BRITISH STANDARD

BS 5072-3: 1975

Incorporating Amendment No. 1

Methods of test for

Sodium fluoride for industrial use —

Part 3: Determination of fluorine content

Confirmed December 2011

UDC 661.833.361:546.33'161:543.24.062:546.16

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*
Department of Trade and Industry — Laboratory of the Government Chemist*
Fertiliser Manufacturers' Association Limited
Ministry of Agriculture, Fisheries and Food
National Sulphuric Acid Association
Royal Institute of Public Health and Hygiene
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The organizations 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
Royal Institute of Chemistry
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 30 September 1975

The following BSI references relate to the work on this standard:
Committee reference CIC/24
Draft for comment 72/52985 DC

ISBN 0 580 08107 9

Amendments issued since publication

Amd. No.	Date of issue	Comments
5348	March 1987	Indicated by a sideline in the margin

Contents

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 sodium fluoride.

In the drafting of this standard account has been taken of the method adopted by the International Organization for Standardization (ISO) in the preparation of which the United Kingdom has been an active participant. It is intended to provide further methods, in the form of Parts of this standard, as the work of ISO/TC 47 — Chemistry (and, in particular, ISO/TC 47/SC 7 — Alumina and related compounds) advances.

This Part of BS 5072 is based on International Standard ISO 2833 *"Sodium 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 not 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 5072.

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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 5072 specifies a modified Willard-Winter method for the determination of fluorine content of sodium fluoride for industrial use by titration with thorium nitrate solution.

2 References

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

3 Principle

The fluorine is separated from a test portion 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 as indicator.

4 Reagents

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

4.1 *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.

4.2 *Perchloric acid,* approximately N solution.

4.3 *Sodium hydroxide,* 20 g/l solution. Dissolve 20 g of sodium hydroxide in water and, after cooling, dilute to 1 000 ml.

4.4 *Sulphuric acid,* approximately 23N. Carefully add, in small quantities, 200 ml of sulphuric acid, ρ approximately 1.84 g/ml, about 98 % (*m*/*m*) solution, to approximately 100 ml of water and, after cooling, dilute to 300 ml.

4.5 *Buffer solution.* Either of the following may be used:

a) 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

b) 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 the N perchloric acid solution (**4.2**) and dilute to 100 ml with water.

4.6 *Thorium nitrate,* standardized solution approximately 0.067N. 1 ml of this solution is equivalent to approximately 1.3 mg of fluorine (F).

4.6.1 *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.

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 200 mg of analytical reagent grade 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 [**5.2** a)] containing several soda-lime glass balls (2 mm to 3 mm diameter).

Stopper the distillation flask and add, through the dropping funnel [**5.2** e)], 50 ml of the sulphuric acid solution (**4.4**).

Carry out the distillation as described in **6.3.1**.

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 about 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 approximately 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 100 ± 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 355 µm complying with the requirements of 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.

4.6.2.2 *Titration.* Transfer a 50.0 ml aliquot portion of the standard reference solution (**4.6.2.1**) to the beaker (**5.5**) and titrate by the procedure described in **6.3.2**.

Towards the end of the titration add the last few drops of the thorium nitrate solution (**4.7.1**) carefully with vigorous stirring.

4.6.2.3 *Blank test.* Carry out a blank test at the same time and following the same procedure (distillation according to **6.3.1** and titration according to **6.3.2**), using the same quantities of all reagents as in the procedure described in **4.6.2.1** and **4.6.2.2** but omitting the sodium fluoride.

4.6.2.4 *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

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

where

m_1 is the mass of sodium fluoride contained in the aliquot portion of the standard reference solution (**4.6.2.1**) taken for the titration (mg);

V_1 is the volume of the thorium nitrate solution (**4.6.1**) used for the titration of the aliquot portion of the standard reference solution (**4.6.2.1**) taken for the titration (ml);

V_2 is the volume of thorium nitrate solution (**4.6.1**) used for the titration of the blank solution (**4.6.2.3**) (ml);

0.4525 is the conversion factor for sodium fluoride to fluorine.

4.7 *Sodium alizarinsulphonate,* 0.5 g/l solution[1]. Dissolve 0.05 g of sodium alizarinsulphonate in water and dilute to 100 ml.

4.8 *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.

4.9 *Methylthymol blue,* 0.5 g/l solution[1]. Dissolve 0.05 g of methylthymol blue in water and dilute to 100 ml.

5 Apparatus

Ordinary laboratory apparatus and the following are required.

5.1 *Steam generator,* for example, such as a flask of capacity 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 steam into the distillation flask [**5.2** a)] (one limb dipping into the distillation flask);

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

c) a safety tube, approximately 1 m long.

5.2 *Steam distillation apparatus,* borosilicate glass, with ground glass joints. A typical apparatus is shown in Figure 1 and consists of the following components:

a) *Claisen flask* (distillation flask), 250 ml capacity, preferably having the following dimensions:

1) diameter of central neck: 36 mm;

2) length of side neck (including the Vigreux column [**5.2** b)]: 275 mm;

3) distance between side neck and central neck: 65 mm;

4) diameter of side neck: 20 mm.

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

1) length of column between the first and last series of indentations: 120 mm;

2) 11 groups of 3 indentations, spaced at 120° on the circumference, at 12 mm separations.

c) *Thermometer sheath.*

d) *Thermometer,* covering the temperature range 0 °C to 200 °C, with an effective length of approximately 250 mm.

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

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

5.3 *Electrical heater,* for heating the distillation flask [**5.2** a)] up to 150 °C and capable of being controlled to within 1 °C.

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

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

5.6 *Burette,* 10 ml with 0.02 ml divisions, complying with the requirements of BS 846.

5.7 *Stirrer, magnetic*

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

6 Procedure

6.1 Test portion. Weigh, to the nearest 0.1 mg, approximately 200 mg of the dried sample[2] into the platinum crucible.

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, but omitting the test portion (**6.1**).

[1] Instead of using the two indicators **4.7** and **4.8** (see **6.3.2**), the sodium alizarinsulphonate solution (**4.7**) may be used alone. Alternatively the methylthymol blue (**4.9**), or any other indicator that gives equivalent results with the appropriate buffer and in the specified pH range, may be used.

[2] See BS 5072-4.

6.3 Determination

6.3.1 *Distillation.* Transfer the test portion (**6.1**), using 20 ml to 30 ml of water, into the distillation flask [**5.2** a)] containing several soda-lime glass balls (2 mm to 3 mm diameter). Place a 500 ml one-mark volumetric flask complying with the requirements of BS 1792 under the condenser [**5.2** f)] to collect the distillate.

Connect the distillation flask [**5.2** a)] to the condenser [**5.2** f)] and start the water circulation.

Stopper the distillation flask and add, through the dropping funnel [**5.2** e)], 50 ml of the sulphuric acid solution (**4.4**).

Using the electrical heater (**5.3**), heat the distillation flask [**5.2** a)] until the solution reaches 150 °C.

When the temperature in the distillation flask [**5.2** a)] has reached 150 °C, pass steam from the generator (**5.1**) into the distillation flask so as to maintain the solution at 150 ± 1 °C and collect approximately 400 ml of distillate over a period of about 90 min.

Disconnect the distillation flask [**5.2** a)] from the steam generator (**5.1**), allowing the steam to escape to the atmosphere, and remove the heater (**5.3**). Wash the condenser with a jet of water.

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

6.3.2 *Titration.* Transfer 50.0 ml of the contents of the collecting flask to the beaker (**5.5**). Add to the beaker approximately 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 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 (**4.7**) and then, still checking with the pH meter (**5.4**), add the appropriate buffer solution (**4.5**) in small portions until the pH is 3.4 ± 0.1 (approximately 1 ml of buffer solution is required).

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 (**5.7**).

Fill the burette (**5.6**) with the thorium nitrate solution (**4.6**) and titrate until a blue-violet colour develops.

Ensure that the same lighting conditions are used as for the standardization of the thorium nitrate solution (**4.6.2**).

NOTE 1 Carry out the titration in daylight or fluorescent light only. The titration is not to be carried out with the illumination provided by tungsten filament lamps.

NOTE 2 If the methylthymol blue (**4.9**) is used as indicator, the pH 3.4 buffer solution [**4.5** b)] should be used instead of the pH 2.7 buffer solution [**4.5** a)] and pH adjustments should be carried out with the perchloric acid solution (**4.2**) instead of the hydrochloric acid solution (**4.1**).

7 Calculation

Fluorine (F) content, expressed as a percentage by mass, is given by the formula

$$\frac{(V_3 - V_4) \times m_2 \times 10}{m_0} \times 100$$

where

m_0 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 (**4.6**) (g);

V_3 is the volume of the standardized thorium nitrate solution (**4.6**) used for the titration of the aliquot portion of the sample solution obtained as described in **6.3.1** (ml);

V_4 is the volume of the standardized thorium nitrate solution (**4.6**) used for the titration of a corresponding aliquot portion of the solution from the blank test (**6.2**) (ml).

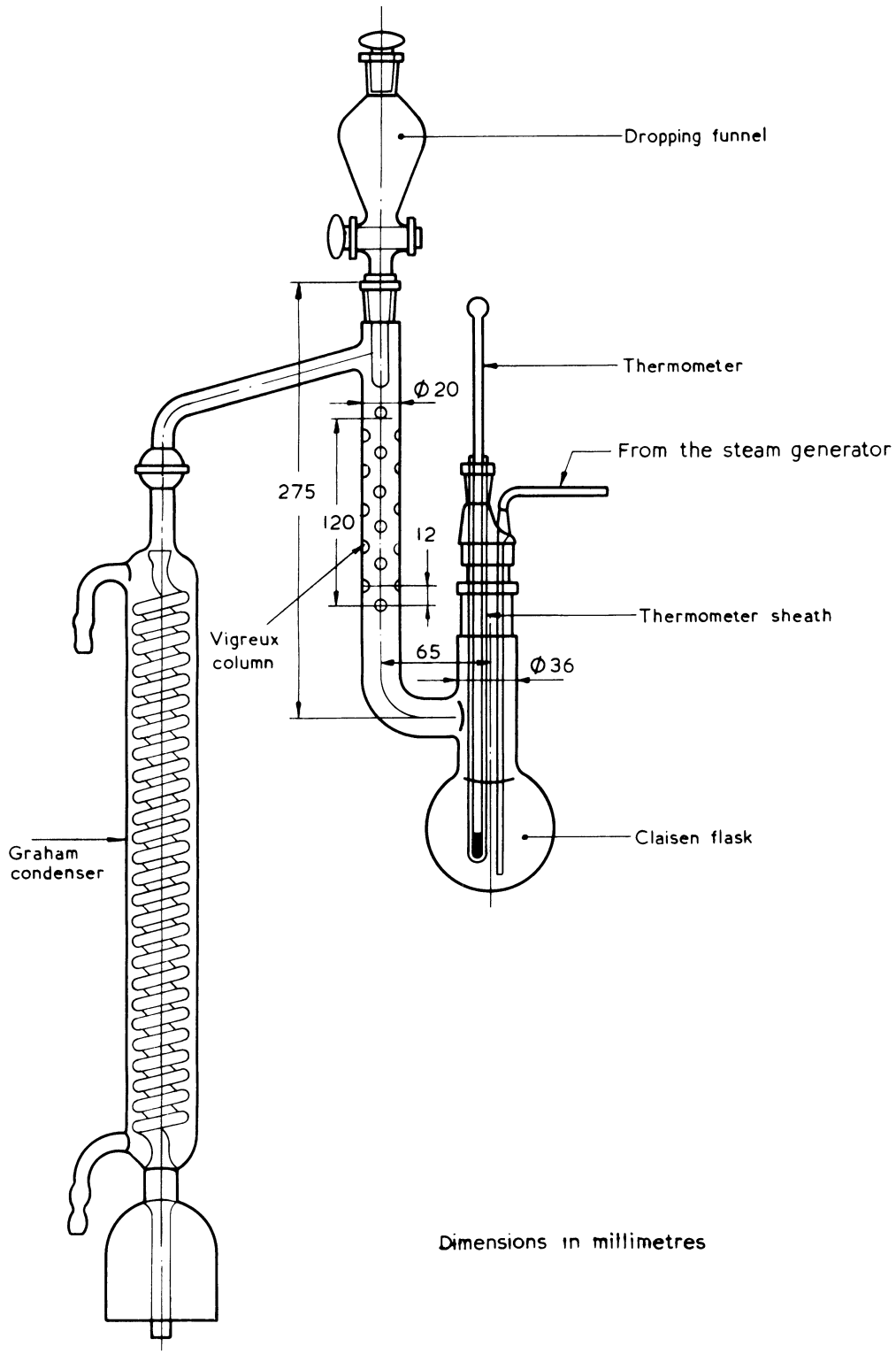

Figure 1 — Typical form of steam distillation apparatus for use in determination of fluorine content

Publications referred to

This standard makes reference to the following British Standards:
BS 410, *Test sieves.*
BS 846, *Burettes and bulb burettes.*
BS 1792, *One-mark volumetric flasks.*
BS 1848, *Glass condensers.*
BS 2586, *Glass electrodes for measurement of pH.*
BS 3145, *Laboratory potentiometric pH meters.*
BS 3422, *Laboratory deflection pH meters.*
BS 3978, *Water for laboratory use.*
BS 5072, *Methods of test for sodium fluoride for industrial use.*
BS 5072-4, *Preparation and storage of samples.*

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