organizations

The Chemicals Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

British Steel Industry
Chemical Industries Association*
Department of Health and Social Security
Department of Trade and Industry
Fertilizer Manufacturers' Association Limited
Ministry of Agriculture, Fisheries and Food
National Sulphuric Acid Association
Royal Institute of Public Health and Hygiene
Soap and Detergent Industry Association

The industrial organization marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

Aluminium Federation
British Ceramic Research Association
Society for Analytical Chemistry
Society of Chemical Industry

This British Standard, having been approved by the Chemicals Industry Standards Committee, was published under the authority of the Executive Board on 28 February 1974

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Foreword

This British Standard has been prepared under the authority of the Chemicals Industry Standards Committee in order to provide methods for the analysis of aluminium fluoride.

For some years the United Kingdom has participated in the work of preparing methods of test applicable to aluminium fluoride for industrial use, organized by Sub-Committee 7 "Alumina and related compounds" of Technical Committee 47 "Chemistry" of the International Organization for Standardization (ISO). As international agreement is reached on the methods, it is proposed to publish them as parts of this British Standard.

This part is based on International Standard ISO 2362 "*Aluminium fluoride for industrial use — Determination of fluorine content — Modified Willard-Winter method*", modified to take into account the comments made by the United Kingdom during its development, in particular by omitting the alternatives of spectrophotometric titration and distillation using perchloric acid.

This standard prescribes methods of test only, and should be used or quoted as a specification defining limits of purity. Reference to the standard should be in a form of words indicating that the methods of test used conform to BS 4993.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 4, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This Part of BS 4993 specifies a modified Willard-Winter method for the determination of the fluorine content of aluminium fluoride for industrial use.

NOTE The titles of the British Standards referred to in this standard are listed on the inside back cover.

2 Principle

A test portion is fused with sodium carbonate and the fluorine is separated by distillation with sulphuric acid. The distillate is titrated with thorium nitrate solution using as indicator either sodium alizarinsulphonate, with or without methylene blue as masking agent, or methylthymol blue.

3 Reagents

The reagents used shall be of recognized analytical reagent quality. Water complying with the requirements of BS 3978 shall be used throughout.

3.1 *Sodium carbonate,* anhydrous.

3.2 *Hydrochloric acid,* approximately 0.06N solution.

Dilute 5 ml of hydrochloric acid, ρ approximately 1.18 g/ml, about 36 % (m/m) solution, with water to 1 000 ml.

3.3 *Perchloric acid,* approximately N solution.

3.4 *Sodium hydroxide,* 20 g/l solution.

Dissolve 20 g of sodium hydroxide in water and, after cooling, dilute to 1 000 ml.

3.5 *Sulphuric acid,* approximately 23N.

Carefully add, in small quantities, 200 ml of sulphuric acid, ρ approximately 1.84 g/ml, about 98 % (m/m), to approximately 100 ml of water, cool and dilute to 300 ml.

3.6 *Buffer solution,* pH 2.7 (for use with sodium alizarinsulphonate indicator)

Dissolve 9.45 g of monochloroacetic acid in 50 ml of N sodium hydroxide solution and dilute to 100 ml with water; or

3.7 *Buffer solution,* pH 3.4 (for use with methylthymol blue indicator)

Dissolve 6.7 g of glycine and 11 g of sodium perchlorate in 11 ml of N perchloric acid and dilute to 100 ml with water.

3.8 *Thorium nitrate,* standardized solution, approximately 0.067N.

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

3.8.1 *Preparation of the solution.* Dissolve 10.01 g of thorium nitrate hexahydrate [$Th(NO_3)_4.6H_2O$] in water and dilute to 1 000 ml.

3.8.2 *Standardization of the solution*

3.8.2.1 *Preparation of the standard reference solution.* Weigh, to the nearest 0.1 mg, about 200 mg of anhydrous sodium fluoride, previously heated at 600 °C in a platinum dish and cooled in a desiccator. Transfer, using 20 ml to 30 ml of water, into the distillation flask (**4.4.1**) containing several soda-lime glass balls (2 mm to 3 mm diameter).

Stopper the distillation flask and add, through the dropping funnel (**4.4.5**), 50 ml of the sulphuric acid (**3.5**).

Carry out the distillation as described in **5.3.2**.

Collect the distillate in a 500 ml one-mark volumetric flask, complying with the requirements of BS 1792, dilute to the mark and mix.

NOTE If analytical reagent grade sodium fluoride is not available, recrystallize the product as follows. Dissolve approximately 5 g of pure sodium fluoride in 125 ml of water and, after dissolution, filter under vacuum through a small Buchner 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, with natural draught, controlled at 110 ± 5 °C.

Remove the dish from the oven, cool in a desiccator, grind the product in an agate mortar and sieve it through a sieve with a mesh size of 0.355 mm (see BS 410). Place the sieved sodium fluoride in a platinum dish, heat for 2 h at 600 °C and then allow to cool in a desiccator.

3.8.2.2 *Titration.* Transfer a 50.0 ml aliquot portion of the standard reference solution (**3.8.2.1**) to the beaker (**4.7**) and titrate as described in **5.3.3**.

Towards the end of the titration add the last few drops of the thorium nitrate solution (**3.8.1**) carefully with vigorous stirring.

3.8.2.3 *Blank test.* Carry out a blank test following the same procedure (distillation as described in **5.3.2** and titration as described in **5.3.3**) using the same quantity of all the reagents as in the procedure described in **3.8.2.1** and **3.8.2.2**, but omitting the sodium fluoride.

3.8.2.4 *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:

$$\frac{m_1 \times 0.4525}{V_1 - V_2}$$

where

m_1 is the mass of sodium fluoride (NaF) contained in the aliquot portion of the standard reference solution (**3.8.2.1**) taken for the titration (mg);

V_1 is the volume of the thorium nitrate solution (**3.8.1**) used for the titration of the aliquot portion of the standard reference solution (**3.8.2.1**) taken for the titration (ml);

V_2 is the volume of thorium nitrate solution (**3.8.1**) used for the titration of the blank solution (**3.8.2.3**) (ml);

0.4525 is the conversion factor from sodium fluoride to fluorine.

3.9 *Sodium alizarinsulphonate,* 0.5 g/l solution[1].

Dissolve 0.05 g of sodium alizarinsulphonate in water and dilute to 100 ml.

3.10 *Methylene blue,* 0.5 g/l solution[1].

Dissolve 0.05 g of methylene blue (oxidation-reduction indicator grade) in water and dilute to 100 ml.

3.11 *Methylthymol blue,* 0.5 g/l solution[1].

Dissolve 0.05 g of methylthymol blue in water and dilute to 100 ml.

4 Apparatus

Ordinary laboratory apparatus and the following are required.

4.1 *Platinum crucible,* flat bottom type, upper diameter approximately 30 mm, lower diameter approximately 15 mm and height approximately 30 mm, fitted with a platinum lid.

4.2 *Electric furnace,* capable of being controlled at 800 ± 20 °C.

4.3 *Steam generator,* such as a flask, capacity approximately 3 000 ml, fitted with a stopper into which are inserted the following three glass tubes, a), b) and c), of internal diameter about 6 mm:

a) a vertical recovery bend tube, for introducing the steam into the distillation flask (**4.4.1**) (one limb dipping into the distillation flask);

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

c) a safety tube, about 1 m long.

4.4 *Steam distillation apparatus,* borosilicate glass, with ground glass joints. A typical form of apparatus is illustrated in Figure 1 and consists of the following components.

4.4.1 *Claisen flask,* 250 ml capacity, preferably having the following dimensions:

diameter of central neck: 36 mm;

length of side neck [including Vigreux distillation column (**4.4.2**)]: 275 mm;

distance between side neck and central neck: 65 mm;

diameter of side neck: 20 mm.

4.4.2 *Distillation column,* Vigreux type, preferably having the following dimensions:

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

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

4.4.3 *Thermometer sheath*

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

4.4.5 *Dropping funnel,* Walter type, about 100 ml capacity, for insertion in the Vigreux column.

4.4.6 *Graham condenser,* with an effective length of about 400 mm, complying with the requirements of BS 1848.

4.5 *Electric heater,* for heating the distillation flask (**4.4.1**) up to 150 °C and capable of being controlled to within 1 °C.

4.6 *pH meter,* fitted with a glass electrode. Essential requirements are given in BS 2586, and in BS 3145 or BS 3422.

4.7 *Beaker,* of borosilicate glass, 250 ml, tall form.

4.8 *Burette,* 10 ml with 0.02 ml divisions.

4.9 *Stirrer,* magnetic.

NOTE All the glassware should be carefully rinsed with a hot chromic-sulphuric acid mixture, then thoroughly rinsed with water and finally with water complying with the requirements of BS 3978.

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[1] Instead of using the two indicators **3.9** and **3.10** (see **5.3.3**), the sodium alizarinsulphonate solution (**3.9**) may be used alone. Alternatively the methylthymol blue (**3.11**), or any other indicator that gives equivalent results with the appropriate buffer and in the specified pH range, may be used.

5 Procedure

5.1 Test portion. Weigh, to the nearest 0.1 mg, about 200 mg of the dried test sample[2] into the platinum crucible (**4.1**).

5.2 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, but omitting the test portion (**5.1**).

5.3 Determination

5.3.1 *Preparation of the test solution.* Introduce into the crucible (**4.1**) containing the test portion (**5.1**) 2 g of the sodium carbonate (**3.1**) and mix carefully, preferably by means of a platinum wire. Place the crucible in the electric furnace (**4.2**), previously heated to about 200 °C, and heat to 800 ± 20 °C. Maintain at this temperature until the carbon dioxide is eliminated and the sample has melted (20 min 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 (**4.4.1**), containing several soda-lime glass balls (2 mm to 3 mm diameter), and wash the crucible carefully with 20 ml or 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 (**4.4.1**).

5.3.2 *Distillation.* Place a 500 ml one-mark volumetric flask under the condenser (**4.4.6**) to collect the distillate.

Connect the distillation flask to the condenser (**4.4.6**) and start the water circulation.

Stopper the distillation flask and add, through the dropping funnel (**4.4.5**), 50 ml of the sulphuric acid (**3.5**).

Using the electric heater (**4.5**), heat the distillation flask until the solution reaches 150 °C.

Pass steam from the generator (**4.3**) into the distillation flask so as to maintain the solution at 150 ± 1 °C and collect about 400 ml of the distillate over a period of about 90 min.

Disconnect the distillation flask from the steam generator (**4.3**), allowing the steam to escape to atmosphere, and remove the heater (**4.5**).

Wash the condenser with a jet of water.

Dilute the distillate to the mark in the collecting flask and mix.

5.3.3 *Titration.* Transfer 50.0 ml of the contents of the collecting flask (**5.3.2**) to the beaker (**4.7**). Add to the beaker about 50 ml of water and 0.50 ml of the sodium alizarinsulphonate solution (**3.9**) and then, in small portions, the sodium hydroxide solution (**3.4**) until a pink coloration appears (pH of the colour change **6.6** to **6.8**).

Checking by means of the pH meter (**4.6**), add the hydrochloric acid solution (**3.2**) 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 and then, still checking with the pH meter, add the buffer solution (**3.6**) 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 (**3.10**) (green coloration of the solution).

Place a small glass-encased iron bar in the solution and stir vigorously using the stirrer (**4.9**).

Fill the burette (**4.8**) with the thorium nitrate solution (**3.8**) 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 (**3.8.2.2**).

NOTE 1 Carry out the titration in daylight or under fluorescent lighting. The titration must not be carried out with the illumination provided by a tungsten filament lamp.

NOTE 2 If the methylthymol blue (**3.11**) is used as indicator, the pH **3.4** buffer solution (**3.7**) should be used instead of pH **2.7** buffer solution (**3.6**) and pH adjustments carried out with the perchloric acid solution (**3.3**) instead of the hydrochloric acid (**3.2**).

6 Calculation

Fluorine content, expressed as a percentage by mass of F, is given by the formula:

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

where

m_o is the mass of the test portion (g);

m_2 is the mass of fluorine corresponding to 1 ml of the standardized thorium nitrate solution (**3.8**) (g);

V_3 is the volume of the standardized thorium nitrate solution (**3.8**) used for the titration of the aliquot portion of the sample solution (**5.3.2**) (ml);

V_4 is the volume of the standardized thorium nitrate solution (**3.8**) used for the titration of a corresponding aliquot portion of the solution from the blank test (**5.2**) (ml).

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[2] Methods for the preparation and storage of test samples of aluminium fluoride are in course of preparation and will be published as a part of this standard.

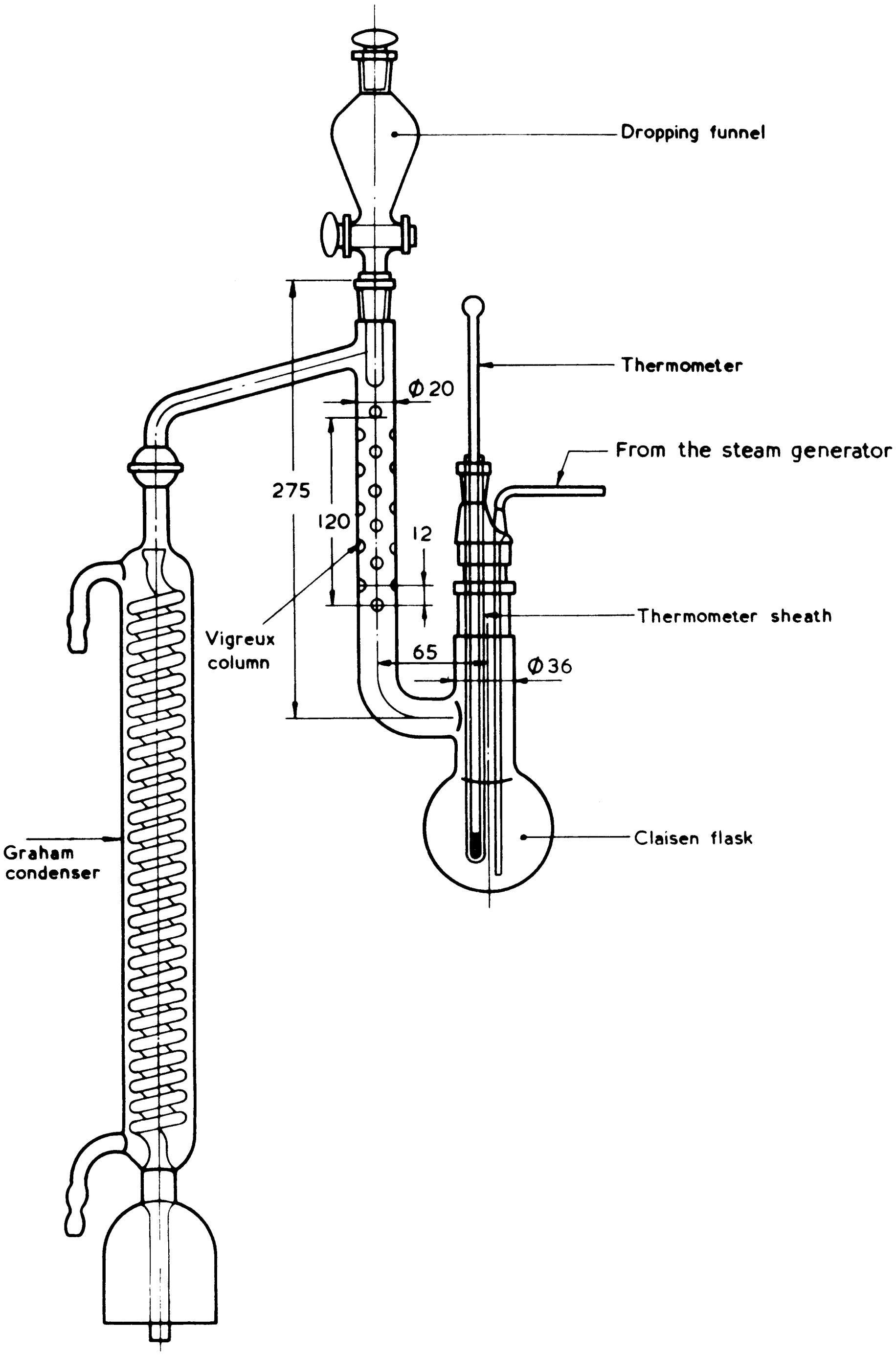

Figure 1 — Typical form of steam distillation apparatus for use in determination of fluorine content

Publications referred to

This standard makes reference to the following British Standards:

BS 410, *Test sieves.*

BS 1792, *One-mark volumetric flasks.*

BS 1848, *Glass condensers.*

BS 2586, *Glass electrodes for the measurement of pH.*

BS 3145, *Laboratory potentiometric pH meters.*

BS 3422, *Laboratory deflection pH meters.*

BS 3978, *Water for laboratory use.*

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